CHAPTER

41 Interhalogen Compounds, Polyhalides and Pseudohalogens

Interhalogen Compounds

We know that halogen atoms have different electronegativity. Due to this difference in electronegativity, the halogen atoms combine with each other and give rise to the formation of binary covalent compounds which are called *interhalogen compounds*. These compounds are of four types : (*i*) *AB type* (+ 1), *e.g.* ClF, BrF, IF (detected spectroscopically), BrCl, ICl, IBr (*ii*) AB_3 *type* (+ 3), *e.g.* ClF_3, BrF_3, IF_3, ICl_3 (*iii*) AB_5 *type* (+ 5), *e.g.* ClF_5, BrF_5, IF_5 (*iv*) AB_7 *type* (+ 7), *e.g.* IF_7. The number given in the bracket indicates the oxidation number of A atom. A halogen atom is larger than B halogen atom, *i.e.* A atom is less electronegative than B atom. Interhalogen compounds are named as the halides of less electronegative halogen atom. Thus ClF is called *chlorine monofluoride* and not *fluorine monochloride*, since the electronegativity of Cl atom is less than that of F.

General Methods of Preparation.

Following are the important general methods by which interhalogen compounds can be prepared.

1. By the direct combination of halogens. All the interhalogens, except IF_7, can be prepared by the direct combination of the halogens under appropriate conditions. The following examples are noteworthy. For the preparation of AB_3 and AB_5 interhalogen compounds excess of B atom must be used in the reaction mixture.

$$\underbrace{Cl_2 + F_2}_{\text{(equal volumes)}} \xrightarrow{250^\circ} 2ClF$$

$$Cl_2 + 3F_2 \text{ (excess)} \xrightarrow{250^\circ} 2ClF_3$$

$$\underbrace{I_2 + Cl_2 \text{ (liquid)}}_{\text{in equimolecular amount}} \longrightarrow 2ICl$$

$$I_2 + 3Cl_2 \text{ (liquid and in excess)} \longrightarrow 2ICl_3$$

$$Br_2 \text{ (vapour)} + 3F_2 \text{ (diluted with } N_2) \longrightarrow 2BrF_3$$

$$I_2 + 3F_2 \text{ (in freon)} \xrightarrow{-78^\circ C} 2IF_3$$

$$Br_2 + 5F_2 \text{ (excess)} \longrightarrow 2BrF_5$$

2. From lower interhalogens. Higher interhalogens can be prepared by the interaction of lower interhalogens with halogens. This method is particularly used for the preparation of *halogen fluorides*. The following examples illustrate the method.

$$ClF + F_2 \longrightarrow ClF_3$$

$$ClF_3 + F_2 \text{ (excess)} \xrightarrow{350^\circ} ClF_5$$

$$BrF_2 + F_2 \xrightarrow{200^\circ} BrF_5$$

$$IF_5 + F_2 \xrightarrow{270^\circ} IF_7$$

3. By miscellaneous methods. Some miscellaneous methods have been illustrated by the following examples :

$$6HCl + KIO_3 + 2KI \longrightarrow 2KCl + 3H_2O + 3ICl$$

$$Cl_2 + ClF_3 \xrightarrow{250\text{–}350^\circ} 3ClF$$

$$KCl + 3F_2 \xrightarrow{200^\circ} KF + ClF_5$$

$$3I_2 + 5AgF \longrightarrow 5AgI + IF_5$$

$$8F_2 + PbI_2 \longrightarrow PbF_2 + 3IF_7$$

General Properties.

1. Physical state. The interhalogen compounds may be covalent gases (*e.g.* ClF, BrF, ClF_3, IF_7), liquids (*e.g.* BrF_3, BrF_5, IF_5) or solids (*e.g.* ICl, IBr, IF_3, ICl_3).

2. Colour. Although many of the interhalogen compounds containing fluorine are *colourless*, yet those made up of heavier halogens are *coloured*. The colour becomes deeper with the increase of the molecular weight of the compound. In this behaviour these compounds resemble the halogens themselves.

3. Diamagnetic nature. Since all the valence electrons in interhalogen compounds are present as bonding or non-bonding (*i.e.* lone pairs) electron pairs, these compounds are diamagnetic in nature.

4. Heat of formation. All these compounds have low heats of formation. For example these values for IBr and BrCl are –25 and –0.34 kcal/mole respectively. These are extremely volatile compounds. In general, compounds containing fluorine are more volatile than those containing chlorine, bromine or iodine.

5. Boiling points. For each type of interhalogen compounds, the boiling points increase with the increase in the electronegativity difference between A and B atoms.

6. Thermal stabitity. Thermal stability of AB type interhalogen compounds decreases with the decrease in electronegativity difference between A and B atoms. Thus the order of stability of some AB compounds is as :

IF (= 1.5) > BrF(1.2) > ClF(1.0) > ICl (0.5) > IBr (0.3) > BrCl(0.2)

In parentheses are given the electronegativity difference between A and B atoms. The above order is also explained by saying that greater is the difference between A and B, the more polar is the A—B bond and hence greater is the thermal stability of AB compound.

7. Reactivity. AB type compounds are more reactive than A_2 and B_2 molecules, since A—B bond in AB compounds is weaker than A—A and B—B bonds in A_2 and B_2 molecules respectively. Thus AB type compounds convert the metals into a mixture of two halides. For example :

$$ICl + 2Na \longrightarrow NaI + NaCl$$

The order of reactivity of some interhalogen compounds has been found as :

$$ClF_3 > BrF_3 > IF_7 > BrF_5 > IF_5 > BrF.$$

8. Hydrolysis. Hydrolysis gives halogen acid and oxy-halogen acid. The oxy-halogen acid is of larger (*i.e.* central) halogen atom. Examples are :

				Halogen acid		*Oxy-halogen acid*
$BrCl$	+	H_2O	$\longrightarrow$	HCl	+	$HOBr$
ICl	+	H_2O	$\longrightarrow$	HCl	+	HIO
ICl_3	+	$2H_2O$	$\longrightarrow$	$3HCl$	+	$HIO2$
IF_5	+	$3H_2O$	$\longrightarrow$	$5HF$	+	HIO_3
BrF_5	+	$3H_2O$	$\longrightarrow$	$5HF$	+	$HBrO_3$
IF_7	+	$6H_2O$	$\longrightarrow$	$7HF$	+	H_5IO_6

It may be noted that the oxidation state of A atom does not change during hydrolysis.

9. Reaction with non-metallic and metallic oxides. Non-metallic and metallic oxides are fluorinated by halogen fluorides to give the corresponding fluorides.

$$4BrF_3 + 3SiO_2 \longrightarrow 3SiF_4 + 2Br_2 + 3O_2$$
$$4BrF_3 + 2WO_3 \longrightarrow 2WF_6 + 2Br_2 + 3O_2$$

10. Addition reactions. The diatomic interhalogens (AB type compounds) add at olefinic double bond sites.

$$-CH=CH- + ICl \longrightarrow -\underset{\displaystyle I}{\underset{|}{CH}}-\underset{\displaystyle Cl}{\underset{|}{CH}}-$$

$$CH_2=CH_2 + BrCl \longrightarrow \underset{\displaystyle Br}{\underset{|}{CH_2}}-\underset{\displaystyle Cl}{\underset{|}{CH_2}}$$

11. Reaction with alkali metal halides. Reaction with alkali metal halides gives polyhalides.

$$IBr + NaBr \longrightarrow NaIBr_2$$
$$ICl + KCl \longrightarrow KICl_2$$
$$BrCl + CsI \longrightarrow CsIBrCl$$
$$ICl_3 + KCl \longrightarrow KICl_4$$
$$BrF_3 + KF \longrightarrow KBrF_4$$

Polyhalides

Uses of Interhalogen Compounds.

Uses of some interhalogen compounds are given below :

(*i*) (*a*) A solution of ICl in glacial acetic acid is used for the estimation of iodine number which is a measure of the unsaturation of oils and fats.

$$-CH=CH- + ICl \longrightarrow \underset{\displaystyle I}{\overset{\displaystyle |}{-CH-}}\underset{\displaystyle Cl}{\overset{\displaystyle |}{-CH-}}$$

(*b*) ICl is also used to iodonate and chlorinate organic compounds. For example :

Salicylic acid + ICl (vapours) $\longrightarrow$ chlorinated product of salicylic acid

Salicylic acid + ICl (solution in nitrobenzene) $\longrightarrow$ Iodonated product of salicylic acid

(*b*) The solution of ICl is commonly used as a catalyst in oxidising As_2O_3 by $Ce(SO_4)_2$. ICl is also used to prepare polyhalides.

(*ii*) (*a*) BrF_3 is used as a fluorinating agent since it converts many metals, metallic oxides and chlorides into their fluorides. For example :

$$6M + 2BrF_3 \longrightarrow 6MF + Br_2$$
$$3MCl + BrF_3 \longrightarrow 3MF + BrCl_3$$

(*b*) Many metal fluorides have been converted into complex fluorides. For example :

$$\left.\begin{aligned} KF + BrF_3 &\longrightarrow K^+[BrF_4]^- \\ SbF_3 + BrF_3 &\longrightarrow Sb^{3+}[BrF_6]^{3-} \end{aligned}\right\} \text{polyhalides}$$

Thus BrF_3 is used to prepare polyhalides.

(*iii*) ClF_3 has been used as a fluorinating agent, as an incendiary and in cutting oil well tubes. It is also used as an oxidiser for propellants. It is also used to prepare polyhalides.

(*iv*) ICl_3 is used in medicine. It is also used to prepare polyhalides.

(*v*) BrF_5 is used in organic synthesis. It is also used as an oxidiser for propellants.

Some Important Interhalogen Compounds

1. Iodine Monochloride, ICl.

Preparation. It is prepared as a dark red liquid by passing Cl_2 over I_2 or by heating I_2 with $KClO_3$.

$$I_2 + Cl_2 \longrightarrow 2ICl$$
$$KClO_3 + I_2 \longrightarrow KIO_3 + ICl$$

Properties. (*i*) It solidifies on standing even at room temperature (15–25°). From this solid two forms of the compound may be obtained. These are (*a*) α-form which is ruby-red. It is a stable form (m.pt. = 27.2°) (*b*) β-form which is red rhombic. It is a meta stable form (m.pt. = 14.0°, b.pt. = 97.4°). These two forms are identical in the gaseous state. These can be separated by cooling the liquid ICl below 14° and by adding to the liquid a crystal of either of the two forms.

(*ii*) ICl is soluble in water and gets hydrolysed by it.

$$5ICl + 3H_2O \longrightarrow 2I_2 + HIO_3 + 5HCl$$

(*iii*) It also dissolves in alkalies to form I_2, iodate and chloride

$$5ICl + 6NaOH \longrightarrow 2I_2 + NaIO_3 + 5NaCl + 3H_2O$$

(*iv*) ICl is an electrical conductor when in the molten state. Thus when ICl is in the molten state, it ionises as :

$$2ICl \rightleftarrows I^+ + ICl_2^-$$

$$2I^+ + 2e^- \longrightarrow I_2 \text{ (}At\ cathode\text{)}$$

$$2ICl_2^- \longrightarrow I_2 + 2Cl_2 + 2e^- \text{ (}At\ anode\text{)}$$

The liberation of I_2 at cathode and both I_2 and Cl_2 at anode shows that ICl is an ionic compound and in it iodone is present as I^+ ion (*unipositive iodine*).

Uses. (*i*) A solution of ICl in glacial acetic acid is used for the dertermination of iodine number which measures the unsaturation of oils and fats. (*ii*) RICl is also used to iodate and chlorinate organic compounds. (*iii*) The solution of ICl is used as a catalyst in oxidising As_2O_3 by $Ce(SO_4)_2$. (*iv*) It is also used to prepare polyhalides (*v*) Because of the formation of I^+ cation, ICl is also used as an electrophilic iodinating agent. For example, it converts acetanitride into 4-iodoacetanitride and salicylic acid into 3, 5-diodosalicylic acid in nitrobenzene.

2. Iodine Monobromide, IBr.

Preparation. It is obtained by the direct combination of the elements.

$$I_2 + Br_2 \longrightarrow 2IBr$$

Properties. (*i*) It is a hard, crystalline solid of grey-violet colour.

(*ii*) Its vapour dissociates to a small extent on heating.

$$2IBr \rightleftarrows I_2 + Br_2$$

(*iii*) IBr is an electrical conductor when in the molten state. It ionises as :

$$IBr \longrightarrow I^+ + Br^-$$

Thus in IBr, iodine is present as I^+.

3. Iodine Trichloride, ICl_3.

Preparation. (*i*) It is obtained by the action of excess of Cl_2 on I_2 or on ICl at 100°C.

$$3Cl_2 \text{ (}Excess\text{)} + I_2 \longrightarrow ICl_3$$

$$Cl_2 \text{ (}Excess\text{)} + ICl \longrightarrow ICl_3$$

(*ii*) It is also formed when dry HCl gas reacts with heated I_2O_5.

$$I_2O_5 \text{ (heated)} + 10HCl \text{ (dry gas)} \longrightarrow 2ICl_3 + 5H_2O + 2Cl_2$$

(*iii*) It is also formed along with ICl by the action of HI on Cl_2

$$4HI + 5Cl_2 \longrightarrow 4HCl + I_2 + ICl + ICl_3$$

Properties. (*i*) It is a lemmon-yellow crystalline solid which fumes readily. It is soluble in organic solvents, liq.NH_3 and liq.SO_2.

(*ii*) It forms crystalline additive compounds with metallic chlorides. These compounds dissociate on exposure to air, giving ICl_3 and MCl.

$$MCl + ICl_3 \rightleftarrows \underset{\text{Additive compound}}{MICl_4}$$

(*iii*) With fluorides of K, Rb, Cs, it gives polyhalides of $MICl_3F$ type.

(*iv*) ICl_3 is completely hydrolysed by H_2O.

$$2ICl_3 + 3H_2O \longrightarrow 5HCl + HIO_3 + ICl$$

(*v*) ICl_3 dissociates on heating at 68° giving ICl and Cl_2.

$$ICl_3 \longrightarrow ICl + Cl_2$$

(*vi*) It reacts with CS_2 as :

$$4ICl_3 + 3CS_2 \longrightarrow CCl_4 + 2CSCl_2 + 2S_2Cl_2 + 2I_2$$

(*vii*) Like ICl, ICl_3 is also decomposed by KOH solution

$$3ICl_3 + 12KOH \longrightarrow 9KCl + KI + 2KIO_3 + 6H_2O$$

(*viii*) Molten ICl_3 has a high conductivity (= 8.4×10^{-3} ohm^{-1} cm^{-1}). The liberation of I_2 and Cl_2 at both electrodes indicates that ICl_3 is ionised into $[I^{3+}Cl_2]^+$ and $[I^{3+}Cl_4]^-$ ions.

$$2ICl_3 \rightleftarrows [ICl_2]^+ + [ICl_4]^-$$

$$2[ICl_2]^+ + 2e^- \longrightarrow I_2 + 2Cl_2 \ (At\ cathode)$$

$$2[ICl_4]^- - 2e^- \longrightarrow I_2 + 4Cl_2 \ (At\ anode)$$

Uses. ICl_3 is used in medicines. It is also used in the preparation of polyhalides.

4. Chlorine Trifluoride, ClF_3.

Preparation. It is prepared when Cl_2 is heated with excess of F_2 in a copper vessel at 250°C.

$$Cl_2 + 3F_2 \longrightarrow 2ClF_3$$

Properties. It is a colourless gas which condenses to give a pale-green liquid (b.pt. = – 12°C). It is exceedingly reactive and attacks a number of metals. It also attacks glass vigorously. It reacts with water to give a red liquid which crystallises at –70°C. The compound formed is ClFO.

Uses. (*i*) ClF_3 has been used as a fluorinating agent, as an incendiary and in cutting oil well tubes. (*ii*) It is also used as an oxidiser for propellants (*iii*) It is also used for the preparation of polyhalides.

5. Iodine Pentafluoride, IF_5.

Preparation. It is formed by the direct combination of the elements or by the action of F_2 on heated I_2O_5.

$$2I_2O_5 \text{ (heated)} + 10F_2 \longrightarrow 4IF_5 + 5O_2$$

It may also be prepared by heating together I_2 and AgF.

$$5AgF + 3I_2 \xrightarrow{\text{Red heat}} IF_5 + 5AgI$$

or

$$10AgF + I_2 \longrightarrow 2IF_5 + 10Ag$$

Properties. It is a colourless liquid (b.pt. = 98°). Its vapours attack the respiratory organs. It is a very poor conductor. It decomposes on heating to I_2 and IF_7

$$7IF_5 \longrightarrow I_2 + 5IF_7$$

When heated with H_2O, it is hydrolysed giving successively IOF_3, IO_2F and finally I_2O_5.

$$2IF_5 + 5H_2O \longrightarrow I_2O_5 + 10HF$$

Sulphur is converted to SF_6. Phosphorus in an atmosphere of IF_5 forms I_2 and PF_3. I_2O_5 when boiled with IF_5 gives white crystals of IOF_3.

$$3IF_5 + I_2O_5 \longrightarrow \underset{\substack{\text{iodine}\\\text{oxy-}\\\text{fluoride}}}{5IOF_3}$$

These crystals decompose at 100° to give back IF_5 and IO_2F which is a white stable solid.

$$2IOF_3 \xrightarrow{100^\circ} IF_5 + IO_2F$$

I_2O_4 dissolves in IF_5 to give IOF_3 and some I_2.

The oxides P_2O_5, V_2O_5, Sb_2O_5, Cr_2O_3 and WO_3 dissolve in hot IF_5 to form POF_3, VOF_3, $SbF_5.IO_2$, CrO_2F_2 and $WO_3.2IF_5$ respectively. Nitrogen (IV) oxide, NO_2, dissolves in IF_5 to give a cream coloured crystalline compound, $IF_5.NO_2$.

It is a good conductor of electricity and ionises as :

$$2IF_5 \rightleftarrows IF_4^+ + IF_6^-$$

6. Iodine Heptafluoride, IF_7.

Preparation. It may be prepared by refluxing IF_5 in a current of excess of F_2 through a tube of Pt heated to 270°

$$IF_5 + F_2 \xrightarrow{270^\circ} IF_7$$

When iodine reacts with excess of F_2 at 300°C, IF_7 is formed.

Properties. It is a colourless gas having mustly odour. It can be condensed to a colourless liquid or to a colourless crystalline solid. It reacts with most metals (except the platinum group), non- metals including Cl_2 and I_2, water to give periodate and fluoride ions, many inorganic compounds and a variety of organic materials. It explodes when heated with H_2. It is slowly decomposed by water. Two of fluorine atoms present in IF_7 can easily be removed.

Structure of Interhalogen Molecules

1. Structure and Shape of AB Type Interhalogen Molecules.

The structure and shape of AB type molecules can be illustrated by considering ICl molecule. In this molecule the central atom *viz.* I atom is sp^3 hybridised and the molecule has *linear shape* with I—Cl bond length = 2.32A°. For the details see chapter 8.

2. Structure and Shape of AB_3 Type Interhalogen Molecules.

The structure and shape of this type of intorhalogen compounds can be illustrated by considering ClF_3 molecule. In this molecule the central atom *i.e.* Cl atom is sp^3d hybridised and ClF_3 molecule has *slightly bent T-shape.* For details see chapter 8. Like ClF_3, BrF_3 molecule also has *T-shaped structure.*

4. Structure and Shape of AB_5 Type Molecules.

In IF_5 molecule the central atom *viz.* I atom is sp^3d^2 hybridised and the molecule has *square pyramidal* shape. For details see chapter 8. Like IF_5, ClF_5 and BrF_5 molecules also have square pyramidal shape which results from sp^3d^2 hybridisation of Cl and Br atoms respectively.

4. Structure and Shape of IF_7 Molecule.

This molecule has *pentagonal bipyramidal shape* which results from sp^3d^3 hybridisation of I atom (central atom). For details see chapter 8.

Polyhalide Ions and Polyhalides

The ions like I_3^-, IBr_2^-, $IBrF^-$, ICl_4^-, I_7^-, I_9^- (anions), ICl_2^+, BrF_2^+, ClF_2^+ (cations) etc. which contain more than two same or different halogen atoms are called *polyhalide ions.* The ionic compounds like $Cs^+[IBr_2]^-$, $K^+[ICl_4]^-$, $[N(CH_3)_4]^+[ICl_4]^-$, $[ICl_2]^+[SbCl_6]^-$, $[BrF_2]^+[SbF_6]^-$ etc. which contain polyhalide cations or anions are called *polyhalides.* As in case of interhalogens, here too the heavier halogen atom plays the role of central atom.

Preparation of Polyhalides

(*i*) Simple polyhalides like $K^+Cl_3^-$, $NH_4^+I_5^-$ etc. can be prepared by the action of halogen on metallic halides, *e.g.*

$$Cl_2 + KCl \longrightarrow K^+Cl_3^- \; ; \; 2I_2 + NH_4I \longrightarrow NH_4^+I_5^-$$

(*ii*) Mixed polyhalides like $Cs^+[ClF_4]^-$, $K^-[ICl_2]^-$ etc. can be prepared by the action of an appropriate gaseous halogen or interhalogen on a solid metallic halide in the absence of a solvent, *e.g.*

$$2F_2 + CsCl \longrightarrow Cs^+[ClF_4]^- \; ; \; ICl + KCl \longrightarrow K^+[ICl_2]^-.$$

(*iii*) Polyhalides of one type can be converted into the other type by the action of halogen or interhalogen on them. *e.g.*

$$K[ICl_2] + Cl_2 \longrightarrow K[ICl_4]$$
$$K[ClIBr] + ICl \longrightarrow K[Cl_2] + IBr$$

Properties

(*i*) Colour. All the polyhalides are coloured compounds. The depth of the colour increases with the increase of the atomic number of the halogen atoms present. Thus the bromoiodides are red and chlorobromides are yellow.

(*ii*) Dissociation in aqueous solution. The polyhalides are usually very soluble in water from which they can often be crystallised. Some of them get dissociated in water to free halogen and halide ion (metallic monohalide). For example :

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

The stability of metallic trihalides of MX_3 type having the same cation in the same oxidation state and different trihalide anions in aqueous solution towards dissociation to free halogen and metallic monohalide (MX halide) is in the order :

$$MI_3 > MBr_3 > MCl_3.$$

For the metallic trihalides having the same trihalide anion and different cations in the same oxidation state, the stability increases with the increase of the size of the cation. For example : $NaI_3 < KI_3 < RbI_3 < CsI_3$. Note that the size of Na^+, Rb^+ and Cs^+ cations increases from Na^+ to Cs^+.

The polyhalides containing ICl_4^- anion dissociate in aqueous solution to metal chloride and ICl_3; the latter then hydrolyses to iodate, IO_3^-.

$$M^+[ICl_4]^- \longrightarrow MCl + ICl_3] \times 5$$
$$5ICl_3 + 9H_2O \longrightarrow 3HIO_3 + 15HCl + I_2$$
$$5M^+[ICl_4]^- + 9H_2O \longrightarrow 5MCl + 3HIO_3 + 15HCl + I_2$$

or
$$5ICl_4^- + 9H_2O \longrightarrow 20Cl^- + 18H^+ + 3IO_3^- + I_2$$

***(iii)* Formation of complexes.** Some of the polyhalide ions form complexes with organic donor molecules. Some examples of such complexes are : $LiI_3 . 4C_6H_5CN$, $MI_3 . 2C_6H_5CN$ (M = Na or K).

***(iv)* Effect of heat : Thermal decomposition.** When the solid polyhalides are heated, they dissociate more or less readily. The ease of dissociation of a given polyhalide decreases with the increase of the size of the cation with which the polyhalide anion is associated. This means that *the stability of the solid polyhalides towards dissociation is maximum when the cation with which the polyhalide anion is associated is large.*

On thermal dissociation the polyhalides give the metal monohalide and halogen molecule or interhalogen molecule. For example :

$$CsI_3 \xrightarrow{\Delta} CsI + I_2$$
$$RbICl_2 \longrightarrow RbCl + ICl$$

When a polyhalide containing more than one type of halogen atoms undergoes thermal dissociation, the metal monohalide formed is always that which *has highest lattice energy.* Thus when $Cs^+[ICl_2]^-$ undergoes thermal dissociation, the products formed are CsCl + ICl and not CsI + Cl_2, since CsCl has higher lattice energy than CsI.

For trihalide ions formed by the same metal, the order of thermal stability is : $I_3^- > IBr_2^- > ICl_2^- > I_2Br^- > Br_3^- > BrCl_2^- > Br_2Cl^-$

***(v)* Reaction with halogens.** Sometimes when a polyhalide is allowed to react with a halogen molecule, one or two atoms of halogen present in the polyhalide are substituted by one or two atoms of the reacting halogen, as the case may be.

$$KIBr_2 + Cl_2 \longrightarrow KICl_2 + Br_2$$
$$CsBr_3 + I_2 \longrightarrow CsIBr_2 + IBr$$

Sometimes a higher polyhalide is formed.

$$KICl_2 + Cl_2 \longrightarrow KICl_4$$

***(vi)* Dissolution in liq. halogen or interhalogen.** Polyhalides may dissolve in liquid halogen or interhalogen to give solution from which the original polyhalide may be crystallised on evaporation. The polyhalides like $K^+[IBr_2]^-$, $NH_4^+[IBr_2]^-$ and $Rb^+[IBr_2]^-$ form solution in bromine.

Structure of Polyhalide Ions

1. Structure and Shape of Trihalide Anions.

Trihalide anions like ICl_2^-, I_3^- etc. have *symmetrical linear shape* (see chapter 8). This shape results from sp^3d hybridisation of I atom.

2. Structure and Shape of Trihalide Cations.

The trihalide cations like ICl_2^+, BrF_2^+, ClF_2^+ etc. have *angular shape* which results from sp^3 hybridisation of the central atom. For the details of the structure of ICl_2^+ ion see chapter 8.

Pseudohalides and Pseudohalogens

There are certain uninegative ions (*e.g.* CN^-, OCN^-, N_3^- etc.) which are made up of two or more electronegative atoms and resemble halide ions in some respects. These uninegative ions are called *pseudohalide ions.* Examples of some important pseudohalide ions are : cyanide ion (CN^-), isocyanide ion (NC^-), fulminate ion (ONC^-), cyanate or oxycyanide ion (OCN^-), isocyanate ion (NCO^-), thiocyanate ion (SCN^-), isothiocyanate ion (NCS^-), tellurocyanate ion ($TeCN^-$), selenocyanate ion ($SeCN^-$), isoselenocyanate ion ($NCSe^-$), azide ion (N_3^-), azidothiocarbonate ion or azido carbondisulphide ion ($SCSN_3^-$). The salts (ionic compounds) given by the pseudohalide ions [*e.g.* AgCN, $Pb(CNS)_2$ etc.] are called *pseudohalides.*

As the dimers of halide ions are called halogens, the covalent dimers of the pseudohalide ions are called *pseudohalogens* or *halogenoids.* So far only a limited number of pseudohalogens have been isolated and characterised. Examples of some pseudohalogens or halogenoids are : cyanogen, $(CN)_2$; oxy cyanogen $(OCN)_2$; thiocyanogen, $(SCN)_2$; tellurocyanogen, $(TeCN)_2$; selcnocyanogen, $(SeCN)_2$; azidocarbun disulphide $(SCSN_3)_2$.

Similarities between Halide Ions and Pseudohalide Ions.

Following are the important similarities between halide ions and pseudohalide ions.

1. Formation of ionic as well as covalent compounds. Like halide ions, pseudohalide ions also form ionic as well as covalent compounds. Ionic compounds are given by these ions with metals while covalent compounds ore given by the combination of these ions with non-metals or metalloids. Examples are :

Ionic compounds : AgCl(AgCN), $PbCl_2[Pb(CNS)_2]$, AgCl(AgCNS)

Analogous covalent compounds : ICl(ICN), $SiCl_4[Si(NCS)_4]$, $COCl_2[CO(N_3)_2]$, $SO_2Cl_2[SO_2(N_3)_2]$

The compounds given in parentheses are the analogous compounds given by pseudohalide ions.

2. Oxidation of hydracids. HX acids (X = Cl^-, Br^-, I^-) can he oxidised to free halogen (X_2). Similarly HY acids (Y = SCN^-, CN^- etc.) can also be oxidised to free pseudohalogen (Y_2). For example :

$$4HCl + MnO_2 \longrightarrow MnCl_2 + 2H_2O + Cl_2$$
$$4HSCN + MnO_2 \longrightarrow Mn(SCN)_2 + 2H_2O + (SCN)_2$$

3. Thermal decomposition of Pb (IV) salts. On heating some of the Pb(IV) salts of halide ions (*e.g.* $PbCl_4$) decompose to give Pb (II) salts and free halogen molecule. Similarly some Pb(IV) salts of pseudohalide ions [*e.g.* $Pb(SCN)_4$, $Pb(SeCN)_4$] decompose to give Pb(II) salts and free pseudohalogens. For example :

$$PbCl_4 \xrightarrow{\Delta} PbCl_2 + Cl_2$$
$$Pb(SCN)_4 \xrightarrow{\Delta} Pb(SCN)_2 + (SCN)_2$$

4. Formation of complex ions. Like halide ions, pseudohalide ions also form complex ions with transition metal ions. Examples are given below :

Complex ions given by halide ions : $[FeF_6]^{3-}$, $[CoCl_4]^{2-}$, $[Hg1_4]^{2-}$

Analogous complex ions given by pseudohalide ions : $[Fe(CN)_6]^{3-}$, $[Co(SCN)_4]^{2-}$, $[Hg(CN)_4]^{2-}$

5. Formation of inter-pseudohalogen and inter-halogen compounds. Halide ions can combine together to form inter-halogen compounds like ClF, ICl, IBr etc. Similarly pseudohalides can also combine together to form inter-pseudohalogen compounds like $CN.N_3$, CN.SCN etc.

6. Formation of monobasic hydracids. Like halide ions, pseudohalide ions also combine with H_2 to form monobasic hydracids.

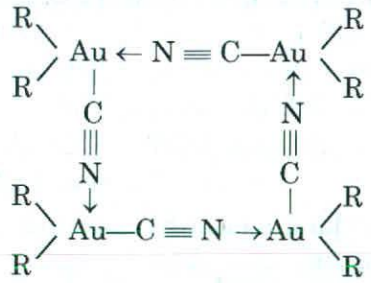
$$H_2 + 2Cl^- \longrightarrow 2HCl + 2e^-$$
$$H_2 + 2CN^- \longrightarrow 2HCN + 2e^-$$

7. Formation of insoluble salts. Like halide ions, pseudohalide ions give insoluble salts with Ag^+, Pb^{2+} and Hg^+ cations.

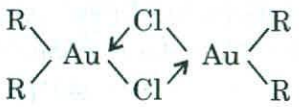
$$(a)\begin{cases} Ag^+ + Cl^- \longrightarrow AgCl\downarrow \\ Ag^+ + CN^- \longrightarrow AgCN\downarrow \end{cases} \qquad (c)\begin{cases} Pb^{2+} + 2Cl^- \longrightarrow PbCl_2\downarrow \\ Pb^{2+} + 2CNS^- \longrightarrow Pb(CNS)_2\downarrow \end{cases}$$

$$(b)\begin{cases} Hg^+ + Cl^- \longrightarrow HgCl\downarrow \\ Hg^+ + CNS^- \longrightarrow HgCNS\downarrow \end{cases}$$

8. Acting as bridging ligands. Like halide ions, pseudohalide ions also have more than one pair of electrons and hence can coordinate with two metal ions simultaneously. Consequently like halide ions, pseudohalide ions also can act as



$[R_2Au(CN)]_4$ compound
(Tetrameric)



$[R_2AuCl)]_2$ compound
(Dimeric)

bridging ligands. For example in $[R_2Au(CN)]_4$ which is a tetrameric compound, four CN^- ions act as bridging ligands. Similarly in $[R_2AuCl]_2$ which is a dimeric compound, two Cl^- ions at as bridging ligands.

Note that in each of the above compounds the geometry of Au atoms is square planar.

Dissimilarities between Halide Ions and Pseudohalide Ions.

The differences between the two classes of ions are given as follows :

(*i*) The hydracids formed by the pseudohalide ions on combination with hydrogen are relatively weaker than the analogous hydracids formed by the halide ions. For example HCN is a very weak acid while HCl is a very strong acid in aqueous medium. The weak nature of hydracids given by pseudohalide ions may be due to the poor electronegativity of the pseudohalogens.

(*ii*) Pseudohalide ions are stronger coordinating ligands than the halide ions and hence the complexes formed by pseudohalide ions are *low spin* (*i.e.* inner-orbital involving d^2sp^3 hybridisation) while those formed by halide ions are *high spin* (outer-orbital involving sp^3d^2 hybridisation). For example $[Fe(CN)_6]^{3-}$ is a low spin complex while $[FeF_6]^{3-}$ is a high spin complex.

That the pseudohalide ions are stronger ligands than the halide ions is due to the ability of the electron deficient pseudo halides to form a bond (from the pseudohalide to the metal) as well as π-bond (from the metal to the pseudohalide).

(*iii*) Pseudohalide ions, being made up of two hetero atoms, can function as *ambidentate* ligands. For example class *a* metals form isothiocyanate complexes like $[Co(NCS)_4]^{2-}$ in which N atom is coordinated to Co^{2+} ion while class *b* metals form thiocyanate complexes like $Pd(SCN)_4]^{2-}$ in which S atom is bonded to Pd^{2+} ion. Halide ions have no tendency to act as ambidentate ligands.

Similarities between Halogens and Pseudohalogens.

Following are the points showing the similarities between the two classes of compounds.

1. Volatile and dimeric nature. Like halogens, pseudohalogens are also dimeric and fairly volatile (with the exception of polymeric thiocynogen) in the free state.

2. Isomorphous nature. Pseudohalogens are isomorphous to halogens when in the free or solid state. For example Cl_2 is isomorphous to $(CN)_2$ and similarly Br_2 is isomorphous with $(SCN)_2$.

3. Addition to ethylenic double bond. Like halogens, pseudohalogens also add to ethylenic double bond linkage. For example :

$$H_2C = CH_2 + Cl_2 \longrightarrow \underset{\displaystyle Cl\ \ Cl}{\overset{\displaystyle H_2C-CH_2}{|\quad\ |}}$$

$$H_2C = CH_2 + (SCN)_2 \longrightarrow \underset{\displaystyle SCN\ \ SCN}{\overset{\displaystyle H_2C\ -\ CH_2}{|\quad\ |}}$$

4. Reaction with alkalies. Like halogens. pseudohalogens also react with alkalies. For example :

(*i*) $(SCN)_2 + 2KOH$ (*cold and dilute*) $\longrightarrow KSCN + KOSCN + H_2O$

$Cl_2 + 2KOH$ (*cold and dilute*) $\longrightarrow KCl + KOCl + H_2O$

(*ii*) $3(SCN)_2 + 6KOH$ (*hot and concentrated*) $\longrightarrow 5KSCN + KSCNO_3 + 3H_2O$

$3Cl_2 + 6KOH$ (*hot and concentrated*) $\longrightarrow 5KCl + KClO_3 + 3H_2O$

5. Formation of monobasic hydracids. Like halogens, pseudohalogens also combine with H_2 to form monobasic hydracids.

$$Cl_2 + H_2 \longrightarrow 2HCl$$

$$(CN)_2 + H_2 \longrightarrow 2HCN$$

Dissimilarity between Halogens and Pseudohalogens.

Pseudohalogens undergo polymerisation and form polymerised species. For example :

$$n(CN)_2 \xrightarrow{500°C} 2(CN)_n$$

$$n(SCN)_2 \xrightarrow{\text{Room temp.}} 2(SCN)_n$$

$$n(SeCN)_2 \xrightarrow{\text{On standing}} 2(SeCN)_n$$

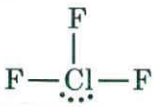
Halogens have no tendency to undergo polymerisation.

Conceptual Questions with Answers

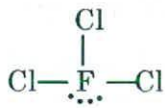
Q.1 Give reasons for the following :

(*i*) ClF_3 exists but FCl_3 does not.

Ans. Let us write down Lewis structure of the given molecules



σ-*bps* = 3, *lps* = 2,
Sum = 3 + 2 = 5 (sp^3d hybridisation of Cl-atom)
(correct structure)



σ-*bps* = 3, *lps* = 2,
Sum = 3 + 2 = 5 (sp^3d hybridisation of F-atom)
(wrong structure)

These structures show that central halogen atom should be sp^3d hybridised. sp^3d hybrisation of F-atom for the formation of FCl_3 is not possible since F-atom does not have d-orbitals. Thus due to the absence of d-orbitals in F-atom, F-atom is not able to undergo sp^3d hybridisation and hence cannot form FCl_3 molecule.

Since Cl-atom is bigger in size than F-atom, this atom can accomdate three small F-atoms round it but F-atom (smaller atom) cannot accomdate three larger Cl-atoms round it.

(*ii*) Interhalogens are more reactive than halogens.

Ans. We know that in the formation of X–Y bond in interhalogen molecule (XY), the overlapping between the two orbitals of dissimilar halogen atoms takes place while in the formation of X–X bond in halogen molecule (X_2), the overlapping between the two orbitals of similar halogen atoms takes place. Now, since the overlapping between the orbitals of similar atoms in X_2 molecule is more effective than that between the orbitals of dissimilar atoms in XY molecule, X–X bond in X_2 molecule is strong than X–Y bond in XY molecule. Due to weaker X–Y bond, interhalogen (XY) are more reactive than halogen (X_2).

Q.2 Discuss the structure of I_3^+ ion on the basis of hydrisation.

Ans. Positive charge on I_3^+ ion may be regarded as being present on central I-atom. Hence the structure of I_3^+ can be written as $:\ddot{I}-\overset{+}{\ddot{I}}-\ddot{I}:$. Since the central I^+ atom is surrounded by σ-*bps* + *lps* = 2 + 2 = 4, I^+ atom is sp^3 hybridised. Due to sp^3 hybridisation and the presence of two *lps* of electrons, I_3^+ ion has ***angular*** geometry.

Q.3 Write the structures of the following pseudohalide ions (*i*) Cyanide ion (*ii*) Isocyanide ion (*iii*) Cyanate ion (*iv*) Isocyanate ion (*v*) Thiocyanate ion (*vi*) Isothiocyanate ion (*vii*) Fulminate ion.

Ans. The structures of the given pseudohalide ions can be obtained by removing H^+ from the parental acids of these ions. Thus :

(*i*) $H-C\equiv N: \xrightarrow{-H^+} :\bar{C}\equiv N: + H^+$

Hydrocyanic acid or hydrogen cyanide — Cyanide ion

(*ii*) $H-N\rightleftarrows C: \xrightarrow{-H^+} :\bar{N}\rightleftarrows C: + H^+$

Isohydrocyanic acid or isohydrogen cyanide — Isocyanide ion

(*iii*) $H-\ddot{O}-C\equiv N: \xrightarrow{-H^+} :\bar{\ddot{O}}-C\equiv N: + H^+$

Cyanic acid — Cyanate ion or oxycyanide ion

(*iv*) $H-\ddot{N}=C=\ddot{O}: \xrightarrow{-H^+} :\bar{\ddot{N}}=C=\ddot{O}: + H^+$

Isocyanic acid — Isocyanate ion

(*v*) $H-\ddot{S}-C\equiv N: \xrightarrow{-H^+} :\bar{\ddot{S}}-C\equiv N: + H^+$

Thiocyanic acid — Thiocyanate ion

(*vi*) $H-\ddot{N}=C=\ddot{S}: \xrightarrow{-H^+} :\bar{\ddot{N}}=C=\ddot{S}: + H^+$

Isothio cyanic acid — Isothiocyanate ion

(*vii*) $\bar{\ddot{C}}\equiv\overset{+}{N}-\bar{\ddot{O}}:$

Fulminate ion

University Questions

1. Write a note on "Interhalogen Compounds". *(Bundelkhand 88)*
2. Give the reasons for the following :
   (*i*) All known interhalogen compounds are diamagnetic and contain an even number of atoms. *(Delhi Hons. 87)*
   (*ii*) Interhalogen compounds have covalent character. *(GND 84 S)*
   (*iii*) ClF_3 can be prepared but FCl_3 cannot be prepared. *(Punjab 85)*
   (*iv*) In halogen fluorides the number of fluorine atoms is always odd.
   (*v*) Interhalogen compounds are diamagnetic. *(Delhi 84, 85)*
   (*vi*) Interhalogen compounds are more reactive than halogens.
3. Write a concise account of polyhalides. *(Calcutta 86; Meerut M.Sc. 83, 84, 85)*
4. Discuss the similarities between halogens and pseudohalogens. *(Delhi 99)*
5. Give a brief account of interhalogen compounds. *(Kanpur 2000)*
6. What are interhalogen compounds? Discuss their preparation, important properties and structure. *(Lucknow 2000)*
7. How are IF_5 and BrF_3 prepared? *(Bharathiar 2000)*

CHAPTER

42

Elements of Group 18 (Zero) : Noble Gases

Zero group of the periodic table consists of six elements namely *helium* (Z = 2); *neon*, Ne (Z = 10); *argon*, Ar (Z = 18); *krypton*, Kr (Z = 36); *xenon*, Xe(Z = 54) and *radon*, Rn (Z = 86). These elements are also called by other names like *inactive gases, inert gases, rare gases* and *noble gases.*

Position of Inert Gases in the Periodic Table

The inert gases were not known at the time of Mendeleef when he gave his original classification of elements. He did not leave gaps for these gases although he left gaps for several other unknown elements. After their discovery a new group was introduced into the periodic table. In the modern periodic table, these may be placed in the zero group as well as in the VIII group because of the following reasons.

1. Reasons for placing in zero group. (*i*) *Chemical inertness.* These elements are chemically inert. The existence of such a group is expected from the fact that there must be a separating group between strongly electronegative halogens of VII A group and strongly electropositive alkali metals of IA group. Therefore, these elements should be placed in between VII A group and I A group, *i.e.*, in the zero group.

(*ii*) *Valency.* Valenoy is defined as the combining capacity of the element. The electronic configurations of these elements given as : He $\rightarrow 2(1s)$, Ne $\rightarrow$ 2, 8 $(2s^2p^6)$, Ar $\rightarrow$ 2, 8, 8 $(3s^2p^6)$, Kr $\rightarrow$ 2, 8, 18, 8 $(4s^2p^6)$, Xe $\rightarrow$ 2, 8, 18, 18, 8 $(5s^2p^6)$, Rn $\rightarrow$ 2, 8, 18, 32, 18, 8 $(6s^2p^6)$ indicate that the atoms of these elements have saturated shells. They have, therefore, no tendency either to lose, gain or hare electrons with the atoms of other elements. In other words, their combining capacity or valency is zero. Therefore, these elements should be placed in the zero group.

2. Reasons for placing in VIII group. (*i*) *Electronic cofiguration.* Electronic configurations of inert gases as given above, indicate that, except helium which has $1s^2$ configuration, all the elements have eight electrons in the outermost shell. Therefore, on this basis they should be placed in the VIII group.

(*ii*) *Analogy with other groups.* In the modern periodic table, all the groups, except VIII, are divided into two sub-groups A and B each. The elements of A sub-groups are normal elements, whereas those of B sub-groups are transitional. If the VIII group is also considered parallel to others, it should also be divided into two sub-groups *viz.* VIII A and VIII B. The VIII A group should contain inert elements and VIII B group should contain transitional elements. In such a case, the periodic table will be more symmetrical. Thus, from the above discussion it

is clear that the inert gases may be placed in both the groups, *i.e.*, zero and VIII. However, for the general reference they are still considered as the members of the zero group. The position of these gases is further justified because of the facts namely : (*a*) They are all colourless, odourless and tasteless gases, under ordinary conditions. (*b*) The specific heat ratio, *i.e.*, C_p/C_v is the same (1.66) for all gases, which indicates their mono-atomic character. (*c*) They show a regular gradation in their physical and chemical properties. (*d*) They do not have any resemblance with the elements of their neighbouring groups. (*e*) They are all chemically inert.

Occurrence of Noble Gases.

Excepting radon, all other noble gases occur throughout the universe in atomic state. Since radon is a radioactive element and hence decays rapidly, it does not occur in the free state. Other rare gases occur in the following sources :

(*i*) **In the stars and interstellar space.** The masses of the major planets Jupiter and Saturn are estimated to be due to 23% and 27% of helium respectively. The atmosphere of Mars consists of mostly N_2 and argon.

(*ii*) **In the earth's atmosphere.** The non-radioactive rare gases are present in the atmosphere to the extent of 1% by volume. The volume of each rare gas in 100 litres of this is as : He = 0.524 c.c., Ne = 1.82 c.c., Ar = 9.34 c.c., Kr = 0.114 c.c., Xe = 0.0087 c.c.

(*iii*) **In natural gas.** Helium and traces of neon are found in natural gas which is found in the wells of certain oil fields in U.S.A. At present most of helium is isolated from natural gas as the concentration of helium in it varies from 2 to 7%.

(*iv*) **In minerals and spring waters.** Noble gases are also found in certain minerals. Except helium, the concentration of other noble gases in minerals is quite low. For example, the concentration of helium in thorianite is 10.5 c.c. gm. Certain spring waters give off gases which contain helium and argon. The percentage of these gases in spring water is so low that these cannot be isolated.

Why Are the Rare Gases Chemically Inert?

The chemical inertness of these elements is due to the following reasons :

(*i*) We have already seen that the atoms of rare gases have saturated shells. They all have eight electrons in their outermost shells, except helium, which has two. They have, therefore, no tendency either to lose, gain or share electrons with atoms of other elements. These elements, thus, do not enter into chemical combination.

(*ii*) The atoms of these elements have all the electrons paired. Thus, the electrons are not available for sharing with the electrons of other atoms. Hence, they can not form covalent compounds.

(*iii*) The electronegativity and electron affinity of these elements are zero. Thus) these elements have no tendency to attract or accept electrons and hence, are unable to form compounds.

(*iv*) The ionization potentials of these gases are very high. Hence, the removal of the electron from the outermost shell is very difficult.

Facts Indicating the Mono-atomic Character of Inert Gases.

The mono-atomic character of inert gases can be established by the following facts :

(*i*) **Specific heat ratio.** The specific heat ratio, *i.e.*, Cp/Cu for all inert gases has been found to be 1.66, which is the theoretical ratio for all mono-atomic gases.

(*ii*) **Value of physical constants.** The values of other physical constants such as dielectric constant, refractive index etc., also confirm their .mono-atomic character.

(*iii*) **Electronic configuration.** The atoms of these elements have saturated shells. They have, therefore, no tendency to combine together to form polyatomic molecules and hence exist as single atoms.

History of Discovery of Rare Gases.

The credit for the discovery of rare gases goes to Lord Rayleigh and William Ramsay.

1. Discovery of argon—Cavendish in 1785, repeatedly sparked a mixture of purified air and excess of oxygen and absorbed the resulting oxides of nitrogen and unused oxygen in caustic potash and potassium pentasulphide solutions, respectively. He found that a small volume of the gas which was about 1/120 part of the original air, was left. It was neither nitrogen nor oxygen. Cavendish, however, could not draw any conclusion regarding the nature of the residual gas.

The experimental observation of Cavendish was not given any importance for a long time. Rayleigh in 1892, observed that the density of nitrogen isolated from air was 0.5% more than the density of nitrogen obtained by chemical means, *i.e.*, by the decomposition of urea or ammonium nitrite. Ramsay suggested that this difference of density was due to the presence of some heavier gas of the atmosphere. Rayleigh and Ramsay repeated Cavendish's experiment in a modified apparatus and found that the residual gas was chemically inert. They also removed various constituents of air. The residual gas thus obtained was the same as obtained by Cavendish's experiment. This gas was completely unreactive and different from all the known gases. On sparking in a discharge tube, it gave red light and a spectral line never observed before. This indicated the presence of a new element. It was named argon derived from the Greek word argon, meaning lazy.

2. Discovery of helium—Lockeyer and Frankland in 1868, observed a new yellow line in the chromosphere of the sun, during total solar eclipse. This line did not coincide with the D_1 and D_2 lines of sodium and Lockeyer called it D_3 line. This indicated the presence of a new element. It was named helium derived from the Greek word helios, meaning sun.

Hillebrand in 1888, observed that uranium minerals such as clevite, on treatment with dil. H_2SO_4 gave out a gas which he thought to be nitrogen. Ramsay who was constantly in the search of some other sources of argon. suspected the same gas to be argon. He examined the spectrum of the gas which indicated the presence of helium, the element already discovered by Lockeyer and Frankland in the chromosphere of the sun.

3. Discovery of neon, krypton and xenon. After the discovery of argon and helium, Ramsay and Travers collected large amounts of argon by the fractional evaporation of liquid air. This argon was then subjected to systematic fractional evaporation under different reduced pressures. From the first fraction, they isolated a new element which gave a number of red lines in the spectrum. It was named neon (meaning new). From the final fraction they isolated two more inert gases—krypton (meaning hidden) which gave green spectral lines and xenon (meaning strange) which gave a blue glow.

4. Discovery of radon—Dorn in 1900, discovered radon as one of the disintegration products of radium.

$$^{226}_{88}\text{Ra} \xrightarrow{-\,^{4}_{2}\text{He}} {}^{222}_{86}\text{Rn} + {}^{4}_{2}\text{He}$$

Isolation of Rare Gases From Dry Air (*Chemical Method*)

The method used for the isolation of rare gases from dry air is the chemical method. This method consists of the following two steps :

1. Isolation of Inert Gases Mixture from the Dry Air.

Different constituents of the air *viz.* CO_2, water vapour, O_2 and N_2 are removed from the air by any of the following methods and thus inert gases mixture which is free from CO_2, water vapour, O_2 and N_2 is obtained.

(i) Rayleigh and Ramsay first method. In this method, the different constituents of air, *i.e.*, carbon dioxide, water vapour, oxygen and nitrogen are removed, one by one, as shown below :

(*a*) ***Carbon dioxide.*** By passing over soda lime.

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

(*b*) ***Water vapour.*** By passing over P_2O_5.

$$P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4$$

(*c*) ***Oxygen.*** By passing over red hot Cu.

$$2Cu + O_2 \longrightarrow 2CuO$$

(*d*) ***Nitrogen.*** By passing over heated Mg.

$$3Mg + N_2 \longrightarrow Mg_3N_2$$

The process of passing air successively over red hot copper and heated magnesium is repeated till it is completely free from nitrogen and oxygen. The residual gas is a mixture of inert gases.

(ii) Rayleigh and Ramsay second method. In this method, 9 volumes of air and 11 volumes of oxygen are introduced into a glass globe of 50 litres capacity. This glass globe is fitted with two heavy platinum electrodes through which a transformer discharge of 600–800 volts is passed (Fig. 42.1). The nitrogen of the air combines with excess of oxygen to form oxides of nitrogen. Now a continuous stream of caustic soda solution is introduced into the glass globe through a tube. The oxides of nitrogen are absorbed by the alkali and used up caustic soda solution is taken away by another tube.

$$N_2 + O_2 \xrightarrow{\text{Electric}} 2NO$$

$$2NO + O_2 \xrightarrow{\text{Discharge}} 2NO_2$$

$$2NaOH + 2NO_2 \longrightarrow NaNO_2 + NaNO_3 + H_2O$$

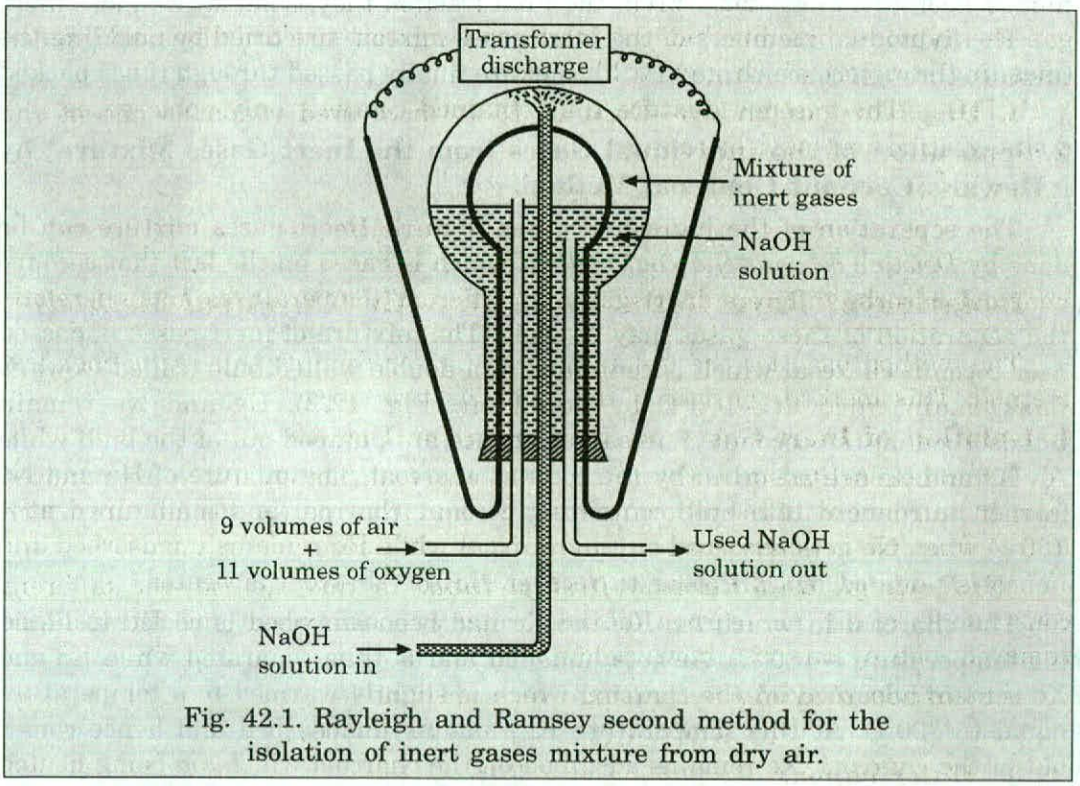


Fig. 42.1. Rayleigh and Ramsey second method for the isolation of inert gases mixture from dry air.

As a result of the above method, most of O_2 and N_2 is removed from the air in the glass globe. The mixture of residual gases contains noble gases with traces of O_2. The mixture of residual gases is passed through tubes containing alkaline pyrogallol in which O_2 gas gets absorbed and the mixture of rare gases which is free from O_2 gas comes out.

(iii) Fisher Ringe's method. In this method, the air free from moisture and carbon dioxide is passed over a heated (800°C) mixture containing 90% calcium carbide and 10% calcium chloride in an iron tube, when the following reactions take place :

$$CaC_2 + N_2 \xrightarrow{800°C} \underset{\text{calcium cyanamide}}{CaCN_2} + C$$

$$C + \tfrac{1}{2}O_2 \longrightarrow CO$$

$$C + O_2 \longrightarrow CO_2$$

$$2CaC_2 + 3CO_2 \longrightarrow 2CaCO_3 + 5C$$

The mixture of gases containing CO and CO_2 so obtained is passed over heated copper oxide when CO is oxidized to CO_2 and CO_2 thus formed is absorbed by caustic potash solution.

$$CuO + CO \longrightarrow Cu + CO_2$$
$$2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$$

The individual members of the inert gases mixture are dried by bubbling the mixture through concentrated H_2SO_4 and are finally passed through tubes packed with P_4O_{10}. The gaseous mixture thus obtained contains only noble gases.

2. Separation of the Individual Gases from the Inert Gases Mixture by Dewar's Coconut Charcoal Method.

The separation of the individual gases from the inert gases mixture can be done by *Dewar's coconut charcoal method* which is based on the fact that coconut charcoal adsorbs different inert gases at different temperatures and, therefore, the separation of these gases may be done. The mixture of inert gases is passed over coconut charcoal which is contained in a double walled bulb (called Dewar's flask) maintained at –100°C by liquid air (Fig. 42.2). He and Ne remain unadsorbed on the coconut charcoal and hence are pumped out of the bulb while Ar, Kr and Xe are adsorbed by the coconut charcoal. The mixture of He and Ne is then introduced into bulb containing coconut charcoal and maintained at –180°C when Ne gets adsorbed on the charcoal while He remains unadsorbed and hence is pumped out. In order to recover Ne the charcoal is heated.

The charcoal in which Ar, Kr and Xe had been adsorbed is cooled to liquid air temperature (–180°C). Ar gets liquefied and is thus separated while Kr and Xe remain adsorbed on the charcoal which is slightly warmed to a temperature equal to –90°C. At this temperature Kr ramains unadsorbed and hence comes out of the charcoal. Xe remains adsorbed on the charcoal which, on being heated at 0°C, gives Xe.

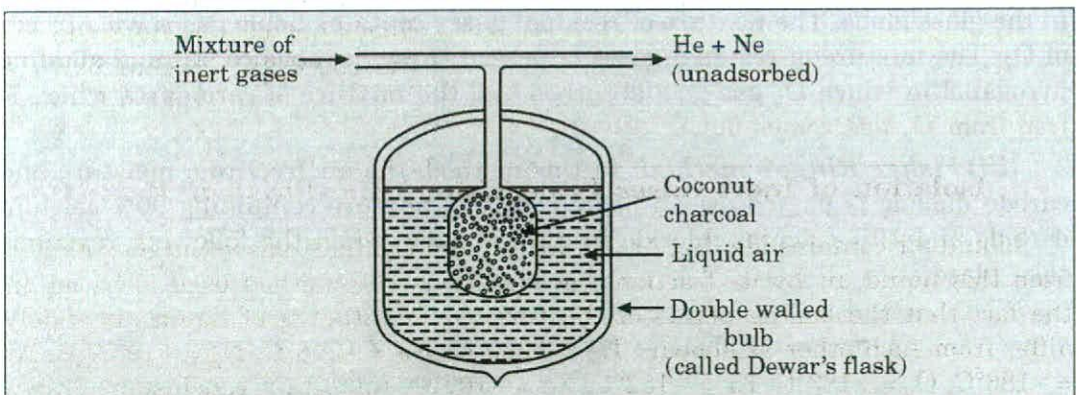
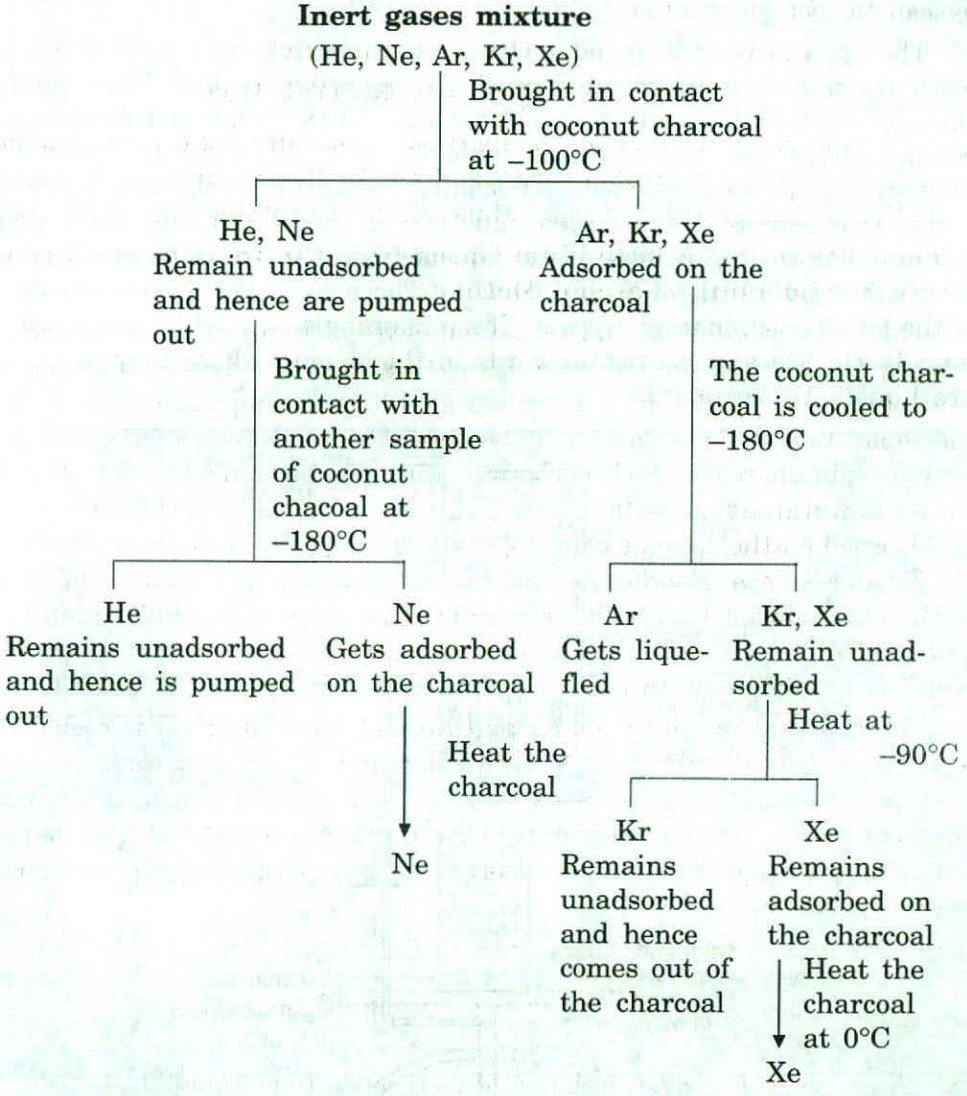


Fig. 42.2. Dewar's coconut charcoal method for the separation of inert gases from the inert gases mixture.

Flow sheet given below illustrates the various steps of this method.

Flow sheet for the separation of inert gases by Dewar's coconut charcoal method



Isolation of Inert Gases From Liquid Air (*Physical Method*).

Liquid air contains He, Ne, Ar, Kr, Xe, N_2 and O_2. Inert gases can be obtained from this liquid air by its fractional evaporation. The method used is based on the fact that the boiling points of the various constituents of liquid air widely differ from each other as shown : He = −269°C, Ne = −246°C, N_2 = −195.7°C, Ar = −186°C, O_2 = −183°C, Kr = −152°C, Xe = −107°C. Important conclusions drawn from these values can be summarised as : (*i*) He and Ne have very low b.pts. and hence during the process of liquefying the air, He and Ne will remain as gases while other constituents will change into liquids. (*ii*) There is little difference between the b.pts of Ar and O_2 and hence these gases will be collected more or less as a single fraction, (*iii*) Kr and Xe have fairly high boiling points as compared

to those of N_2, Ar and O_2. Therefore, Kr and Xe are always found in the less volatile portion of the liquid air and are always easily separated from other gases.

The apparatus used in this method consists of two fractionating columns *viz. lower fractionating column* and *upper fractionating column.* These columns are provided with baffle plates on the inner side. There is a reservoir between these columns. This reservoir contains liquid O_2. (Fig. 42.3). Air free from CO_2 and moisture (as these substances, on cooling, change into solid and hence clog the pipes) is compressed and cooled and then is introduced into the fractionating column. The cooling results in the liquefaction of less volatile gases namely O_2, Ar, Kr, Xe and a little of N_2 (*Fraction A*). These gases get collected at the bottom of the lower fractionating column. The remaining gases (which are more volatile) namely He, Ne and N_2 rise upwards in the column where they are cooled and are liquefied (*Fraction B*).

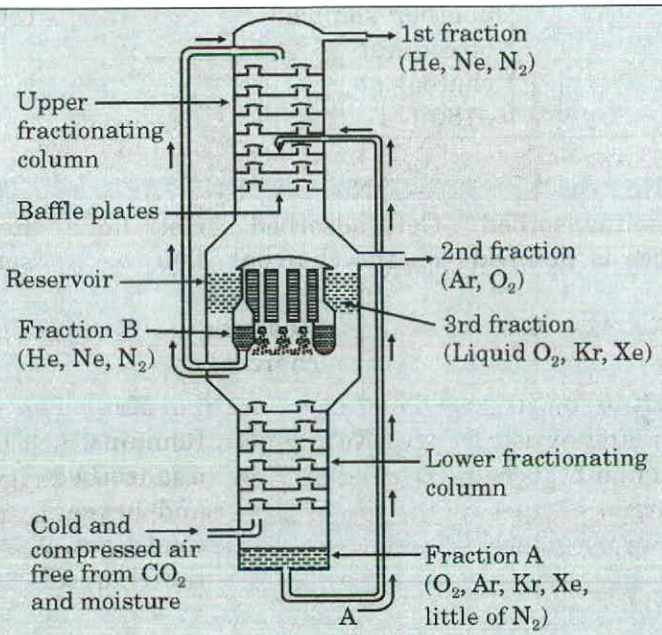


Fig. 42.3. Isolation of inert gases from liquid air.

Now the fraction A (O_2, Ar, Kr, Xe and a little of N_2) is pumped up from the bottom and is dropped from the middle of the upper fractionating column. The fraction B (He, Ne and N_2) is also pumped and is dropped from the top of the upper fractionating column. By this operation the liquid air gets separated into three fractions *viz.* (*a*) *1st fraction.* This fraction contains most volatile gases namely He, Ne and N_2. The mixture of these gases escapes from the top of the upper fractionating column. (*b*) *2nd fraction.* This fraction contains Ar and O_2. The mixture of these gases escapes from the top of central reservoir. (*c*) *3rd fraction.* This fraction contains liquid O_2, Kr and Xe. The mixture of these gases gets collected at the bottom of the reservoir.

Now from these fractions the individual inert gases are obtained as follows :

(i) Separation of helium and neon from the 1st fraction. The first fraction containing He, Ne and N_2 is passed through a spiral tube cooled by liquid nitrogen. Here most of the nitrogen is condensed and a mixture of He, Ne and some N_2 passes out. The remaining N_2 is removed by passing the mixture over heated calcium carbide.

$$CaC_2 + N_2 \xrightarrow{800°C} CaCN_2 + C$$

The gaseous mixture containing He and Ne is then passed through a spiral tube cooled by liquid H_2 at –253°C when Ne solidifies (b. pt. –246°C) and is collected at the bottom, while helium in the gaseous state escapes from the top (Fig. 42.4).

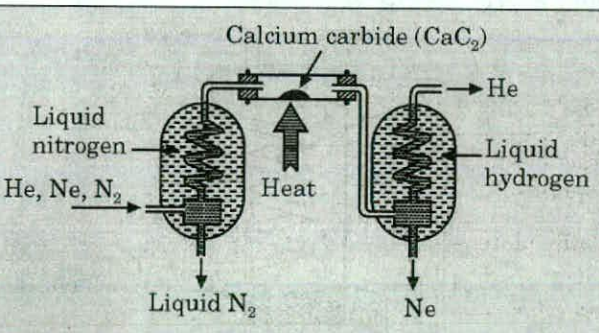


Fig. 42.4. Separation of He and Ne from *1st* fraction.

(ii) Separation of argon from the 2nd fraction. The second fraction containing argon and oxygen is passed through a column which is provided with a coil in which liquid N_2 is being circulated. Here most of the oxygen is condensed while more of argon escapes at the top (Fig. 42.5). The argon, so obtained, still contains some oxygen which is removed by passing over heated copper.

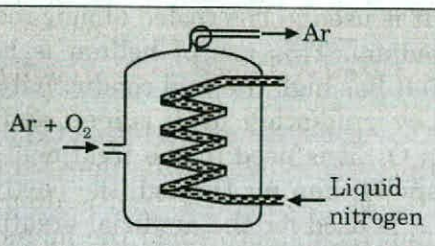


Fig. 42.5. Separation of Ar from the *2nd* fraction.

(iii) Separation of krypton and xenon from the 3rd fraction. From the third fraction containing liquid O_2, Kr and Xe, oxygen is removed by evaporation. The remaining liquid becomes richer in krypton and xenon. These two may be

separated easily by fractional evaporation as there is a wide difference in their boiling points (Kr = –152°C, Xe = –107°C) (Fig. 42.6).

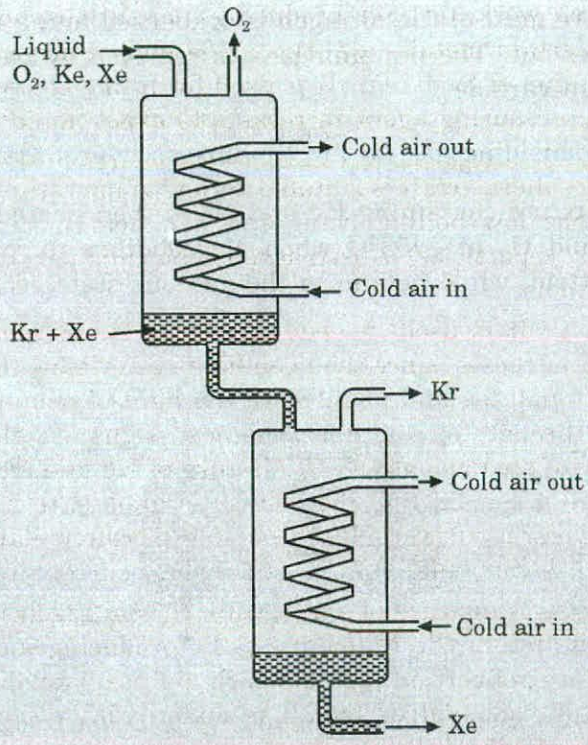


Fig. 42.6. Separation of Kr and Xe from in nature *3rd* fraction

Uses of Noble Gases.

Of all the noble gases, only He and Ar which are available easily and in plenty have got many uses. The uses are due to their chemical inertness and low boiling points. Important uses of noble gases are given below :

Uses of Helium. (*i*) It is used in gas cooled atomic reactors as a heat transfer gas, *i.e.* as a cooling medium. This use of helium is because of the following properties of this gas : (*a*) It has high thermal conductivity. (*b*) It has low viscosity. (*c*) It remains unaffected by irradiation. (*d*) It is inert and hence does not undergo corrosion. (*ii*) Mixed with O_2, it is used in the treatment of asthma. Being light, this gas diffuses more rapidly than air through the partly choked lung passages. The mixture of He and O_2 is used for the artificial breathing of asthma patients. This mixture keeps breathing steady. (*iii*) It is used for filling in balloons and airships as it is a light and non-combustible gas. For this purpose, a mixture of 85% helium and 15% hydrogen is generally used. (*iv*) The mixture of helium and oxygen is used for respiration by sea divers. The air proves harmful because nitrogen of the air dissolves in the blood at high pressure when the diver is under deep sea. When he comes to the surface, the pressure is suddenly decreased.

The bubbles of nitrogen gas now escape from the blood and are collected at joints which cause pains. Helium taken in the place of air is much less soluble in blood at high pressure. (*v*) Liquid helium is used for producing low temperatures required for research work. (*vi*) For producing inert atmosphere in the welding and metallurgy of certain metals (*e.g.* Mg, Al, Ti etc.) which are easily oxidised. (*vii*) In the preservation of food. (*viii*) It is used for filling electrical transformers. (*ix*) It is used as a pressuring agent in rockets to expel liquid O_2 and liquid H_2. (*x*) It is used as a shielding gas for arc welding as it protects both the arc and the metal from atmosphere. (*xi*) It is suitable for low temperature gas thermometry because this gas has low boiling point and has nearly ideal gas behaviour. (*xii*) Helium nucleus (α-particles) is used as a bombarding particle for the artificial disintegration of atoms.

Uses of Neon. (*i*) It is used in neon discharge lamps and signs which are used for advertising purposes, since the neon lights are visible from long distances and even visible through fog and mist. Since the light of neon signs has a better penetrating power through fog and mist, the neon signs are also used in beacon lights for the safety of air navigation. (*ii*) Mixture of He and Ne does not conduct electric current until a certain limiting voltage is applied to it and thereafter it starts conducting electric current. Based on this property, it is used in certain protective electrical devices like voltage stabilisers, current rectifiers etc.

Uses of Argon. (*i*) A mixture of argon with 15% nitrogen is filled in electric bulbs to increase the life of the filament. (*ii*) Fr producing inert atmosphere in welding and metallurgy of certain metals which are easily oxidised. (*iii*) In filling fluorescent tubes and radio-valves. (*iv*) It is mixed with neon in neon signs to obtain the lights of varying colours.

Uses of Krypton. (*i*) It is used in high efficiency miner's cap lamps. (*ii*) It is used in filling luminous tubes. (*iii*) Krypton-85, one of the isotopes of Kr, is used in electronic tubes for regulating the voltage and for testing the leaks. (*iv*) Krypton-85 is also used for the measurement of the thickness of sheets of metals and plastics.

Uses of Xenon. (*i*) It is used in discharge tubes for producing high speed flash of bluish light used in quick photography. (*ii*) Liquid xenon is used in bubble chamber for the detection of gamma photon and neutral mesons.

Uses of Radon. (*i*) It is used in the preparation of ointment for the treatment of cancer and other diseases. (*ii*) It is used for photographing the interior of opaque materials for locating the defects in steel castings.

Importance of Inert Gases in Theoretical Chemistry.

The inert gases have an important role in the development of theoretical chemistry as follows :

(*i*) **In the periodic table.** The introduction of these gases between strongly electronegative halogens and strongly electropositive alkali metals, has removed one of the anomalies of Mendeleef's periodic table. The zero group of inert gases acts as a separating group between these two classes of elements.

(*ii*) **In the elucidation of distribution of electrons in atoms.** The outermost shell of the atoms of inert gases has eight electrons, except helium which has two. This configuration accounts for the inertness of these elements. On this basis Bohr and Bury postulated that outermost shells of the atoms cannot have more than eight electrons.

(*iii*) **In the development of electronic theory of valency.** The modern concept of valency is based upon the structure of inert gases. According to the concepts of Kossel and Lewis, the atoms tend to acquire inert gas type of electronic configuration by transference of electrons from one atom to another (electrovalency), by sharing of electrons between two atoms (covalency) and by the combination of both the processes, *i.e.*, transference and sharing (co-ordinate).

(*iv*) **In the discovery of isotopes.** Neon was the first non-radioactive substance whose isotopes were first of all separated. On this basis, it was concluded that other elements may also consist of a mixture of two or more isotopes and thereafter, a number of isotopes of other elements have been identified and separated.

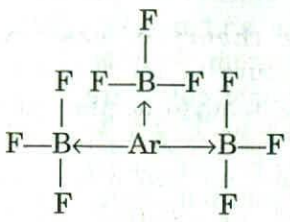
(*v*) **In radioactivity.** Helium is one of the disintegration products of some radioactive elements. This fact has been useful in the development of the theory of the radioactive disintegration and group displacement law.

Types of Compounds Formed by Inert Gases.

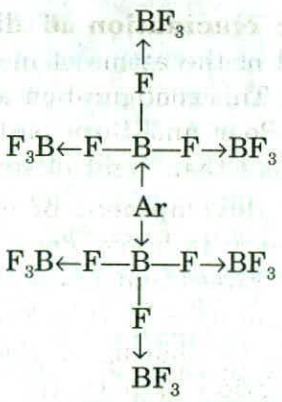
The atoms of inert gases have saturated shells and, therefore, they are chemically inert. Recent researches have shown that under certain specified conditions, they enter into chemical combinations and form some rare chemical compounds. The specified conditions and types of compounds formed by these gases are described below :

1. Compounds formed under excited conditions : Compounds of helium. These compounds known as helides are formed by sparking helium at low pressure in presence of mercury, tungsten etc., to form $HgHe_2$, $HgHe_{10}$, WHe_2. In addition, metal electrodes in the discharged tubes also form compounds, with helium like $BiHe_2$, FeHe, Pt_3He, PdHe. In these compounds, it is supposed that helium is adsorbed on the surface of the metal and, therefore, these compounds are not considered as true chemical compounds.

2. Compounds formed through co-ordination : Compounds of argon. Booth and Wilson in 1935 reported that argon forms a number of unstable compounds with varying number of BF_3 molecules, *e.g.*, $Ar.BF_3$, $Ar.2BF_3$, $Ar.3BF_3$, $Ar.6BF_3$, $Ar.8BF_3$ and $Ar.16BF_3$. In these compounds, argon atom donates a pair of electrons to boron atom. In the case of higher compounds, the fluorine atoms also donate pair of electrons. The structure of $Ar.3BF_3$ and $Ar.8BF_3$ are given below.



Structure of $Ar.3BF_3$



Structure of $Ar.8BF_3$

3. Compounds of inert gases with water : Formation of hydrates. The inert gases Ar, Kr and Xe form compounds with water at low temperature and high pressure. These compounds are known as hydrates. The compounds like $Ar.6H_2O$, $Kr.6H_2O$ and $Xe.6H_2O$ have been obtained and studied.

4. Compounds formed by physical trapping : Clathrate compounds. The inert gases argon, krypton and xenon form solid compounds with certain organic molecules such as phenol, hydroquinone, $C_6H_4(OH)_2$ under pressure. In these compounds the inert gases are enclosed into the crystal lattices of the organic molecules. These compounds are known as clathrates. (Latin : *clathrate* = enclosed or protected by cross bars or grating). These are also referred to as *cage compounds.*

In clathrates *the noble gases are trapped into the cavities of crystal lattices of certain organic and inorganic compounds.*

The organic or inorganic substance having the cavities of crystal lattices is called the *'host'* while the atom of noble gases entrapped in it is called the *'guest'.*

Organic or inorganic molecule (Host component) + Inert gas (Guest component) $\longrightarrow$ *Clathrate.*

Thus a simple clathrate can be represented by the formula *mH.n*G where H and G are the host und guest components . *m* and *n* represent the number of their molecules.

In these compounds the guest components are held by Van der Waals forces in crystalline cages formed by the host substances and consequently there is no chemical bonding involved in these compounds. It is not necessary that all the cavities in the host structure are filled. As a result the clathrates are normally *nonstoichiometric compounds.* The 'guest' can escape from the 'host' by heating the crystals or by dissolving them in a suitable solvent such as alcohol.

Conditions for the formation of clathrates.

(*i*) The crystal lattice of the host component should contain cavities of appropriate size. (*ii*) Size of the guest component should be such that it should fit in the cavities of the host component without bringing any atoms closer together than which corresponds to the van der Waals radii of the atoms.

Types and Preparation of Clathrates.

(*i*) ***Gas hydrates.*** Clathrates of Ar, Kr and Xe in which water molecule is the host component are called gas hydrates. These have been prepared by solidifying water in presence of Ar, Kr and Xe. The general formula of these is 5.75 H_2O.G where G = Ar. Kr or Xe. No gas hydrate of He and Ne has yet been prepared even under high pressure due to their small size and highly volatile nature. The stability of the gas hydrates increases as the atomic number of the *'guest'* atom increases. In noble gas hydrates the water molecules are linked together by hydrogen bonds, leaving roughly spherical voids which are occupied by gas atoms.

(*ii*) ***Quinol clathrates.*** Clathrates of Ar, Kr and Xe have been obtained by dissolving any of these in aqueous saturated solution of quinol under a pressure of 10–40 atmospheres followed by slow cooling.

These compounds are crystalline and can be stored for several years. However, when heated or dissolved in water, the gas atoms escape and quinol remains behind as such. Quinol molecules which form the cavities are held together by H-bonds.

(*iii*) ***Phenol and β-hydroquinone clathrates.*** Clathrates given by phenol and β-hydroquinone with Ar, Kr and Xe have been prepared by dissolving any of these gases in phenol or β-hydroquinone followed by slow crystallisation. These clathrates are also quite stable. Clathrate of β-hydroquinone can be represented by the formula, 3.β-hydroquinone. G or 3.β-$C_6H_4(OH)_2$.G where G = Ar, Kr or Xe.

Reasons for the Stability of Clathrates.

The stability of clathrates is due to the reasons namely : (*i*) The guest molecules are tightly held in the cavities of the host molecules. (*ii*) The guest molecules within the cages are at minimum potential energy. The guest molecules can be made to leave the cavities in host lattices only when the forces holding the molecular cages together are overcome. The forces can be overcome either by heating the crystals, or by dissolving the crystals in a suitable solvent such as alcohol.

Uses of clathrates.

(*i*) In the separation of noble gases, *e.g.*, Ne can be separated from Ar, Kr and Xe, since Ne is the only gas that does not form a clathrate with quinol. (*ii*) Kr-85 clathrate is used as a safe and useful source of beta radiations which are used for measuring thickness of guages. (*iii*) Xe-133 clathrate provides a compact source for gamma radiations. (*iv*) Clathrates play an important role in some physiological actions.

Compounds of Noble Gases

1. Xenon Difluoride, XeF_2.

Preparation. It has been prepared :

(*i*) by irradiating a mixture of xenon and fluorine with light from a high pressure mercury arc.

$$Xe + F_2 \xrightarrow[\text{mercury lamp}]{\text{Light from a}} XeF_2$$

(*ii*) by heating xenon and fluorine in the ratio of 1 : 3 in a nickel tube at 400°C. On cooling the vapours, it is obtained as colourless solid.

$$Xe + F_2 \xrightarrow[400°C]{\text{Ni tube}} XeF_2$$

(*iii*) by the action of dioxygen difluoride on xenon at –118°C

$$Xe + O_2F_2 \xrightarrow{118°C} XeF_2 + O_2$$

Properties. ***(i) Physical state.*** XeF_2 is a white crystalline solid at room temperature and can be sublimed. Its melting point is 140°C. It can be stored for an indefinite period in a nickel or Monel metal container.

(ii) Fluorinating properties. XeF_2 is a fluorinating agent, since it can fluorinate ethylene (C_2H_4) to $FH_2C—CH_2F$ and $F_2HC—CH_3$, C_6H_6 to C_6H_5F, propylene (C_3H_6) to $F_2HC—CH_2—CH_3$, NO to NOF, NO_2 to NO_2F and SO_3 to $S_2O_6F_2$.

$$2XeF_2 + 2H_2C = CH_2 \longrightarrow FH_2C—CH_2F + F_2HC—CH_3 + 2Xe$$
$$C_6H_6 + XeF_2 \longrightarrow C_6H_5F + Xe + HF$$
$$C_3H_6 + XeF_2 \longrightarrow F_2HC—CH_2—CH_3 + Xe$$
$$2NO + XeF_2 \longrightarrow 2NOF + Xe$$
$$2NO_2 + XeF_2 \longrightarrow 2NO_2F + Xe$$
$$2SO_3 + XeF_2 \longrightarrow S_2O_6F_2 + Xe$$

(iii) Substitution reactions. XeF_2 undergoes substitution reactions when reacted with strong protonic acids like HSO_3F, $HClO_4$, CF_3COOH etc.

$$XeF_2 + 2HX \longrightarrow XeX_2 + 2HF$$

Here X is SO_3F^-, ClO_4^-, CF_3COO^- etc.

(iv) Oxidising properties. XeF_2 can oxidise a number of compounds and is itself reduced to Xe. For example XeF_2 oxidises H_2 to HF, I_2 to IF (in presence of BF_3), Cl^- to Cl_2, Ce^{3+} to Ce^{4+}, NH_3 to N_2, HCl to Cl_2 etc.

$$H_2 + XeF_2 \longrightarrow 2HF + Xe$$
$$I_2 + XeF_2 \xrightarrow{BF_3} 2IF + Xe$$
$$2Cl^- + XeF_2 \longrightarrow Cl_2 + 2F^- + Xe$$
$$2Ce^{3+} + XeF_2 \longrightarrow 4Ce^{4+} + 2F^- + Xe$$
$$8NH_3 + 3XeF_2 \longrightarrow N_2 + 6NH_4F + 3Xe$$
$$2HCl + XeF_2 \longrightarrow Cl_2 + 2HF + Xe$$

(v) Hydrolysis reactions. (*a*) XeF_2 dissolves unchanged in water or in acidic solutions, but, on standing hydrolysis occurs slowly.

$$2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$$

(*b*) It is rapidly hydrolysed in an aqueous solution of a base.

$$2XeF_2 + 4OH^- \longrightarrow 2Xe + 4F^- + 2H_2O + O_2$$

(vi) Formation of addition compounds. XeF_2 can react with covalent pentafluorides like PF_5, AsF_5, SbF_5 and transition metal fluorides like NbF_5,

TaF_5 etc. In these reactions XeF_2 acts as a fluoride ion-donor (*Lewis base*) and the pentafluoride acts as a fluoride ion-acceptor (*Lewis acid*). The products are called adducts. These *adducts* are *ionic compounds.*

Lewis base		***Lewis acid***		***Adduct***
XeF_2	+	MF_5 (M = Sb, As)	$\longrightarrow$	$XeF_2.MF_5$ or $[XeF]^+[MF_6]^-$
XeF_2	+	$2SbF_5$	$\longrightarrow$	$XeF_2.2SbF_5$ or $[XeF]^+[Sb_2F_{11}]^-$
$2XeF_2$	+	MF_5	$\longrightarrow$	$2XeF_2.MF_5$ or $[Xe_2F_3]^+[MF_6]^-$
XeF_2	+	IF_5	$\longrightarrow$	$XeF_2.IF_5$

$XeF_2.IF_5$ has molecular lattice while other adducts are ionic compounds.

(vii) Action of HF. XeF_2 dissolves in HF without any reaction. The solution does not show any change in conductivity.

Structure. See chapter 8.

2. Xenon Tetrafluoride, XeF_4.

Preparation. It is prepared by heating a mixture of fluorine and xenon in the ratio of 5 : 1 in a nickel vessel at 400°C and 6 atmospheric pressure for a few hours. After heating, the reaction is quenched by cooling the nickel vessel rapidly in cold water. The excess of fluorine is removed by pumping at –78°C.

$$Xe + 2F_2 \xrightarrow[400°C,\ 6\ atoms]{Nickel\ vessel} XeF_4$$

The tetrafluoride prepared under the above mentioned conditions contains less than 8% XeF_3 and XeF_6 as impurities. These impurities can be removed from XeF_4 by sublimation.

Properties. ***(i) Physical State.*** XeF_4 is a white crystalline solid at room temperature and can be sublimed readily. Its melting point is 117.1°C. It is less volatile than XeF_6. It dissolves in CF_3COOH.

(ii) Storing. It can he stored for an idefinite period in a nickel or Monel metal container, but since XeF_4 is very susceptible to hydrolysis, even traces of water must be excluded.

(iii) Fluorinating properties. XeF_4 is a strong fluorinating agent, since it can fluorinate a number of compounds. For example XeF_4 fluorinates SF_4 to SF_6, Pt to PtF_4, C_6H_6 to C_6H_5F, ethylene (C_2H_4) to $FH_2C—CH_2F$ and $F_2HC—CH_3$, NO to NOF and NO_2 to NO_2F.

$$2SF_4 + XeF_4 \longrightarrow 2SF_6 + Xe$$
$$Pt + XeF_4 \longrightarrow PtF_4 + Xe$$
$$2C_6H_6 + XeF_4 \longrightarrow 2C_6H_5F + 2HF + Xe$$
$$2C_2H_4 + XeF_4 \longrightarrow FH_2C—CH_2F + F_2HC—CH_3 + Xe$$
$$4NO + XeF_4 \longrightarrow 4NOF + Xe$$
$$4NO_2 + XeF_4 \longrightarrow 4NO_2F + Xe$$

(iv) Reaction with Xe. Whan XeF_4 is warmed with excess of Xe, XeF_2 is formed.

$$XeF_4 + Xe\ (excess) \xrightarrow{\text{Warm}} 2XeF_2$$

(v) Oxidising properties. XeF_4 can oxidise a number of compounds and itself is reduced to Xe. For example XeF_4 oxidises H_2 to HF at 130°C, Hg to HgF_2, I^- to I_2, BCl_3, to Cl_2, Cl^- to Cl_2, NH_3 to N_2 etc.

$$XeF_4 + 2H_2 \xrightarrow{130°C} 4HF + Xe$$
$$XeF_4 + 2Hg \longrightarrow 2HgF_2 + Xe$$
$$XeF_4 + 4I^- \longrightarrow 2I_2 + 4F^- + Xe$$
$$3XeF_4 + 4BCl_3 \longrightarrow 4BF_3 + 6Cl_2 + 3Xe$$
$$XeF_4 + 4Cl^- \longrightarrow 2Cl_2 + 4F^- + Xe$$
$$XeF_4 + 6NH_3(g) \longrightarrow N_2 + 4NH_4F + H_2 + Xe$$

(vi) Hydrolysis reactions. (*a*) XeF_4 undergoes *disproportionation* in H_2O to form a highly explosive solid compound, XeO_3.

$$2XeF_4 + 3H_2O \longrightarrow Xe + XeO_3 + 6HF + F_2$$
$$6XeF_4 + 12H_2O \longrightarrow \underset{(Xe = 0)}{4Xe} + \underset{(Xe = +6)}{2XeO_3} + 24HF + 3O_2$$
$$(Xe = +4)$$

(*b*) Hydrolysis of XeF_4 at –80°C gives xenon oxydifluoride, $XeOF_2$

$$XeF_4 + H_2O \xrightarrow{-80°C} XeOF_2 + 2HF$$

(vii) Formation of addition compounds. XeF_4 can react with covalent pentafluorides like PF_5, AsF_5, SbF_5 and transition metal fluorides like NbF_5, TaF_5, RuF_5, OsF_5, RhF_5, IrF_5 and PtF_5. In these reactions XeF_4 acts as a fluoride ion-donor (*Lewis base*) and the covalent pentafluoride acts as a fluoride ion-acceptor (*Lewis acid*). The products are called *adducts*. These adducts are *ionic compounds*.

Lewis base		***Lewis acid***		***Adduct***
XeF_4	+	SbF_5	$\longrightarrow$	$XeF_4.SbF_5$ or $[XeF_3]^+[SbF_6]^-$
XeF_4	+	$2MF_5$	$\longrightarrow$	$XeF_4.2MF_5$ or $[XeF_3]^+[M_2F_{11}]^-$

Structure. See chapter 8.

3. Xenon Hexafluoride, XeF_6.

Preparation. (*i*) It is very difficult to prepare. However, it is prepared by heating a mixture of xenon and fluorine in the ratio of 1 : 20 in a nickel vessel and at 200–250°C and 50 atmospheric pressure.

$$Xe + 3F_2 \xrightarrow[50\ atm]{200–250°C} XeF_6$$

The yield of this method is 95%. It becomes 100% when the pressure is 2 atmospheres and the temperature is 702°C.

(*ii*) XeF_6 is also formed by the reaction of XeF_4 with O_2F_2 at –130°C.

$$XeF_4 + O_2F_2 \longrightarrow O_2 + XeF_6$$

Properties (*i*) *Physical state.* XeF_6 is white solid and can be sublimed at room temperature. It can be stored for an indefinite period in nickel or Monel

metal container, but, since XeF_6 is more susceptible to hydrolysis, even traces of water must be excluded. The melting point of XeF_6 is equal to 495°C at which XeF_6 melts to give a yellow liquid,. It is best stored in nickel container, since it attacks glass and silica (SiO_2)

$$2XeF_6 + SiO_2 \longrightarrow 2XeOF_4 + SiF_4$$
$$[XeOF_4 + SiO_2 \longrightarrow SiF_4 + XeO_3] \times 2$$
$$2XeF_6 + 3SiO_2 \longrightarrow 3SiF_4 + 2XeO_3$$

(ii) Fluorinating properties. Out of the three xenon fluorides, XeF_6 is the best fluorinating agent.

(iii) Oxidising properties. XeF_6 can oxidise a number of compounds and is itself reduced to Xe. For example :

$$XeF_6 + 3H_2 \longrightarrow 6HF + Xe$$
$$XeF_6 + 6HCl \longrightarrow 3Cl_2 + 6HF + Xe$$
$$XeF_6 + 8NH_3 \longrightarrow N_2 + 6NH_4F + Xe$$

(iv) Hydrolysis reactions. (*a*) Slow hydrolysis of XeF_6 by atmospheric moisture gives the solid XeO_3

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

(*b*) Small quantities of water bring about partial hydrolysis of XeF_6 to give a colourless liquid containing xenon oxyfluoride, $XeOF_4$

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$

(*c*) In *strongly basic solution* (2.5 M NaOH solution), XeF_6 is converted into xenate ion, $HXeO_4^-$ which slowly disproportionates into perxenate ion. XeO_6^{4-} and Xe.

$$[XeF_6 + 7OH^- \longrightarrow \underset{\text{Xenate ion}}{HXeO_4^-} + 3H_2O + 6F^-] \times 2 \quad ...(i)$$

$$2HXeO_4^- + 2OH^- \longrightarrow \underset{\substack{\text{Perxenate ion} \\ (Xe = +8)}}{XeO_6^{4-}} + \underset{(Xe = 0)}{Xe} + 2H_2O + O_2 \quad ...(ii)$$

On adding (*i*) and (*ii*) we get the final equation as :

$$2XeF_6 + 16OH^- \longrightarrow 8H_2O + 12F^- + XeO_6^{4-} + Xe + O_2$$

(v) Formation of addition compounds. XeF_6 reacts with covalent fluorides like PF_5, AsF_5, SnF_4, BF_3 etc. and transition metal fluorides like NbF_5, TaF_5 etc. In these reactions XeF_6 acts as a fluoride ion-donor (*Lewis base*) and the covalent pentafluoride acts as fluoride ion-acceptor (*Lewis acid*). The products are called adducts which are ionic compounds.

$$XeF_6 + AsF_5 \longrightarrow XeF_6.AsF_5 \text{ or } [XeF_5]^+[AsF_6]^-$$
$$4XeF_6 + SnF_4 \longrightarrow 4XeF_4.SnF_4 \text{ or } [Xe_4F_{15}]^+[SnF_5]^-$$
$$XeF_6 + BF_3 \longrightarrow XeF_6.BF_3 \text{ or } [XeF_5]^+[BF_4]^-$$
$$2XeF_6 + MF_5 \longrightarrow 2XeF_6.MF_5 \text{ or } [Xe_2F_{11}]^+[MF_6]^-$$

The formation of addition compounds shows that XeF_6 acts as a F^- ion-donor. However, there are many reactions in which XeF_6 acts as a F^- ion-acceptor as

is evident from the fact that XeF_6 can accept F^- ion from alkali metal fluorides (except LiF) like RbF, CsF etc. to form heptafluoro xenates (VI), $M^+[XeF_7]^-$

$$XeF_6 + \underset{(M = Rb, Cs)}{MF} \longrightarrow [M]^+[XeF_7]^-$$

On heating $M^+[XeF_7]^-$ salts decompose to form octafluoro xenates (VI), $M_2^+[XeF_8]^{2-}$

$$2M^+[XeF_7]^- \xrightarrow{50°C} XeF_6 + M_2^+[XeF_8]^{2-}$$

XeF_6 also reacts with NOF as follows :

$$2NOF + XeF_6 \longrightarrow [NO]_2^+[XeF_8]^-$$

(vi) Reaction with HF. XeF_6 reacts with HF and forms $[XeF_5]^+[HF_2]^-$ which is appreciably ionised.

$$HF + XeF_6 \longrightarrow [XeF_5]^+[HF_2]^- \longrightarrow [XeF_5]^+ + [HF_2]^-$$

(vii) Action of heat. On strong heating, it decomposes to give XeF_2 and XeF_4.

$$2XeF_6 \xrightarrow{\Delta} XeF_2 + XeF_4$$

Structure. See chapter 8.

4. Xenon Trioxide, XeO_3.

Preparation. (*i*) It can be obtained in small quantity by the hydrolysis of XeF_4 or XeF_6.

(*ii*) It can also be prepared by allowing the reaction between XeF_6 and quarts (SiO_2) to run for a prolonged period.

(*iii*) It can also be prepared by hydrolysing $XeOF_4$

$$XeOF_4 + 2H_2O \longrightarrow 4HF + XeO_3$$

Great care must be taken in the preparation of XeO_3, since it is highly explosive.

Properties (*i*). XeO_3 is a white non-volatile deliquescent solid and soluble in water. It explodes violently, when dry, on gentle heating, rubbing or pressing. It produces the same effect as T.N.T.

(*ii*) Its aqueous solution is weakly acidic, since it gives xenic acid, $H(HXeO_4)$ in water.

$$XeO_3 + H_2O \longrightarrow \underset{\text{Xenic acid}}{H_2XeO_4} \longrightarrow H^+ + \underset{\text{Xenate ion}}{HXeO_4^-}$$

With more quantity of H_2O, it gives H_6XeO_6 acid

$$XeO_3 + 3H_2O \longrightarrow H_6XeO_6 \longrightarrow H^+ + H_5XeO_6^-$$

(*iii*) In basic medium XeO_3 slowly disproportionates.

$$XeO_3 + OH^- \longrightarrow HXeO_4^-] \times 2 \qquad ...(i)$$

$$2HXeO_4^- + 2OH^- \longrightarrow XeO_6^{4-} + Xe + O_2 + 2H_2O \qquad ...(ii)$$

On adding (*i*) and (*ii*), we get the final equation as :

$$\underset{(Xe = +6)}{2XeO_3} + 4OH^- \longrightarrow \underset{\substack{(Xe = +8)\\ \text{Perxenate ion}}}{XeO_6^{4-}} + \underset{(Xe = 0)}{Xe} + O_2 + 2H_2O$$

(*iv*). XeO_3 is a strong oxidising agent. For example it oxidises Pu^{3+} to Pu^{4+} in presence of H^+ ions

$$6Pu^{3+} + XeO_3 + 6H^+ \longrightarrow 6Pu^{4+} + Xe + 3H_2O$$

XeO_3 can quantitatively be reduced by I^- ion

$$XeO_3 + 6H^+ + 9I^- \longrightarrow 3I_3^- + Xe + 3H_2O$$

(*v*) When a solution of XeO_3 is treated with KF or CsF, an oxo-fluoro salt, $M^+[XeO_3F]^-$ is obtained

(*vi*) With $XeOF_4$, XeO_3 gives XeO_2F_2

$$XeO_3 + XeOF_4 \longrightarrow 2XeO_2F_2$$

Structure. XeO_3 molecule has pyramidal shape as shown in Fig. 42.7. This shape results from sp^3 hybridisation of Xe atom. Each of Xe—O bond distances is equal to 1.76 A° and each OXeO bond angle is equal to 103°.

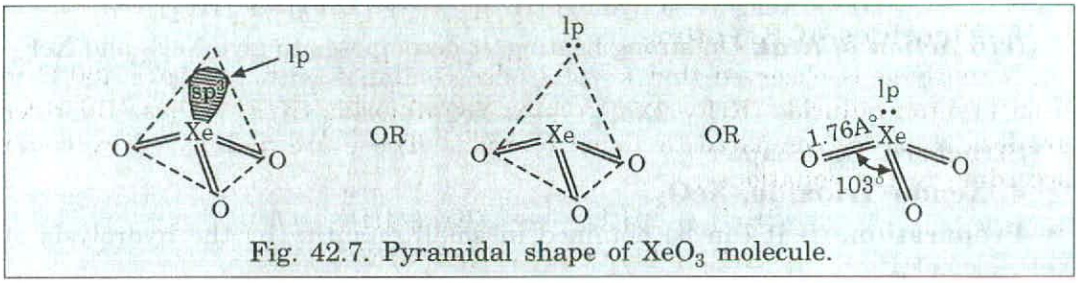


Fig. 42.7. Pyramidal shape of XeO_3 molecule.

5. Xenon Oxytetrafluoride, $XeOF_4$.

Preparation. (*i*) It is prepared by the controlled hydrolysis of XeF_6 with equimolar quantity of water (See the hydrolysis reactions of XeF_6).

(*ii*) $XeOF_4$ may also be prepared by heating XeF_6 in a silica tube at 50°C. When the yellow colour of XeF_6 disappears, the bulb is immediately cooled with solid CO_2. The vapours of SiF_4 are pumped out and $XeOF_4$ is collected.

$$2XeF_6 + SiO_2 \xrightarrow{50°C} 2XeOF_4 + SiF_4$$

Properties. (*i*) It is a clear, colourless mobile liquid which can be stored unchanged in nickel containers for long period.

(*ii*) It reacts with hydrogen to form xenon gas at 300°C,

$$XeOF_4 + 3H_2 \xrightarrow{300°C} Xe + H_2O + 4HF$$

(*iii*) With silica, it results in the formation of explosive trioxide, XeO_3.

$$XeOF_4 + SiO_2 \longrightarrow SiF_4 + XeO_3$$

(*iv*) With water it undergoes hydrolysis forming the explosive oxide, XeO_3 (See the preparation of XeO_3).

(*v*) (*a*) $XeOF_4$ also forms a few complexes with fluoride-ion acceptors (*e.g.* $XeOF_4.2SbF_5$). These complexes are probably ionic compounds and can, therefore, be represented as $[XeOF_3]^+[Sb_2F_{11}]^-$.

(*b*) $XeOF_4$ also forms complexes with fluoride-ion donors (*e.g.* $CsF.XeOF_4$; $3KF.XeOF_4$). In these complexes $[XeOF_5]$ ions or more complex ions containing fluorine-bridges may be present.

(*vi*) The interaction of $XeOF_4$ and XeO_3 gives XeO_2F_2

$$XeOF_4 + XeO_3 \longrightarrow 2XeO_2F_2$$

Structure. $XeOF_4$ molecule has square pyramidal shape as shown in Fig. 42.8. This shape results from sp^3d^2 hybridisation of Xe atom.

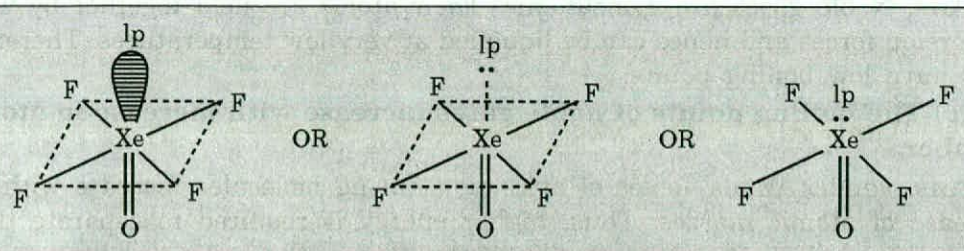


Fig. 42.8. Square pyramidal shape of $XeOF_4$ molecule.

6. Fluorides of Krypton.

Recently, it is observed that krypton also combines with F_2 above 400°C to from krypton difluride (KrF_2) and krypton tetrafluoride (KrF_4). These fluorides are lees stable as compared to xenon fluorides. These are hydrolysed by water according to the equations :

$$2KrF_2 + 2H_2O \longrightarrow 2Kr + 4HF + O_2$$

$$KrF_4 + 2H_2O \longrightarrow Kr + 4HF + O_2$$

KrF_2 is a colourless solid. It is a powerful oxidising and fluorinating agent. KrF_2 also forms addition compound with SbF_5

$$KrF_2 + 2SbF_5 \longrightarrow KrF_2.2SbF_5 \longrightarrow [KrF]^+[Sb_2F_{11}]^-$$

Just like XeF_2, KrF_2 has linear shape which results from sp^3d hybridisatinn of Kr atom.

Conceptual Questions with Answers

Q.1 Explain the following :

(*i*) Noble gases are mostly inert.

Ans. Noble gases are chemically inert because of the following reasons.

(*i*) They have completely filled ns^2np^6 electronic configurations in thier valence shells.

(*ii*) They have high ionization enthalpies.

(*iii*) Electron affinities of noble gases are almost zero.

(*ii*) Noble gases have comparatively large atomic sizes.

Ans. The atomic radii of noble gases are by far the largest in their respective periods. This is due to the reason that noble gases (because they do not form molecules) have only *vander Waals radii* while other elements have covalent radii. vander Waals radii, by definition, are larger than covalent radii. That is why noble gases have comparatively large atomic sizes.

(*iii*) Elements of group 18 are known as noble gases.

Ans. The elements of group 18 have their valence shell orbitals completely filled. As a result, they react with only a few elements (oxygen and fluorine) only under certain conditions. Therefore, they are called noble gases.

(*iv*) Noble gases have very low boiling points.

Ans. Noble gases are monoatomic. Their atoms are held together by weak dispersion forces and hence can be liquefied at very low temperatures. Therefore, they have low boiling points.

(*v*) The boiling points of noble gases increase with increase in atomic number.

Ans. vander Waals' forces of attraction among molecules increase with the increase of atomic masses. Thus, higher energy is required to separate these molecules as to get them in gaseous state. Hence, the boiling points increase with increase of atomic masses.

(*vi*) Argon does not form diatomic molecules like oxygen and nitrogen?

Ans. All the orbitals which are occupied by the electrons are completely filled in argon and hence it has no tendency to lose, gain or share electrons with other atom of Ar to form diatomic molecules. O and N, on the other hand, have unpaired electrons and hence share with other O and N atom respectively to form O_2 and N_2 molecules.

(*vii*) Helium is used in diving apparatus?

Ans. Since helium has low solubility (as compared to N_2) in blood, a mixture of oxygen and helium is used in diving apparatus used by deep sea divers.

(*viii*) Neon is generally used for warning signals.

Ans. Neon lights are visible from long distances even in fog and mist and hence neon is generally used for warning signals.

(*ix*) The group in which inert gases are acommodated was called zero group.

Ans. Inert gases do not show chemical activity under ordinary conditions due to possession of completed outermost shell *i.e.*, they show zero valency. On account of zero valency, the group in which inert gases were placed was called zero group.

(*x*) Zero group elements do not form compounds under ordinary conditions.

Ans. Zero group elements have complete electronic configuration of their outermost shells, *i.e*, s^2p^6 (except helium which has $1s^2$). Hence they do not have any tendency either to lose or accept electron/electrons or share electrons with other atoms.

Q.2 Explain the following :

(*i*) Helium and neon do not form compounds with fluorine.

Ans. He and Ne do not contain *d*-orbitals in thier respective valence shells and hence their electrons cannot be promoted to higher energy levels like that in Xe to form bonds. Therefore, *He and Ne do not form compounds with fluorine.*

(*ii*) Noble gases form compounds with fluorine and oxygen only.

(A.I.S.B. 1998)

Ans. The electronegativity of both fluorine and oxygen is very high. Moreover, fluorine is a highly reactive element.

***(iii)* (*a*) Xenon does not form fluorides such as XeF, XeF_3 and XeF_5.**

(*b*) Out of noble gases, only xenon is known to form established chemical compounds. (D.S.B. 2003, A.I.S.B. 2004 S, D.S.B. 2005)

Ans. (*a*) All the filled orbitals of Xe have paired electrons. The promotion of one, two or three electrons from the *p*-filled orbitals to the 5*d*-vacant orbitals will give rise to two, four and six half-filled orbitals. So Xe can combine with even but not with odd number of F-atoms. Hence, it cannot form XeF, XeF_3 and XeF_5.

(*b*) Except radon which is radioactive, Xe has least ionization energy among noble gases and hence it readily forms chemical compounds particularly with O_2 and F_2.

***(iv)* Xenon forms compounds with fluorine and oxygen even though xenon has a closed-shell electronic configuration.**

Ans. Since Xe has low ionisation energy (= 1170KJ/mol) and flurine and oxygen both have high electronegativity, these elements can excite paired electrons present in 5*s* and 5*p* orbitals to vacant 5*d* orbitals so that unpaired electrons become available. These unpaired electrons are used in forming bonds with fluorine and oxygen atoms.

***(v)* He, Ne and Ar donot form chemical compound while O and F do.**

Ans. Since the ionization enthalpies of He, Ne and Ar are sufficiently higher than those of oxygen and fluorine.

***(vi)* He and Ne donot form clathrate compounds with quinol.**

Ans. The size of the cavities formed during crystallisation of quinolol is more than the size of He and Ne atoms.

Q.3 Complete the following equations :

(i) $XeF_2 + H_2O \longrightarrow$ .....

(ii) $XeF_4 + H_2O \longrightarrow$ .....

(iii) $XeF_6 + H_2O \longrightarrow$ .....

(iv) $XeF_6 + NaF \longrightarrow$ .....

(v) $XeF_2 + PF_5 \longrightarrow$ .....

(vi) $XeF_6 + SiO_2 \longrightarrow$ .....

(vii) $XeF_6 + NH_3 \longrightarrow$ .....

Ans. (*i*) XeF_2 undergoes slow hydrolysis with H_2O evolving O_2.

$$2XeF_2 + 2H_2O \longrightarrow 2Xe + 3HF + O_2$$

(*ii*) XeF_4 reacts with H_2O and undergoes disproportionation reaction giving Xe and XeO_3.

$$\underset{(Xe = +4)}{6XeF_4} + 12H_2O \longrightarrow \underset{(Xe = 0)}{4Xe} + \underset{(Xe = +6)}{2XeO_3} + 24HF + 3O_2$$

(*iii*) XeF_6 undergoes hydrolysis with H_2O in two ways :

(*a*) Complete hydrolysis of XeF_6 gives XeO_3

$$XeF_6 + 3H_2O \xrightarrow[\text{hydrolysis}]{\text{Complete}} XeO_3 + 6HF$$

(*b*) Partial hydrolysis of XeF_6 gives $XeOF_4$ and XeO_2F_2

$$XeF_6 + H_2O \longrightarrow XeOF_4 + HF$$

$$XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 2HF$$

(*iv*) In this reaction NaF acts as fluoride ion donor and XeF_6 behaves as fluoride ion acceptor. Hence the reaction between XeF_6 and NaF gives fluoroanion, $[XeF_7]^-$.

$$NaF \longrightarrow Na^+ + F^-$$

$$XeF_6 + F^- \longrightarrow [XeF_7]^-$$

$$\underset{\substack{F^- \text{ ion} \\ \text{donor}}}{NaF} + \underset{\substack{F^- \text{ ion} \\ \text{acceptor}}}{XeF_6} \longrightarrow Na^+ + [XeF_7]^- \text{ or } Na^+ [XeF_7]^-$$

(*v*) In this reaction XeF_2 acts as F^- ion donor and PF_5 behaves as F^- ion acceptor. Hence the reaction between XeF_2 and PF_5 gives caionic species, $[XeF]^+$

$$XeF_2 \longrightarrow XeF^+ + F^-$$

$$PF_5 + F^- \longrightarrow PF_6^-$$

$$\underset{\substack{F^- \text{ ion} \\ \text{donor}}}{XeF_2} + \underset{\substack{F^- \text{ ion} \\ \text{acceptor}}}{PF_5} \longrightarrow [XeF]^+ [PF_6]^-$$

(*vi*) $2XeF_6 + SiO_2 \longrightarrow 2XeOF_4 + SiF_4$

$2XeOF_4 + SiO_2 \longrightarrow 2XeO_2F_2 + SiF_4$

$2XeO_2F_2 + SiO_2 \longrightarrow 2XeO_3 + SiF_4$ (Explosive)

(*vii*) $XeF_6 + 8NH_3 \longrightarrow Xe + N_2 + 6NH_4F$

Q.4 Discuss the reaction between fluorides of Xe and pentafluorides like AsF_5, SbF_5 etc. and alkali metal fluorides.

Ans. (*i*) **XeF_2.** In BrF_3 solution, XeF_2 reacts with AsF_5, SbF_5 etc. In this reaction XeF_2 molecule acts as F^- donor (Lewis base) and MF_5 molecule (M = As, Sb) acts as F^- ion acceptor [Lewis acid]

F^- ion donor (Lewis base)		F^- ion acceptor (Lewis acid)		Adduct
XeF_2	+	SbF_5	$\longrightarrow$	$[XeF]^+ [SbF_6]^-$
$2XeF_2$	+	AsF_5	$\longrightarrow$	$[Xe_2F_3]^+ [AsF_6]^-$

The formation of $[XeF]^+ [SbF_6]^-$ takes place through the following steps :

$$XeF_2 \longrightarrow [XeF]^+ + :\ddot{\underset{\cdot\cdot}{F}}:^-$$

$$SbF_5 + :\ddot{\underset{\cdot\cdot}{F}}:^- \longrightarrow \begin{matrix} & :\ddot{\underset{\cdot\cdot}{F}}: \\ & \downarrow \\ F & \\ F & \rangle Sb \langle \begin{matrix} F \\ F \end{matrix} \\ & | \\ & F \end{matrix} \quad \text{or } [SbF_6]^-$$

On adding : XeF_2 + SbF_5 $\longrightarrow$ $[XeF]^+ [SbF_6]^-$

F^- ion donor (Lewis base) — F^- ion acceptor (Lewis acid) — Adduct

(*ii*) **XeF_4.** This molecule reacts with SbF_5. In this reaction XeF_4 acts as F^- ion donor and SbF_5 molecule behaves as F^- ion acceptor.

XeF_4 (*F^- ion donor*) + SbF_5 (*F^- ion acceptor*) $\longrightarrow$ $[XeF_3]^+ [SbF_6]^-$ (*Adduct*)

(*iii*) **XeF_6** (*a*) XeF_6 reacts with AsF_5, SbF_5 etc. In this reaction XeF_6 acts as F^- ion donor and MF_5 molecule (M = As, Sb) behaves as F^- ion acceptor.

XeF_6(*F^- ion donor*) + MF_5 (*F^- ion acceptor*) $\longrightarrow$ $[XeF_5]^+ [MF_6]^-$ (*Adduct*)

(*b*) XeF_6 molecule also reacts with alkali metal fluorides. In this reaction XeF_6 acts as F^- ion acceptor and MF molecule (M = Na, K, Rb, Cs) acts as F^- ion donor.

MF (*F^- ion donor*) + XeF_6 (*F^- ion acceptor*) $\longrightarrow$ $M^+ [XeF_7]^-$ (*Adduct*)

Q.5 In the following molecules (*i*) Write the hybridisation of Xe atom (*ii*) Draw the structure/geometry of the molecule (*iii*) Locate the position of *lps* of electrons, if any. XeO_4, $XeOF_2$, XeO_2F_2, XeO_3F_2 and XeO_2F_4.

Ans. The structure of the given molecules are given in Fig. 42.9. Form this figure the following points may be noted.

(*i*) XeO_4 molecule. In this molecule, σ-*bps* + *lps* = 4 + 0 = 4. Hence Xe atom XeO_4 molecule is sp^3 hybridised. XeO_4 has **tetrahedral geometry** shown in Fig. 42.10. This molecule has no *lp* of electrons.

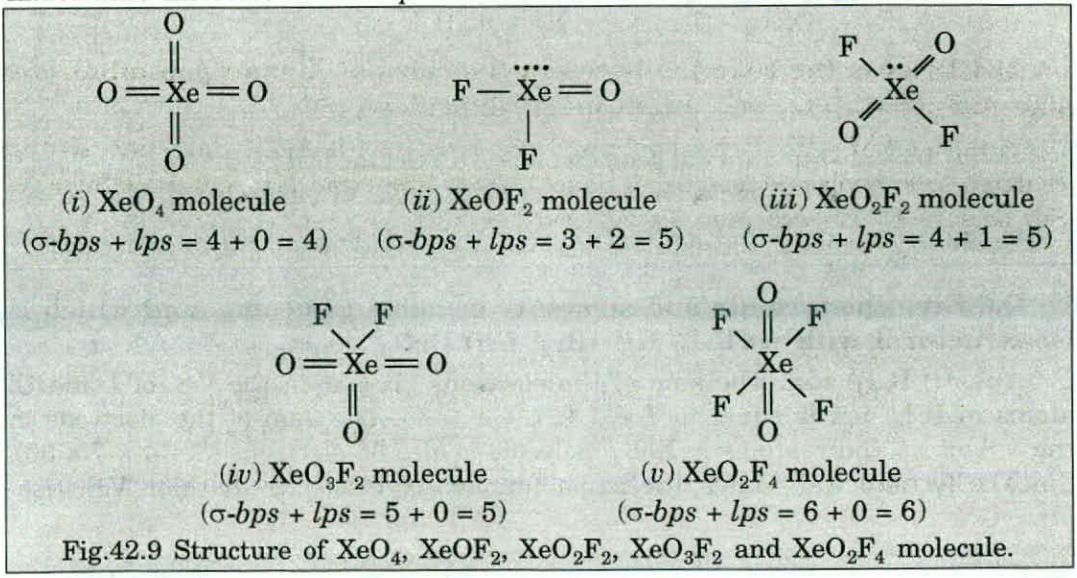


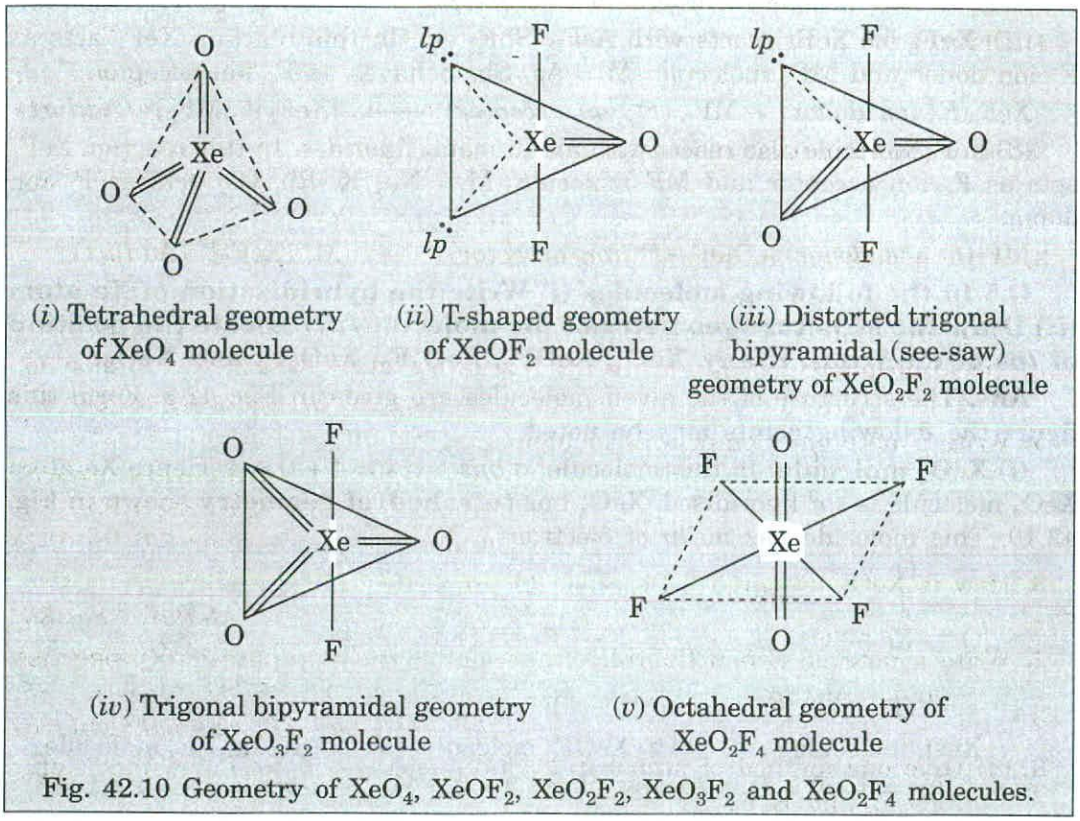
Fig.42.9 Structure of XeO_4, $XeOF_2$, XeO_2F_2, XeO_3F_2 and XeO_2F_4 molecule.

***(ii)* $XeOF_2$ molecule.** In this molecule, σ-*bps* + *lps* = 3 + 2 = 5. Hence Xe-atom is sp^3d hybridised and $XeOF_2$ has **T-shaped geometry**. Two *lps* of electrons occupy the **equatorial positions** of the trigonal bipyramid. (See Fig. 42.10)

***(iii)* XeO_2F_2 molecule.** In this molecule σ-*bps* + *lps* = 4 + 1 = 5. Hence Xe-atom is sp^3d hybridised and XeO_2F_2 has **see-saw geometry**. *lp* of electrons occupies one of the three **equatorial positions** of the trigonal pyramid. (See Fig. 42.10)

***(iv)* XeO_3F_2 molecule.** In this molecule, σ-*bps* + *lps* = 5 + 0 = 5. Hence Xe atom is sp^3d hybridised and XeO_3F_2 has **trigonal bipyromidal geometry**. This molecule has no *lp* of electrons (See Fig. 42.10)

***(v)* XeO_2F_4 molecule.** In this molecule, σ-*bps* + *lps* = 6 + 0 = 6. Hence Xe atom is sp^3d^2 hybridised and XeO_2F_4 has **octahedral geometry**. This molecule has no *lp* of electrons. (See Fig 42.10)



(*i*) Tetrahedral geometry of XeO_4 molecule

(*ii*) T-shaped geometry of $XeOF_2$ molecule

(*iii*) Distorted trigonal bipyramidal (see-saw) geometry of XeO_2F_2 molecule

(*iv*) Trigonal bipyramidal geometry of XeO_3F_2 molecule

(*v*) Octahedral geometry of XeO_2F_4 molecule

Fig. 42.10 Geometry of XeO_4, $XeOF_2$, XeO_2F_2, XeO_3F_2 and XeO_2F_4 molecules.

Q.6 Give the formula and structure of noble gas compound which is iso-structural with (*i*) ICl_4^- (*ii*) IBr_2^- (*iii*) BrO_3^-.

Ans. (*i*) **ICl_4^- ion.** The sum of the electrons present in the V.S. of I and Cl atoms in ICl_4^- ion is equal to $7 + 4 \times 7 + 1 = 36$. The sum of the electrons in the V.S. of Xe and F atoms in XeF_4 molecule is also 36 electrons ($8 + 4 \times 7 = 36$). Since ICl_4^- and XeF_4 have the same number of electrons in thier V.S. (iso-

electronic species), these species have the same geometry (iso-sturctural species). Both these species have **square planar geometry.**

(*ii*) **IBr_2^- ion.** The sum of the electrons present in the V.S. of I and Br atoms in IBr_2^- ion is equal to $7 + 7 \times 2 + 1 = 22$. The V.S. of Xe and F atoms in XeF_2 also has 22 electrons ($8 + 2 \times 7 = 22$). Since IBr_2^- and XeF_2 have the same number of electrons in their V.S. (iso-electronic species), these species have the same geometry (iso-structural species). Both these species have **linear geometry.**

(*iii*) **BrO_3^- ion.** The sum of the electrons present in the valence shell of Br and O-atom in BrO_3^- ion is equal to $7 + 3 \times 6 + 1 = 26$. The V.S. of Xe and F atom in XeO_3 also has 26 electrons ($8 + 6 \times 3 = 26$). Since BrO_3^- and XeO_3 have the same number of electrons in their V.S. (iso-electronic species), these species have the same geometry. Both these species have **pyramidal geometry.**

University Questions

1. Discuss the position of inert gases in the periodic table.
(Meerut 82, 83; Raj. 84, 86; Jiwaji 84; Panjab 84; Andhra 86; Bharathiar 86)

2. State the important industrial uses of noble gases.
(Indore 86; Sagar 85; Punjab 86; Madurai 85; Raj. 86; M.D. Rohtak 84)

3. Write a note on the history of the discovery of noble gages.
(Raj. 87, 87 S)

4. Give an account of different methods for the isolation of inert gases from the atmosphere. *(Meerut 82, 85; Indore 86; Raj. 87 S; Jiwaji 84; Sagar 85)*

5. Write a note on "Compounds of inert gases".
(Meerut 83, 86, 87, 88, 89 S; Allahabad 86, 89; Agra 89; Utkal 85; Andhra 86; Gorakhpur 83; Raj. 87)

6. How is XeO_3 prepared ? Describe its properties and structure.
(Madurai 85, 86)

7. Write a note on xenon fluorides, mentioning their preparation, properties uses and structure. *(Meerut 84, 85, 88; Madurai 85; Jodhpur 84; Utkal 86; Bundelkhend 88)*

8. (*a*) Give one method of preparation and structure of the following : XeF_6, XeO_2F_6 and KrF_2.

(*b*) What are clathrate compounds of noble gases? Give conditions to form stable clathrates. Which inert gases do not form clathrates and why?
(Himachal Pradesh 2000)

9. Give a brief description of the compounds of xenon. Write the structures of XeF_2 and XeF_4. Why He and Ne do not form such compounds.
(Kanpur 2000)

10. Discuss the position of inert gases in the periodic table, their isolation and structure of any two important compounds of xenon. *(Kumaon 2000)*

11. Write a note on "Compounds of noble gases." *[Gauhati (General) 2000]*

12. What are possible oxidation states of xenon ? Give preparation and structure of one compound in each of its oxidation states. *(Lucknow 2000)*

13. What are noble gases? Write their electronic configuration. *(Avadh 2000)*

14. Write notes on the following : (*a*) Clatherate compounds (*b*) Hybridization and geometrical shape of : XeF_2, XeF_4, XeF_6. *(Avadh 2000)*

15. (*a*) Explain the isolation of noble gases in detail.

(*b*) Write the structure and shape of XeF_4 molecule *(Meerut 2009)*

CHAPTER

43 Co-ordination Compounds

Definitions of Some Terms

A. Addition or Molecular Compounds ?

When solutions of two or more salts in simple molecular ratio are mixed together and allowed to evaporate, crystals of a new compound are obtained. This new compound is called *addition or molecular compound.* Molecular compounds are of two types as discussed below :

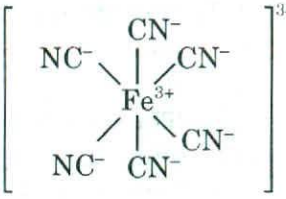
1. Double Salts. There are the addition compounds which have the properties *viz.* (*i*) These compounds are stable in the solid state only but are broken into their individual compounds when dissolved in water or any other ionic solvent. Their solutions, therefore, have the same properties as a mixture of the individual compounds. For example, a solution of Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$ which is a double salt, shows the same physical and chemical properties as a mixture of the solutions of $FeSO_4$ and $(NH_4)_2SO_4$. (*ii*) The physical and chemical properties of a double salt are the same as those of their individual compounds. Examples of double salts are carnallite, $KCl.MgCl_2.6H_2O$; Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$; potash alum, $K_2SO_4.Al_2(SO_4)_3.24H_2O$.

2. Coordination or complex compounds. These are also the addition compounds which have the following properties : (*i*) These compounds retain their identities (*i.e.* do not lose their properties) in the solid as well as when dissolved in water or any other ionic solvent. (*ii*) Their properties are completely different from those of their individual constituents. For example when aqueous NH_3 is added to a green solution of $NiCl_2$ and the solution thus obtained is evaporated, purple crystals of a new compound having the composition, $[Ni(NH_3)_6]Cl_2$ are obtained. This new compound, when dissolved in water, ionizes as :

$$[Ni(NH_3)_6]Cl_2 \rightleftharpoons [Ni(NH_3)_6]^{2+} + 2Cl^-,$$

showing that the solution of the complex compound has neither Ni^{2+} ions nor NH_3 molecules. The properties of the complex compound, $[Ni(NH_3)_6]Cl_2$ are entirely different from those of Ni^{2+} ions and NH_3 molecules. The ion, $[Ni(NH_3)_6]^{2+}$ is called complex ion. A complex ion can be defined as *an electrically charged radical which is obtained by the combination of a metal cation with one or more neutral molecules or simple anions.* For example $[Ni(NH_3)_6]^{2+}$ which is a complex ion is obtained by combining one Ni^{2+} cation with six NH_3 molecules Similarly $[Fe(CN)_6]^{4-}$ which is a complex ion is obtained by combining one Fe^{2+} cation and six CN^- ions.

B. Ligands or Coordinating Groups.



The neutral molecules or ions (usually anions) which are attached with the central ion in complex compounds are called *ligands* or *co-ordinating grounds.* For example in the complex ion, $[Fe(CN)_6]^{3-}$ the six CN^- ions which are attached with the central Fe^{3+} ion as shown in the margin act as ligands. In Lewis sense, in most of the complex compounds the ligands act as Lewis bases (electron pair donors) and the central metal ion acts as a Lewis acid (electron pair acceptor), *i.e.* in most of the complex compounds the ligands donate one or more electron pairs to the central metal ion.

M^{n+}	$+ xL$	$\longrightarrow$	$[ML_x]^{n+}$
Central metal ion (Lewis acid or electron pair acceptor)	Ligand (Lewis base or electron pair donor)		Complex compound

In some complex compounds the ligand acts both as donor and acceptor. For example in metallic carbonyls CO molecules which act as ligands act both as donor and acceptor ($M \rightleftarrows CO$). In a ligand the atom which actually donates the electron pair to the central metal ion is called *donor atom.* The ligands are attached with the central metal ion through their donor atom (or atoms).

The ligands are arranged round the central metal ion inside the first sphere of attraction in preferred geometries which are : *linear, equilateral triangular, tetrahedral, square planar, trigonal bipyramidal, square pyramidal and octahedral.*

C. Monodentate or Unidentate Ligands.

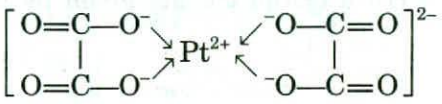
The ligands which have only one donor atom or are co-ordinated through one electron pair are called *monodentate* or *unidentate ligands.* Such ligands are coordinated to the central metal ion at one site or by one metal—ligand bond only. These ligands may be neutral molecules or in anionic form. Examples of such ligands are given below. Abbreviations, if any, for the ligands are given in parenthesis and the donor atoms are indicated by asterisk. (*A*) *Neutral monodentate ligands.* Examples are : thiourea (abbreviated as *tu*), $\overset{*}{S} = C\begin{matrix}NH_2\\NH_2\end{matrix}$; pyridine (*py*) $C_5H_5\overset{*}{N}$; ammine, $\overset{*}{N}H_3$; aqua or aquo, $H_2\overset{*}{O}$; $\overset{*}{S}PMe_3$; $\overset{*}{P}H_3$; $\overset{*}{P}R_3$; (*e.g.* $PEtPh_2$); $\overset{*}{C}O$; $R_2\overset{*}{S}$; $R_3\overset{*}{A}s$; $\overset{*}{N}O$ etc. (*B*) *Anionic monodentate ligands.* Examples are F^-, Cl^-, Br^-, I^-, CN^-, NCS^-, NO_2^-, $\overset{*}{N}H_2^-$: $\overset{*}{N}H^{2-}$, N^{3-}, $\overset{*}{O}H^-$, O^{2-}, $CH_3C\overset{*}{O}O^-$, OCN^-, H^-, S^{2-} etc.

D. Polydentate Ligands.

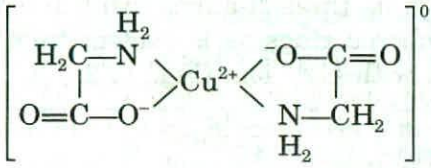
The ligands having two or more donor atoms are called polydentate ligands. These ligands may be of the following types, depending on the number of donor atoms present in them.

1. Bidentate ligands. The ligands having two donor atoms are called bidentate ligands. Examples of such ligands are :

(*A*) *Anionic bidentate ligands.* Examples are : (*i*) *Oxalato*, $C_2O_4^{-2}$ (abbreviated as ox^{2-}). This is a bidentate dibasic ligand and its co-ordination to the metal ion occurs through its both negatively-charged O-atoms (acidic donor atoms), forming a 5-membered chelate as is evident from the structure of dioxalato platinate (II) ion, $[Pt^{2+}(C_2O_4)_2]^{2-}$ or $[Pt^{2+}(ox)_2]^{2-}$ shown below. (*ii*) *Glycinato*, $\overset{*}{NH_2}.CH_2—\overset{\overset{O}{\|}}{C}—\overset{*}{O^-}$ (gly^-). It is a didentate monobasic ligand and its co-ordination to the metal ion occurs through neutral N-atom (neutral donor atom) and negatively-charged O-atom (acidic donor atom), forming a 5-memberod ring as is avident from the structure of bis-(glycinato) copper (II) ion, $[Cu^{2+}(NH_2.CH_2.COO)_2]^0$ or $[Cu(gly)_2]^0$ as shown below.

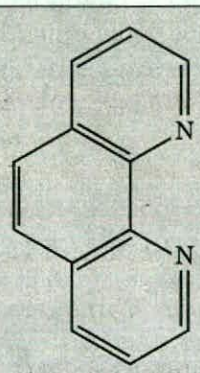


Dioxalato platinate (II) ion,
$[Pt^{2+}(C_2O_4)_2]^{2-}$ or $[Pt^{2+}(ox)_2]^{2-}$

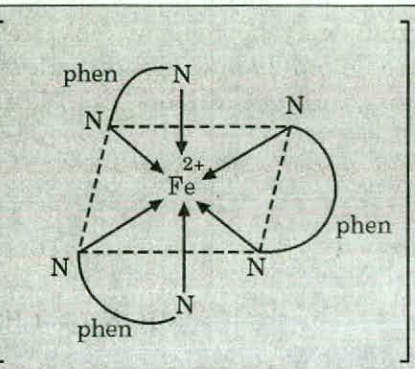


Bis (glycinato) copper (II) ion,
$[Cu^{2+}(NH_2.CH_2.COO)_2]^0$ or $[Cu^{2+}(gly)_2]^0$

(*B*) *Neutral bidentate ligands. o-phenanthroline (phen or phenan)* is an important example of this type of bidentate ligand. It has two N-atoms as its donor atoms (neutral donor atoms). Its co-ordination to the metal ion takes place through these N-atoms as is evident from the structure of ferrous orthophenanthroline ion, $[Fe^{2+}(phen)_3]^{2+}$ shown in Fig. 43.1.



Ortho phenanthroline (phen or phenan)



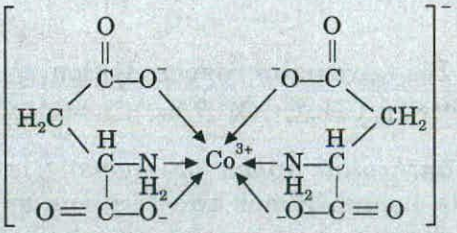
Ferrous orthophenanthroline ion,
$[Fe^{2+}(phen)_3]^{2+}$

Fig. 43.1. Structure of $[Fe^{2+}(phen)_3]^{2+}$ ion.

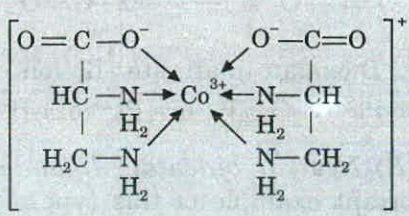
2. Tridentate ligands. The ligands having three donor atoms are called tridentate ligands. Examples are:

(A) *Anionic tridentate ligands.* Example of such ligands are (*i*) *Anion of aspartic acid* whose structure is $^{-}\overset{*}{O}OC—CH_2—CH(\overset{*}{NH_2})—\overset{*}{COO}^{-}$ and is abbreviated as Asp^{2-}. It is a tridentate dibasic ligand and its coordination to the metal ion occurs through its N-atom (neutral donor atom) and two negatively-charged O-atoms (acidic donor atoms) as is evident from the structure of the chelate formed by this ligand with Co^{3+} ion [Fig. 43.2 (*a*)]. (*ii*) *Anion of diaminopropionic acid*, $H_2C(\overset{*}{NH_2})—CH(\overset{*}{NH_2})—\overset{*}{COO}^{-}$. Obviously it is a tridentate mono-basic ligand and its coordination to the metal ion takes place through its two N-atoms (neutral donor atoms) and one negtively-charged O-atom (acidic donor atom) as is evident from the structure of the chelate formed by this ligand with Co^{3+} ion [Fig. 43.2 (*b*)]

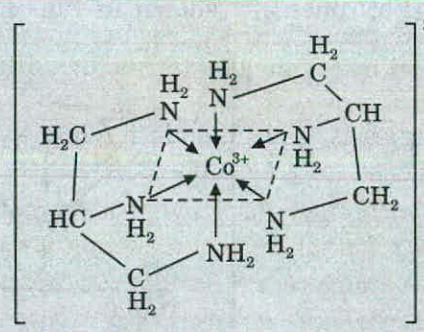
(*B*) *Neutral tridentate ligands.* Such ligands can be exemplified by triamino propane, $CH_2(\overset{*}{NH_2})—CH(\overset{*}{NH_2})—CH_2(\overset{*}{NH_2})$ which coordinates to the metal ion through its three N-atoms (neutral donor atoms), leading to the formation of two 5-membered rings as is evident from the structure of the cholate given by this ligand with Co^{3+} ion. [Fig. 43.2 (*c*)].



(*a*) $[Co^{3+}(OOC—CH_2—CH(NH_2)—COO)_2]^-$



(*b*) $[Co^{3+}(CH_2(NH_2)—CH(NH_2)—(COO)_2]^+$



© $[Co^{3+}(CH_2(NH_2)—CH(NH_2)—CH_2(NH_2)]^{3+}$

Fig. 43.2. Structure of the chelates given by tridentate ligands

3. Tetradentate ligands. The ligands having four donor atoms are called tetradentate ligands. These may be anionic or neutral ligands.

(*A*) *Anionic tetradentate ligands.* Nitrilotriacetate (nta^{3-}) is an important example of the anionic tetradentate ligand. Its structure is $*N(CH_2—\overset{*}{COO}^{-})_3$ which

shows that it is a tribasic tetradentate ligand. The coordination of this ligand to the metal ion takes place through N-atom (neutral donor atom) and three negatively-charged O-atoms (acidic donor atoms) of COO^- groups. This type of coordination gives rise to the formation of a chelate having three 5-membered rings [Fig. 43.3 (*a*)].

(B) Neutral tetradentate ligands. Triethylentetramine (trien), $\overset{*}{NH_2}—CH_2—CH_2—\overset{*}{NH}—CH_2—CH_2—\overset{*}{NH}—CH_2—CH_2—\overset{*}{NH_2}$ is an important example of this type of tetradentate ligands. This ligand has four N-atoms as its donor atoms (neural donor atoms). Coordination of this ligand to the metal ion takes place through these N-atoms, forming a chelated complex containing 5-membered rings as shown in Fig. 43.3 (*b*).

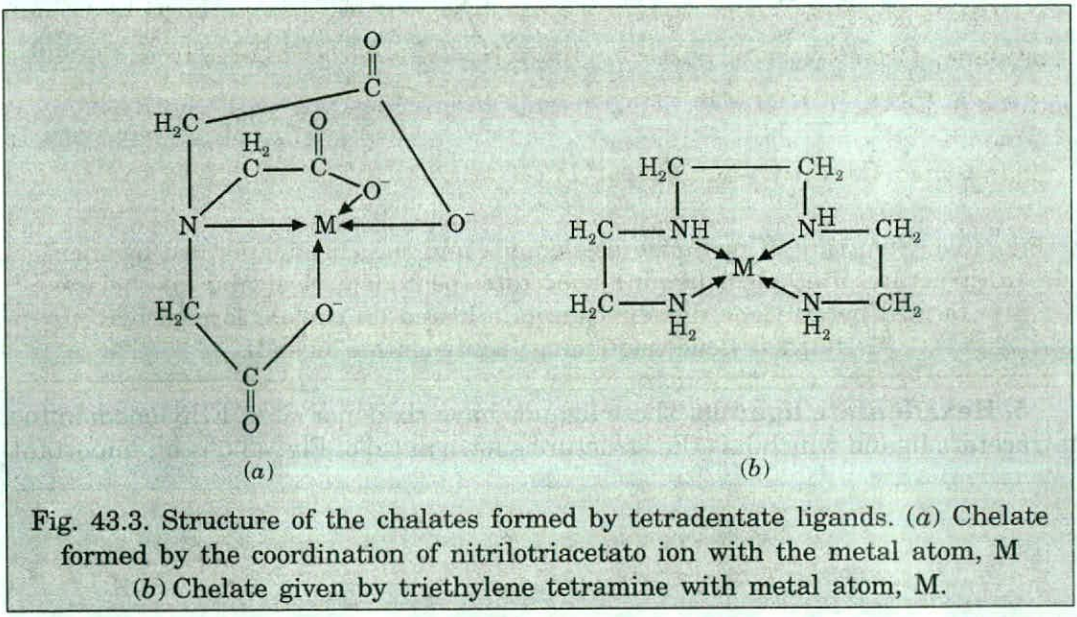


Fig. 43.3. Structure of the chalates formed by tetradentate ligands. (*a*) Chelate formed by the coordination of nitrilotriacetato ion with the metal atom, M (*b*) Chelate given by triethylene tetramine with metal atom, M.

4. Pentadentate ligands. The ligands having five donor atoms are called pentadentate ligands. These may be anionic or neutral ligands.

(*A*) *Anionic pentadentate ligands.* Ethylenediaminetriacetato whose structure is shown at (*a*) of Fig. 43.4 is an important example of this type of ligands. Its coordination to the metal atom occurs through two N-atoms (neutral donor atoms) and three negatively-charged O-atoms (acidic donor atoms) of COO^- groups, forming four 5-membered rings as shown at (*b*) of Fig. 43.4.

(*B*) *Neutral pentadentate ligands.* Tetraethylenepentamine (tetraen) is an important example of this type of pentadentate ligands. Its structure is $\overset{*}{NH_2}—(CH_2)_2—\overset{*}{NH}—(CH_2)_2—\overset{*}{NH}—(CH_2)_2—\overset{*}{NH}—(CH_2)_2—\overset{*}{NH_2}$, showing that it has five N-atoms as its donor atoms (neutral donor atoms). Thus this ligand coordinates to the metal atom through these five N-atoms and forms four 5-membered rings as shown at (*c*) of Fig. 43.4.

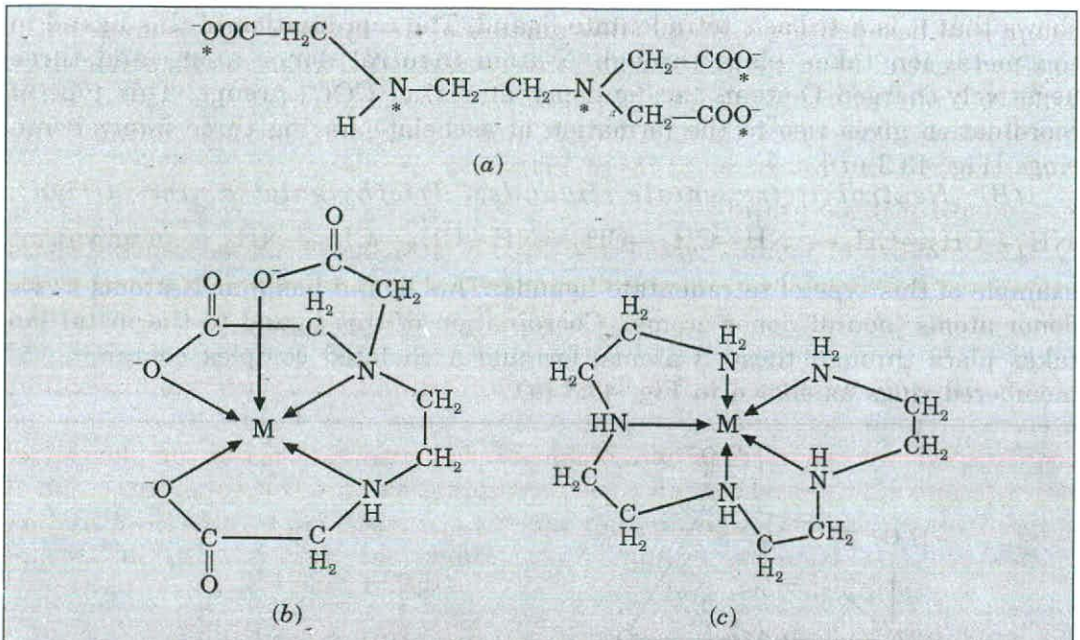


Fig. 43.4. Structure of pentadentate ligands and the chelates formed by them. (*a*) structure of ethylenediamine triacetato (pentadentate ligand (*b*) chelate formed by ethylene diaminetriacetato ligand (*c*) chelate formed by tetraethylene pentamine (pentadentate ligand).

5. Hexadentate ligands. These ligands have six donor sites. Ethylenediamine tetracetato ligand which has the structure shown at (*a*) of Fig. 43.5 is an important

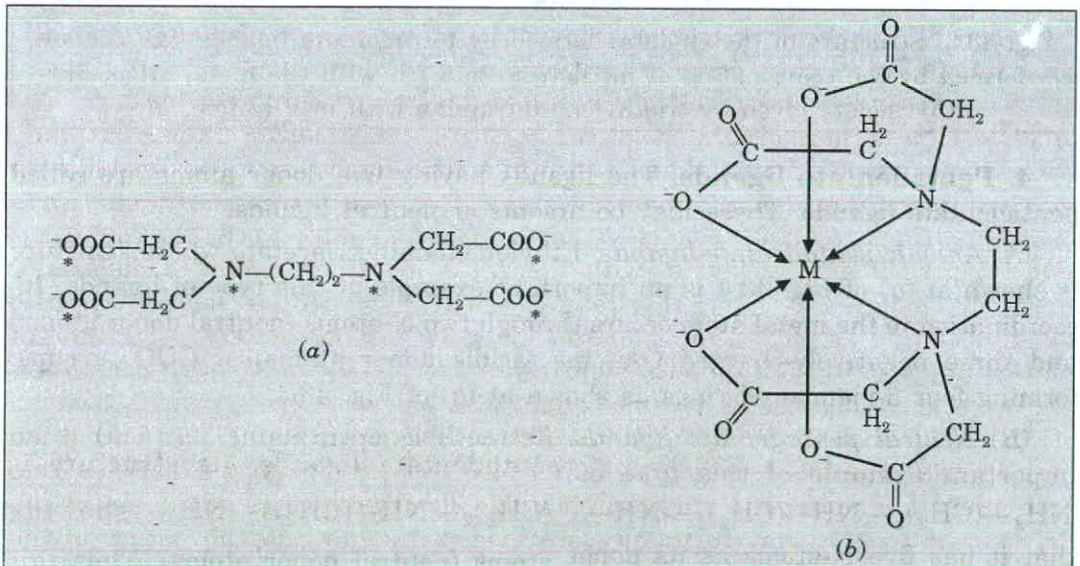


Fig. 43.5. Structure of (*a*) ethylene diamine tetraacetato ion (hexa dentate ligand) (*b*) chelate complex given by ethylene diamine tetraacetato ligand with metal atom, M.

example of hexadentate ligands. The structure of the ligand clearly shows that it has two neutral N-atoms and four negatively-charged O-atoms as its donor sites. Thus it is a tetrabasic hexadentate ligand. The coordination of this ligand to the metal atom takes place through two N-atoms and four O-atoms, forming five 5-membered rings as shown at (*b*) of Fig. 43.5.

E. Coordination Number.

The number of ligands which are directly attached with the central metal atom/ion is known as the coordination number of that metal atom/ion. For example the co-ordination number of Ag^+ ion in $[Ag(NH_3)]^{2+}$ is two. 2, 3, 4 and 6 coordination numbers are very common. Light transition metal atoms prefer to attain 4 and 6 coordination numbers while the heavier transition metal atoms exhibit coordination numbers greater than 6. A metal atom may exhibit more than one coordination number in different complexes. For example in the complexes *viz.* $[FeCl_4]^-$ and $[FeCl_6]^{3-}$, Fe^{3+} ion shows coordination number equal to 4 and 6 respectively. Normally the coordination number of a metal ion is twice the oxidation state of the metal ion. For example the coordination numbers of Ag^+, Cu^{2+} and Cr^{3+} ions are 2, 4 and 6 respectively.

F. Coordination Sphere.

While writing the structural formula of a given complex ion, the ligands which are directly linked with the metal atom are enclosed in square bracket which is called coordination sphere. Thus coordination sphere consists of the central metal atom/ion and the ligands attached with it. Thus in the complex compound, $[Co(NH_3)_6]Cl_3$, the coordination sphere consists of one Co^{3+} ion and six NH_3 molecules which are acting as ligands.

G. Tendency of Polydentate Ligands to Form Chelates : Chelation.

When all the donor atoms of a polydentate ligand get coordinated with the same metal ion, we get a complex compound which contains one or more rings in its structure and hence is called a *chelated* (or *cyclic*) *complex* or *chelate.* The process of the formation of a chelated complex is called *chelation* or *cyclisation.* For example when oxalato ligand, $C_2O_4^{2-}$ (bidentate ligand) gets coordinated with Pt^{2+} ion, we get dioxalato platinate (II) ion, $[Pt^{2+}(C_2O_4)_2]^{2-}$ which contains two 5-membered rings and hence is a chelated complex. In simple words the complexes given by the polydentate ligands with the central metal ion are called chelates or chelated complexes. It is for this reason that the polydentate ligands are also called chelating ligands. The complexes given by a monodentate ligand do not contain any ring in their structure and hence are called *non-chelated complexes.* The word chelating ligand does not apply to a bidentate ligand which forms a bridge system with its two donor atoms bonded to separate metal ions. A chelating ligand must have two or more lone pairs which should be at such a distance from each other that the ligand may form suitable strain-free rings at the metal ion. Polydentate ligands may further be subdivided according to the nature of the donor atoms present in them. A polydentate ligand may contain all neutral donor atoms or all acidic (anionic) donor atoms or some of the donor atoms may be neutral and the remaining may be acidic. Neutral donor atoms are generally N, O, S etc atoms which are from the groups like $-NH_2$ (primary, secondary and

tertiary amines), = NOH (oxime), –OH (alcoholic hydroxyl), = CO (carbonyl) and –S–(thioether). The acidic donor atoms are from the anions obtained by removing one or more H-atoms from the acidic groups like –COOH (carboxyl), $-SO_3H$ (sulphonic), –OH (enolia hydroxyl) and = NOH (oxime). Diehal (1937) has classified the chelates on the basis of the fact whether the chelating ligand has all neutral donor atoms or all acidic (anionic) donor atoms or some of the donor atoms are neutral and the remaining arc acidic.

H. Applications of Chelate Formation.

Applications of chelate formation can be studied under the following heads.

1. Formation of chelates in analytical chemistry. Examples are :

(*i*) *Estimation and identification of Ni^{2+} ions by dimethyl glyoxime.* Dimethyl glyoxime solution reacts with Ni^{2+} ions in ammoniacal medium and forms a red coloured precipitate of *bis*- (dimethyl glyoximato) nickel (II). Thus the formation of this precipitate can be used for the identification, estimation of Ni^{2+} and also for the separation of Ni^{2+} ions from Co^{2+} ions

(*ii*) *Estimation of Mg^{2+} and Ca^{2+} ions by EDTA.* Disodium salt of ethylene diamine tetraacetic acid (abbreviated as $EDTAH_2Na_2$) has been used for the estimation of M^{2+} metal ions like Mg^{2+}, Ca^{2+} etc. by complexometric titrations. In these titrations an organic dye is used as an indicator. A good indicator should meet the following requirements (*a*) The indicator must form a coloured complex with the metal ion at the same *p*H at which the $EDTA^{4-}$ ion forms complex with the same metal ion. (*b*) The colour of the metal- indicator complex should be different from that of the free indicator ion. (*c*) The stability of the metal-indicator complex should be low compared to that of metal-EDTA complex.

Suppose in the complexometric titration of Mg^{2+} or Ca^{2+} ions with $EDTAH_2Na_2$, we use Erio-chrome Black T (abbreviated as H_3D) as an indicator. In this titration the solution containing Mg^{2+} or Ca^{2+} ions is buffered to *p*H = 10 (This *p*H is obtained by using NH_4Cl—NH_4OH buffer), a few drops of the indicator are added and the solution is titrated with a standard solution of $EDTAH_2Na_2$. In this titration, indicator ions (D^{3-} ions) form red metal-indicator complex, $[MD]^-$ with M^{2+} (M^{2+} = Mg^{2+} or Ca^{2+}) ions.

$$\underset{\substack{\text{Metal ion}\\(M^{2+} = Mg^{2+} \text{ or } Ca^{2+})}}{M^{2+}} + \underset{\substack{\text{Indicator}\\\text{ion (blue)}}}{D^{3-}} \overset{p\text{H} = 10}{\rightleftarrows} \underset{\substack{\text{Metal-indicator}\\\text{complex (red)}}}{[M^{2+}D]^-}$$

Metal-indicator complex reacts with $EDTA^{4-}$ ion and forms metal-EDTA complex.

$$\underset{\substack{\text{Metal-indicator}\\\text{complex}\\\text{(red)}}}{[M^{2+}D]^-} + \underset{\substack{\text{EDTA}\\\text{ion}}}{EDTA^{4-}} \rightleftarrows \underset{\substack{\text{Metal-EDTA}\\\text{complex}}}{[M^{2+}(EDTA)]^{2-}} + \underset{\substack{\text{Indicator}\\\text{ion}\\\text{(blue)}}}{D^{3-}}$$

$EDTA^{4-}$ ion also forms metal-EDTA complex with the free Ca^{2+} or Mg^{2+} ions (present. in the titration solution) that have not reacted with D^{3-} ions to form $[MD]^-$ complex.

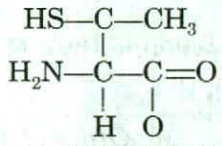
Thus we see that free indicator ion is obtained at the end point. The release of the free indicator is marked by a change form red (colour of $[M^{2+}D]^{2-}$ complex) to blue (colour of D^{3-} ion) colour.

2. Formation of chelates in softening of water. Ethylenediamine tetracetic acid ($EDTAH_4$) has been used for softening water which does a lot of harm in industrial boilers and other equipments by forming a scale in them. Ethylenediamine tetracetic acid is added to the boilers in which $EDTA^{4-}$ forms water-soluble chelated complex with Ca^{2+} and Mg^{2+} ions present In hard water and thus these ions are removed.

3. Formation of chelates in medicines. Some applications are :

(*i*) *In the removal of poisonous metals from the body.* In this case injection of $CaNa_2EDTA$ is given to the patient. $CaNa_2EDTA$ reacts with Pb in the body and forms Pb-EDTA complex which is rapidly excreted in urine. Since EDTA is not readily metabolised, most of Ca-EDTA complex also goes out of the body in urine.

(*ii*) *Disorder of lever.* The desease regarding the disorder of the lever leads to the malfunctioning of the central nervous system. This disease is due to the fact that free Cu^{2+} ions accumulate in the lever. The excess of Cu^{2+} ions is removed by giving penicillamine (I) to the patient. (The structure of (I) is shown in the margin). Cu^{2+} ions form a soluble complex with (I) by coordinating with S, N and O donor atoms of (I).



Penicillamine (I)

4. Formation of chelates in living systems. Metal chelates play vital role in living systems. For example :

(*i*) The green colouring matter present in plants which is called chlorophyll is a square planar complex of Mg^{2+}. This substance converts CO_2 and water to starches and sugars in the plants. Solar system provides the energy for this conversion.

(*ii*) Hemoglobin imparts red colour to the human blood and is porphyrin complex of Fe^{2+} ion. In human livings blood is saturated with air and the hemoglobin is completely changed to the oxyhemoglobin form.

$$Hemoglobin + O_2 \rightleftarrows Oxyhemoglobin + H_2O$$

As the blood runs through the arteries to the tissues, the oxygen pressure dwindles and the bound oxygen gets liberated. This liberated O_2 is used in the combustion of food. By this reversible process hemoglobin serves as an oxygen carrier to all the cells of the organism. Oxygen carriers in the blood of various invertebrates are the chelates of Cu, Mn and V.

(*iii*) At present it is believed that all the essential trace metals in human body probably function through processes involving chelate formation.

(*iv*) Within the animal cell another Fe(II)–Fe(III) protein, coordination compound of hemoglobin family, called *cytochrome-C* acts as a catalyst for the utilisation of oxygen in the basic cell metabolism of the fundamental life process.

Nomenclature of Coordination Compounds

Coordination compounds are named according to the rules suggested by the *International Union of Pure and Applied Chemistry*, IUPAC (1976). For naming

all types of complex compounds the ligands are named first and the central metal atom is named in the end.

1. Naming the Ligands. The ligands are named as :

(*i*) *Naming the anionic ligands.* The name of anionic ligands ends in *o*. Examples are CH_3COO^-, acetato; CN^-, cyno; NO_2^- (ONO^-), nitrito; NO_3^-, nitrato; $NH_2CH_2.COO^-$, glycinato; Cl^-, chloro; $C_2O_4^{2-}$, oxalato etc.

(*ii*) *Naming the neutral inorganic ligands.* For neutral inorganic ligands the names are not systematic. Examples are N_2, dinitrogen; H_2O, aquo or aqua; NH_3, ammine; CO, carbonyl etc.

(*iii*) *Naming the cationic ligands.* Positively-charged ligands have the suffix *ium* in the end. Examples are $NH_2.NH_3^+$, hydrazinium; NO^+, nitrosylium; NH_4^+, ammonium etc.

(*iv*) *Naming the organic ligands.* Organic free radicals are given their own names. Examples are CH_3, methyl; C_2H_5, ethyl; C_6H_5, phenyl. For organic neutral molecules their names are used, *e.g.*, $P(C_6H_5)_3$, triphenylphosphine; C_5H_5N, pyridine (py); $S=C\begin{matrix}NH_2\\NH_2\end{matrix}$, thiourea (*tu*); $NH_2.CH_2.CH_2.NH_2$, ethylene diamine (en).

(*v*) *Order of naming ligands.* If there are two or more different kinds of ligands, the order of naming such ligands is *negative* (*anionic*) *ligands, neutral ligands* and *positive* (*cationic*) *ligands* without separation of hyphens (*i.e.* as single words). Within the ligands of the same category, the ligands are named in the order of their increasing complexity. The anionic ligands are named in the order : H^-, O^{2-}, OH^-, other simple monoatomic anionic ligands, polyatomic anionic ligands and finally organic anions in alphabetical order. Where the two ligands have the same number of atoms, the order is that of decreasing atomic number of the central metal species in the ligand, *e.g.* CrO_4^{2-} first and then SO_4^-. Neutral ligands are named in the following order : *first* : H_2O (*aquo*), then NH_3 (*ammine*), *second* : other neutral coordinated ligands in the order in which the coordinated atom falls in the series : B, Si, C, Sb, As, P. N, H, Te, Se, S, At, I, Br, Cl, O, F, *third* : neutral organic ligands in alphabetical order.

(*vi*) *Indication of the number of ligands.* The number of simple ligands such as Cl^-, CH_3COO^-, $C_2O_4^{2-}$ etc. is indicated by using before them the Greek prefixes : *di-*, *tri-*, *tetra-*, *penta-*, *hexa-* etc. In case of chelating ligands like ethylenediamine, trialkyl phosphine which contain the prefixes *di-*, *tri-*, etc. in their ligand names, the prefixes *bis-* (for two), *tris-*, (for three), *tetrakis-* (for four), *pentakis*. (for five), *hexakis-* (for six) etc. are used before their names.

(*vii*) *Naming the bridging ligands.* There are many monodentate ligands like OH^-, NH^{2-}, NH_2^-, NO_2, Cl^-, O_2^{2-}, CO etc. which can coordinate simultaneously with more than one metal ion and thus form a bridge between the metal ions. Such ligands are called *bridging ligands* and the complexes containing such ligands are called *bridged* or *poly-nuclear complexes.* For naming a bridging ligand in such complexes the Greek prefix μ is used before its name and for naming two or more bridging ligands of the same kind the prefixes *di-*μ. *tri-*μ, etc. are used before their name. The bridging ligand (or ligands) is written in the name of the complex by separating it from the remaining name of the complex by a hyphen.

(*viii*) *Naming the ambidentate ligands.* Some of the ligands possess two different donor atoms. For example CN^- ion contains C and N as donor atoms and SCN^- ion contains S and N as donor atoms. When such ligands get coordinated to the metal ion as monodentate ligands, they use either of their two donor atoms, *i.e.* these ligands bond to the metal ion through one type of donor atom in one complex and through another type of donor atom in another complex. Such ligands are called *ambidentate* (or *ambident*) *ligands.* Ambidentate ligands are named by adding the italicised symbol (or symbols) of the element (or elements) coordinated to the metal ion at the end of the name of the ligand. However, some such ligands are also given special names.

2. Naming the Central Metal Atom. Different rules are used for naming the central metal atom in different complexes. For example :

(*i*) *In cationic and neutral complexes.* In cationic and neutral complexes the name of the central metal atom remains the same. Its name is followed by its oxidation number or state in Roman numeral in parentheses. For example nickel (0), iron (II), copper (III) etc.

(*ii*) *In anionic complexes.* In such complexes the name of the central metal atom is modified to end in *ate*. For example chromate (for Cr), ferrate (for Fe), cobaltate (for Co), cuperate (for Cu), argentate (for Ag), palladate (for Pd), rhenate (for Re), stannate (for Sn), iridate (for Ir), ruthenate (for Ru), osinate (for Os), platinate (for Pt), cadmate (for Cd), zincate (for Zn), silicate (for Si). *Marcurate* and *tungstate* are the exceptions. The modified name of the central metal atom is followed by its oxidation state (or number) in Roman numerals in parantheses.

3. Naming the Complex Compounds. In naming the complex compounds the ligands are named first and then the central metal atom is named. The rules for naming the ligands have already been discussed.

(*i*) *Naming the cationic and neutral complexes.* Cationic complexes such as $[CrCl_2(H_2O)_4]^+$, $[Co(H_2O)_6]^{3+}$ etc. and neutral complexes like $[Co(NH_3)_2(NO_2)_3Cl]$, $[Co(NH_3)_3(SCN)_3]$ etc. are named by giving the number and the name of the ligands followed by the name of the central metal atom with its oxidation number (or state) in Roman numerals in parentheses. *e.g.* $[CrCl_2(H_2O)_4]^+$, tetraaquadichloro chromium (III) ; $(Co(NH_3)_4(NO_2)Br]$, tetraamrninenitro cobalt (III); $[(en)_2 Co^{3+}\begin{matrix}\diagup \\ \diagdown\end{matrix}\begin{matrix}NH_2 \\ O_2\end{matrix}\begin{matrix}\diagdown \\ \diagup\end{matrix} Co^{3+}(en)_2]^{4+}$, μ-amido μ-superoxo *tetrakis* (ethylenediamine) cobalt (III) (Cationic complexes); *cis*-$(Pt(NH_3)_2Cl_2]$, *cis*-dichloro diammine platinum (II); $[Co(en)_2Cl_2]$, dichloro *bis* (ethylenediamine) cobalt (II); $[Co(NH_3)_3(SCN)_3]$, tristhiocyanate (*S*) triammine cobalt (III) (Neutral complexes).

(*ii*) *Naming the anionic complexes.* The anionic complexes like $[Ag(CN)_2]^-$, $[Fe(CN)_6]^{3-}$, $[Si F_6]^{2-}$ etc. are named by giving the number and the name of the ligands followed by the name of the central metal atom with an *ate* ending and its oxidation state in Roman numeral in parentheses. For example $[Ag(CN)_2]^-$, dicyano argentate (I); $[Fe(CN)_6]^{3-}$, hexacyanoferrate (III); $[(C_2O_4)_2 Cr^{3+}\begin{matrix}\diagup \\ \diagdown\end{matrix}\begin{matrix}OH \\ OH\end{matrix}\begin{matrix}\diagdown \\ \diagup\end{matrix} Cr^{3+}(C_2O_4)_2]^{4-}$, μ-dihydroxo *tatrakis* oxalato chromate (III).

(iii) Naming the complex compounds having complex cation and simple anion. $[Co(NH_3)_4Cl_2]Cl$, $[Cr(H_2O)_4Cl_2]NO_3$, $[Cu(NH_3)_4]SO_4$ etc. are the examples of such complex compounds. In naming such complex compounds the complex cation is named first and then the simple anion is named as we do for an ionic simple salt like NaCl (sodium chloride). The complex cation of such complex compounds is named according to the rule used for naming the cationic complexes, *i.e.* this complex cation is named by giving the number and the name of the ligands followed by the name of the central metal atom with its oxidation state in Roman numerals in parentheses. Simple anion present in the complex compound is named as usual. For example : $[Co(NH_3)_4Cl_2]Cl$, dichlorotetraaminine cobalt (III) chloride; $[(NH_3)_5 Cr^{3+} —OH—Cr^{3+} (NH_3)_5] Cl_5$, μ-hydroxo decaammine chromium (III) chloride; $[Cu(NH_3)_4] [SO_4$, tetraammine copper (II) sulphate.

(iv) Naming the complex compounds having simple cation and complex anion. $K[Ag(CN)_2]$, $Fe[Fe(CN)_6]$, $Hg[Co(CNS)_4]$. $K_2[HgI_4]$ etc. are the examples of such complex compounds. In naming such complex compounds the simple cation is named first and then the complex anion is named as we do for a simple ionic salt like NaCl (sodium chloride). The complex anion of such complex compounds is named according to the rule used for naming anionic complexes, *i.e.* this complex anion is named by giving the number and the name of the ligands followed by the name of the central metal atom with an *ate* ending and its oxidation state in Roman numeral in parentheses. Simple cation is named as usual. For example $K[Ag(CN)_2]$, potassium dicyano argentate (I); $K_4[Fe(CN)_6]$, potassium hexacyano ferrate (II); $Na_2[Fe(NO)(CN)_5]$, sodium pentacyano nitrosyl ferrate (II); $Hg[Co(CNS)_4]$, mercury tetrathiocyanato (N) cobaltate (III).

(v) Naming the complex compounds having complex cation and complex anion. $[Pt(py)_4] [PtCl_4]$, $[Co(NH_3)_6] [CdCl_5]$ etc are the examples of such complex compounds. In naming such complex compounds the complex cation is named first and then the complex anion is named. The complex cation of such complex compounds is named by giving the number and the name of the ligands followed by the name of the central metal atom with its oxidation state in Roman numerals in parentheses while the complex anion is named by giving the number and the name of the ligands followed by the name of the central metal atom with an *ate* ending and its oxidation state in Roman numeral in parentheses. For example : $[Pt(py)_4] [PtCl_4]$, tetrakisphyridine platinum (I) tetrachloro platinate (IV) ; $[Cr(NH_3)_6] [Co(CN)_6]$, hexaammine chromium (III) hexacyano cobaltate (III).

Isomerism

The compounds having the same molecular formula but having different structural arrangement of their atoms are called isomers and the phenomenon that gives rise to isomers is called isomerism. Coordination compounds show two types of isomerism namely *structural isomerism* and *stereo-isomerism or space isomerism*.

Structural Isomerism

This isomerism is of the following types :

1. Conformation Isomerism. In this two isomers have different geometries but are otherwise identical. For example $[Ni^{2+}(P.Et.Ph_2)_2Br_2]$ complex (four coordinated complex) gives two conformation isomers. One of these is green and paramagnetic while the other is brown and diamagnetic. The green form is tetrahedral while the brown form is square planar. Thus these have different geometries but the coordination number of Ni^{2+} ion in both the isomers is the same (= 4)

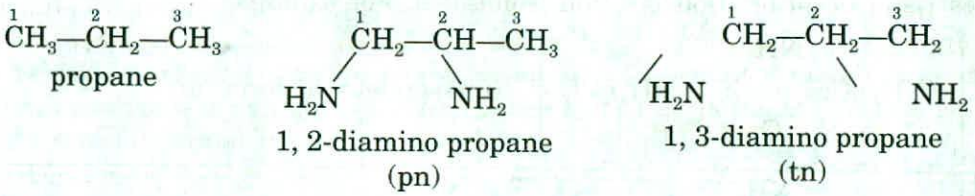
2. Ionisation Isomerism. Complexes which have the same empirical formula and are produced by the interchange of the position of the ligands inside the complex zone (coordination sphere) and the anions outside the complex zone are called isonisation isomers. They give different ions in solution on ionisation. Thus $[Co^{3+}(NH_3)_5Br]SO_4$ and $[Co^{3+}(NH_3)_5(SO_4)]Br$ are the two ionisation isomers, since they give different ions in solution on ionisation as shown below :

$$[Co^{3+}(NH_3)_5Br]SO_4 \rightleftharpoons [Co^{3+}(NH_3)_5Br]^{2+} + SO_4^{2-}$$

$$[Co^{3+}(NH_3)_5(SO_4)]Br \rightleftharpoons [Co^{3+}(NH_3)_5(SO_4)]^{+} + Br^{-}$$

3. Hydrate Isomerism. This type of isomerism arises out of different disposition of water molecules inside and outside the coordination sphere. For example, the compound $CrCl_3.6H_2O$ exists in three hydrate isomers which are : (*a*) $[Cr(H_2O)_6]Cl_3$—violet, does not lose water over H_2SO_4 and all Cl^- ions are immediately precipitated by Ag^+ ions. (*b*) $[Cr(H_2O)_5Cl]Cl_2.H_2O$—green, loses H_2O over H_2SO_4 and two Cl^- ions are precipitated by Ag^+ ion. (*c*) $[Cr(H_2O)_4\ Cl_2]Cl.2H_2O$—green, loses two water molecules over H_2SO_4 and only one Cl^- ion is precipitated by Ag^+ ions.

4. Ligand Isomerism. Some ligands themselves are capable of existing as isomers, *e.g.*, diamino propane can exist both as 1, 2-diamino propane (pn) and 1, 3-diamino propane, also called trimethylene diamino (tn).



When these ligands (*i.e.*, pn and tn) form complexes, the complexes are isomers of each other. One example of isomeric complexes having this ligand is : $[Co(pn)_2Cl_2]^+$ and $[Co(tn)_2\ Cl_2]^+$ ions. The structural formulas of these complex ions are shown below in Fig. 43.6.

5. Linkage Isomerism. The tendency of ambidentate ligands due to which they can be linked to the metal ion in two different ways gives rise to linkage isomerism in the complexes given by these ambidentate ligands. As an example we can consider the linkage isomers given by NO_2^- ion. NO_2^- ion is an ambidentate ligand and possesses two different donor atoms *viz.* N and O. This ion can, therefore, coordinate to the metal ion either through N-atom or through O-atom. Thus NO_2^- ion gives two linkage isomers which are called *nitro-N* or *nitro isomer* and *nitro-O* or *nitrito isomer.*

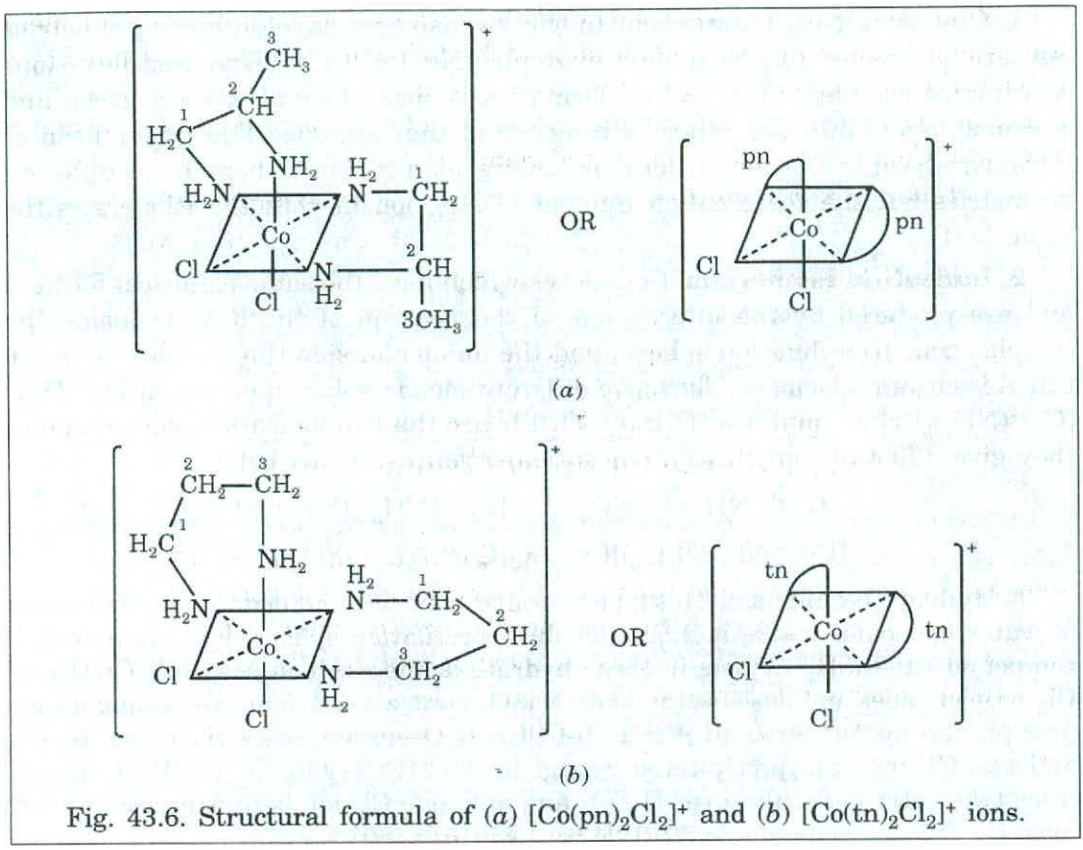


Fig. 43.6. Structural formula of (*a*) $[Co(pn)_2Cl_2]^+$ and (*b*) $[Co(tn)_2Cl_2]^+$ ions.

6. Coordination Position Isomerism. In some poly-nuclear complexes, to interchange the ligands between the metal atoms which are present as part of the complex is possible. This type of interchange of ligands between the metal atoms gives rise to coordination position isomerism. For example

$$\left[(NH_3)_4Co\begin{matrix}NH_2\\ \diagup\ \ \diagdown\\ O_2\end{matrix}Co(NH_3)_2Cl_2\right]^{2+}$$ (unsymmetrical form) and

$$\left[Cl(NH_3)_3Co\begin{matrix}NH_2\\ \diagup\ \ \diagdown\\ O_2\end{matrix}Co(NH_3)_3Cl\right]^{2+}$$ (symmetrical form) are coordination position isomers.

7. Coordination Isomerism. If both cation and anion of a complex compound are complex, there may be an exchange of ligands between the two coordination spheres, giving rise to isomers known as coordination isomers and the isomerism thus obtained is called coordination isomerism. For example $[Cr(NH_3)_6]^{3+}$ $[Cr(SCN)_6]^{3-}$ and $[Cr(NH_3)_4(SCN)_2]^+[Cr(NH_3)_2(SCN)_4]^-$ are coordination isomers to each other.

8. Polymerisation Isomerism. This type of isomerism is found in those complex compounds whose formulae appear to be polymers of some simple complex

compound. All these complex compounds have the same ratio of different metal atoms and ligands in them. For example the following complex compounds are polymerisation isomers to each other, since (*ii*) and (*iii*) complexes appear to be dimer of (*i*) complex and (*iv*) complex appears to be the pentamer of (*i*) complex. The ratio Co^{3+} : NH_3 : NO_2^- in all the complexes is 1 : 3 : 3.

Complex compound	***Number of***		
	Co^{3+}	NH_3	NO_2^-
(*i*) $[Co(NH_3)_3(NO_2)_3]$	1	3	3
(*ii*) $[Co(NH_3)_6][Co(NO_2)_6]$	2	6	6
(*iii*) $[Co(NH_3)_4(NO_2)_2][Co(NH_3)_2(NO_2)_4]$	2	6	6
(*iv*) $[Co(NH_3)_5(NO_2)]_3[Co(NO_2)_6]_2$	5	15	15

Stereo (or Space) Isomerism

When two compounds contain the same ligands coordinated to the same central ion, but the arrangement of ligands in space is different, the two compounds are said to be stereo-isomers and the type of isomerism is called *stereo-isomerism.* It is also called *space isomerism.* Stereisomers are quite similar. *e.g.*, optical isomers (which are stereisomers) differ only in their optical activity. On the other hand structural isomers differ from each other in various ways. Stereo isomerism is of two types : (*i*) *Geometrical or cis-trans isomerism*, and (*ii*) *Optical or mirror-image isomerism.*

Geometrical Isomerism

In this isomerism, the ligands occupy different positions round the central metal ion. If the two identical ligands occupy adjacent positions. the isomer is called a *cis*-isomer (*cis* means *same* in Latin), *i.e.* in *cis*-isomer the ligands in question are next to one another. On the other hand, when the two identical ligands are placed opposite to each other, the isomer is called a *trans*-isomer (*trans*-means *across* in Latin), *i.e.* in trans-isomer the line connecting the two identical ligands passes through the central point at which the metal ion is placed.

Geometrical Isomerism in Tetrahedral Complexs (C.N. = 4)

Geometrical isomerism cannot arise in tetrahedral complexes (C.N. = 4) because this geometry contains all the ligands in cis (*i.e.*, adjacent) position with respect to each other, *i.e.* each ligand is equidistant from the other three ligands and all the bond angles are the same (= 109.5°). Thus we see that in tetrahedral complexes all the four positions of the ligands are adjacent to each other and hence geometrical isomerism can not be expected.

Geometrical Isomerism in Square Planar Complexes (C.N. = 4)

Square planar complexes of $[Ma_4]$, $[Ma_3b]$ and $[Mab_3]$ type (*a* and *b* are monodentote ligands) do not show geometrical isomerism, since every conceivable

spatial arrangement of ligands round the metal ion is exactly equivalent. However, the square planar complexes of $[Ma_2b_2]$, [Mabcd] etc. type do show geometrical isomerism as discussed below :

1. $[Ma_2b_2]$ type complexes. Square planar complexes of this type (M is the central metal ion and *a* and *b* are monodentate ligands) exist as *cis*-and *trans* isomers. For example $[Pt^{2+}(NH_3)_2Cl_2]$ exists in *cis*- and *trans*- isomers as shown below in Fig. 43.7. $[Pt^{2+}(NH_3)_2Br_2]$ and $[Pd^{2+}(NH_3)_2(NO_2)_2]$ are other examples of square planar complexes which, like $[Pt(NH_3)_2Cl_2]$, also exist in *cis*- and *trans*-isomers.

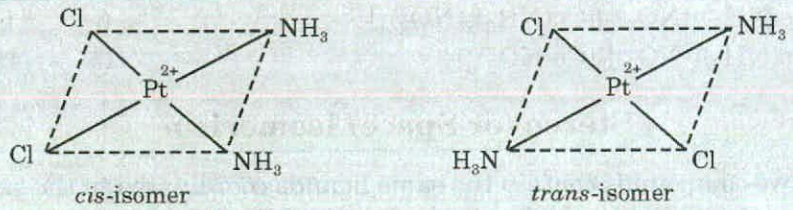


Fig. 43.7. Cis- and trans-isomers of $[Pt^{2+}(NH_3)_2Cl_2]$.

2. [*Mabcd*] type complexes. Square planar complexes of this type exist in three isomeric forms. For example $[Pt^{2+}(NH_3)$ (py)(Cl) (Br)] exists in three isomeric forms shown below in Fig. 43.8. These isomeric forms can be obtained by selecting one ligand, say NH_3, and then placing the remaining three ligands, one by one, *trans* to NH_3.

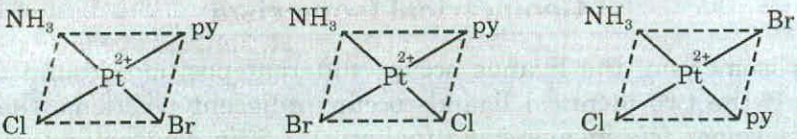


Fig. 43.8. Three isomeric forms of $[Pt^{2+}(NH_3)(py)(Cl)(Br)]$

$[Pt^{2+}(NO_2)(py)(NH_3)(NH_2OH)]^+$ and $[Pt^{2+}(C_2H_4)(NH_3)(Cl)(Br)]$ are other examples of square planar complexes which exist in three isomeric forms.

The existence of three isomeric forms in case of the complexes mentioned above indicates that these complexes have square planar geometry.

3. $[Ma_2bc]$ type complexes. Square planar complexes of this type also show *cis-trans* isomerism. For example $[Pd^{2+}Cl_2BrI]^{2-}$ ion exists in *cis* and *trans*-isomers as shown below in Fig. 43.9.

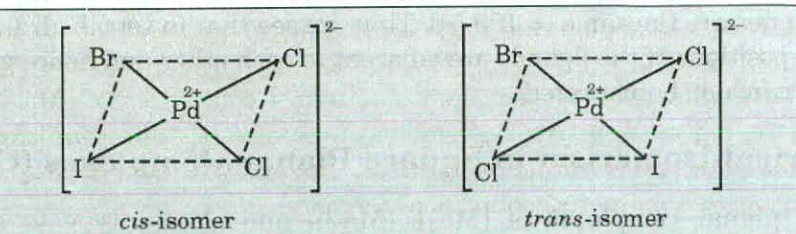


Fig. 43.9. Cis-and trans-isomers of $[Pd^{2+}Cl_2BrI]^{2-}$ ion.

4. $[M(AB)_2]$ type complexes. Here M is the central metal ion and AB represents an unsymmetrical bidentate ligand in which *A* and *B* are two different coordinating (donor) atoms. Square planar complexes of this type also exist in *cis*- and *trans*-isomers. For example $[Pt^{2+}(gly)_2]$ exists in *cis*- and *trans*-isomers as shown below in Fig. 43.10. Here gly represents the glycinato ligand, $NH_2.CH_2COO^-$ which has N and O atoms as its donor atoms (*i.e.* A = N and B = O).

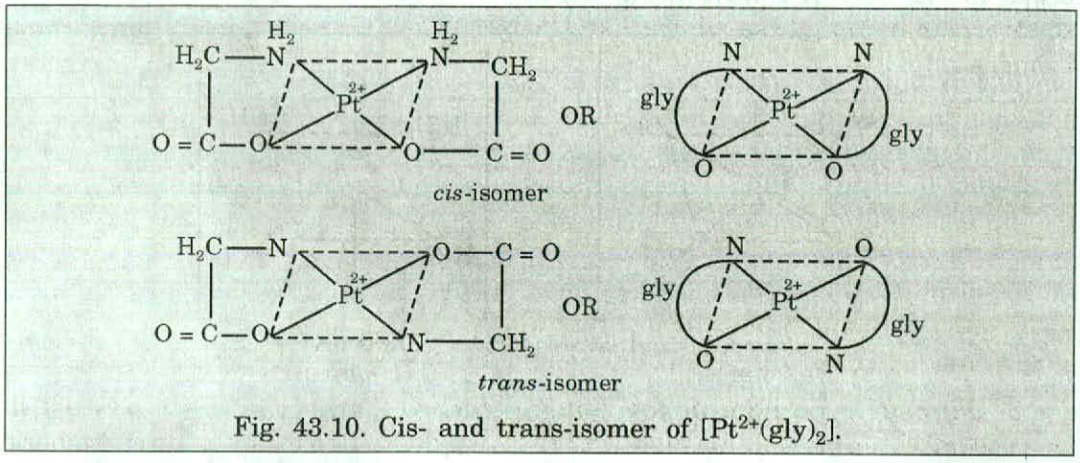


Fig. 43.10. Cis- and trans-isomer of $[Pt^{2+}(gly)_2]$.

Geometrical Isomerism in Octahedral Complexes (C.N. = 6)

We know that a complex compound having the central metal ion with coordination number equal to 6 has octahedral shape. The system used for numbering different positions of the ligands in an octahedral geometry has been shown below in Fig. 43.11.

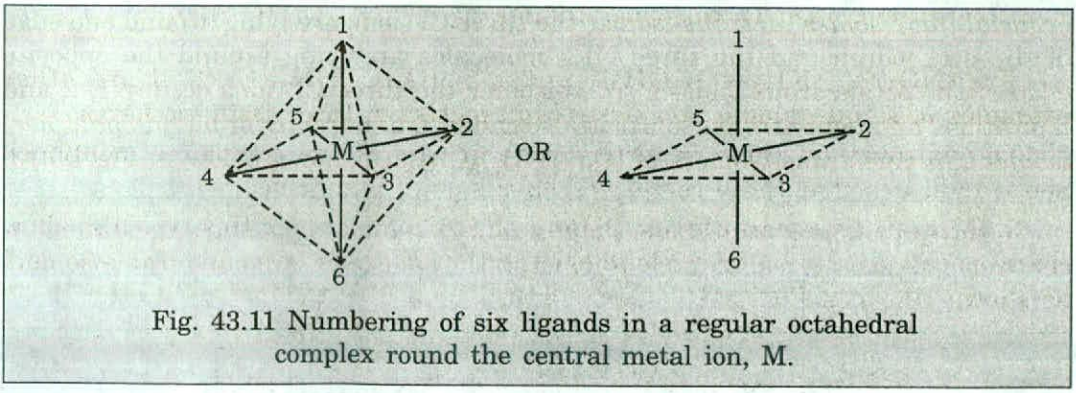


Fig. 43.11 Numbering of six ligands in a regular octahedral complex round the central metal ion, M.

It has been shown by Werner that octahedral complexes of $[Ma_6]$, $[M(AA)_3]$ and $[Ma_5b]$ type give only single geometrical isomer, *i.e.* the complexes of these types do not show geometrical isomerism. However, the following octahedral complexes give two or more geometrical isomers.

1. $[Ma_4b_2]$ type complexes. Octahedral complexes of this type exist in *cis* and *trans* isomers. In *cis*-isomer the two monodentate *b* ligands occupy adjacent positions (*i.e.* 1 and 2 positions) of the octahedron while in *trans*-isomer these ligands occupy the opposite positions (*i.e.* 1 and 6 positions) of the octahedron. For example $[Co^{3+}(NH_3)_4Cl_2]^+$ ion exists in *cis*- and *trans*-isomers. In *cis*-isomer the two Cl^- ions occupy 1 and 2 positions while in *trans*-isomer these ions occupy 1 and 6 positions as shown in Fig. 43.12.

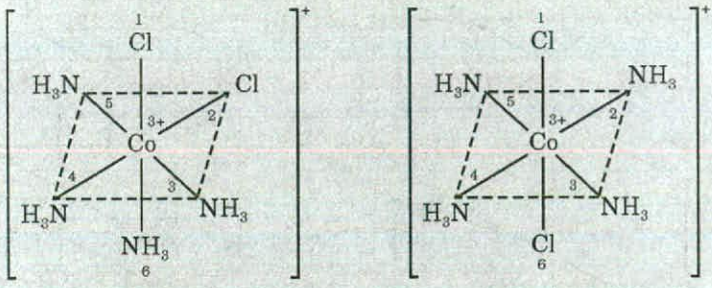


Fig. 43.12. Cis-and trans-isomers of $[Co^{3+}(NH_3)_4Cl_2]^+$ ion.

$[Co^{3+}(NH_3)_4(NO_2)_2]^+$ is another example of $[Ma_4b_2]$ type octahedral complex which exists in *cis*- and *trans*- isomers.

2. $[Ma_3b_3]$ type complexes. Octahedral complexes of this type also exist in *cis*- and *trans*-isomers. For example $[Co^{3+}(NH_3)_3Cl_3]$ exists in *cis*- and *trans*-isomers. In *cis*-isomer the three Cl^- ions lie on the corners of one of the triangular face of the octahedron and the three NH_3 molecules are lying on the corners of the opposite triangular face of the octahedron. Thus in *cis*-isomer the three Cl^- ions occupy 1, 2 and 3 positions and hence this isomer is also called *1, 2, 3 isomer* or *facial* (*fac*) *isomer*. In *trans*-isomer the three Cl^- ions are lying around one edge of the octahedron and the three NH_3 molecules are lying around the opposite edge of the octahedron. Thus in *trans*-isomer the three Cl^- ions occupy 1, 2 and 6 positions and hence *trans*-isomer is also called *1, 2, 6 isomer* or *meridional* (*mer*) *isomer*. *Cis* and *trans*-isomers of $[Co^{3+}(NH_3)_3Cl_3]$ are shown below in Fig. 43.13.

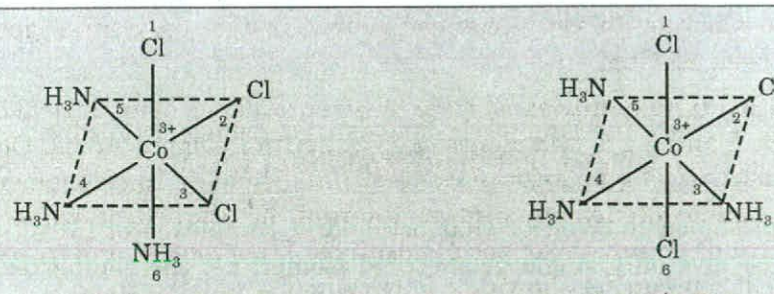


Fig. 43.13. Cis- and trans- isomers of $[Co^{3+}(NH_3)_3Cl_3]$

$[Cr^{3+}(H_2O)_3F_3]$, $[Rh^{3+}(py)_3Cl_3]$, $[Cr^{3+}(NH_3)_3Cl_3]$, $[Ru^{3+}(H_2O)_3Cl_3]$, $[Pt^{4+}(NH_3)_3Br_3]^+$, $[Pt^{4+}(NH_3)_3I_3]^+$, $[Ir^{3+}(H_2O)_3Cl_3]$, $[Ru^{3+}(MeCN)_3Cl_3]$ and $[Co^{3+}(NH_3)_3(NO_2)_3]$ are other examples of $[Ma_3b_3]$ type octahedral complexes which exist in *cis*- and *trans*-isomers.

3. $[Ma_2b_2c_2]$ type complexes. Octahedral complexes of this type can exist theoretically in five geometrical isomers. Out of these only three have been prepared. All the five geometrical isomers for $[Pt^{4+}(NH_3)_2(py)_2Cl_2]^{2+}$ ion have been shown in Fig. 43.14.

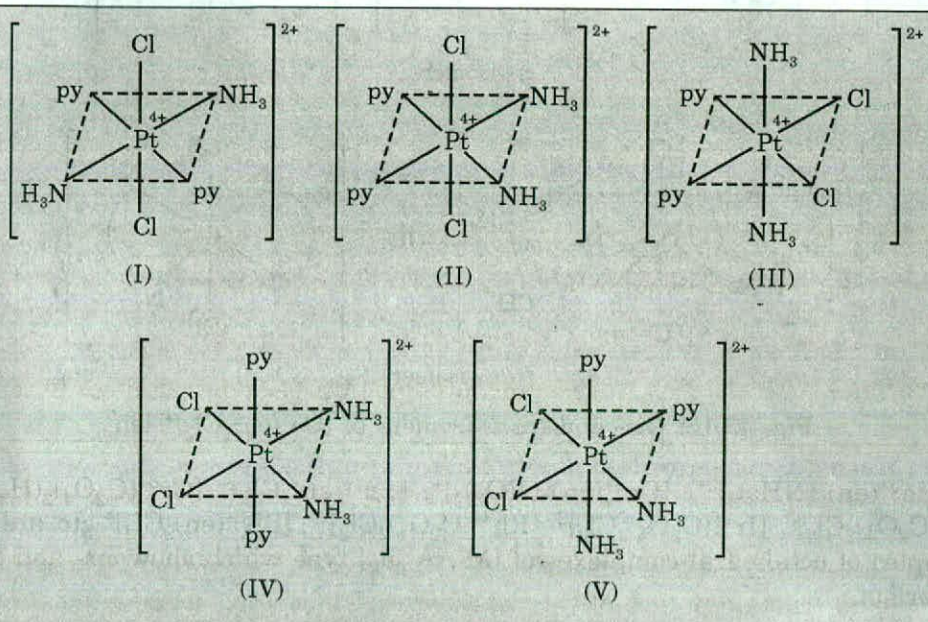


Fig. 43.14. All possible five geometrical isomers of $[Pt^{4+}(NH_3)_2(py)_2Cl_2]^{2+}$ ion. Note that the two like groups in isomer (*V*) are *cis* to each other.

4. [Mabcdef] type complexes. Octahedral complexes which have different monodentate ligands have been prepared for Pt(IV). $[Pt^{4+}(py)\ (NH_3)\ (NO_2)\ (Cl)\ (Br)\ (I)]$ is the only complex of this type of complexes. Theoretically 15 geometrical isomers are possible for this complex compound. In fact only three geometrical isomers have been isolated.

5. $[M(AA)_2a_2]$ type complexes. Here (AA) represents a symmetrical bidentate ligand in which A and A are two identical coordinating (donor) atoms. Octahedral complexes of $[M(AA)_2a_2]$ type exist in *cis*-and *trans*-isomers. In *cis*-isomer the two monodenate *a* ligands occupy adjacent positions of the octahedron while in *trans*-isomer these ligands occupy the opposite positions. Thus the *cis*- and *trans*-isomers of $[Co^{3+}(en)_2Cl_2]^+$ ion can be shown as follows in Fig. 43.15.

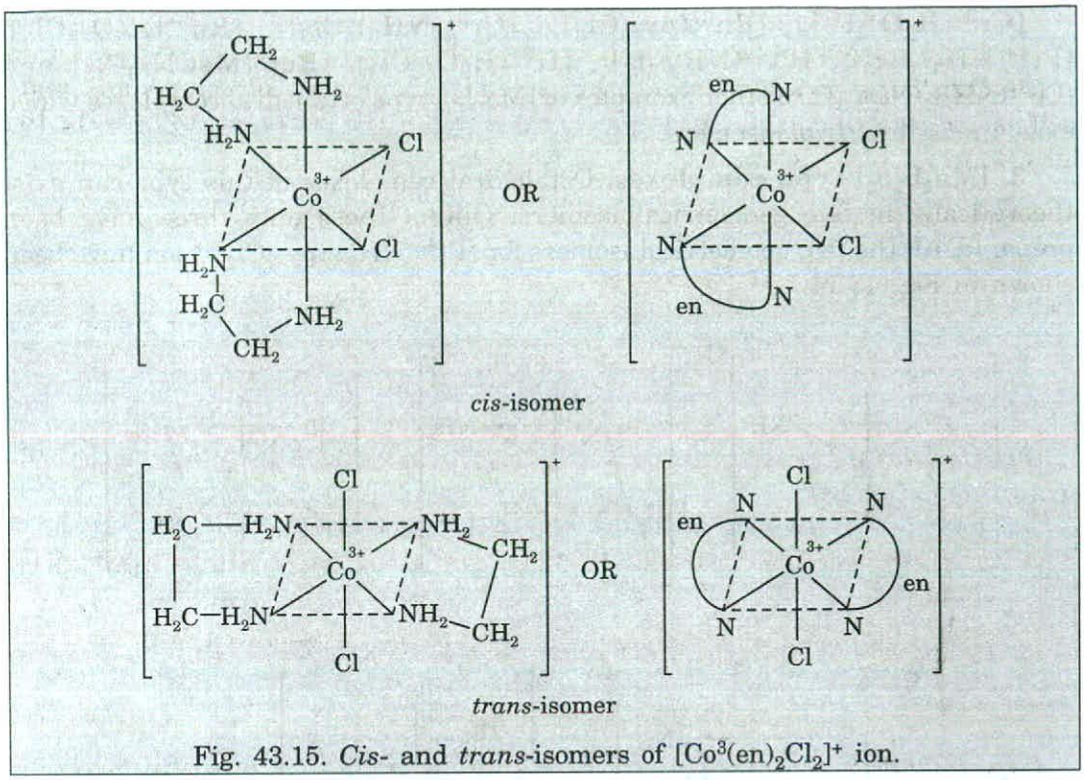


Fig. 43.15. *Cis-* and *trans*-isomers of $[Co^{3}(en)_2Cl_2]^+$ ion.

$[Co^{3+}(en)_2(NH_3)_2]^{3+}$, $[Co^{3+}(en)_3(NO_3)_2]^+$, $[Cr^{3+}(en)_2Cl_2]^+$ $[Cr^{3+}(C_2O_4)_2(H_2O)_2]^-$, $[Ir^{3+}(C_2O_4)_2Cl_2]^{3-}$ $[Ir^{4+}(C_2O_4)_2Cl_2]^{2-}$ $[Rh^{4+}(C_2O_4)_2Cl_2]^{2-}$. $[Rh^{3+}(en)_2Cl_2]^+$ etc. are other examples of octahedral complexes of $[M(AA)_2a_2]$ type which show *cis-* and *trans*-isomerism.

6. $[M(AA)_2ab]$ type conplexes. Octahedral complexes of this type exist in *cis-* and *trans*-isomers. In *cis*-isoiner the two monodentate *a* and *b* ligands occupy the adjascent (*i.e. cis*) positions of the octahedron while in *trans*-isomer these ligands occupy the opposite (*i.e. trans*) positions. Thus *cis-* and *trans*-isomers of $[Co^{3+}(en)_2(NH_3)(Cl)]^{2+}$ ion can be shown as follows in Fig. 43.16.

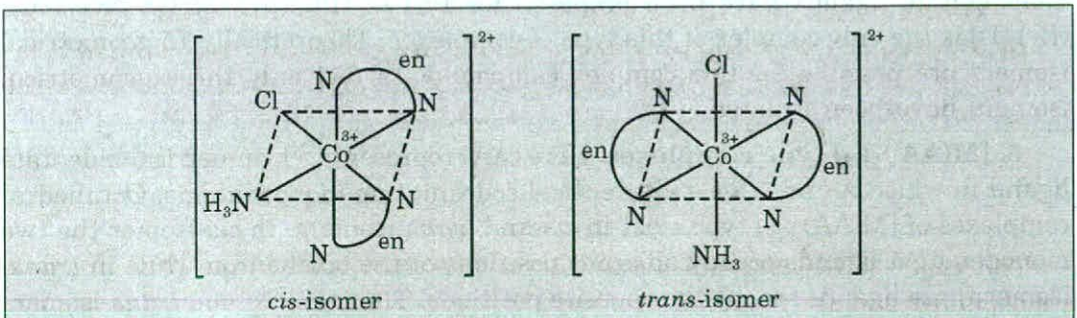
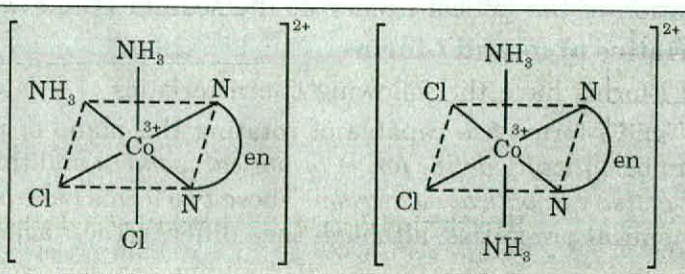


Fig. 43.16. *Cis-* and *trans*-isomers of $[Co^{3+}(en)_2(NH_3)(Cl)]^{2+}$ ion.

$[Ru^{3+}(C_2O_4)_2(py)(NO)]^-$ is another example of octahedral complex of $[M(AA)_2ab]$ type which shows *cis-* and *trans*-isomerism.

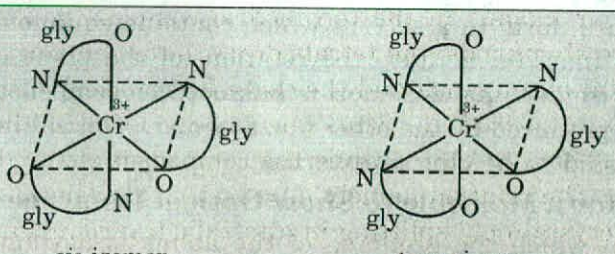
7. $[M(AA)a_2b_2]$ type complexes. Octahedral complexes of this type exist in *cis*- and *trans*-isomers. In *cis*-isomer both monodentate *a* and *b* ligands occupy *cis* positions while in *trans*-isomer these ligands occupy *trans* positions. For example in *cis*- isomer of $[Co^{3+}(en)(NH_3)_2Cl_2]^+$ ion both NH_3 and Cl^- ion are *cis* to each other while in *trans*-isomer both NH_3 and Cl^- ion are *trans* to each other (See Fig. 43.17).



cis-isomer *trans*-isomer

Fig. 43.17. *Cis*- and *trans*-isomers of $[Co^{3+}(en)(NH_3)_2Cl_2]^+$ ion.

8. $[M(AB)_3]$ type complexes. Here (AB) represents an unsymmetrical bidentate ligand in which A and B are two different coordinating (donor) atoms. Octahedral complexes of this type exist in *cis*- and *trans*-isomers. As an example the *cis*- and *trans*-isomers of $[Cr^{3+}(gly)_3]$ has been shown in Fig 43.18. Each of these forms is optically active and hence each has a pair of optical isomers.



cis-isomer *trans*-isomer

Fig 43.18. *Cis*- and *trans*- isomers of $[Cr^{3+}(gly)_3]$.

Optical Isomerism

Definition of Some Terms.

Before discussing the optical isomerism shown by various types of complexes we will define some important terms related to this isomerism.

When the solutions of certain complex compounds are placed in the path of a *plane-polarised light* (the waves of the plane-polarised light vibrate only in one direction; vibrations in other directions are cut off), they rotate its plane through a certain angle which may be either to the left or to the right. *This property of a complex of rotating the plane of polarised light is called its optical activity and the complex possessing this property is said to be optically active.* Optically active

complexes are said to exist in the following forms (*a*) One which rotates the plane of polarised light towards right (*i.e.* in clockwise direction) is said to be *dextro-rotatory* or *d*-form. *d-form* is also represented by placing (+) sign before its name or formula. (*b*) One which rotates the plane of polarised light towards left (*i.e.* in anti-clockwise direction) is called *levo-rotatory* or *l*-form. *l*-form is also represented by putting (–) sign before its name or formula. (+), dextro, and (–), levo, refer to the sign of rotation of the optical isomer at the sodium D line wavelength.

Characteristics of *d*- and *l*-forms

The *d*- and *l*-forms have the following characteristics :

(*i*) Since *d*- and *l*-forms are capable of rotating the plane of polarised light, these are said to be *optically active forms or optical isomers* and this phenomenon is called *optical activity* or *optical isomerism.* These two forms have exactly identical physical and chemical properties, although they differ in their action on polarised light.

(*ii*) *d*- and *l*-forms are mirror-images to each other just as left hand is the mirror image of the right hand. Thus *d*- and *l*-forms can be superimposed on each other. Since these forms are related to each other as mirror-images, they are commonly called *enantiomorphs* (Latin : *enantio* = opposite, *morphs* = forms) or *enantiomers.* Thus optical isomerism is now often referred to as *enantiomerism.*

(*iii*) The isomer which is not capable of rotating the plane of polarised light is called *optically inactive.* Such an isomer is called *racemic, dl-or* (±) *form.* A racemic substance is composed of 50% *d*- and 50% *l*-form. The solution of a racemic (*dl* mixture) form in a solvent which contains equimolecular amounts of *d*- and *l*-forms is inactive, because the rotation (of the plane of polarised light) produced by one isomer, say *d*-isomer, is balanced or compensated by equal but opposite rotation produced by the other (*i.e. l*-isomer). Optical inactivity produced in *dl*-mixture is said to be clue to external compensation.

Conditions for a Molecule to Show Optical Isomerism.

A molecule in which the grouping of the atoms is asymmetric is called an *asymmetric* or *dissymmetric molecule.* An asymmetric molecule has the following features :

(*i*) An asymmetric molecule never has a plane of symmetry (also called mirror-image plane) which is defined as an imaginary plane dividing the molecule in such a way that the part of it on one side of the plane is the mirror image of that on the other side of the plane. The molecules possessing such a plane of symmetry are always *inactive while those having no plane of symmetry are optically active and hence show optical isomerism.*

(*ii*) An asymmetric molecule cannot be superimposed on its mirror image. Thus the most necessary and sufficient condition for a molecule to show optical isomerism (*i.e.* to exist in *d*- and *l*-forms) is that *the molecule should be asymmetric, (i.e., it should have no plane of symmetry) and should not be superimposable on its mirror image.*

Optical Isomerism in Tetrahedral Complexes (C.N. = 4)

Tetrahedral complexes of $[Ma_4]$ and $[Ma_3b]$ type are not able to show optical isomerism because all the possible arrangements of the ligands round the central metal ion, M are exactly equivalent. By analogy with organic tetrahedral molecules in which carbon atom is surrounded by four different atoms or groups, it is expected that a tetrahedral metal complex of [*Mabcd*] type should also exhibit optical isomerism, *i.e.* it should be possible for us to isolate optically active *dextro* and *levo* forms of tetrahedral metal complex of [*Mabcd*] type. However it has not been possible to isolate dextro and levo forms of this complex due to its *labile* nature. Here it may be noted that 4 different groups round the central metal ion are not the only requirement to make the complex to show mirror-image isomerism. All that is required is that the molecule should be asymmetric (*i.e.*, unsymmetrical), *i.e.* it should have no plane of symmetry so that it can exist in two mirror-image forms. Tetrahedral complexes of Be(II), B(III) and Zn(II) with symmetrical bidentate ligands have been made and resolved into optical isomers. Some examples of tetrahedral complexes of this type are *bis* (salicylaldehydato) boron (III) ion, $[B^{3+}(C_6H_4.O.CHO)_2]^+$ and *bis* (benzoylacetonato) beryllium (II), $[Be^{2+}(C_6H_5CO.CH.CH_3CO)_2]^\circ$ whose mirror-image isomers are given in Fig. 43.19 and 43.20 respectively.

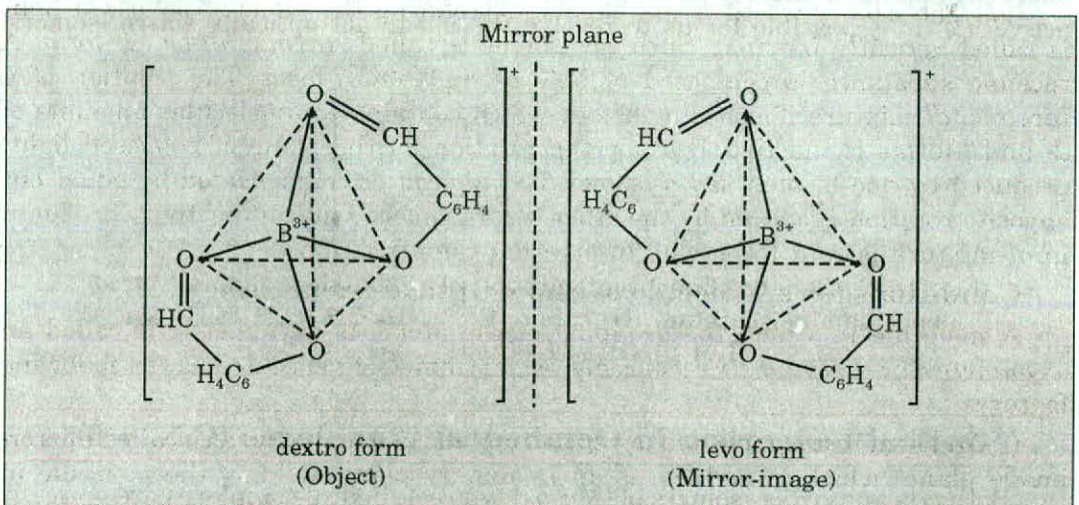


Fig. 43.19. Mirror-image isomers of tetrahedral *bis* (salicyl aldehydato) boron (III) ion, $[B^{3+}(C_6H_4.O.CHO)_2]^+$.

Optical Isomerism in Squar Planar Complexes (C.N. = 4)

Optical isomerism rarely occurs in square planar complexes, since they have all the four ligands and the central metal ion in the same plane and hence contain a plane or axis of symmetry. Thus these complexes are optically inactive, *i.e.* they cannot show optical isomerism even if all the four ligands are different. Although square planar complexes seldom show optical isomerism, yet the square planar complex *viz.* *iso*-butylene diamine-*meso*-stilbenediamine platinum (II) cation,

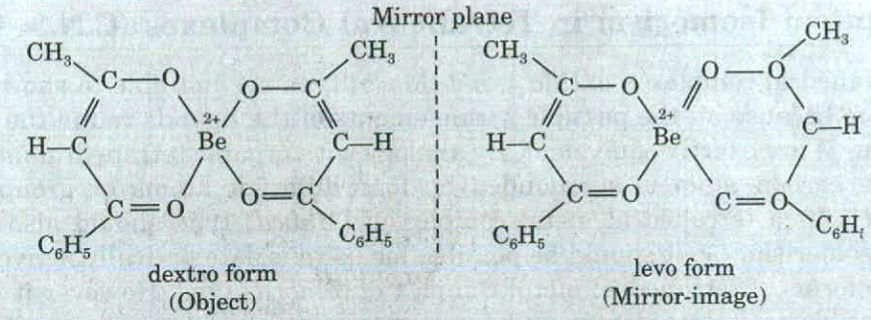


Fig. 48.20. Mirror-image isomers of tetrahedral *bis* (benzoylacetonato) beryllium (II), $[Be^{2+}\ (C_6H_5CO.CH.CH_3CO)_2]^\circ$.

$[Pt^{2+}\ (NH_2.CH\ (C_6H_5).CH(C_6H_5).NH_2)\ (NH_2.CH_2.C(CH_3)_2.NH_2)^{2+}$ has no plane or axis of symmetry (Fig. 43.21) and hence is unsymmetric and optically active, *i.e.* this square planar complex can be resolved into optically active isomers. Why this square planar complex can be resolved into optically active isomers can be explained as follows : In the square planar configuration of this ion as shown in Fig. 43.21 with two rings (I) and (II), since the C_6H_5 groups are below and H-atoms are above the plane of the ring (II), this structure has no plane or axis of symmetry. In the absence of plane or axis of symmetry, the ion in square planar geometry is optically active, *i.e.* it is possible for us to resolve the ion to get optically active isomers.

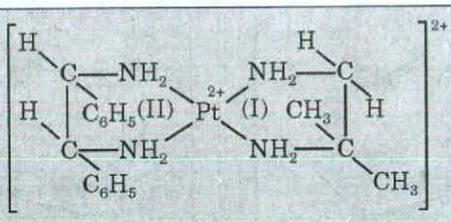


Fig. 43.21. Square planar configuration of *iso*-butylene diamine-*meso*-stilbenediamine platinum (II) cation, $[Pt^{2+}(NH_2.CH\ (C_6H_5).CH\ (C_6H_5).\ (NH_2)\ (NH_2)\ CH_2.C(CH_3)_2.NH_2]^{2+}$.

Optical Isomerism in Octahedral Complexes (C.N. = 6)

Both *cis*- and *trans*-isomers of $[Ma_4b_2]$ type octahedral complexes are optically inactive due to the presence of symmetry and hence do not show optical isomerism. The facial and meridional isomers of $[Ma_3b_3]$ type octahedral complexes are optically inactive and hence do not exist in optical isomers. The following octahedral complexes show optical isomerism.

1. $[Ma_2b_2c_2]$ type complexes. We have seen that the octahedral complexes of this type can exist theoratically in five geometrical isomers which have already been shown in Fig. 43.14. Out of these only three have been prepared. The geometrical isomer with all like groups *cis* to one another occurs in two optical isomers. For example the geometrical isomer of $[Pt^{4+}\ (NH_3)_2\ (py)_2\ Cl_2]^{2+}$ which has all the like groups *cis* to one another occurs in mirror-image isomers as shown in Fig. 43.22.

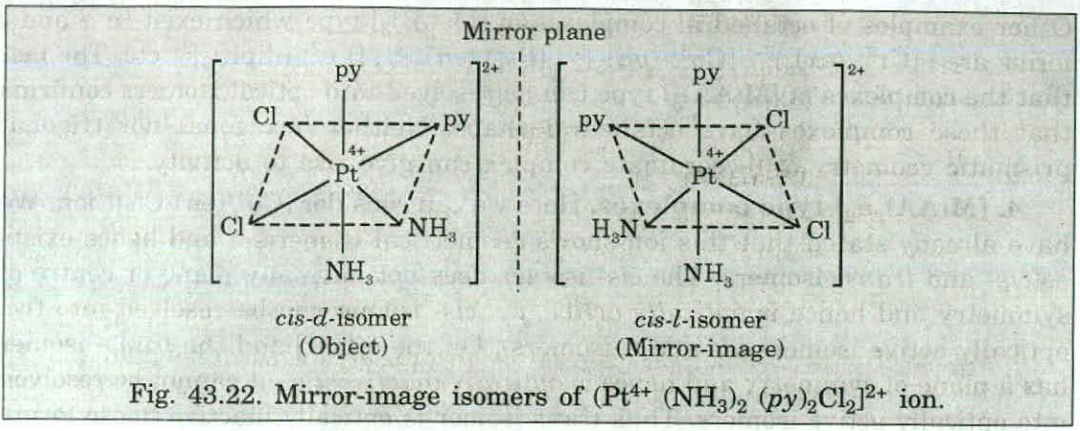


Fig. 43.22. Mirror-image isomers of $(Pt^{4+}\ (NH_3)_2\ (py)_2Cl_2]^{2+}$ ion.

2. [Mabcdef] type complexes. Octahedral complexes of this type for Pt (IV) have only 15 geometrical isomers each of which exists in *d*-and *l*-forms to give a total of 30 isomers. For example *d*- and *l*-forms obtained for one geometrical isomer of $[Pt^{4+}\ (py)\ (NH_3)\ (NO_2)\ (Cl)\ (Br)\ (I)]^{\circ}$ are shown in Fig. 43.23.

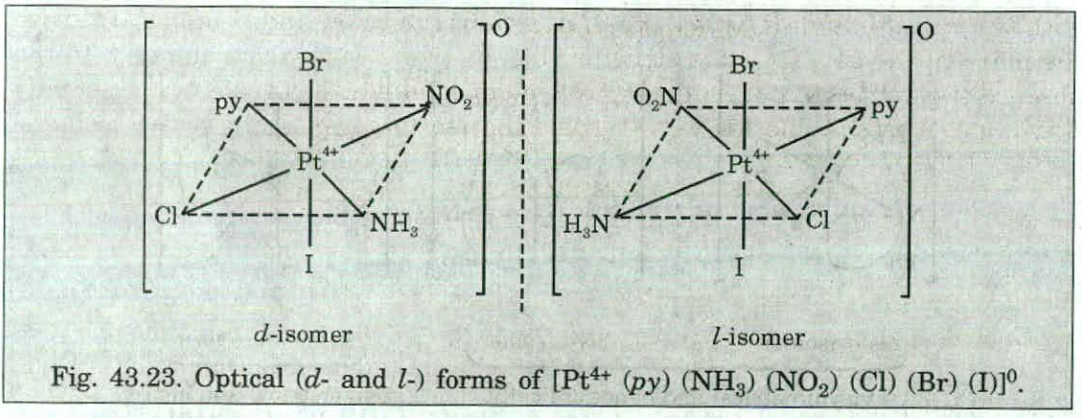


Fig. 43.23. Optical (*d*- and *l*-) forms of $[Pt^{4+}\ (py)\ (NH_3)\ (NO_2)\ (Cl)\ (Br)\ (I)]^0$.

3. $[M(AA)_3]$ type complexes. Due to the absence of a plane or centre of symmetry, the octahedral complexes of this type are resolvable into *dextro* and *levo* forms. For example *d*- and *l*- forms of $[Co^{3+}\ (en)_3]^{3+}$ ion are shown in Fig. 43.24.

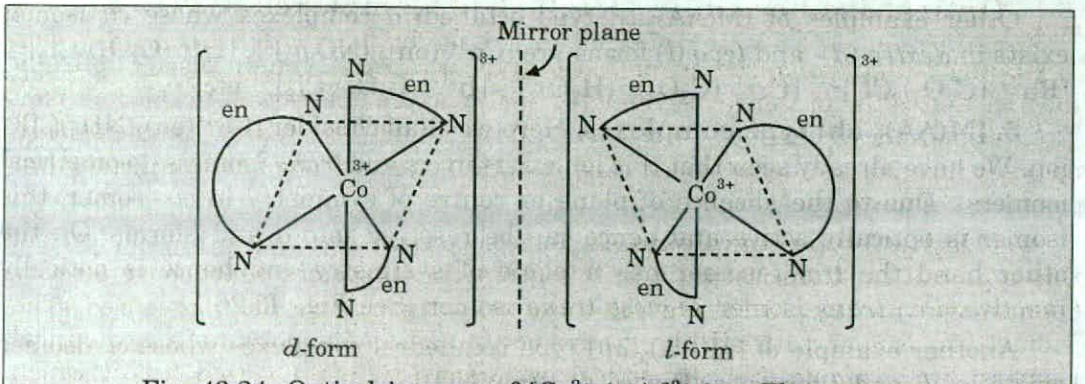


Fig. 43.24. Optical isomers of $[Co^{3+}\ (en)_3]^{3+}$ ion. These cannot be superimposed on each other.

Other examples of octahedral complexes of $[M(AB)_3]$ type which exist in *d* and *l* forms are : $[Cr^{3+}\ (ox)_3]^{3-}$, $[Co^{3+}\ (pn)_3]^{3+}$, $[Pt^{4+}\ (en)_3]^{4+}$, $[Fe^{2+}\ (diph)_3]^{2+}$ etc. The fact that the complexes of $[M(AA)_3]$ type can be resolved into optical isomers confirms that these complexes have octahedral shape. Neither hexagonal nor trigonal prismatic geometry of 6-coordinate complex can give rise to activity.

4. $[M(AA)_2a_2]$ type complexes. Here we can consider $[Co^{3+}(en)_2Cl_2]^+$ ion. We have already stated that this ion shows geometrical isomerism and hence exists as *cis-* and *trans-* isomers. The *cis-* isomer does not have any plane or centre of symmetry and hence is *optically active, i.e. cis-* isomer can be resolved into two optically active isomers (*d-* and *l-* isomers). On the other hand the *trans-* isomer has a plane of symmetry and hence is *optically inactive, i.e.*, it cannot be resolved into optically active isomers. Thus trans isomer is optically inactive (meso form). Consequently $[Co(en)_2Cl_2]^+$ ion has three optical isomers *viz.* : (Also see Fig. 43.25) (*a*) Two optically active isomers corresponding to cis-configuration (*i.e. d-* and *l-* forms). One form is the mirror image of the other. (*b*) One optically inactive form corresponding to trans-form (meso-form).

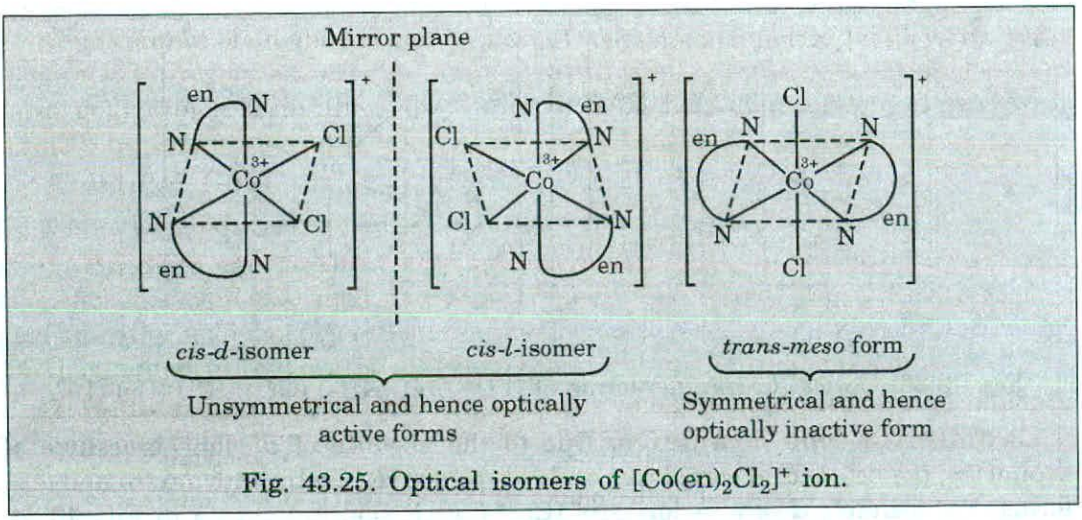


Fig. 43.25. Optical isomers of $[Co(en)_2Cl_2]^+$ ion.

Other examples of $[M(AA)_2a_2]$ type octahedral complexes whose *cis*-isomer exists in *dextro* (*d*)- and *levo* (*l*) forms are $[Co^{3+}\ (en)_2\ (NO_3)_2]^{3+}$, $[Ir^{4+}\ (C_2O_4)_2Cl_2]^{2-}$, $[Rh^{4+}\ (C_2O_4)_2Cl_2]^{2-}$, $[Cr^{3+}\ (C_2O_4)_2\ (H_2O)_2]^-$, $[Ir^{3+}\ (C_2O_4)_2Cl_2]^{3-}$ etc.

5. $[M(AA)_2\ ab]$ type complexes. Here we shall consider $[Co^{3+}(en)_2(NH_3)Cl]^{2+}$ ion. We have already seen that this ion exists in *cis* and *trans*-isomers (geometrical isomers). Due to the absence of plane or centre of symmetry in *cis*-isomer, this isomer is optically active and hence can be resolved into *d* and *l*-forms. On the other hand the *trans*-isomer has a plane of symmetry and hence is optically inactive, *i.e.*, *trans*-isomer is *meso-trans* isomer (See Fig. 43.26).

Another example of $[M(AA)_2\ ab]$ type octahedral complexes whose *cis*-isomer exists in *d-* and *l*-forms is $[Ru^{3+}(C_2O_4)_2(py)(NO)]^-$.

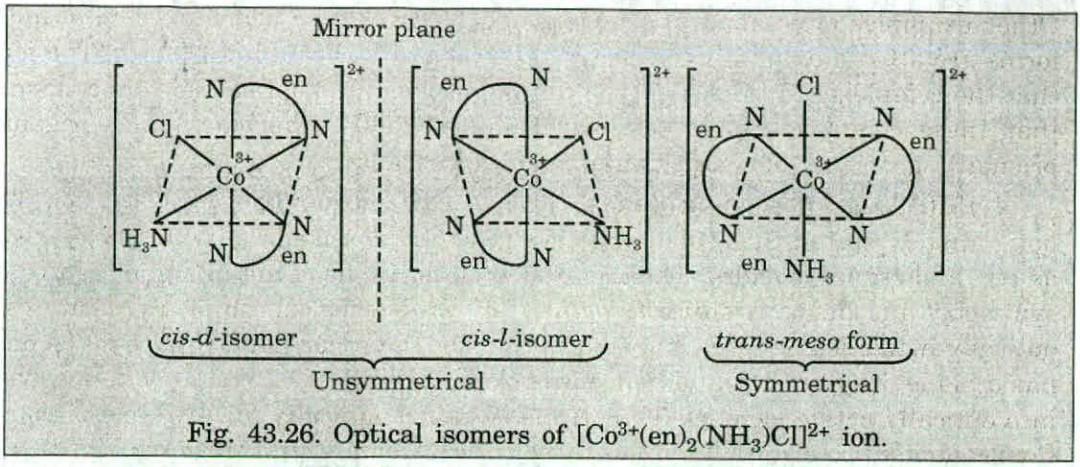


Fig. 43.26. Optical isomers of $[Co^{3+}(en)_2(NH_3)Cl]^{2+}$ ion.

6. $[M(AA)a_2b_2]$ type complexes. Here we shall consider $[Co^{3+}(en)(NH_3)_2Cl_2]^+$ ion. We have seen that this ion exists in *cis*- and *trans*-isomers (geometrical isomers). *Cis*-isomer is optically active and hence gives optically active *d*- and *l*-forms. On the other hand *trans*-isomer is optically inactive and hence does not give any optical active isomer. (See Fig 43.27).

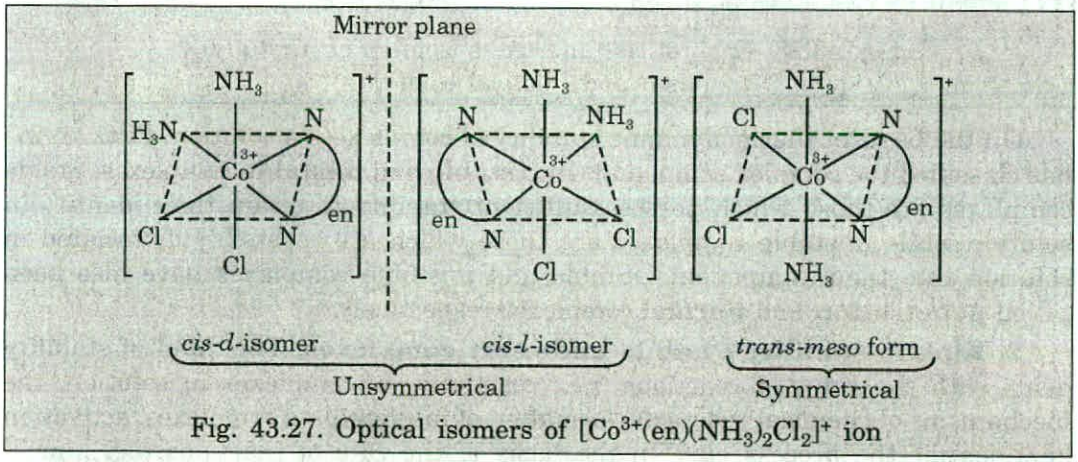


Fig. 43.27. Optical isomers of $[Co^{3+}(en)(NH_3)_2Cl_2]^+$ ion

$[Co^{3+}(C_2O_4)(NH_3)_2(NO)_2]^-$ ion is another important example of $[M(AA)\ a_2b_2]$ type octahedral complexes whose *cis*-isomer gives *d*- and *l*-isomers.

7. $[M(AB)_3]$ type complexes. We have seen that an octahedral complex of this type exists in *cis*- and *trans*-isomers (geometrical isomers). Each of these forms is optically active and hence each gives a pair of optical isomers (*d*- and *l*-forms) as shown below in Fig. 43.28 for $[Cr^{3+}(gly)_3]$ complex compound.

Stability of Complex Compounds in Aqueous Solution

In studying the formation of complex compounds in solution two kinds of stability have to be distinguished. These are :

1. Thermodynamic stability : Stable and unstable complexes. This kind of stability deals with the properties like bond energies, stability constants and redox potentials that affect the equilibrium conditions.

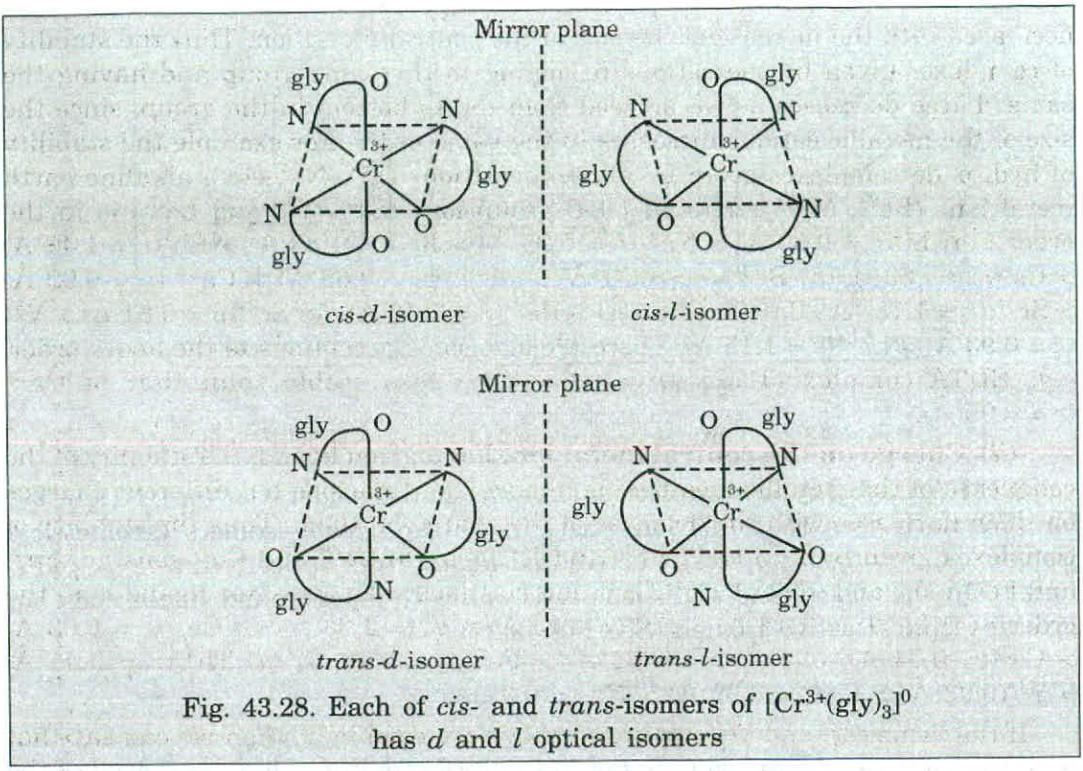


Fig. 43.28. Each of *cis*- and *trans*-isomers of $[Cr^{3+}(gly)_3]^0$ has *d* and *l* optical isomers

On the basis of thermodynamic stability of complexes in solution, Biltz (1927) has classified the complex compounds into **stable** and **unstable** complexes. Stable complexes are those which possess sufficient stability to retain their identity in solution while unstable complexes are those which are reversibly dissociated in solution into their components. Stable and unstable complexes have also been called **penetration** and **normal** complexes respectively.

2. Kinetic stability : Labile and inert complexes. This kind of stability deals with the rates of reactions (*i.e.*, reactivity) of complexes in solution, the mechanisms of chemical reactions, formation of intermediate complexes, activation energies for the process etc. On the basis of the rate of reactions (*i.e.* kinetic stability) of the complexes in solution, Taube (1950) has classified the complexes into **labile** and **inert** complexes. Labile complexes are those whose one or more ligands in the co-ordination sphere can be rapidly replaced by other ligands and the ability of a complex to replace its one or more ligands by other ligands is called its **lability**. Inert complexes are those whose one or more ligands can either not be replaced or can be replaced with difficulty by other ligands.

Factors Affecting the Stability of Metal Complexes.

The stability (or stability constants) of metal complexes depends on the following factors :

1. Properties of central metal ion. The following properties of central metal ion affect the stability of the metal complexes :

***(i)* Size of central metal ion.** For a given ligand the stability (or stability constant) of the complexes of the metallic ions having the same charge on them

decreases with the increase of the size of the central metal ion. Thus the stability of complexes given by the cations belonging to the same group and having the same charge decreases as we proceed from top to bottom in the group, since the size of the metallic cations increases in the same order. For example the stability of hydroxide complexes given by alkali metal ions (Li^+, Na^+ etc.), alkaline earth metal ions (Be^{2+}, Mg^{2+} etc.) and III B group ions (Sc^{3+}, Y^{3+} and La^{3+}) is in the order : (*a*) $Li^+(r = 0.60$ Å) > Na^+ ($r = 0.95$ Å) > $K^+(r = 1.33$ Å) > $Rb^+(r = 1.48$ Å) > $Cs^+(r = 1.69$Å). (*b*) Be^{2+} ($r = 0.31$ Å) > Mg^{2+} ($r = 0.65$ Å) > Ca^{2+} ($r = 0.99$ Å) > Sr^{2+} ($r = 1.13$ Å) >$Ba^{2+}(r = 1.35$ Å) > $Ra^{2+}(r = 1.40$ Å). (*c*) $Sc^{3+}(r = 0.81$ Å) > Y^{3+} ($r = 0.93$ Å) > $La^{3+}(r = 1.15$ Å). There are also some exceptions to the above order, *e.g.* EDTA complex of $Mg^{2+}(r = 0.65$ Å) is less stable than that of Ca^{2+} ($r = 0.99$ Å).

***(ii)* Charge on the central metal ion.** For a given ligand, the stability of the complexes of the metallic ions having almost the same size but different charges on them decreases with the decrease of the charge on them. Thus the stability of complexes given by : (*a*) La^{3+}, Sr^{2+} and K^+ ions. (*b*) Co^{3+} and Co^{2+} ions. (*c*) Fe^{3+} and Fe^{2+} ions, and (*d*) Th^{4+}, Y^{3+},Ca^{2+} and Na^+ ions with the same ligand is in the order : (*a*) $La^{3+}(r = 1.15$ Å) > $Sr^{2+}(= 1.13$ Å) > $K^+(= 1.33$ Å) (*b*) $Co^{3+}(r = 0.63$ Å) > $Co^{2+}(= 0.74$ Å) (*c*) $Fe^{3+}(r = 0.64$ Å) > $Fe^{2+}(r = 0.76$ Å) (*d*) $Th^{4+}(r = 0.95$ Å) > $Y^{3+}(0.93$ Å) > $Ca^{2+}(= 0.99$ Å) > $Na^+(= 0.95$ Å).

If the factors (*i*) and (*ii*) mentioned above are combined, then we can say that with the increase of ionic potential of the central metal ion (Ionic potential of the metal ion = charge on the metal ion/ size of the ion), the stability of the complexes with the same ligand also increases. For example the stability of hydroxide complexes of Li^+, Ca^{2+}, Ni^{2+}, ...Be^{2+} ions whose ionic potential increase from Li^+ to Be^{2+} ions also increases in the same direction as shown below :

Central metal ion (charge on the ion is shown in parentheses)	Ionic radius (A°)	Ionic potential		Order of stability of complexes	
Li^+ (+ 1)	0.60	1/0.60 = 1.6	Increasing ↓		Increasing ↓
Ca^{2+} (+ 2)	0.99	2/0.99 = 2.0			
Ni^{2+} (+ 2)	0.72	2/0.72 = 2.97			
Y^{3+} (+ 3)	0.93	3/0.93 = 3.22			
Th^{4+} (+ 4)	0.95	4/0.95 = 4.20			
Al^{3+} (+ 3)	0.50	3/0.50 = 6.0			
Be^{2+} (+ 2)	0.31	2/0.31 = 6.45			

***(iii)* Electronic configuration of the central metal ion : Irving-William order of stability.** In case of metallic ions which have the same radius and same charge (*e.g.* Na^+ and Cu^+; Ca^{2+} and Cd^{2+} or Sn^{2+} ; Sc^{3+} and Ga^{3+} or Sb^{3+} ions), the outer electronic configuration of the ions plays an important role in determing the stability of the complexes. The complexes given by metal ions possessing inert gas (8-electron ions), pseudo inert gas (18-electron ions) and pseudo inert gas plus

two (18 + 2 electron ions) electronic configuration are less stable than those given by transition metal ions which have $(n-1)d$ orbitals available for accepting the electron pairs donated by the ligands. The stability of transition metal complexes depends on, besides ionic potential, other factors like crystal field stabilisation energy, electron pairing energy, stereochemistry, availability of empty d_z^2, and $d_{x^2-y^2}$ orbitals for π bonding or back donation. The use of inner d-orbitals gives stronger metal-ligand bonding than the use of s-and p-orbitals or outer d-orbitals. The various factors influencing the stability of complexes given by transition metal ions ultimately depends on the number of electrons present in $(n-1)$ d orbitals. The stability constants of the complexes given by the transition metal d^n ions for the equilibirium : $[M(H_2O)_n] + nL \longrightarrow ML_n + nH_2O$ follow the order : $d^0 < d^1 < d^2 < d^3 \lessapprox d^4 > d^5 < d^6 < d^7 < d^8 \lessapprox d^9 > d^{10}$. The sequence $d^3 > d^4$ and $d^8 > d^9$, is expected when the John-Teller effect is low and the coordination number is 6. The sequence $d^3 < d^4$ and $d^8 < d^9$, however, is expected when the John-Teller effect is large and the coordination number is 4. The stability of complexes of the divalent ions of the first transition series from Mn^{2+} to Zn^{2+} with a given ligand increases from Mn^{2+} to Cu^{2+} and then decreases at Zn^{2+}. Thus : $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$. This sequence of stability is commonly known as **Irving-William order of stability** of complexes of M^{2+} ions (M^{2+} = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}. Cu^{2+}, Zn^{2+}) with a given ligand.

***(iv)* Electronegativity and polorising power of the central metal ion.** The bonding between a central metal ion and a ligand is, to some extent, due to the donation of electrons by the ligand to the central ion. Thus, it might be concluded that a central ion with higher electronegativity (*i.e.* a central ion with a strong electron-attracting tendency) would give more stable complexes. Similarly the central metal ion with high polarising power gives more stable complexes. For example complexes given Cu^+ and Cd^{2+} ions are more stable than those given by Na^+ and Ca^{2+} ions respectively.

***(v)* Ionisation energy of the central metal ion.** Generally the stability of complexes given by M^{2+} ions increases with the increase of first plus second ionisation potential for M^{2+} ions.

***(vi)* Class *a* and class *b* metals.** Chatt and Ahrland have classified the metals into three categories : *a*, *b* and *borderline*, on the basis of their electron-acceptor properties. This classification is shown below (normal valence states are assumed). (*a*) *Class a metals* : H, the alkali and alkaline earth metals, the elements Sc $\longrightarrow$ Cr, Al $\longrightarrow$ Cl, Zn $\longrightarrow$ Br, In, Sn, Sb and I, the lanthamides and actinides (*b*) *Class b metals* : Rh, Pd, Ag, Ir, Pt, Au, Hg. (*c*) *Borderline metals* : The elements Mn $\longrightarrow$ Cu, Tl $\longrightarrow$ Po, Mo, Te, Ru, W, Re, Os, Cd.

Class *a* metals form *more stable* complexes with ligands having the coordinating atoms from the second period elements (*e.g.* N, O, F) than those of an analogous ligand in which the donor atom is from third or later period (*e.g.* P, S, Cl). Class *b* metals have the relative stabilities reversed. If the ligand contains the heavier donor atoms, class *a* and *b* metals are characterised by the stability order given below :

$F^- > Cl^- > Br > I^-$
$O > > S > Se > Te$ } Class *a* metals
$N > > P > As > Sb > Bi$

$F^- < Cl^- < Br^- < I^-$
$O < < S \approx Se \approx Te$ } Class *b* metals
$N < < P < As < Sb < Bi$

Class *b* metals are characterised by the presence of a number of *d*-electrons beyond an inert-gas core. These *d*-electrons are used to form π-bond with ligand atoms. It is believed that the stability of the complexes of class *b* metals results from covalent contribution to metal-ligand bonds and from the transfer of electron density from the metal to the ligand *via* π-bonding. The most stable complexes of class *b* metals are formed with ligands like PMe_3, S^{2-} and I^- which have vacant *d*-orbitals or like CO, CN^- which have vacant molecular orbitals of low energy.

For *borderline metals* the stability constants do not display either class *a* or class *b* behaviour uniquely.

2. Properties of the ligand. The following properties of the ligand affect the stability of the metal complexes.

***(i)* Size and charge of ligand.** If a ligand is smaller, it can approach the metal ion more closely forming a stable bond. Similarly, a highly charged ligand would also form a strong bond with the metal. Thus the high charge and small size of a ligand leads to the formation of stable complexes. For example the stability of the complexes of a given metal ion with halide ions used as ligands is in the order : $F^- > Cl^- > Br^- > I^-$. This order is applicable for class *a* metals. When class *b* metals (*e.g.* Pd, Ag, Pt, Hg etc) are used, the above order of stability is reversed, *i.e.* for class *b* metals the order is : $F^- < Cl^- < Br^- < I^-$.

***(ii)* Dipole moment of ligands.** For neutral ligands, the larger the magnitude of permanent dipole moment, the greater is the stability of the complexes. For example the order of stability of complexes formed by some neutral ligands is as : ammonia > ethylamine > diethylamine > triethylamine.

***(iii)* Basic character of ligands.** The more basic is the ligand, more easily it can denote electron pairs to the central ion and hence more easily it can form complexes of greater stability. The ligands that bind H^+ firmly form stable complexes with metal ions. Thus F^- should form more stable complexes than Cl^-, Br^- or I^-, and NH_3 should be better ligand than H_2O which in turn should be better than HF. ($NH_3 > H_2O > HF$). This behaviour is observed for alkali, alkaline earth and other electropositive metals like first-row transition elements, lanthanides and actinides.

***(iv)* π-bonding capacity of ligands.** The ligands like CN^-, CO, PR_3, AsR_3, SR_2, alkenes, alkynes which are capable of forming π-bonds with transition metal ions give more stable complexes.

***(v)* Steric hindrance of bulky groups.** When a bulky group is either attached to or present near a donor atom of a ligand, repulsion between the donor atom

of the ligand and the bulky group is caused and this mutual repulsion weakens the inetal-ligand bonding and hence makes the complex less stable. For example the complex of Ni^{2+} ion with 2-methyl-8-hydroxy quinoline ($\log_{10} \beta = 17.8$) is less stable than that with 8-hydroxy quinoline ($\log_{10} \beta = 21.4$). The effect of the presence of bulky group on the stability of a complex is commonly called *steric hindrance.*

3. Stability of chelates : Chelate effect. Chelates are more stable than similar non-chelated complexes of the same metal ion. Greater stability of chelated complex means that there will be smaller dissociation of the chelated complex into its components in a particular solvent. The enhanced stability conferred on a chelate is called *chelate effect.* The greater stability of a chelated complex as compared to that of a non-chelated complex is due to the increase in entropy. Thus when we consider the formation of $[Co(NH_3)_6]^{2+}$ (non-chelated complex) and $[Co(en)_3]^{2+}$ (chelated complex) from $[Co(H_2O)_6]^{2+}$ as represented by reactions (*a*) and (*b*) given below :

(*a*) $\underbrace{[Co(H_2O)_6]^{2+} + 6NH_3}_{\text{No. of particles} = 1 + 6 = 7} \rightleftharpoons \underbrace{[Co(NH_3)_6]^{2+} + 6H_2O}_{\text{Non-chelated complex; No. of particles} = 1 + 6 = 7}$

(*b*) $\underbrace{[Co(H_2O)_6]^{2+} + 3\ en}_{\text{No. of particles} = 1 + 3 = 4} \rightleftharpoons \underbrace{[Co(en)_3]^{2+} + 6H_2O,}_{\text{Chelated complex; No. of particles} = 1 + 6 = 7}$

we find that number of particles on the right hand side of reaction (*b*) which represents the formation of chelated complex is greater than that on the left hand side while the number of particles on both sides of reaction (*a*) representing the formation of non-chelated complex is the same. Consequently the ehelatel complex, $[Co(en)_3]^{2+}$ is more stable than the non-chelated complex, $[Co(NH_3)_6]^{2+}$.

The stability of chelated complexes increases with the increase of the number of donor atoms present in the chelating ligand. The stability of chelated complexes also depends on the size of the ring formed in the complex. The chelated complexes containing 4- memberod ring are not stable while those containing 5- and 6- membered ring are quite stable. A chelated complex given by a polydentate ligand containing double bonds is more stable than that given by a polydentate ligand containing only single bonds. For example an octahedral complex of acetylacetonato ligand, $\left[M^{2+}(CH_3—\overset{\overset{O}{\|}}{C}—CH=\overset{\overset{O}{|}}{C}—CH_3)_3\right]$ is more stable than the octahedral complex of ethylenediamine with the same metal ion, $[M^{2+}(NH_2—CH_2—CH_2—NH_2)_3]^{2+}$. Note that both the complexes are chelated complexes. With the increase of the number of the rings present in the chelated complex, the complex becomes more stable.

Nature of Metal—Ligand Bonding in Complexes

In order to explain the nature of metal-ligand bonding in complexes the following theories have been suggested : (1) *Werner's Coordination Theory and Sidgwick's Electronic Concept of Coordination Compounds* (2) *Valence Bond Theory* (*VBT*), also called *Atomic Orbital Theory* (*AOT*) (3) *Crystal Field Theory* (*CFT*), and (4) *Ligand Field Theory* (*LFT*), also called *Molecular Orbital Theory* (*MOT*).

Werner's Coordination Theory

In 1893 Werner put forward a theory, called Werner's coordination theory, to explain the formation of complex compounds like the ammines of Pt (IV) (*e.g.* $PtCl_4.6NH_3$, $PtCl_4.5NH_3$, $PtCl_4.4NH_3$, $PtCl_4.3NH_3$, $PtCl_4.2NH_3$) and Co (III) (*e.g.* $CoCl_3.6NH_3$, $CoCl_3.5NH_3$, $CoCl_3.4NH_3$, $CoCl_3.3NH_3$).

Salient Features of Werner's Coordination Theory.

The salient features of Werner's coordination theory are summarized below :

1. Every metal atom or ion exhibits two types of valencies, *viz.*, *primary valency* and *secondary valency*. The primary valency of the central metal ion is satisfied by negative ions. Its attachment to the metal ion is shown by dotted lines. It corresponds to the *oxidation state* of the metal atom or ion and is ionizable. The secondary valency is satisfied by either negative ions or neutral molecules. Its attachment to the metal is shown by thick lines. It corresponds to the *coordination number* of the metal atom or ion and is non-ionizable.

2. Every metal atom or ion wants to satisfy both its primary and secondary valencies. In order to meet this requirement, a negative ion may perform a dual function of satisfying both types of valencies.

3. Every metal has a fixed number of secondary valencies.

4. The ligands which satisfy the secondary valencies are always directed towards fixed positions in space. The geometry of a complex is determined by the number and arrangement of such ligands in space. If a metal ion has a secondary valency of four, the geometry of the complex can be tetrahedral or square palanar. On the other hand, if its secondary valenoy is six, the complex should be octahedral. The primary valencies are non-directional.

Designation and Formulation of Co(III) Ammines on the Basis of Werner's Coordination Theory.

The ammines given by Co(III) are $CoCl_3.6NH_3$, $CoCl_3.5NH_3$, $CoCl_3.4NH_3$ and $CoCl_3.3NH_3$. On the basis of Werner's coordination theory, these ammines can be designated as shown in Fig. 43.29.

1. $CoCl_3.6NH_3$. This ammine has six NH_3 molecules that satisfy the secondary valency of the metal ion, (*viz.*, Co^{3+} ion) and their attachment with the central metal ion is shown by thick lines. The primary valency (*i.e.*, oxidation state of +3) is satisfied by three Cl^- ions whose attachment to Co^{3+} ion has been shown by dotted lines. As all the three Cl^- ions are loosely bound, they are immediately

precipitated as AgCl on the addition of $AgNO_3$ solution. Thus the solution of this compound should conduct current to give four ions in all *viz.* $[Co(NH_3)_6]^{3-}$ and $3Cl^-$ which has been confirmed by conductivity measurements. Thus this ammine is formulated as $[Co(NH_3)_6]^{3+}\ (Cl^-)_3$.

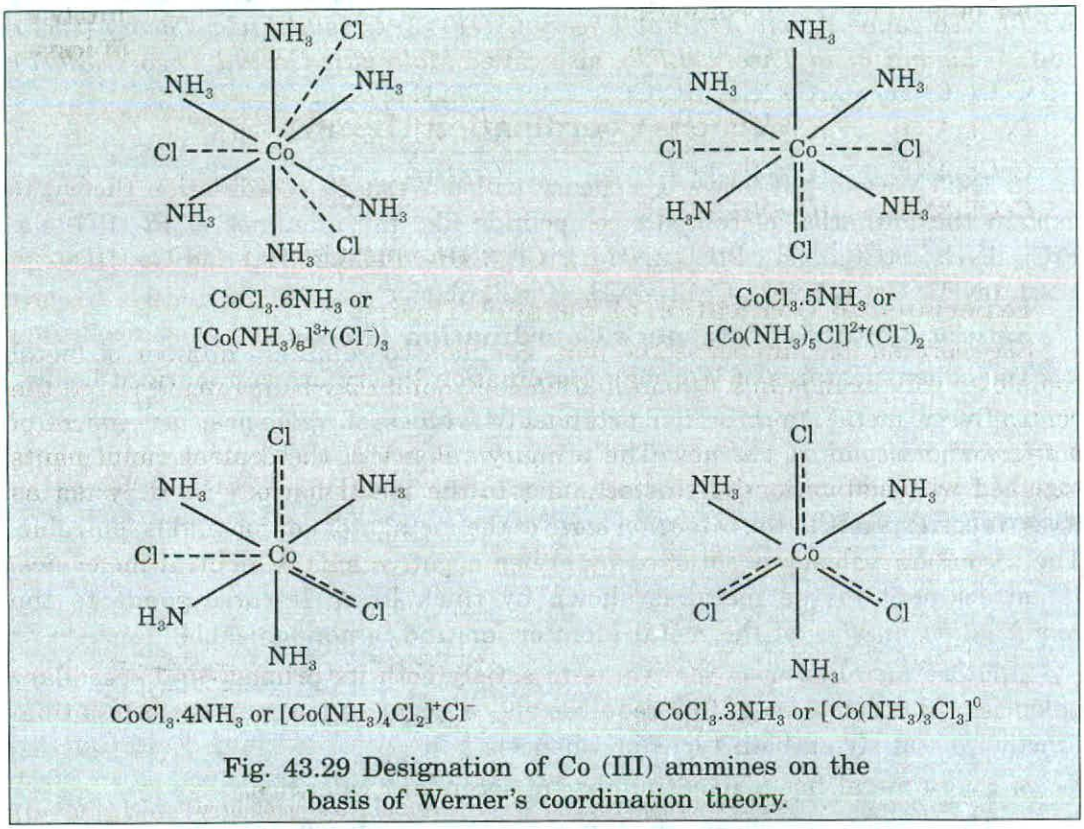


Fig. 43.29 Designation of Co (III) ammines on the basis of Werner's coordination theory.

2. $CoCl_3.5NH_3$. This ammine has five NH_3 molecules. On the basis of Werner's theory one Cl^- ion does the dual function, since it satisfies both primary and secondary valency. Werner, therefore, showed its attachment with the central metal ion by a combined dashed-solid line (-----). This Cl^- ion, being non-ionic, is not precipitated as AgCl by Ag^+ ions and hence it is different from the other two Cl^- ions which, being ionic, are precipitated as AgCl by Ag^+ ions and the total number of ions obtained is three one complex ion, $[Co(NH_3)_5Cl]^{2+}$ and two simple ions, $2Cl^-$. Thus $CoCl_3.5NH_3$ is formulated as $[Co(NH_3)_5Cl]^{2+}(Cl^-)_2$ which satisfies both primary (= +3) and secondary valencies (= C.N. = 6) of Co^{3+}.

3. $CoCl_3.4NH_3$. This ammine has four NH_3 molecules. One ionizable chlorine (primary valency) is shown to be attached by dotted lines. Two non-ionizable chlorine ligands perform dual function of satisfying both types of valencies. Thus this ammine has only one ionic Cl^- ion which gets precipitated is AgCl by $AgNO_3$ solution. Consequently this ammine is formulated as $[Co(NH_3)_4Cl_2]^+\ Cl^-$.

4. $CoCl_3.3NH_3$. All the three chlorine ligands are non-ionizable and perform dual function of satisfying both the primary and secondary valencies. Thus this

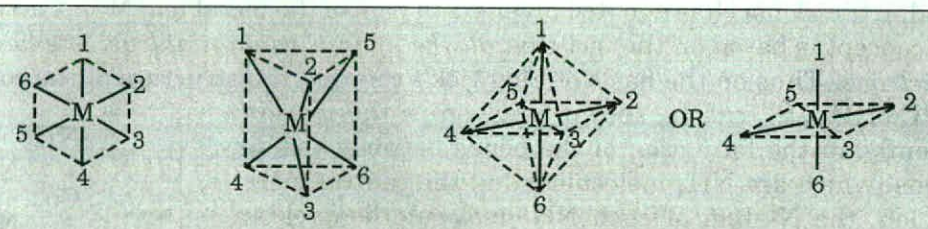
ammine has no ionic Cl^- ions and hence behaves as a non-electrolyte (neutral molecule). Consequently it is formulated as $[Co(NH_3)_3Cl_3]^0$.

The formulation of all these ammines has been shown as follows :

Werner's formulation	Modern formulation	Cation	Anion	Total number of ions
$CoCl_3.6NH_3$	$[Co(NH_3)_6]^{3+}(Cl^-)_3$	$[Co(NH_3)_6]^{3+}$	$3Cl^-$	4
$CoCl_3.5NH_3$	$[Co(NH_3)_5Cl]^{2+}(Cl^-)_2$	$[Co(NH_3)_5Cl]^{2+}$	$2Cl^-$	3
$CoCl_3.4NH_3$	$[Co(NH_3)_4Cl_2]^+Cl^-$	$[Co(NH_3)_4Cl_2]^+$	Cl^-	2
$CoCl_3.3NH_3$	$[Co(NH_3)_3Cl_3]^0$	— (Non-isonisable)	—	—

Experimental Verification of Werner's Theory.

Six coordination number is the most common coordination number of metal complexes. Six ligands in a 6-coordination compound may be arranged round the central metal ion, M, either at the corners of *hexagonal plane* or at the apices of a *trigonal prism* or at the apices of a *regular octahedron.* These arrangements together with mumbers designating substitution positions may be depicted as shown in Fig. 43.30.



Hexagonal planar geometry | Trigonal prismatic geometry | Octahedral geometry

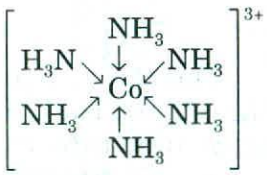
Fig. 43.30. Three possible arrangements of six ligands in a six coordinated complex round the central metal atom, M.

An extensive study of the geometrical and optical isomers of complexes with coordination number six has, however, shown that arrangement of six ligands in a 6-coordination compound is always octahedral and that the arguments concerning other possible geometries (*i.e.* hexagonal planar and trigonal prismatic geometries) are of historical interest only. In order to show that other geometries *viz.* hexagonal planar and trigonal prismatic are not preferred geometries for 6-coordination complex, Werner worked out the theoretical number of geometrical isomers that each of these geometries could give for the complexes Ma_6, Ma_5b, Ma_4b_2 and Ma_3b_3 (a and b are monodentate ligands). He found that the number of geometrical isomers predicted theoretically for these complexes in different geometries are as : *Hexagonal geometry* ⟶ $Ma_6 = 1$, $Ma_5b = 1$, $Ma_4b_2 = 3$ [(1, 2), (1, 3), (1, 4)], $Ma_3b_3 = 3$ [(1, 2, 3), (1, 2, 4), (1, 3, .5)]; *Trigonal prismatic geometry* ⟶

Ma_6 = 1, Ma_5b = 1, Ma_4b_2 = 3 [(1, 2), (1, 3), (1, 4)], Ma_3b_3 = 3 [(1, 2, 3), (1, 2, 5), (1, 2, 6)], *Octahedral geometry* ⟶ Ma_6 = 1, Ma_5b = 1, Ma_4b_2 = 2 [(1, 2), (1, 6)], Ma_3b_3 = 2 [(1, 2, 3), (1, 2 6)]. Werner then took some six-coordinated Co(III) ammines and isolated experimentally their geometrical isomers whose numbers are given as : Ma_6 = 1, Ma_5b = 1, Ma_4b = 2 and Ma_3b_3 = 2. When he compared these numbers with those predicted theoretically for these geometries, he was convinced that the shape of a six-coordinated compound is octahedral, although it is not an absolute proof of this shape, since the correct experimental conditions for preparing all the isomers may not have been found, bot the shape is now known to be octahedral.

Sidgwick's Electronic Concept of Coordinate Bond in Coordination Compounds

In 1916 Lewis introduced a concept of two-electron covalent bond between two atoms in a molecule. According to this concept a covalent bond is formed between two atoms of a molecule by the sharing of an electron pair. Sidgwick (1927) extended this Lewis concept of covalent bond and introduced a new concept of *coordinate bond* which is also some times called *polar* or *dative bond.* According to this Sidgwick's concept the *ligands donate the electron pair to the central metal ion and thus form a coordinate bond,* M ⟵ L which indicates that the ligand, L (*i.e.* donor) has donated an electron pair to the metal ion, M (*i.e.* acceptor). This concept is based on the fact that *all the ligands contain at least one lone pair of electrons.* Thus on the basis of Sidgwick's concept, the structure of the complex ion, $[Co(NH_3)_6]^{3+}$, can be shown as given in the margin. Evidently, in the formation of the bonds between the six ligands (which are NH_3 molecules) and the central metal Co^{3+} ion, the N-atom of each NH_3 molecule donates an electron pair to Co^{3+} ion. Thus in all twelve electrons (*i.e.* six electron pairs) are donated by six NH_3 ligands to Co^{3+} ion. The donation of an electron pair by NH_3 molecule has been represented by an arrow. Coordinate bond formed is not very different from a covalent bond. The only difference lies in the mode of its formation.



Limitations of Sidgwick's Concept of Coordinate Bond.

The donation of one electron pair by each of the ligands to the central metal ion to form L ⟶ M coordinate bond in complexes accumulates negative charge on the central metal ion which is most unlikely. For example in $[Co^{3+}(NH_3)_6]^{3+}$, six NH_3 molecules donate half share of 12 electrons (*i.e.* 6 electrons) to Co^{3+} ion and thus +3 charge on cobalt atom is reduced to –3 (+ 3 – 6 = –3). Such an accumulation of negative charge on the central atom is unlikely.

Pauling suggested that the accumulation of undue negative charge on the central metal ion can be prevented, if it is assumed that *the metal-ligand bond has some ionic character (Electro-neutrality principle) and in addition to σ-bond, the central atom also forms a π-bond with the ligand (π-bonding in complexes)*

Sidgwick's Effective Atomic Number Rule (EAN Rule).

On the basis of his concept of coordinate bond, Sidgwick suggested that after the ligands have donated a certain number of electrons to the central metal ion through L ⟶ M bonding, the total number of electrons on the central atom, including those gained from ligands in the bonding is called the *effective atomic number* (EAN) of the central metal ion and in many cases this total number of electrons (*i.e.* EAN) surrounding the coordinated metal ion is equal to the atomic number of the inert gas which follows the central metal atom in the periodic table. This is called *Effective Atomic Number Rule* or *Noble Gas Rule.* When the EAN is 36 (Kr), 54 (Xe) or 86 (Rn), the rule is said to be followed. EAN of a central metal atom or ion in a given complex is given by the formula *viz.* EAN = $(Z-x) + n \times y$ where Z = atomic number of the central metal atom, x = positive oxidation state of the central metal ion, n = number of ligands and y = number of electrons donated by one ligand. For example EAN of Fe^{2+} ion in $[Fe^{2+}(CN)_6]^{4-}$ is equal to $(26 - 2) + 6 \times 2 = 36$. On the basis of this formula, the EAN's of the central metal atom/ion of some complexes have been calculated and are given as $[Mn^{+}(CO)_5\ (C_2H_4)]^{+} = 36$. $[Fe^{2+}(CN)_6]^{4-} = 36$, $[Co^{3+}(NH_3)_6]^{3+} = 36$, $[Ag^{+}(NH_3)_4]^{+} = 54$, $[Pd^{4+}(NH_3)_6]^{4+} = 54$. $[Pt^{4+}(NH_3)_6]^{4+} = 86$, $[Pt^{4+}Cl_6]^{2-} = 86$.

The EAN of the central metal atom/ion of some complexes has been found to be some units more or less than the atomic number of the next inert gas. Examples of such complexes are : $[Fe^{3+}Cl_4]^{-} = 31$, $[Cu^{+}Cl_2]^{-} = 32$, $[Cr^{3+}(NH_3)_6]^{3+} = 33$, $[Ni(CN)_4]^{2-} = 34$, $[Mn^{2+}(H_2O)_6]^{2+} = 35$, $[Co(CN)_6]^{4-} = 37$, $[Ni^{2+}(NH_3)_6]^{2+ = 38}$, $[Ag^{+}X_2]^{-} = 50$, $[Pd^{2+}Cl_4]^{2-} = 52$, $[Pt^{2+}(NH_3)_4]^{2+} = 84$.

Valence Bond Theory (VBT)

This theory is mainly due to Pauling. It deals with the electronic structure of the central metal ion in its ground state, kind of bonding, geometry and magnetic properties of the complexes.

Assumptions of Valence Bond Theory.

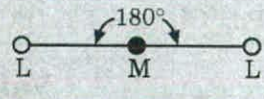
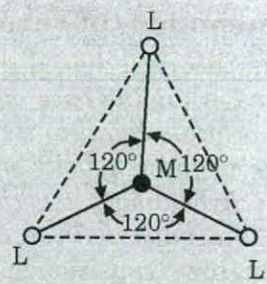
This theory is based on the following assumptions : (1) *The central metal atom or ion (as the case may be) makes available a number of empty s, p and d atomic orbitals equal to its coordination number. These vacant orbitals hybridise together to form hybrid orbitals which are the same in number as the atomic orbitals hybridising together. These hybrid orbitals are vacant, equivalent in energy and have definite geometry.* Important types of hybridisation occuring in the first row transition metal (*3d* metals) complexes and the geometry of the complexes are given in Table 43.1. (2) The ligands have at least one σ-orbital containing *a lone pair of electrons.* (3) Vacant hybrid orbitals of the metal atom or ion *overlap with the filled* (containing lone pair of electrons) σ-orbitals of the ligands to form ligand → metal σ-bond (represented as $M \xleftarrow{\sigma} L$). This bond which is generally known as coordinate bond is a special type of covalent bond and shows the characteristics of both the overlapping orbitals. However, it also possesses a considerable amount of polarity because of the mode of its formation.

(4) The non-bonding electrons of the metal atom or ion are then rearranged in the metal orbitals (*viz.*, pure *d*, *s* or *p* orbitals as the case may be) which do not participate in forming the hybrid orbitals. The rearrangement of non-bonding electrons takes place according to Hund's rule.

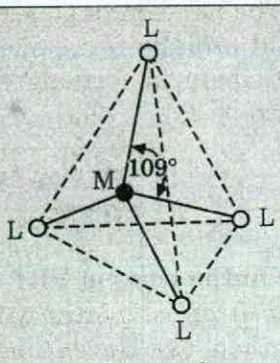
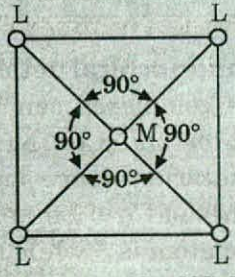
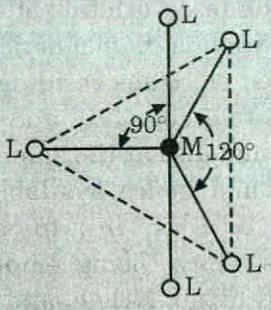
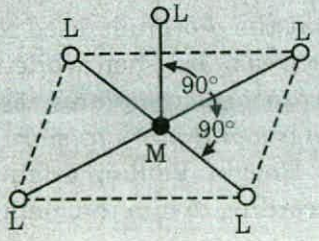
VBT As Applied to Octahedral Complexes (C.N. = 6, d^2sp^3 or sp^3d^2 Hybridisation)

On the basis of VBT, octahedral complexes are of two types : (1) *Inner-orbital octahedral complexes* which result form d^2sp^3 hybridisation of the central metal atom/ion (2) *Outer- orbital octahedral complexes* which result from sp^3d^2 hybridisation.

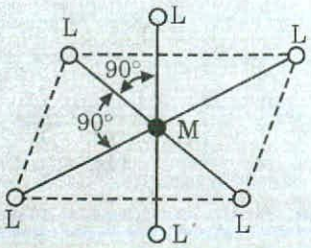
Table 43.1. Important types of hybridisation in the first row transition metal (3d-metal) complexes and the geometry of the complexes. C.N. indicates the coordination number of the central metal atom/ion, M (indicated by black circles) and L (white circles) represents ligands which may be the same or different.

C.N. of the central metal ion/ atom	Type of hybridisation and the atomic orbitals used in hybridisation	Geometry of the complex	Illustration of the geometry and examples
2	*sp* ($4s$, $4p_x$)	Linear or diagonal	 *Examples* : $[Cu^+Cl_2]^-$, $[Cu^+(NH_3)_2]^+$, $[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$ etc.
3	sp^2 ($4s$, $4p_x$, $4p_y$)	Trigonal planar or equilateral triangular	 *Examples* : $[HgI_3]^-$, $\left[Cu^+\left(S{=}C\begin{matrix}NH{-}CH_2\\ \vert \\ NH{-}CH_2\end{matrix}\right)_3\right]^+$, $\left[Cu^+Cl(tu)_2\right]^0$ (distorted trigonal planar geometry) etc.

(*Continued*)

4	sp^3 ($4s$, $4p_x$, $4p_y$, $4p_z$)	Tetrahedral	 *Examples* : $[NiCl_4]^{2-}$, $[Ni(CO)_4]^0$, $[Zn(NH_3)_4]^{2+}$, $[Cu(CN)_4]^{3-}$ etc.
4	dsp^2 ($3d_{x^2-y^2}$, $4s$, $4p_x$, $4p_y$)	Square planar	 *Examples* : $[Cu(CN)_4]^{2-}$, $[Pt(CN)_4]^{2-}$, $[Ni(CN)_4]^{2-}$ etc.
5	dsp^3 ($3d_{z^2}$, $4s$, $4p_x$, $4p_y$, $4p_z$)	Trigonal bipyramidal	 *Examples* : $[Fe^0(CO)_5]^0$, $[Cu^{2+}Cl_5]^{3-}$, $[Ni^{2+}(triars)Br_2]^0$ etc.
5	sp^3d ($3d_{x^2-y^2}$, $4s$, $4p_x$, $4p_y$, $4p_z$)	Square pyramidal	 *Examples* : $[Co^{2+}(triars)\ I_2]^0$, $[Ni^{2+}(CN)_5]^{3-}$, $[SbF_5]^{2-}$etc.

(*Continued*)

6	d^2sp^3 ($3d_{x^2-y^2}$, $3d_z{}^2$, $4s$, $4p_x$, $4p_y$, $4p_z$)	Inner-orbital octahedral	 *Examples* : $[Ti(H_2O)_6]^{3+}$, $[Co(NH_3)_6]^{2+}$, $[Fe(CN)_6]^{4-}$ etc.
	sp^3d^2 ($4s$, $4p_x$, $4p_y$, $4p_z$, $4d_{x^2-y^2}$, $4d_z{}^2$)	Outer-orbital octahedral	*Examples* : $[Cr(H_2O)_6]^{2+}$, $[CoF_6]^{3-}$, $[Zn(NH_3)_6]^{2+}$ etc.

1. Inner-orbital octahedral complexes (d^2sp^3 hybridisation). The formation of these complexes can be explained on the basis of VBT by considering the complex ion *viz.* $[Co^{3+}(NH_3)_6]^{3+}$. In this complex ion Co is present as Co^{3+} ion. We know that the valence-shell electronic configuration of Co atom is $3d^7.4s^2.4p^0$ and hence that of Co^{3+} ion is $3d^6.4s^0.4p^0$. Note that the number of unpaired electrons (n) in Co atom is 3 while that in Co^{3+} ion is 4 as shown at (a) and (b) of Fig. 43.31. The measurement of magnetic moment value (μ value) for $[Co(NH_3)_6]^{3+}$ ion has shown that μ = 0, *i.e.*, $[Co(NH_3)_6]^{3+}$ ion has no unpaired electron or all the electrons in $3d$ orbitals of Co^{3+} ion in this complex ion are paired and hence the complex ion is diamagnetic. In order to make all the $3d$ electrons paired, the two unpaired electrons residing in $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals are forced by the six NH_3 ligands to occupy $3d_{yz}$ and $3d_{zx}$ orbitals. By doing so, all the $3d$ electrons become paired and also at the same time two $3d$ orbitals namely $3d_{z^2}$ and $3d_{x^2-y^2}$ are made vacant and hence available for d^2sp^3 hybridisation [See(c) of Fig. 43.31]. Now $3d_{x^2-y^2}$, $3d_{z^2}$, $4s$, $4p_x$, $4p_y$ and $4p_z$ orbitals hybridise together to give six d^2sp^3 hybrids which, being empty, accept the six electron pairs (represented as ••) donated by six NH_3 ligand molecules to form six $H_3N \rightarrow Co$ coordinate bonds in $[Co(NH_3)_6]^{3+}$ ion. The two electrons of each electron pair (••) have opposite spins. Evidently, since $[Co(NH_3)_6]^{3+}$ ion has no unpaired electron, it should be diamagnetic. Actually the ion has been found to be diamagnetic. It may be seen from Fig. 43.31 that the d-orbitals used in the formation of six d^2sp^3 hybrids belong to the inner shell *viz. 3rd* shell while the s and p orbitals belong to outer shell *viz. 4th* shell. *Octahedral complexes resulted form d^2sp^3 hybridisation, using the inner d and outer s and p orbitals are called inner-orbital octahedral complexes,* as suggested by Heggin. Pauling originally called such complexes as *covalent complexes*, since according to him the metal-ligand bonds in such complexes are primarily covalent.

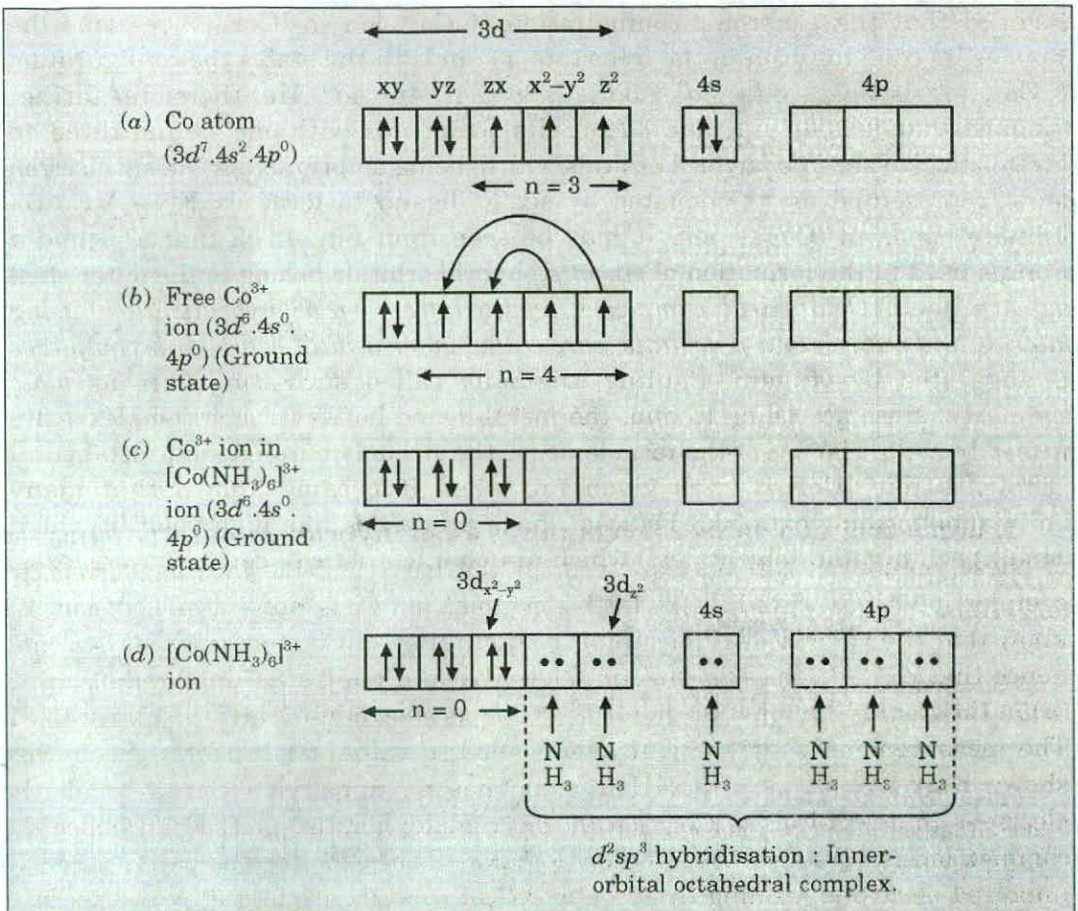


Fig. 43.31. Formation of inner-orbital octahedral complex ion *viz.* $Co(NH_3)_6]^{3+}$ on the basis of valence-bond theory. n represents the number of unpaired electrons. Dots (••) represent an electron pair donated by each of the six NH_3 ligand moleoules. The two electrons of this electron pair have opposite spins.

Examples of inner-orbital octahedral *paramagnetic* complexes are : $[Ti(H_2O)_6]^{3+}$(n = 1), $[Cr(NH_3)_6]^{3+}$ (n = 3), $[Mn(CN)_6]^{4-}$ (n = 1), $[Mn(CN)_6]^{3-}$ (n = 2), $[Fe(CN)_6]^{3-}$ (n = 1), $[Co(CN)_6]^{4-}$ (n = 1 in 5*s* orbital) etc. while the examples of inner-orbital octahedral *diamagnetic* complexes are : $[Fe(CN)_6]^{4-}$ (n = 0), $[Co(CN)_6]^{3+}$ (n = 0), $[Co(H_2O)_6]^{3+}$ (n = 0), $[Co(NH_3)_6]^{3+}$ (n = 0), $[Co(C_2O_4)_3]^{3-}$ (n = 0), $[Co(NO_2)_6]^{3-}$ (n = 0), $[Pt(NH_3)_6]^{4+}$ (n = 0), $[PtCl_6]^{2-}$ (n = 0) etc. In all these complexes n represents the number of unpaired electrons in the complex ion. All these complexes result from d^2sp^3 hybridisation of the central metal ion.

2. Outer-orbital octahedral complexes (sp^3d^2 hybridisation). The formation of these complexes can be explained on the basis of VBT by considering the complex ion *viz.* $[Co^{3+}F_6]$. In this complex ion Co is present as Co^{3+} whose valence-shell configuration is $3d^6.4s^0.4p^0$. $[CoF_6]^{3-}$ is a paramagnetic ion and the value of magnetic moment corresponds to the presence of four unpaired electrons. Now in order to account for the presence of four unpaired electrons in this ion Huggin

assumed that the electronic configuration of Co^{3+} ion in $[CoF_6]^{3-}$ remains the same as its configuration in the free state, *i.e.* in both the states the configuration of Co^{3+} ion is $3d^2_{xy}.\ 3d^1_{yz}.3d^1_{zx}\ 3d^1_{x^2-y^2}.3d^1_{z^2}.4s^0.4p^0\ 4d^0$. He, therefore, further assumed that it is $4d_{x^2-y^2}$, and $4d_{z^2}$ orbitals that mix with one 4*s* and three 4*p* orbitals to give six sp^3d^2 hybrid orbitals which, being empty, accept the six electron pairs (represented as ••) donated by six F^- ligand to form six $F^- \longrightarrow Co$ co-ordinate bonds in $[CoF_6]^3$ ion, It may be seen from Fig. 43.32 that *s*, *p* and *d* orbitals used in the formation of six sp^3d^2 hybrid orbitals belong to the outer shell *viz.* 4*th* shell. *Octahedral complexes resulted from sp^3d^2 hybridisation, using outer d- and outer s and p orbitals, care called outer-orbital octahedral complexes* as suggested by Huggin. Pauling originally called such complexes as *ionic complexes*, since according to him, the metal-ligand bonds in such complexes are primarily ionic. The use of the term ionic for the strongly paramagnetic octahedral complexes like $[CoF_6]^{3-}$ was given up, when it became known that many paramagnetic complexes like $Fe(acac)_3$ have properties like high volatility, high solubility in organic solvents etc. which are characteristic of covalent complexes.

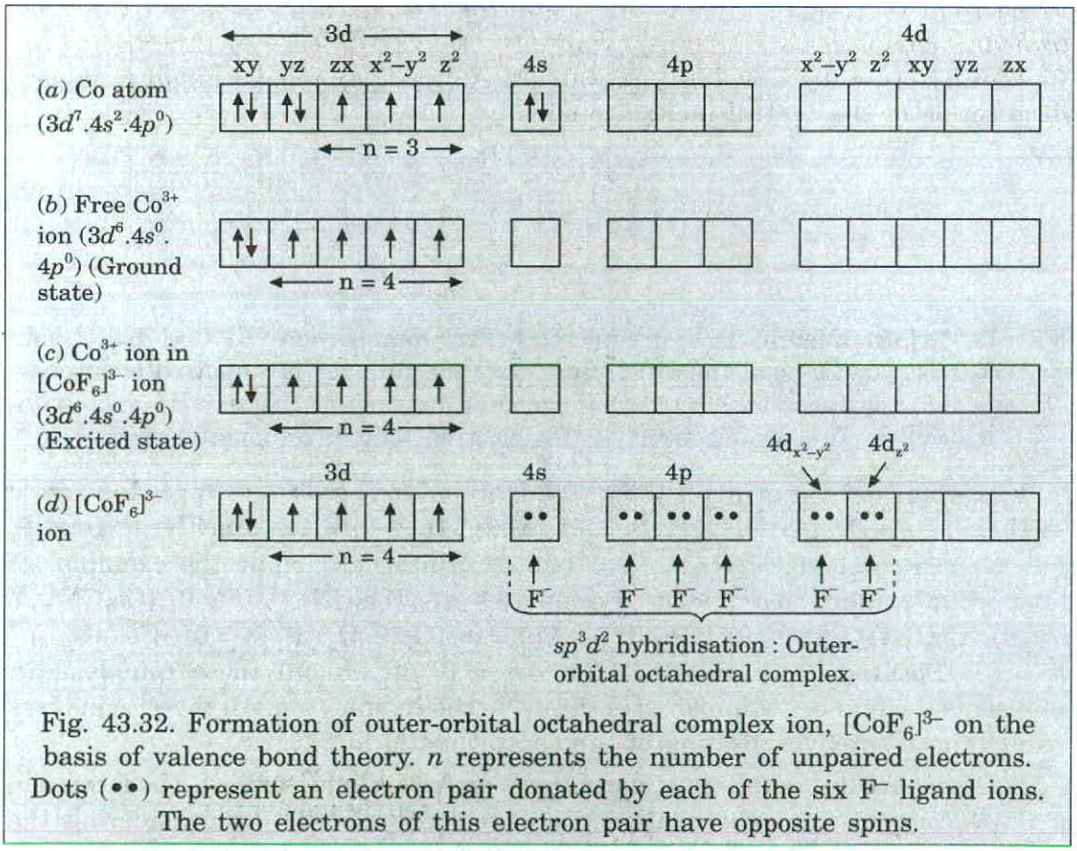


Fig. 43.32. Formation of outer-orbital octahedral complex ion, $[CoF_6]^{3-}$ on the basis of valence bond theory. *n* represents the number of unpaired electrons. Dots (••) represent an electron pair donated by each of the six F^- ligand ions. The two electrons of this electron pair have opposite spins.

Examples of outer-orbital octahedral *paramagnetic* complexes are : $[Cr(H_2O)_6]^{2+}$ ($n = 4$), $[Mn(H_2O)_6]^{2+}$ ($n = 5$), $[Fe(H_2O)_6]^{2+}$ ($n = 4$), $[Fe(NH_3)_6]^{2+}$ ($n = 4$), $[Fe(NH_3)_6]^{3+}$

(n = 4), $[Fe(H_2O)_6]^{3-}$ (n = 5), $[FeF_6]^{3-}$ (n = 5), $[CoF_6]^{3-}$ (n = 4), $[Co(NH_3)_6]^{2+}$ (n = 3), $[Co(H_2O)_6]^{2+}$ (n = 3), $[Ni(NH_3)_6]^{2+}$ (n = 2), $[Ni(H_2O)_6]^{2+}$ (n = 2), $[Ni(NCS)_6]^{4-}$ (n = 2), $[Ni(NO_2)_6]^{4-}$ (n = 2), $[CuF_6]^{3-}$ (n = 2). $[Zn(NH_3)_6]^{2+}$ (n = 0), is an example of outer-orbital octahedral diamagnetic complex. All these complexes result from sp^3d^2 hybridisation.

VBT As Applied to Tetrahedral Complexes (C.N. = 4, sp^3 hybridisation)

Tetrahedral complexes result from sp^3 hybridisation. In sp^3 hybridisation s- and three p-orbitals should belong to the same shell. The formation of tetrahedral complexes by VBT can be explained by considering the complex ion like $[MnCl_4]^{2-}$. This complex ion is parmagnetic corresponding to the presence of five unpaired electrons and hence the configuration of Mn^{2+} ion in the free state and in the complex ion remains the same as shown in Fig. 43.33.

Examples of some *paramagnetic* tetrahedral complexes are : $[NiCl_4]^{2-}$ (n = 2) $[Ni(NH_3)_4]^{2+}$ (n = 2), $[MnBr_4]^{2-}$ (n = 5), $[FeCl_4]^{2-}$ (n = 5), $[CoCl_4]^{2-}$ (n = 3), $[CuCl_4]^{2-}$ derived from $Cs_2[CuCl_4]$ (n = 1) etc. while the examples of some *diamagnetic tetrahedral* complexes are : $[Ni(CO)_4]^0$ (n = 0), $[Cu(CN)_4]^{3-}$ (n = 0), $[Zn(NH)_4]^{2+}$ (n = 0), $[ZnCl_4]^{2-}$ (n = 0), $[Cd(CN)_4]^{2-}$ (n = 0) etc. All these complexes result from sp^3 hybridisation of the central metal atom/ion.

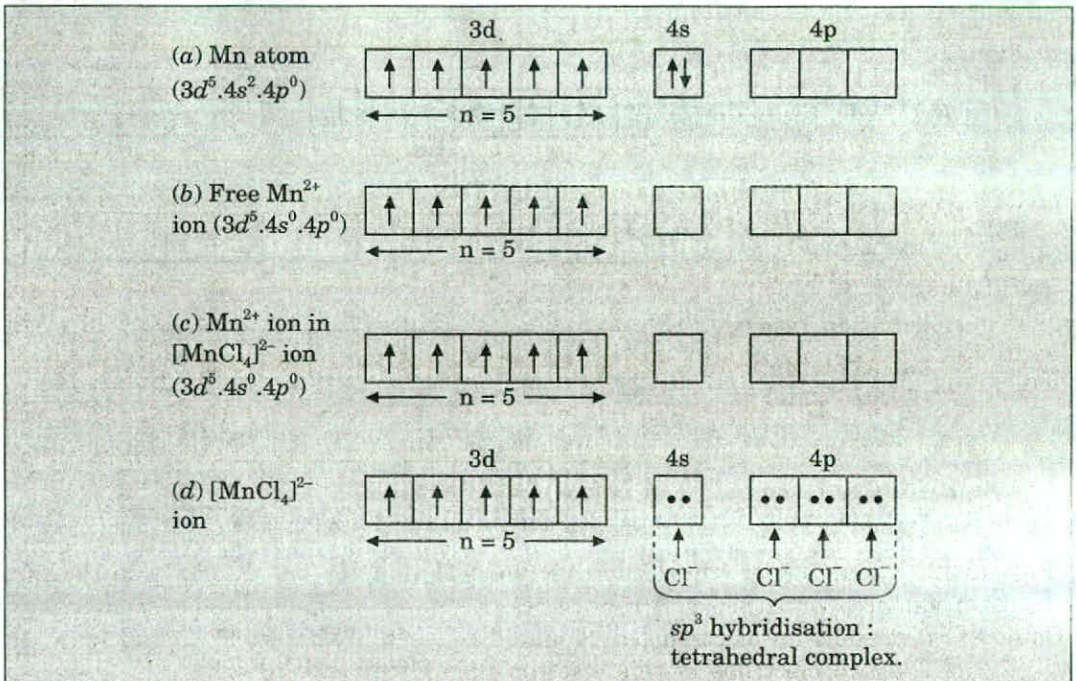


Fig. 43.33. Formation of tetrahedral $[MnCl_4]^{2-}$ ion on the basis of valence bond theory. n represents the number of unpaired electrons.

VBT As Applied to Square Planar Complexes (C.N. = 4, dsp^2 hybridisation)

Square planar complexes result from dsp^2 hybridisation. In dsp^2 hybridisation d-orbital should be $d_{x^2-y^2}$ orbital belonging to the lower shell while s and p orbitals should be from the higher shell. The two p-orbitals should be p_x and p_y orbitals. The selection of $d_{x^2-y^2}$, p_x and p_y orbitals is based on the fact that all these orbitals lie in xy plane. The formation of square planar complexes by VBT can be explained by considering the complex ion like $[Ni(CN)_4]^{2-}$ in which Ni is present as Ni^{2+} whose valence-shell configuration is $3d^8.4s^0.4p^0$ having two unpaired electrons. The measurement of magnetic moment value for $[Ni(CN)_4]^{2-}$ ion has shown that $\mu = 0$, *i.e.* the complex ion has no unpaired electron or all the electrons in $3d$ orbitals of Ni^{2+} ion in $[Ni(CN)_4]^{2-}$ ion are paired and hence the complex ion is diamagnetic. In order to make all the $3d$-electrons paired, one unpaired electron residing in $3d_{x^2-y^2}$ orbital is forced by the four CN^- ligands to occupy $3d_{z^2}$ orbital. By doing so, all the $3d$-electrons become paired and also at the same time $3d_{x^2-y^2}$ orbital becomes vacant and hence available for dsp^2 hybridisation. Now $3d_{x^2-y^2}$, $4s$, $4p_x$ and $4p_y$ orbitals mix together to form four dsp^2 hybrid orbitals which, being empty, accept the four electron pairs (represented as ••) donated by four CN^- ligand ions to form four $NC^- \longrightarrow Ni$ co-ordinate bonds in $[Ni(CN)_4]^{2-}$ ion (See Fig. 43.34).

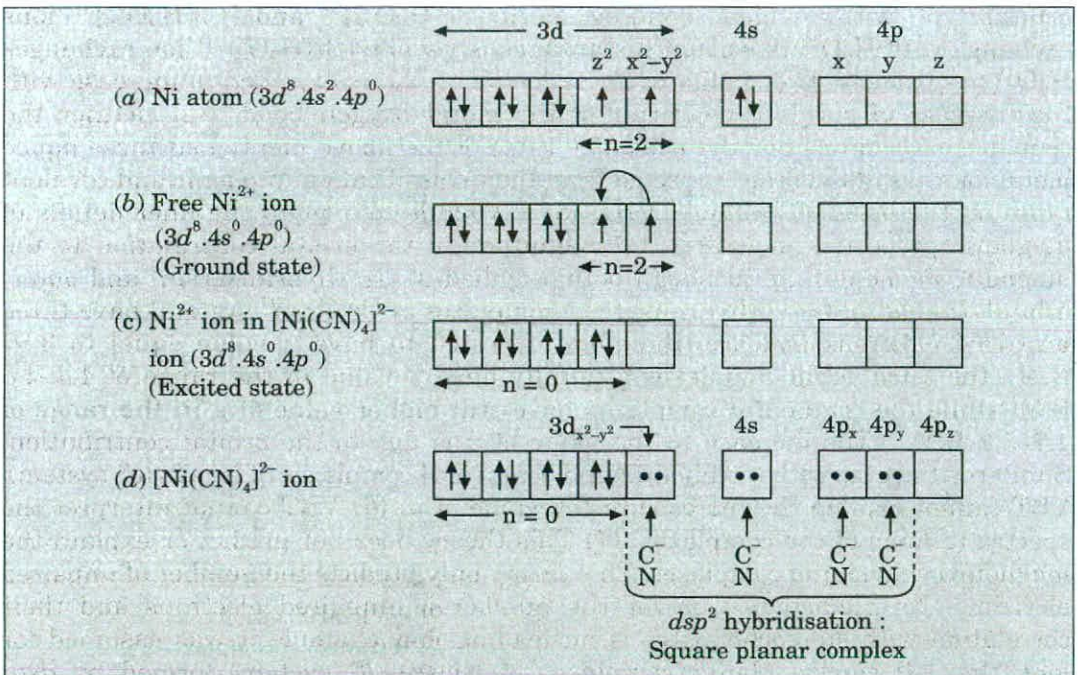


Fig. 43.34. Formation of square planar $[Ni(CN)_4]^{2-}$ complex ion on the basis of valence bond theory. n represents the number of unpaired electrons. Dots (••) represent an electron pair donated by each of the four CN^- ligand ions. The two electrons of this electron pair have opposite spins.

Examples of *paramagnetic* square-planar complexes are : $[Cu(CN)_4]^{2-}$ (n = 1), $(Cu(NH_3)_4]^{2+}$(n = 1), $[CuCl_4]^{2-}$ derived from $(NH_4)_2[CuCl_4]$(n = 1) etc. while the examples of *diamagnetic* square planar complexes are : $[Ni(CN)_4]^{2-}$ (n = 0), $[CuO_2]^-$ (n = 0), $[PtCl_4]^{2-}$ (n = 0), $[Pt(NH_3)_4]^{2+}$ (n = 0) etc.

Limitations of VBT.

(1) VBT cannot account for the relative stabilities for different shapes and different coordination numbers in metal complexes, *e.g.* it cannot explain satsifactorily as to why Co(+ 2)(d^7 system) forms both octahedral and tetrahedral complexes while Ni(+2) (d^8 system) rarely forms tetrahedral complexes. Similarly Fe(+3)(d^5 system) forms both tetrahedral and octahedral complexes while Cr(+3) (d^3 system) gives only octahedral complexes. **(2)** VBT cannot explain as to why Cu(+2) forms only distorted octahedral complexes even when all the six ligands are identical. **(3)** This theory cannot account for the relative rates of reactions of analogous metal complexes. *e.g.* $[Mn(phen)_3]^{2+}$ dissociates *instantaneusly* in acidic aqueous solution while $[Fe(phen)_3]^{2+}$ dissociates at a stow rate. **(4)** The classification of metal complexes on the basis of their magnetic behaviour into *covalent* (*inner-orbital*) and *ionic* (*outer-orbital*) complexes is not satisfactory and is often misleading, *e.g.* many of the so-called ionic complexes like $[Fe^{3+}(acac)_3]^0$ have properties like high volatility, high solubility in organic solvents etc. which are characteristic of covalent compounds, Also it is known that the aquo ion, $[Cr(H_2O)_6]^{3+}$ (pK_a = 3.8 at 25°C) is a much weaker acid than $[Fe(H_2O)_6]^{3+}$(pK_a = 2.2) and $[Co(H_2O)_6]^{3+}$(pK_a = 0.7) ions, despite the fact that only $[Fe(H_2O)_6]^{3+}$ is of outer-orbital type with ionic bonding while the other two aquo ions are of outer-orbital type with covalent bonding. Both $[Fe(H_2O)_6]^{3+}$ and $[Co(H_2O)_6]^{3+}$ ions exchange with H_2O^{18} in solvent instantaneously while $[Cr(H_2O)_6]^{3+}$ ion exchanges H_2O^{18} very slowly. The acidity of an aqueo metal ion is expected to increase with the increase of covalent character of the metal–oxygen bond. But neither the sequence of acidities nor the exchange rates of the above mentioned three aqueo metal ions are in the order expected from their classification into ionic and covalent types on the basis of Pauling's VBT. **(5)** VBT fails to explain the finer details of magnetic properties including the magnitude of the orbital contribution to the magnetic moments, *e.g.* although both tetrahedral (sp^3 hybridisation) and outer-orbital octahedral (sp^3d^2 hybridisation) complexes of Co(+2)(d^7 system) have three unpaired electrons and are, therefore, expected to have μ value equal to 3.87 B.M.; the tetrahedral complexes generally have μ value in the range of 4.4–4.8 B.M. while the octahedral complexes have still higher value of μ in the range of 4.7–5.2 B.M. . The increase in the value of μ is due to the orbital contribution, Similar is the case with tetrahedral and octahedral complexes of Ni(+2) (d^8 system). VBT cannot explain the increase in the value of μ. **(6)** VBT cannot interpret the spectra (colour) of the complexes. **(7)** This theory does not predict or explain the magnetic behaviour of complexes. This theory only predicts the number of unpaired electrons. Its prediction even for the number of unpaired electrons and their correlation with stereochemistry is misleading. For example it was assumed for long that all square planar complexes of Ni(+2) (d^8 system) formed by dsp^2 hybridisation were diamagnetic (n = 0), while all tetrahedral complexes of Ni(+2) formed by sp^3 hybridisation were paramagnetic due to the presence of two unpaired electrons (n = 2). X-ray study of 4-coordinate Ni (+ 2) complexes has shown that one and the same complex can he obtained in both a *paramagnetic form* (having

blue colour) and a *diamagnetic form* (having yellow colour). VBT has no explanation for it. VBT cannot explain the temperature dependent paramagnetism of the complexes. **(8)** VBT cannot give any explanation for the order of reactivities of the inner-orbital inert complexes of d^3, d^4 d^5 and d^6 ions and of the observed differences in the energies of activation in a series of similar complexes. **(9)** The magnetic moment values of the complexes of certain ions (*e.g.* Co^{2+}, Ni^{2+}, etc.) are much higher than those expected by spin only formula. VBT can not explain the enhanced values of magnetic moment.

Crystal Field Theory (CFT)

This theory determines the effect of different electrostatic fields caused by the different geometries of the complexes and different basic strengths of the ligands, on the energies of *d*-orbitals of the central metal ion.

Salient Features of Crystal Field Theory.

(1) The central metal cation is surrounded by ligands which contain one or more lone pairs of electrons (2) The ionic ligands (*e.g.* F^-, Cl^-, CN^- etc.) are regarded as negative point charges (also called point charges) and the neutral ligands (*e.g.* H_2O, NH_3 etc.) are regarded as point dipoles or simply dipoles, *i.e.* according to this theory neutral ligand are dipolar. If the ligand is neutral, the negative end of this ligand dipole is oriented towards the metal cation. (3) The interaction between the metal cation and the ligands is regarded as purely electrostatic, *i.e.* the metal–ligand bond is considered to be 100% ionic.

CFT As Applied to Octahedral Complexes

Splitting of d-orbitals in Octahedral Complexes.

In case of free metal ion all the five *d*-orbitals are degenerate, *i.e.* these have the same energy. Now let us consider an octahedral complex, $[ML_6]^{n+}$ in which the central metal cation, M^{n+} is placed at the centre of the octahedron and is surrounded by six ligands which reside at the six corners of the octahedron as shown in Fig. 43.35. The three axes *viz.* *x*-, *y*-, and *z*-axes which point along the corners have also been shown. Now suppose both the ligands on each of the three axes are allowed to approach towards the metal cation, M^{n+} from both the ends of the axes. In this process the electrons in *d*-orbitals of the metal cation are repelled by negative point charge or by the negative end of the dipole of the ligands. (Remember CFT ragards the ionic ligands as negative point charges and neutral ligands as dipoles). This repulsion will raise the energy of all the five *d*-orbitals. If all the ligands approaching towards the central cation are at an equal distance from each of the

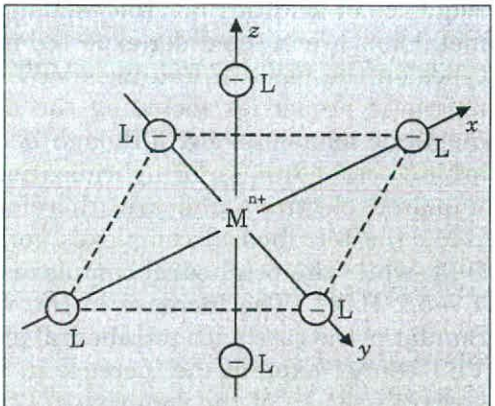


Fig. 49.35. Position of the central metal cation, M^{n+} and six ligands, L's in an octahedral complex, $[ML_6]^{n+}$.

d-orbitals (*i.e.* the ligand field is spherically symmetrical), the energy of each of five *d*-orbitals will raise by the same amount, *i.e.* all the *d*-orbitals will still remain degenerate, although they will have now higher energy than before. This is only a *hypothetical situation. Since the lobes of the two* e_g *orbitals* (*i.e.* d_{z^2} and $d_{x^2-y^2}$ orbitals) *lie directly in the path of the approaching ligands, the electrons in these orbitals experience greater force of repulsion than those in three* t_{2g} *orbitals* (*i.e.* d_{xy}, d_{yz} and d_{zx} orbitals) *whose lobes are directed in space between the path of the approaching ligands i.e.* the energy of e_g orbitals is increased while that of t_{2g} is decreased (Remember : *greater is the repulsion, greater the increase in energy*). Thus we find that under the influence of approaching ligands the five *d*-orbitals which were originally degenerate in the free metallic cation are now split (or resolved) into two levels *viz.* t_{2g} level which is triply degenerate and is of lower energy, and e_g level which is doubly degenerate and is of higher energy (*See* Fig. 43.36). In other words the degeneracy of the five *d*-orbitals is removed under the influence of the ligands. *The separation of five d-orbitals of the metal ion into two sets having different energies is called crystal field splitting or energy level splitting.* This concept of crystal field splitting makes the basis of CFT.

The energy gap between t_{2g} and e_g sets is denoted by Δ_0 or 10Dq (Δ_0 = 10Dq) where Δ_0 indicates an octahedral arrangement of the ligands round the central metal cation. This energy difference arises because of the difference in electrostatic field exerted by the ligands on t_{2g} and e_g sets of orbitals of the central metal cation. Δ_0 or 10Dq is called *crystal field splitting energy.* With the help of simple geometry it can be shown that the energy of t_{2g} orbitals is 0.4 Δ_0 (= 4Dq) *less* than that of hypothetical degenerate *d*- orbitals (No splitting state shown by dotted line in Fig. 43.36) and, hence, that of e_g orbitals is 0.6Δ_0 (= 6 Dq) *above* that of the hypothetical degenerate *d*-orbitals. Thus, we find that t_{2g} set *loses* an energy equal to 0.4 Δ_0 (= 4Dq) while e_g set gains an energy equal to 0.6Δ_0 (= 6Dq). In Fig. 43.36 the loss and gain in energies of t_{2g} and e_g orbitals is shown by negative and positive signs respectively.

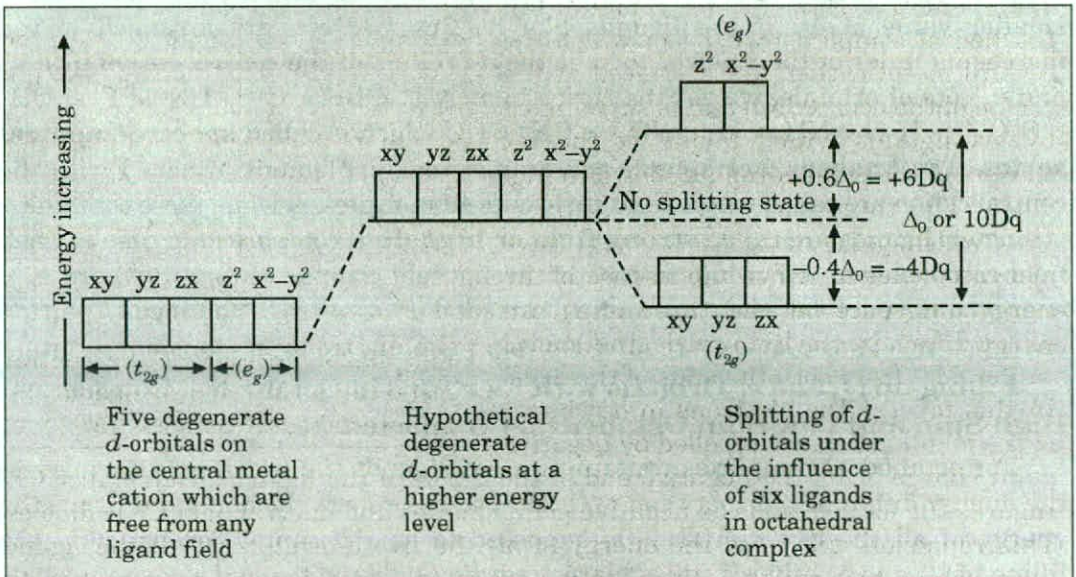


Fig. 43.36. Crystal field splitting of *d*-orbitals in octahedral complex.

Factors Affecting the Magnitude of Δ_0.

Following are important factors which influence the magnitude of Δ_0.

1. Nature of the central cation. Here we shall consider the complex compounds having the same geometry and same ligands. (*a*) The complex compound having the central cation with higher oxidation state (*i.e.* higher charge) has higher value of Δ_0 than that having the central cation with lower oxidation state. For example Δ_0 for $[Fe^{3+}(H_2O)_6]^{3+}$ (= 13,700 cm^{-1}) > Δ_0 for $[Fe^{2+}(H_2O)_6]^{2+}$ (= 10,400 cm^{-1}). Similarly $[Cr^{3+}(H_2O)_6]^{3+}$ (= 17,400 cm^{-1}) > $[V^{2+}(H_2O)_6]^{2+}$ (= 12,400 cm^{-1}). The increase in the value of Δ_0 with the increase of oxidation state is explained by saying that the metal cation with higher oxidation state polarises the ligands more effectively and hence the ligands approach this cation more closely than they approach the cation with lower oxidation state, resulting in a larger splitting of *d*-orbitals. (*b*) In case of complexes having the central cations with the same oxidation state but with different number of *d*-electrons in the central cation, the magnitude of Δ_0 decreases with the increase of the number of *d*-electrons. For example Δ_0 for $[Co^{2+}(H_2O)_6]^{2+}$ (= 9,300 cm^{-1}) in which Co^{2+} ion has seven d-electrons is higher than that for $[Ni(H_2O)_6]^{2+}$ (= 8,500 cm^{-1}) in which Ni^{2+} ion has eight d-electrons. (*c*) The value of Δ_0 for the complexes having the central cations with the same oxidation state but with different principal quantum number (n) of their d-orbitals increases with the increase of the value of n. For example $[Co^{2+}(NH_3)_6]^{3+}$ (= 23,000 cm^{-1}, $Co^{3+} \rightarrow 3d^6$ with $n = 3$) < $[Rh^{3+}(NH_3)_6]^{3+}$ (= 34,000 cm^{-1}, $Rh^{3+} \rightarrow 4d^6$ with $n = 4$) < $[Ir^{3+}(NH_3)_6]^{3+}$ (= 41,000 cm^{-1}, $Ir^{3+} \rightarrow 5d^6$ with $n = 5$).

2. Nature of the ligand : Spectrochernical series. The ligands which split the *d*-orbitals of the central metal cation into t_{2g} and e_g sets of orbitals to a greater extent are called *strong(er) ligands* while those which split the *d*-orbitals to a lesser extent are called *weak(er) ligands.* Thus strong (er) ligands (*e.g.* CN^-, CO etc.) give larger value of Δ_0 and weak(er) ligands (*e.g.* I^-, Br^- etc) yield a smaller value of Δ_0. If the ligands like I^-, Br^-, Cl^- etc. are arranged in the increasing order of their power to split the *d*-orbitals of the central cation into t_{2g} and e_g sets of orbitals, we get the series namely $I^- < Br^- < Cl^- \sim CN^- < F^- < OH^- < C_2O_4^{2-} \sim H_2O < NH_3 <$ en $< NO_2^- < CN^- <$ CO which is called **spectrochemical series**. The octahedral complexes containing weak(er) ligands attached with the central cation are called **weak field or low field complexes** while those containing strong(er) ligands are called **strong field or high field** complexes. In case of weak field complexes $\Delta_0 <$ P while in case of strong field complexes $\Delta_0 >$ P where Δ_0 = energy difference between t_{2g} and e_g sets and P = average (or mean) pairing energy which is the energy required to pair two electrons in the same orbital.

Filling up t_{2g} and e_g Orbitals with Electrons in Octahedral Complexes : High Spin and Low Spin Octahedral Complexes.

For octahedral complexes containing weak ligands (*i.e.* weak field complexes) the energy difference, Δ_0 between t_{2g} and e_g sets is relatively small and hence the energy of all the five *d*-orbitals is supposed to be the same. Consequently the filling of t_{2g} and e_g orbitals takes place according to Hund's rule, *i.e.* electrons pair

up only when each of the five *d*-orbitals is at least singly filled. Thus: (*a*) in case of weak field complexes the distribution of d^1 to d^{10} electrons t_{2g} and e_g orbitals takes place as : $d^1 = t_{2g}^1 e_g^0$ ($n = 1$, $S = n/2 = 1/2$); $d^2 = t_{2g}^2 e_g^0$ ($n = 2$, $S = 1$); $d^3 = t_{2g}^3 e_g^0$ ($n = 3$, $S = 3/2$); $d^4 = t_{2g}^3 e_g^1$ ($n = 4$, $S = 2$); $d^5 = t_{2g}^3 e_g^2$ ($n = 5$, $S = 5/2$); $d^6 = t_{2g}^4 e_g^2$ ($n = 4$, $S = 2$); $d^7 = t_{2g}^5 e_g^2$ ($n = 3$, $S = 3/2$); $d^8 = t_{2g}^6 e_g^2$ ($n = 2$, $S = 1$); $d^9 = t_{2g}^6 e_g^3$ ($n = 1$, $S = 1/2$); $d^{10} = t_{2g}^6 e_g^4$ ($n = 0$, $S = 0$). Here n = number of unpaired electrons and S = resultant spin which is equal to $n/2$.

(*b*) For octahedral complexes containing strong ligands (*i.e.* strong field complexes) all the three *d*-orbitals of low energy t_{2g} set are filled up first and then the two *d*-orbitals of high energy e_g set are filled. Thus in this ease the distribution of d^1 to d^{10} electrons in t_{2g} and e_g orbitals takes places as : $d^1 = t_{2g}^1 e_g^0$ ($n = 1$, $S = 1/2$); $d^2 = t_{2g}^2 e_g^0$ ($n = 2$, $S = 1/2$); $d^3 = t_{2g}^3 e_g^0$ ($n = 3$, $S = 3/2$); $d^4 = t_{2g}^4 e_g^0$ ($n = 2$, $S = 1$); $d^5 = t_{2g}^5 e_g^0$ ($n = 1$, $S = 1/2$); $d^6 = t_{2g}^6 e_g^0$ ($n = 0$, $S = 0$); $d^7 = t_{2g}^6 e_g^1$ ($n = 1$, $S = 1/2$); $d^8 = t_{2g}^6 e_g^2$ ($n = 2$, $S = 1$); $d^9 = t_{2g}^6 e_g^3$ ($n = 1$, $S = 1/2$); $d^{10} = t_{2g}^6 e_g^4$ ($n = 0$, $S = 0$).

It may be seen that the weak field octahedral complexes of d^4, d^5, d^6 and d^7 ions have greater number of unpaired electrons (n) than those of (same ions) strong field complexes and hence have higher value of S. It is for this reason that weak field complexes of d^4, d^5, d^6 and d^7 ions are also called **high spin** or **spin free** complexes. Similarly strong field complexes are also called **low spin** or **spin paired** complexes. Recall that VBT has called high spin complexes as ionic (Pauling) or outer orbital (Huggin) complexes while the same theory has called low spin complexes as covalent or inner orbital complexes.

Crystal Field Stabilisation Energies (CFSEs) of Octahedral Complexes.

We have seen that, according to CFT, under the influence of the six ligands approaching towards the central metal ion during the formation of an octahedral complex, the *d*-orbitals of the central metal ion are split into two sets of orbitals *viz.*, *lower energy triplet* (or *trio*) t_{2g} and *higher energy doublet* (or *pair*) e_g sets. t_{2g} set of orbitals is triply degenerate while e_g set is doubly degenerate The energy gap between these two sets is equal to Δ_0 (or 10Dq). The energy of t_{2g} set is lowered by 2/5 Δ_0 (= $0.4\Delta_0$) or 4Dq while that of e_g set is raised by 3/5 Δ_0 (= $0.6\Delta_0$) or 6Dq relative to the energy of hypothetical degenerate *d*-orbitals. Thus each electron occupying t_{2g} orbitals decreases the energy of *d*-orbitals by $-0.4\ \Delta_0$ (= –4Dq) while that going into e_g orbitals increases its energy by $+\ 0.6\ \Delta_0$ (= + 6Dq). – and + signs indicate respectively the decrease and increase in the energy of *d*-orbitals caused by their splitting under the influence of six ligands. Now let us consider a d^x ion containing $t_{2g}^p e_g^q$ configuration in which p is the number of electrons in t_{2g} set, q is the number of electrons in e_g set and $x = p + q$. Quite obviously :

Change in energy (in terms of Δ_0) for $t_{2g}^p e_g^q$ configuration

= Loss in energy due to p electrons in t_{2g} set

+ gain in energy due to q electrons in e_g set.

$= -0.4\ \Delta_0 \times p + 0.6\ \Delta_0 \times q$

$= [-0.4\ p + 0.6q]\ \Delta_0$ ...(*i*)

Now since Δ_0 = 10Dq, the above expression can also be written as :

Change in energy (in terms of Dq) for $t_{2g}^{p}e_g^{q}$ *configuration*

$$= [-0.4p + 0.6q] \times 10Dq$$

$$= [-4p + 6q]Dq \quad ...(ii)$$

Thus equations (*i*) and (*ii*) give the energies of d^x ion containing $t_{2g}^{p}e_g^{q}$ configuration. The change in energy for d^x ion containing $t_{2g}^{p}\,e_g^{q}$ configuration calculated as above is called *crystal field stabilisation energy* (CFSE) of d^x ion, since it stabilises *d*-orbitals by lowering their energy which results from their splitting into t_{2g} and e_g orbitals.

In the derivation of equations (*i*) and (*ii*) we have not considered the pairing energy, P of d^x ion which is the energy required to pair two electrons against electron-electron repulsion in the same orbital. If the pairing energy of the ion is also involved in any $t_{2g}^{p}e_g^{q}$ configuration of a given d^x ion, then CFSE of the ion is given by the expression. :

$$= [-0.4p + 0.6q]\,\Delta_0 \times m\,p \quad ...(iii)$$

$$= [-4p + 6q]\,Dq + mp \quad (\because \Delta_0 = 10\,Dq) \quad ...(iv)$$

Here m is the total number of paired electrons in t_{2g} and e_g sets of orbitals. Equations (*iii*) and (*iv*) have been used to calculate the CESE values (in terms of Δ_0 and Dq respectively) for d^0 to d^{10} ions of high spin and low spin octahedral complexes. These values, as calculated from the above equations, are given below :

(*a*) For high spin (or spin free or weak field) octahedral complexes : d^0 ($t^0{}_{2g}\,e^0{}_g$, $p = 0$, $q = 0$) = 0.0 Δ_0 or 0.0 Dq; d^1 ($t_2{}^1{}_g\,e^0{}_g$, $p = 1$, $q = 0$) = – 0.4 Δ_0 or – 4Dq; d^2 ($t^2{}_{2g}\,e^0{}_g$, $p = 2$, $q = 0$) = – 0.8 Δ_0 or –8 Dq; d^3 ($t^3{}_{2g}\,e^0{}_g$, $p = 3$, $q = 0$) = – 1.2 Δ_0 or – 12 Dq; d^4 ($t^3{}_{2g}\,e_g{}^1$, $p = 3$, $q = 1$) = – 0.6 Δ_0 or – 6 Dq; d^5 ($t^3{}_{2g}\,e_g{}^2$, $p = 3$, $q = 2$) = 0.0 Δ_0 or 0.0 Dq; d^6 ($t_{2g}{}^4\,e_g{}^2$, $p = 4$, $q = 2$, $m = 1$) = – 0.4 Δ_0 + P or – 4 Dq + P; d^7 ($t^5{}_{2g}\,e_g{}^2$, $p = 5$, $q = 2$, $m = 2$) = – 0.8 Δ_0 + 2P or – 8 Dq + 2P; d^8 ($t^6{}_{2g}\,e_g{}^2$, $p = 6$, $q = 2$, $m = 3$) = – 1.2 Δ_0 + 3P or – 12 Dq + 3P; d^9 ($t^6{}_{2g}\,e_g{}^3$, $p = 6$, $q = 3$, $m = 4$) = – 0.6 Δ_0 + 4P or – 6 Dq + 4P; d^{10} ($t^6{}_{2g}\,e_g{}^4$, $p = 6$, $q = 4$, $m = 5$) = 0.0 Δ_0 + 5P or 0.0 D + 5P.

(*b*) For low spin (or spin paired or strong field) octahedral complexes : d^0 ($t^0{}_{2g}\,e_g{}^0$, $p = 0$, $q = 0$) = 0.0 Δ_0 or 0.0 Dq; d^1 ($t^1{}_{2g}\,e_g{}^0$, $p = 1$, $q = 0$) = – 0.4 Δ_0 or – 4Dq; d^2 ($t^2{}_{2g}\,e_g{}^0$, $p = 2$, $q = 0$) = – 0.8 Δ_0 or – 8 Dq; d^3 ($t^3{}_{2g}\,e_g{}^0$, $p = 3$, $q = 0$) = – 1.20 Δ_0 or – 12 Dq; d^4 ($t^4{}_{2g}\,e_g{}^0$, $p = 4$, $q = 0$, $m = 1$) = – 1.6 Δ_0 + P or – 16 Dq + P; d^5 ($t^5{}_{2g}\,e_g{}^0$, $p = 5$, $q = 0$, $m = 2$) = 2.0 Δ_0 + 2P or – 20 Dq + 2P; d^6 ($t^6{}_{2g}\,e_g{}^0$, $p = 6$, $q = 0$, $m = 3$) = – 2.4 Δ_0 + 3P or – 24 Dq + 3P; d^7 ($t^6{}_{2g}\,e_g{}^1$, $p = 6$, $q = 1$, $m = 3$) = – 1.8 Δ_0 + 3P or – 18 Dq + 3P; d^8 ($t^6{}_{2g}\,e_g{}^2$, $p = 6$, $q = 2$, $m = 3$) = – 1.2 Δ_0 + 3P or – 12 Dq + 3P; d^9 ($t^6{}_{2g}\,e_g{}^3$, $p = 6$, $q = 3$, $m = 4$) = – 0.6 Δ_0 + 4P or – 6 Dq + 4P; d^{10} ($t^6{}_{2g}\,e_g{}^4$, $p = 6$, $q = 4$, $m = 5$) = 0.0 Δ_0 + 5P or 3.0 Dq + 5P.

CFSE values as given above show that, (*i*) When Δ_0 = P, each of d^4, d^5, d^6 and d^7 ions gives the same value of CFSE for both spin states. (*ii*) When Δ_0 > P, the

CFSE of the low spin state becomes smaller than that of the high spin state and hence the low spin state becomes the preferred state of the ion. In this condition (*i.e.* when $\Delta_0 > P$), the electrons tend to pair and hence low spin complexes are obtained (*iii*) When $\Delta_0 < P$, the CFSE of the high spin becomes smaller than the low spin state and hence high spin state becomes the preferred state of the ion. Under this condition (*i.e.* when $\Delta_0 < P$) the electrons tend to remain unpaired and hence high spin complexes are obtained.

Thus we see that the spin state of an ion in a complex depends on whether the crystal field splitting (Δ_0) is bigger or smaller than the pairing energy (P).

CFT As Applied to Tetrahedral Complexes

Splitting of d-orbitals in Tetrahedral Complexes.

In order to understand the splitting of *d*-orbitals in tetrahedral complexes, a tetrahedron should be pictured as being placed in a cube as represented in Fig 43.37. It may be seen from the figure that the four negative ligands (represented by circles with negative signs) placed at the four corners of the tetrahedron are located at the four corners of the cube. Thus these four ligands are lying between the three axes *viz.* x, y and z axes which pass through the centres of the six faces of the cube and thus go through the centre of the cube. Now since the lobes of t_2 orbitals (d_{xy}, d_{yz} and d_{zx}) are lying between the axes, *i.e.* are lying directly in the path of the ligands, these orbitals will experience greater force of repulsion from the ligands than those of e orbitals (d_{z^2} and $d_{x^2-y^2}$) whose lobes are lying along the axes, *i.e.* are lying in space between the ligands. Thus the energy of t_2

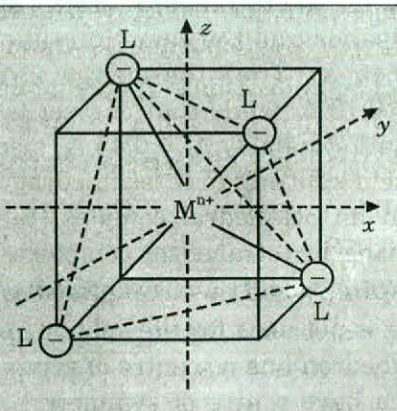


Fig. 43.37. A tetrahedron placed in a cube. The centre of the cube is the centre of the tetrahedron at which is placed central metallic cation, M^{n+}. Four corners of the cube are the four corners of the tetrahedron at which are placed the four negative ligands which have been shown by circles with negative signs.

orbitals will be *increased* while that of e orbitals will be *decreased.* Consequently the d orbitals are again split into two sets as shown in Fig. 43.38 from which it may be seen that the order of energy of t_2 and e sets is the reverse of that seen for t_{2g} and e_g sets in octahedral complexes.

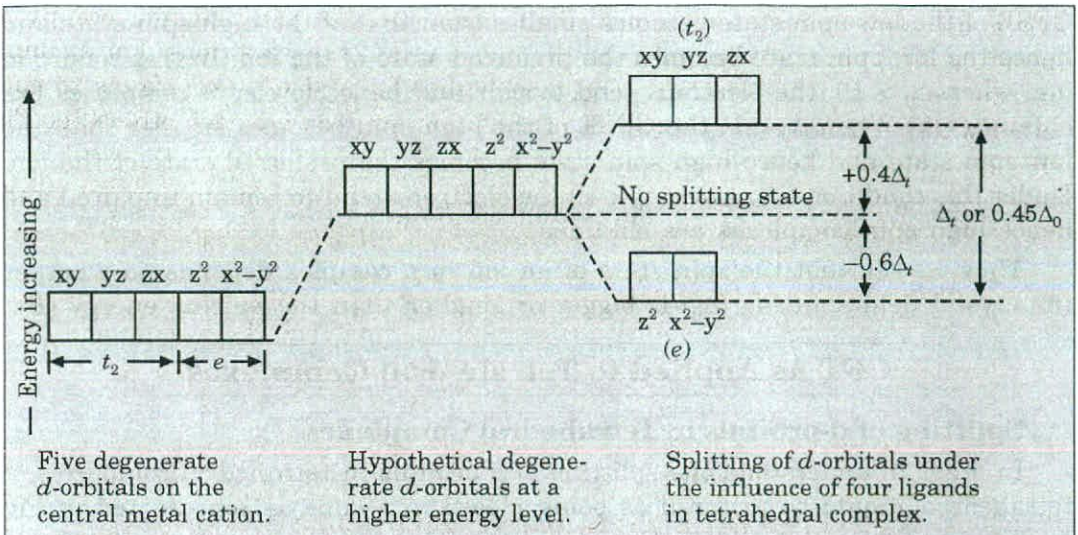


Fig. 43.38. Crystal field splitting of *d*-orbitals in tetrahedral complex.

The energy difference between t_2 and e sets for tertrahedral complex is represented as Δ_t. In has been shown that $\Delta_t < \Delta_0$, the cause of which is that t_2-orbitals, although now closest to the ligands, do not point directly at the ligands, *i.e.* in an octahedral complex there is a ligand along each axis and in a trahedral complex no ligand lies directly along any axis. For this reason and also because there are only four ligands in the tetrahedral complex, while in an octahedral complex there are six ligands, the tetrahedral orbital splitting, Δ_t is less than Δ_0, for the same metal and ligands and the same internuclear distances. It has also been shown that $\Delta_t = 0.45\ \Delta_0$. Thus the energy level of the t_2 set is raised by $0.4\ \Delta_t = 0.4 \times 0.45\Delta_0 = 0.18\ \Delta_0$ while that of e set is lowered by $0.6\ \Delta_t = 0.6 \times 0.45\ \Delta_0 = 0.27\ \Delta_0$. The relation namely $\Delta_t = 0.45\ \Delta_0$ also shows that, other things being equal, the crystal field splitting in a tetrahedral complex will be about half the magnitude of that in an octahedral complex. Since Δ_t is relatively small orbital splitting, spin-pairing in tetrahedral complexes is rather unlikely. Since $\Delta_t < \Delta_0$, *crystal field splitting favours the formation of octahedral complexes.*

Note : The subscript g is not used for the splitting of *d*-orbitals in tetrahedral complexes because a tetrahedron has no centre of symmetry. The symbol *g* is used for the ligand fields which have centre of symmetry.

Splitting of *d*-orbitals in Tetragonally Distorted Octahedral and Square Planar Complexes.

Before considering the splitting of *d*-orbitals of the central metal cation in these complexes, we should undrstand how tetragonally distorted octahedral and square planar geometries are obtained from regular octahedral geometry. Consider a regular (symmetrical) octahedral complex, $[M(L_b)_4\ (L_a)_2]$ in which L_a are two *trans*-ligands (*i.e.* L_a are the ligands lying along the *z*-axis) and L_b are the basal ligands lying in *xy* plane. In this complex all the six bond distances (four M–L_b

and two M–L_a distances) are equal [See Fig. 43.39(*a*)]. Now if two L_a ligands are moved slightly away from the central metal cation, M so that each of the two M–L_a distances becomes slightly greater than each of the four co-planar M–L_b distances, the symmetrical shape of octahedral complex becomes tetragonally distorted octahedral shape [See Fig 43.39 (*b*)]. Now if the two L_a ligands are completely removed away from the *z*-axis, the tetragonally distorted octahedral shape becomes square planar (Fig. 43.39 (*c*)].

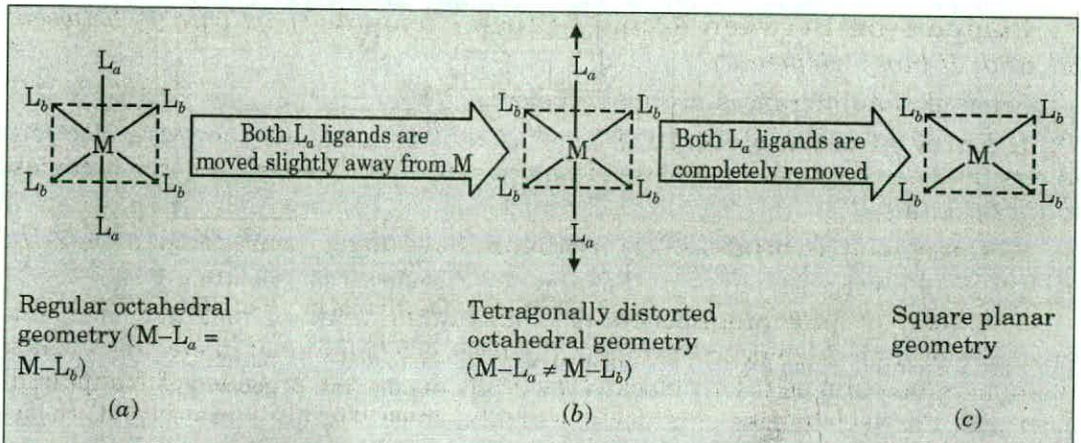


Fig. 43.39. Distortion in regular octahedral geometry leading to the formation of tetragonally distorted octahedral geometry and square planar geometry.

Now in order to consider the splitting of *d*-orbitals in tetragonally distorted octahedral and square planar complexes, we start with the splitting of *d*-orbitals in octahedral complexes. We have already seen that in octahedral complexes, the energy of d_{xy}, d_{yz} and d_{zx} orbitals (t_{2g} orbitals) is decreased while that of d_{z^2} and $d_{x^2-y^2}$ orbitals (e_g orbitals) is increased [Fig. 43.40(*a*)]. Now in tetragonally distorted octahedral complex, since the distance of the *trans*-ligands (L_a ligands) is increased from the central metal ion by removing them away along the *z*-axis, *d*-orbitals along the *z*-axis (*i.e.* d_{z^2} orbital), in *xz* (*i.e.* d_{xz}) and *yz* (*i.e.* d_{yz}) planes experience less repulsion from the ligands than they do in the octahedral complex while the *d*-orbitals in *xy* plane (*i.e.* d_{xy} and $d_{x^2-y^2}$ orbitals) experience more repulsion than they do in the octahedral complex. Consequently the energy of d_{zy}, d_{yz} and d_{zx} orbitals decreases while that of $d_{x^2-y^2}$ and d_{z^2} orbitals increases [Fig.43.40(*b*)]. Note that d_{yz} and d_{zx} orbitals still remain degenerate as they are in the octahedral complex. In square planar geometry the energies of d_{z^2}, d_{yz} and d_{zx} orbitals again fall down while those of $d_{x^2-y^2}$ and d_{xy} orbitals rise up [see Fig. 43.40 (*d*)].

The crystal field splitting energy in square planar complexes is denoted by Δ_{sp} and is given by :

$$\Delta_{sp} = E(d_{x^2-y^2}) - E(d_{xz}, d_{yz}) \qquad \text{[See Fig. 43.40(d)]}$$
$$= \Delta_1 + \Delta_2 + \Delta_3$$

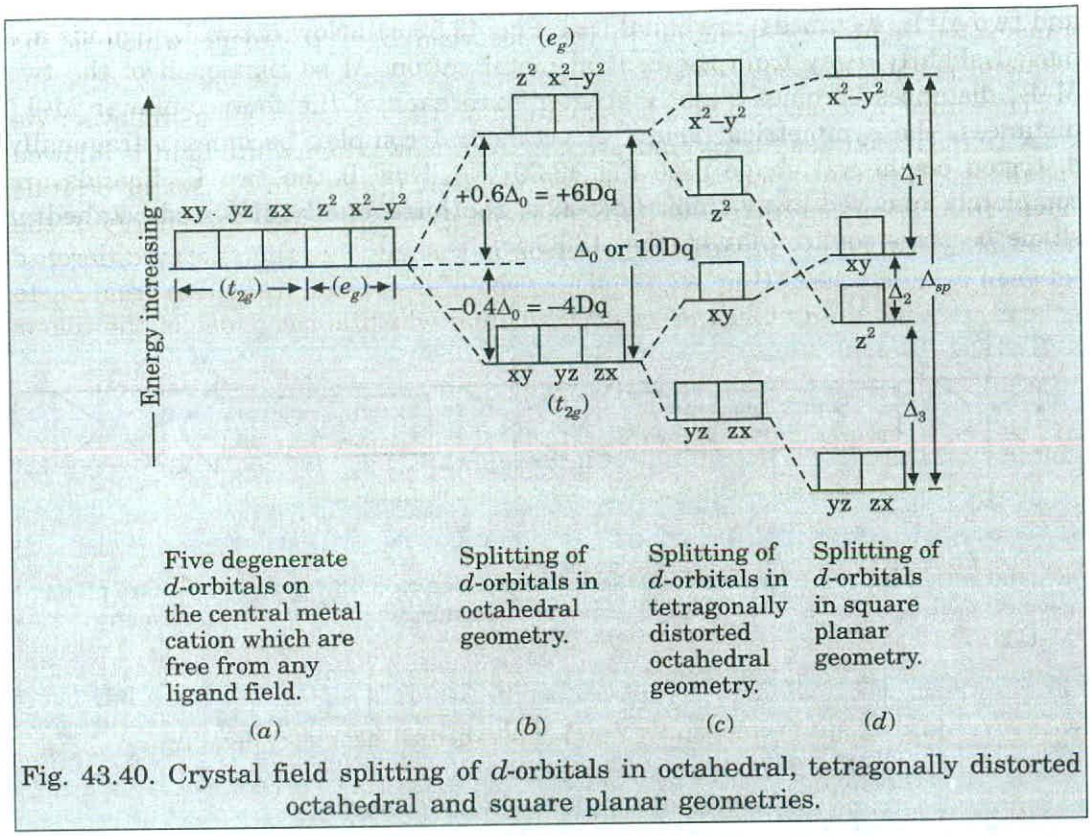


Fig. 43.40. Crystal field splitting of *d*-orbitals in octahedral, tetragonally distorted octahedral and square planar geometries.

The value of Δ_{sp} has been found larger than Δ_0 ($\Delta_{sp} = 1.3\ \Delta_0$) because of the reason that d_{xz} and d_{yz} orbitals interact with only two ligands in the square planar complexes, while in octahedral complexes the interaction takes place only with four ligands.

Applications of Crystal Field Theory

The following properties of transition metal complexes can well be explained on the basis of CFT.

1. Colour of transition metal complexes.

It has been seen that the solution of transition metal complexes formed by metal cations having no unpaired electrons in *d*-orbitals (*i.e.* having completely filled or vacant *d*-orbitals) are colourless while the solution of transition metal complexes given by transition metal cations having one or more unpaired electrons in *d*-orbitals are coloured. The colour of transition metal complexes having unpaired electrons in *d*-orbitals can well be explained by considering the example of $[Ti(H_2O)_6]^{3+}$ ion which is an octahedral complex and has purple colour. Now when white light is allowed to fall on this complex ion, the ion absorbs radiation from the white light (*i.e.* visible spectrum). The maximum absorption takes place at a wavelength of 5000Å. The absorbed light of this wavelength is green and the

transmitted light corresponding to this absorbed light it purple which is the colour of $[Ti(H_2O)_6]^{3+}$ solution.

The cause of colour can also be explained on the basis of CFT as follows : We know that Ti^{3+} ion has the configuration $t_{2g}^{\ 1}\, e_g^{\ 0}$. Now when white light is allowed to fall on $[Ti(H_2O)_6]^{3+}$ ion, the unpaired electron present in t_{2g} set of orbitals moves from lower energy t_{2g} set to higher energy e_g set, since the energy of the radiation absorbed by unpaired t_{2g} electron is the same as the energy difference between t_{2g} and e_g sets (Fig. 43.41). This type of electronic transition from t_{2g} to e_g level is called *d—d* or *ligand—field transition* which is the cause of the colour of $[Ti(H_2O)_6]^{3+}$ ion.

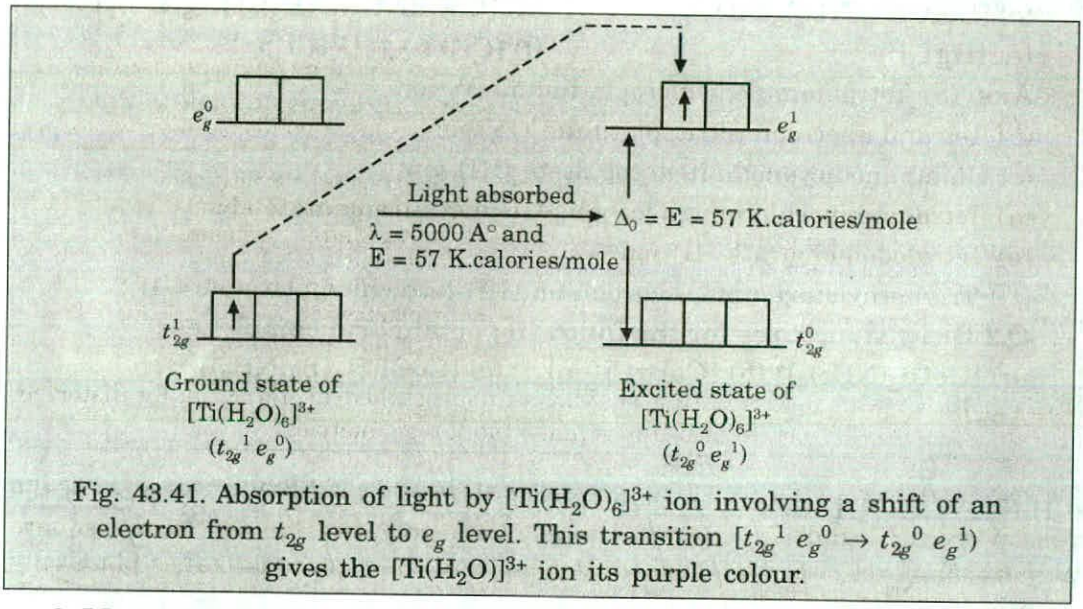


Fig. 43.41. Absorption of light by $[Ti(H_2O)_6]^{3+}$ ion involving a shift of an electron from t_{2g} level to e_g level. This transition $[t_{2g}^{\ 1}\, e_g^{\ 0} \rightarrow t_{2g}^{\ 0}\, e_g^{\ 1})$ gives the $[Ti(H_2O)]^{3+}$ ion its purple colour.

2. Magnetic moment values of complex compounds.

CFT can be used to find out the number of unpaired electrons (n) in a given octahedral complex. The substitution of n value in the spin-only formula, $\mu = \sqrt{n(n+2)}$ gives the value of magnetic moment of the given complex compound. From the knowledge of μ-value the valence state of the central metal cation and the nature of bonding in the complex (*i.e.* whether the complex is high spin or low spin) can be known.

Comparison between VBT and CFT.

The points showing the comparison between the two theories are given below.

1. Inner orbital octahedral complexes of VBT are the same as the spin-paired or low-spin octahedral complexes of CFT. Simalarly outer-orbital complexes of VBT are the same as the spin-free or high-spin octahedral complexes of CFT.

2. In the formation of some inner-orbital octahedral complexes of VBT, the promotion of an electron from *d*-orbital to *s*-orbital is required, while in the formation of spin-paired octahedral complexes of CFT no such promotion is required.

3. According to VBT, the metal-ligand bonding in complexes is only covalent, since VBT assumes that ligand electrons are donated to the vacant *d*-orbitals on the central cation. On the other hand, CFT considers the bonding to be entirely electrostatic. Thus CFT does not allow the ligand electrons to enter the metal *d*-orbitals.

Questions with Answers

Q.1 Name the following species :

(*a*) $[PtCl_2(NH_3)_4]^{2+}$ **(*b*) $[PtCl(NO_2)(NH_3)_4]^{2+}$**

(*c*) $[Co(CN)_2(NO_2)_2(NH_3)_2]^-$ **(*d*) $[CoCl(NO_2)(NH_3)_4]$ $[Ag(CN)_2]$**

(*e*) $[HgI_4]^{2-}$ **(*f*) $[Cr(en)_3]_2$ $[PtCl_4]_3$**

Ans. (*a*) Tetraamminedichloroplatinum (IV) ion

(*b*) Tetramminechloronitritoplatinum (IV) ion

(*c*) Diamminedicyanodinitritocobaltate (III) ion

(*d*) Tetraamminechloronitritocobalt (III) dicyanoargentate (I)

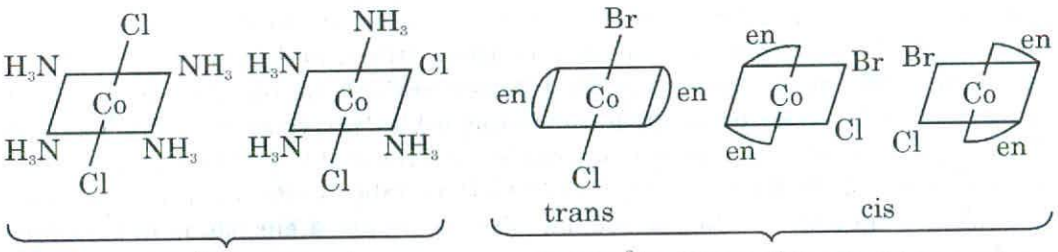
(e) Tetraiodomercurate (II) ion

(*f*) Tris (ethylenediamine) chromium (III) tetrachloroplatinate (II)

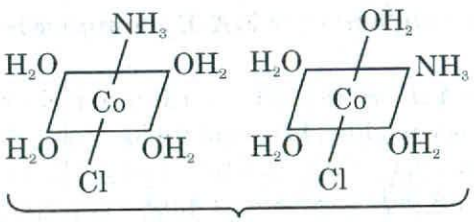
Q.2 Draw structures for the following octahedral complexes :

(*a*) $[CoCl_2(NH_3)_4]^+$ (*b*) $[CoBrCl(en)_2]^+$ (*c*) $[CoCl(H_2O)_4(NH_3)]^{2+}$

Ans.



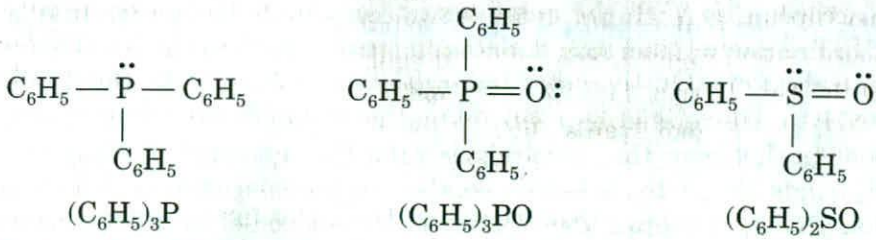
(*a*) $[Co^{3+}Cl_2(NH_3)_4]^+$ (*b*) $[Co^{3+}BrCl(en)_2]^+$ (optical isomers)



(*c*) $[Co^{3+}Cl(H_2O)_4(NH_3)]^{2+}$

Q.3 How do you expect $(C_6H_5)_3P$, $(C_6H_5)_3PO$ and $(C_6H_5)_2SO$ to behave as coordinating ligands ?

Ans. The structures of the given molecules are given below :



$(C_6H_5)_3P$ $(C_6H_5)_3PO$ $(C_6H_5)_2SO$

In the structure of $(C_6H_5)_3P$, since P-atom has a *lp* of electrons, this molecule can act as a monodentate ligand. P-atom is the donor atom.

In the structure of $(C_6H_5)_3PO$, since O-atom has two *lps* of electrons, this molecule can act as a ligand, coordinating through O-atom. Now since two *lps* reside on the same atom (*i.e.* O-atom), this molecule can act only as a monodentate ligand and not as a bidentate ligand.

In the structure of $(C_6H_5)_2SO$, since S and O both have *lps* of electrons, this molecule can act as a ligand. Now since *lps* reside on different atoms, this molecule can act as an ambidentate ligand, coordinating through S or through O-atom. This molecule coordinates with Pt(II), Pd(II) through S-atom and with Co(II), Ni(II), Zn(II)etc. through O-atom.

Q.4 Molecular N_2 is a weaker sigma donor as well as weaker pi acceptor than CO molecule, although both molecules are isoelectronic and have the same bonding patter. Explain.

Ans. It is true that CO and N_2 are isoelectronic and have the same bonding pattern. Both have a triple bond and a lone pair on each of the two atoms. Oxygen has more protons in the nucleus than carbon and hence oxygen orbitals are more stable than those of carbon. Therefore the bonding orbitals of CO have more oxygen character while the anti-bonding orbitals have more carbon character. Bonding orbitals of N_2 are little more stable than those of CO while the antibonding orbitals are less stable than those of CO. (Remember that in N_2 the two atomic orbitals are the same). Thus molecular nitrogen is a weaker sigma donor as well as a weaker pi acceptor than carbon monoxide.

Q.5 (*a*) How would you distinguish between *cis* and *trans* isomer of $[CrCl_2(NH_3)_4]Cl$?

(*b*) How would you decide whether MA_2B_2 complex is square planar or tetrahedral?

Ans. (*a*) The *cis* isomer has the two coordinated chloro groups as near neighbours. Hence it will react readilly with oxalate ion ($C_2O_4^{2-}$) giving tetrammine (oxalato) chromium (III) ion, $[Cr^{3+}(NH_3)_4C_2O_4]^+$ .The *trans* isomer will not react as readily as the *cis* isomer. A bidenate oxalato group can span only two adjacent positions as in the *cis* but not in the *trans*.

(*b*) A square planar MA_2B_2 complex is capable of giving *cis* and *trans* isomers while a tetrahedral MA_2B_2 complex cannot do so.

Q.6 $[PtCl_2(NH_3)_2]$ has been isolated in two isomer. One isomer has a good dipole moment while the other has nearly zero dipole moment. Elucidate their structures.

Ans. Bipositive platinum in these two compounds has a coordination number four. Coordination number four admits of a tetrahedral or a square planar geometry. A tetrahedral MA_2B_2 complex cannot give isomers. So the two forms of $[PtCl_2(NH_3)_2]$ are related as *cis-trans* geometrical isomers. Individually each of the bonds in the *cis* or the *trans* is polar, the Pt–Cl bonds being more so than the Pt–NH_3 bonds. In the *trans* isomer bonds of equal polarity are oriented in opposite direction giving an overall non-polarity to the molecule. In the *cis* isomer the two chlorine ends will have more negative charge than the ammonia end. Effectively then there will be separation of charge : the positive centre being on the platinum and the negative centre being in between the two chlorine atoms. Therefore that isomer which has nearly zero dipole moment is the *trans* while the other with a good value of dipole moment is the *cis* variety.

Q.7 10 Dq of $[Mn(H_2O)_6]^{3+}$ is known from electronic spectrum to be 21,000 cm^{-1}. The pairing enrgy of Mn(III) is 28,800 cm^{-1}. Predict whether the complex is high-spin or low-spin.

Ans. $[Mn(H_2O)_6]^{3+}$ has Mn^{3+} ion which is a d^4 ion.

CFSE for d^4 ion in H.S. state ($t_{2g}^3\, e_g^1$ having $m = 0$),

$$(CFSE)_{H.S.} = -6Dq + mP = -6 \times \frac{21000}{10} + 0 \times P$$
$$= -12{,}600 \text{ cm}^{-1}$$

CFSE for d^4 ion in L.S. state ($t_{2g}^4 e_g^\circ$ having $m = 1$),

$$(CFSE)_{L.S.} = -16Dq + mP = -16 \times \frac{21000}{10} + 1 \times 28{,}800$$
$$= -33600 + 28800$$
$$= -4800 \text{ Cm}^{-1}$$

Now since $(CFSE)_{H.S.}$ is more negative than $(CFSE)_{L.S.}$, the given complex ion is more stable in H.S. state.

Alternatively, since $10Dq$ (= 21,000 cm^{-1}) < P (= 28,000 cm^{-1}), the given complex is a high spin complex.

Q.8 $10Dq$ values of $[Ru(H_2O)_6]^{2+}$ and $[RuCl_6]^{3-}$ are nearly the same but according to spectrochemical series, the value for $10Dq$ for the chloride complex should be lower than H_2O complex. How do you explain the similarity of the $10Dq$ values of the two complexes ?

Ans : $[Ru(H_2O)_6]^{2+}$ ion has Ru in +2 O.S. while $[Ru(H_2O)_6]^{3-}$ ion has Ru in +3 O.S. It is true that chloride ion is a far weaker ligand than H_2O. In one of the two complexes we have ruthenium (II) associated with H_2O and in the other ruthenium (III) is associated with the weaker ligand, chloride. $10Dq$ depends on several factors of which a very important one is the oxidation state. It is empirical fact that with an increase in the oxidation state by one unit (from +2 to +3), $10Dq$ increases by about 100%. This explains why even a weaker lignad (chloride) produces with ruthenium(III) nearly the same $10Dq$ as does hexaaquaruthenium(II).

Q.9 Chromium(III) under forcing conditions forms hexachloro complex ion, $[CrCl_6]^{3-}$ but the corresponding complexes are never found in Mn(III) and Fe(III). Why ?

Ans. Cr(III), Mn(III) and Fe(III) are d^3, d^4 and d^5 systems respectively. Since chloride ion is a weak field ligand, all the complexes, if found at all, must be high-spin. The *CFSE's* are $-12Dq$, $-6Dq$ and $0Dq$ (in respective *Dq's*) respectively. These values show that since Cr(III) (d^3 ion) has the most negative value of CFSE, Cr(III) has the maximum possibilty of forming hexachloro complex ion, $[CrCl_6]^{3-}$.

Q.10 Arrange the following species in the order of increasing Jhan Teller distortion in an octahedral enviroment : high-spin Co(III), low-spin Co(II), copper(II) and Ti(III).

Ans. Jhan Teller effect becomes more severe when the e_g level is unsymmetrically occupied than when the t_{2g} level is unsymmetrically occupied. $t_{2g}^{p}\, e_g^{2}$ configurations of the given ions are given below :

H.S. Co(III) = $3d^6 = t_{2g}^{4}\, e_g^{2}$,

L.S. Co(II) = $3d^7 = t_{2g}^{6}\, e_g^{1}$

Cu(II) = $3d^9 = t_{2g}^{6}\, e_g^{3}$,

Ti(III) = $3d^1 = t_{2g}^{1}\, e_g^{\circ}$

These configurations show that Jhan Teller distortion of the given ions is in the order :

Ti(III) = H.S. Co(III) < Cu(II) = L.S. Co(II)

Q.11 $(NH_4)_2$ $[VF_6]$ shows one electronic transition around 20.1 *KK* while $[VO(acac)_2]$ in chloroform gives three bands around 14.8, 16.8 and 25.0 *KK*. Explain.

Ans. Both the complexes have $3d^1$ vanadium(IV). $(NH_4)_2$ $[VF_6]$ may be viewed as octahedral with some slight Jhan-Teller distrotion while $[VO(acac)_2]$ is under heavy tetragonal compression. The vanadly oxygen bond is much too short compared to the other equatorial vanadium-oxygen bonds. Hence the spiliting of the d orbitals is unlike what obtains in octahedral complexes. So in the former compound one transition ($t_{2g} \rightarrow e_g$) is expected while in the latter as many as three ($d_{xy} \rightarrow d_{xz}$, d_{yz}; $d_{xy} \rightarrow d_{x2-y2}$; $d_{xy} \rightarrow d_z^2$) are expected. The three bands around 14.8, 16.8 and 25.0 *KK* are due to these electronic transitions.

Q.12 Magnetic moment measurement of potassium hexacyanomanganate(III), $K_3[Mn^{3+}(CN)_6]$ indicates the presence of two unpaired electrons. Predict whether the complex compound is outer orbital octahedral or inner orbital octahedral.

Ans. Mn^{3+} ion is a $3d^4$ ion. The formation of outer orbital octahedral complex ion, $[Mn^{3+}(CN)_6]^{3-}$ and that of inner orbital octahedral complex ion, $[Mn^{3+}(CN)_6]^{3-}$ has been at (*a*) and (*b*) respectively of Fig. 43.42. It may be seen from the figure that $[Mn(CN)_6]^{3-}$ ion is an inner orbital octahedral complex ion.

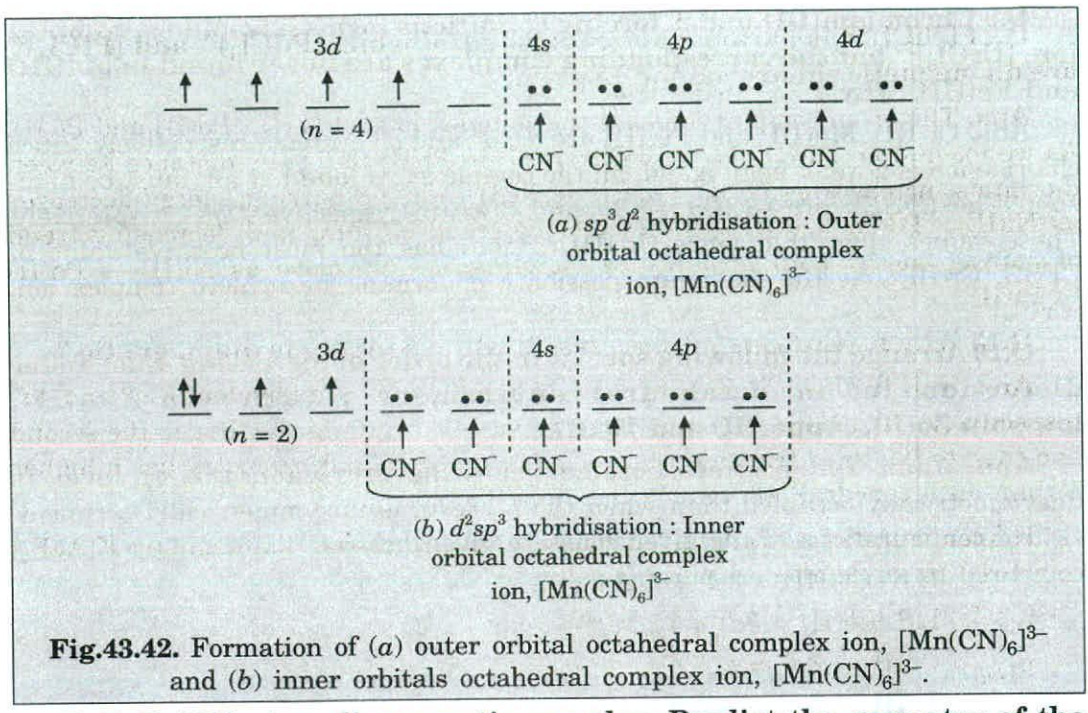


Fig.43.42. Formation of (*a*) outer orbital octahedral complex ion, $[Mn(CN)_6]^{3-}$ and (*b*) inner orbitals octahedral complex ion, $[Mn(CN)_6]^{3-}$.

Q.13 $Fe(CO)_5$ is a diamagnetic complex. Predict the geometry of the complex.

Ans. In $Fe(CO)_5$, Fe is present in zero oxidation state. Hence Fe is present as Fe° whose V.S.E.C. is $3d^64s^2$ or $3d^8$. Since C.N. of Fe is 5 in $Fe(CO)_5$, $Fe(CO)_5$ can have trigonal bipyramidal geometry (dsp^3 hybridisation of Fe atom) or square pyramidal geometry (d^2sp^2 hybridisations of Fe atom). Both these hybridisations shown in Fig.43.43. indicate that $Fe(CO)_5$ molecule has $n = 0$ and hence is diamagnetic. For d^2sp^2 hybridisation two $3d$ electrons have to be promoted to higher energy $4p$ orbitals. This process is unfavourable since the promotion of electrons to higher energy orbitals will make these electrons valnerable to oxidation. Hence trigonal bipyramidal geometry is preferred.

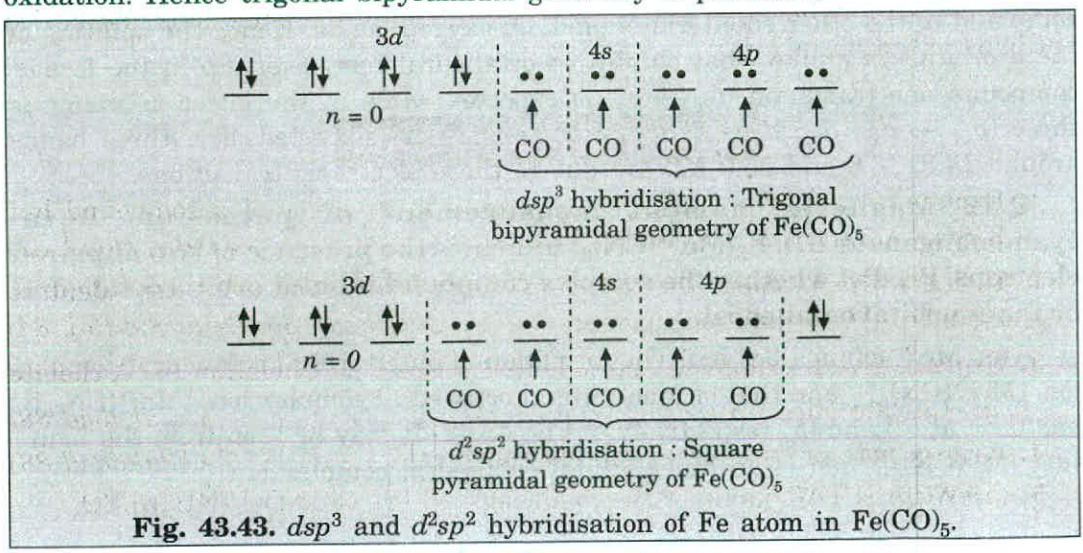


Fig. 43.43. dsp^3 and d^2sp^2 hybridisation of Fe atom in $Fe(CO)_5$.

Q.14 $[NiCl_4]^{2-}$ is paramagnetic tetrahedral while $[PdCl_4]^{2-}$ and $[PtCl_4]^{2-}$ are diamagnetic square palnar. Explain.

Ans. The given complex ions are the complex ions of Ni(II), Pd(II) and Pt(II). As we move from Ni(II) ($3d^8$) to Pd(II) ($4d^8$) to Pt(II) ($5d^8$), the distance between d-orbitals increases as Ni(II) < Pd(II) < Pt(II) but the parring energy decreases as Ni(II) > Pd(II) > Pt(II). The increasing trend of $10Dq$ and decreasing trend of pairing energy both favour L.S. complexes as we move as Ni(II) $\rightarrow$ Pd(II) $\rightarrow$ Pt(II).

Q.15 Why $K_3[CuF_6]$ is paramagnetic while $K[AgF_4]$ is diamagnetic ?

Ans. In $K_3[CuF_6]$ and $K[AgF_4]$ both the metal ions are trivalent ($3d^8$ and $4d^8$ respectively). In general Δ increases as we move down from the first to the second and then to the third transition series. Also square palnar geometry has a higher Δ than an octahedral one having the same ligand.

Higher value of Δ in Ag(III) favours a square planar diamagnetic $K[AgF_4]$ compared to an octahedral paramagnetic $K_3[CuF_6]$.

$K_3[CuF_6]$: $t_{2g}^6\ e_g^2$: 2 unpaired electrons.

$K[AgF_4]$: $d^2_{z2}\ d^2_{xz}\ d^2_{yz}\ d^2_{xy}\ d^0_{x2-y2}$: no unpaired electron.

Q.16 The divalent metal ions in the oxides MO are octahedraly surrounded by weak field oxide ions in the crystal lattice. Explain the trend seen in the following lattice enthalpies :

CaO	TiO	VO	MnO	
3460	3878	3913	3810	KJ/mole

Ans. Calcium(II), titanium(II), vanadium(II) and managanese(II) are d^0, d^2, d^3 and d^5 ions respectively. Calcium (d^0) and high-spin managnese(II) (d^5) have $CFSE = 0$. $CFSE$ of titanium(II) and vanadium(II) are $-8Dq$ and $-12Dq$. So the MO oxides of Ti(II) and V(II) will be stabilished compared to Ca(II). MnO will be having no extra stablisation due to the crystal field of the oxide ions and lattice enthalpy will drop in MnO.

University Questions

1. Explain why K_3 [Fe $(CN)_6$] is considered to be a complex compound but K_2SO_4. $Al_2(SO_4)_3.24H_2O$ is not? *(Delhi Hons. 82)*
2. Define with examples, the following terms : (*i*) Ligand (*ii*) A pentadentate ligand. (*iii*) Coordination number. *(Allahabad 86; Delhi 89; Raj. 84)*
3. Explain, giving examples, the following terms : (*i*) Chelation (*ii*) A chelate (*iii*) Chelate effect in coordination chemistry. *(Allahabad 88)*
4. Write a note on "stepwise stability constants". *(Allahabad 88)*
5. (*a*) Write IUPAC name of the following : (*i*) [Pt Cl (NO_2) $(NH_3)_4$] SO_4.

(*ii*) $\left[(en)_2 Co\begin{matrix}NH_2\\NH_2\end{matrix}Co(en)_2 Br_4\right]$ (*iii*) $NH_4[Cr(NCS)_2(NH_3)_3]$ Also calculate the EAN of the central metal atom (Cr = 24, Co = 27, Pt = 78).

(*b*) Write the structural formula for dichloro*bis* (ethyleneamine) platinum (IV) tetrachloroplatinate (II). (*Allahabad 99*)

6. (*a*) Write the formulae of the following compounds : (*i*) Hexa aquiron (II) sulphate (*ii*) Potassium tetracyanonickelate (III) (*iii*) Trans-Chloronitro-diammine platinum (II).

(*b*) Write the IUPAC names of $Fe(CO)_5$ and $[(CO)_3 Co(CO)_2 Co(CO)_3]$ (*Himachal Pradesh 2000*)

7. What are various types of isomerism exhibited by coordination compounds? Write in detail giving examples. (*Lucknow 2001*)

8. (*i*) $[Co F_6]^{3-}$ is paramagnetic while $[CO(NH_3)_6]^{3+}$ is diamagnetic.

(*ii*) $[Fe(CN)_6]^{3-}$ is less paramagnetic than $[Fe(H_2O)_6]^{3+}$ (*Avadh 2000*)

9. (*i*) Explain why $[FeF_6]^{3-}$ and $[Fe(CN)_6]^{3-}$ ions are paramagnetic but their magnetic moments are quite different.

(*ii*) Write a note on : High spin and low spin complexes.

(*iii*) What are inner and outer complexes? Give two examples of each.

(*iv*) Write a note on "Crystal field theory" (*Lucknow 2001*)

10. (*a*) What is CFSE ? Explain.

(*b*) Discuss in brief the limitations of VBT.

(*c*) Give an elementry idea of CFT and explain the spliting of d-orbitals in octahedral and tetrahedral complexes. (*Agra 2008*)

11. Which of the following has larger value of CFSE ? $[Co(NH_3)_6]^{2+}$ and $[Co(NH_3)_6]^{3+}$. (*H.N. Bahugura 2008*)

12. $[FeF_6]^{3-}$ in has less magnetic moment than $[Fe(CN)_6]^{3-}$, though both are octahedral complex ions. Explain. (*C.S.J.M. Kanpur 2009*)

13. (*a*) Discuss VBT of complex compounds. Explain different geometric and magnetic character of complex compounds on the basis of this theory with suitable examples.

(*b*) Write oxidation number and coordination number of Cr-atom in $[Cr)NH_3)_6]Cl_3$.

14. (*c*) Explain :

(*i*) Zn^{2+} salts are white but Cu^{2+} salts the blue

(ii) Cu+ is diamagnetic but Cu^{2+} is paramagnetic (*Meerut 2009*)

15. (*a*) What are the important features of CFT. Discuss its applications and limitations.

(*b*) Write a note on "Jahn – Teller Effect".

(*c*) Write a note on "Spectrochemical Series". (*Meerut 2009*)

CHAPTER

44

Characteristics of d- and f- Block Elements (Transition and Inner-transition Elements)

d-block Elements : Transition Elements

What are d-Block Elements ?

The definition of *d*-block elements has already been given in chapter 3.

Why are d-Block Elements Called Transition Elements ?

The *d*-block elements are called transition elements because they exhibit transitional behaviour between highly reactive ionic-compound forming *s*-block elements (electropositive elements) on one side and mainly covalent-compound forming *p*-block elements (electronegative elements) on the other side.

Position of d-Block Elements in the Periodic Table.

d-block elements are located in between *s*-(ionic-compound forming elements) and *p*-(covalent-compound forming elements) block elements as shown in Fig. 44.1. Thus these elements are located in the middle of the periodic table and occur in fourth ($n = 4$) and subsequent periods of the periodic table. It is because of their inclusion in between *s*- and *p*-block elements that the properties of *d*-block elements are intermediate between those of *s*- and *p*-block elements. Thus the elements of groups 3 (IIIB), 4 (IVB), 5 (VB), 6 (VIB), 7 (VIIB), 8, 9, 10 (VIII), 11 (IB) and 12 (IIB) belong to this block.

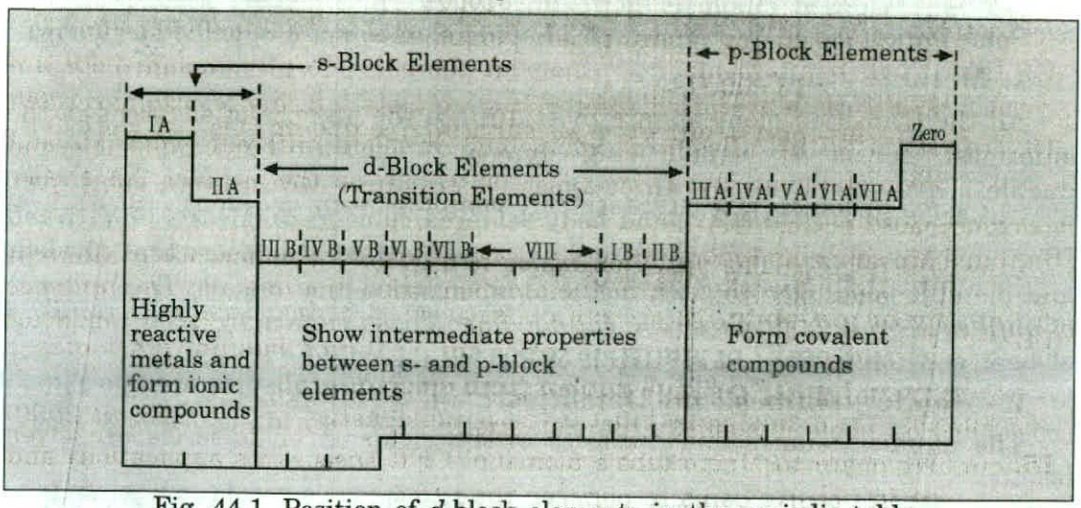


Fig. 44.1. Position of *d*-block elements in the periodic table.

Electronic Configurations of d-Block Elements.

Complete and valence-shell configurations of *d*-block elements namely (*a*) Sc (Z = 21) to Zn (Z = 30); (*b*) Y (Z = 39) to Cd (Z = 48); (*c*) La(Z = 57), Hf (Z = 72) to Hg (Z = 80); and (*d*) Ac (Z = 89), Ku(Z = 104), Ha (Z = 105) have already been given in chapter 3. From these configurations these points may be noted (*i*) In atoms of *d*-block elements two outermost shells [*i.e. nth* and $(n-1)th$ shells] are partially filled while the remaining inner-shells [*i.e. 1st, 2nd*.....$(n-2)th$ shells] are completely filled. (*ii*) With the exception of Cr, Cu, Nb, Mo, Ru, Rh, Pd, Ag, Pt and Au, in the atoms of these elements the *ns*-orbital is completely filled (ns^2 configuration) and the differentiating electron enters $(n-1)$d orbital Thus the valence- shell configuration of most of these elements varies from $(n-1)d^1$. ns^2 (Group IIIB) to $(n-1)d^{10}.ns^2$ (Group IIB) configuration. The elements of the groups IIIB, IVB, VB, VIB, VIIB, VIII, IB and IIB belong this block as is evident from their configurations. (*iii*) It may be noted from the valence-shell configurations of the atoms of these elements that in the elements like Cr, Cu, Nb, Mo, Ru, Rh, Pd, Ag, Pt and Au one or both the electrons from *ns* orbital get shifted to $(n-1)d$ orbital and hence such elements have one or no electron in *ns* orbital (instead of two electrons in *ns* orbital). This type of shifting makes the $(n-1)$ *d* orbitals half-filled or completely filled and such $(n-1)$ *d* orbitals are more stable than other $(n-1)$ *d* orbitals. Thus the shifting of one or both the electrons from *ns* orbital to $(n-1)d$ orbital gives more stable configuration to the atom.

Classification of d-Block Elements.

Based on whether the differentiating electron goes to *3d, 4d, 5d* or *6d* orbitals, *d*-block elements have been classified into *four series viz. 3d, 4d, 5d* and *6d* series as discussed in chapter 3.

General Characteristics of d-Block Elements

Some important characteristics of 3*d*-series elements are described as follows :

1. Metallic Character.

All the transition elements are metals, since the number of electrons in the outermost shell is very small, being equal to 2. They are hard, malleable and ductile. They exhibit all the three types of structures face centred cubic (*fcc*), hexagonal close packed (*hcp*), and body centered cubic (*bcc*). Metals of VIII and IB groups are softer and more ductile than other metals. It appears that covalent and metallic bonding both exist in the atoms of transition metals. *The presence of unfilled d-orbitals favours covalent bonding.* These metals are good conductor of heat and electricity.

2. Atomic Volumes and Densities.

The atomic volumes and densities of the elements of 3*d*-series are given below :

Elements :	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic volume : (cm^3)	15.0	1.66	8.3	7.2	7.3	7.1	6.7	6.6	7.1	9.2
Density (g/cm^3) :	3.0	4.5	6.1	7.2	7.4	7.8	8.9	8.9	8.9	7.1

In *d*-block elements $(n-1)d$ sub-shell is filled and the increased nuclear charge pulls the electrons in. This leads to the comparatively low atomic volumes of these elements compared to those of the neighbouring *s*- and *p*-block elements. The densities of *d*-block elements are very high in comparison to those of group IA and IIA elements. This is understandable because of their decreasing volumes.

3. Melting and Boiling Points.

The melting and boiling points of the elements of 1*st* transition series are given below :

Elements :	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Boiling point (°C) :	2730	3260	3450	2665	2150	3000	2900	2730	2595	906
Melting point (°C) :	1539	1668	1900	1876	1245	1536	1495	1453	1083	419.5

It is evident from the values that the *d*-block elements have high melting and boiling points. It shows that they are held by strong forces. It can be seen from the table that the melting and boiling points have highest values in the middle of the series. In this region the elements have maximum number of unpaired *d*-electrons available for bonding. The elements also exhibit the highest oxidation states in this region. The trend in melting and boiling points shown by 3*d*-series elements is also followed by 4*d* and 5*d*-series elements. However Zn, Cd and Hg have relatively low values (melting and boiling points for these metals are : Zn = 419.5°C, 906°C; Cd = 320.9°C, 765°C and Hg = –38.4°C, 357°C respectively). The reason of these low values is that these metals have completely filled *d*-orbitals with no unpaired electron (Zn = $3d^{10}.4s^2$ with $n = 0$; Cd = $4d^{10}.4s^2$ with $n = 0$ and Hg = $5d^{10}.6s^2$ with $n = 0$) that may be available for *covalent bonding* amongst the atoms of these metals and is responsible for high melting and boiling points.

Generally the melting and boiling points of *d*-block elements increase on descending a group. Melting and boiling points of Ag are lower than those of Cu and Au. This can be explained on the basis that both Cu and Au have greater tendency to acquire higher oxidation state than +1, suggesting that in these metals the involvement of *d*-orbitals for metallic bonding is to a greater extent than in Ag.

4. Atomic (Covalent) Radii.

The atomic (covalent) radii of *d*-block elements are given below :

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
1.44 A°	1.32	1.22	1.18	1.17	1.17	1.16	1.15	1.17	1.25
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
1.62 A°	1.45	1.34	1.30	1.27	1.25	1.25	1.28	1.34	1.48
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
1.68 A°	1.44	1.34	1.30	1.28	1.26	1.27	1.30	1.34	1.49

These points may be noted : (*i*) As is evident, these values generally decrease on moving from left to right in the series (*i.e.* period). This is due to the fact that as the nuclear charge increases with increasing atomic number across any series, the attraction of the electrons towards the nucleus increases and this increase in attraction leads to a decrease in the radii values across each period. There are, however, a few exceptions. The atomic radii of the elements form Cr to Cu are very close to one another. This is explained as follows. As we move across the period, there is an increase in nuclear charge which tends to pull the 4*s*-electron inward near the nucleus, *i.e. it tends to reduce the size.* At the same time the addition of extra electrons to the 3*d*-orbitals also provides a screening effect which shields the 4*s*-electrons from the inward pull of the positive nucleus on these electrons. This screening effect increases as the number of extra electrons being added to 3*d*-orbitals increases. This effect *opposes the increase in size.* Thus there are operating two effects namely *screening effect* and the *nuclear charge effect* which *oppose each other*, resulting in that the effect of increase in the screening effect *almost* compensates the corresponding effect in increase in nuclear charge and hence very slight variations in the atomic radii from Cr to Cu are observed. (*ii*) In a particular series the atomic radius attains a minimum value for the elements of VIII group and increases again towards the end of the series. This is explained in terms of the increased force of repulsion among the added electrons which exceeds the attractive force due to the increased nuclear charge and results in the expansion of the electron cloud. (*iii*) On descending a group *n* increases. The atomic size is, therefore, expected to increase from top to bottom. But this increase is not the same for all the members. The difference in radius of the second and third series elements is very small (~ 0.02 A°) as compared to the first and second series members. This is due to lanthanide contraction. Due to the inclusion of 14 lanthanides between La (Z = 57, Group IIIB) and Hf (Z = 72, Group IV B), Hf is not as large as it would have been, if it had followed directly after La. The nuclear charge in the second series members are 18 units greater than the first series members, but this difference between the 2*nd* and 3*rd* series elements is 32. Thus, the increase in *n* [from 2*nd* series (*n* = 5) to 3*rd* series (*n* = 6)], though tends to increase the size, the excessive increase in nuclear charge annuls this effect. Consequently *the elements of 2nd and 3rd series are very similar in size.*

5. Ionic Radii.

The ionic radii follow the same trend as the atomic radii. It may be seen that the radii of the ions having the same charge (valency) decrease with the increase in atomic number.

Sc^{2+}	Ti^{2+}	V^{2+}	Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
0.95 A°	0.90	0.88	0.74	0.80	0.76	0.74	0.72	0.69	0.74
Sc^{3+}	Ti^{3+}	V^{3+}	Cr^{3+}	Mn^{3+}	Fe^{3+}	Co^{3+}	Ni^{3+}	—	—
0.81 A°	0.76	0.74	0.69	0.66	0.64	0.63	0.62	—	—

Decreasing →

6. Ionisation Potentials.

The ionisation potential values of most of the *d*-block elements lie in between those of *s*- and *p*-block elements. This indicates that the *d*-block elements are *less electropositive than s*-block elements *and more so than p-block elements.* Thus *d*-block elements do not form ionic compounds so readily as the alkali and alkaline earth metals do. Unlike *s*-block elements, *d*-block elements form covalent compounds as well. *1st*, *2nd* and *3rd* ionisation potentials (in KJ/ mole) of the elements of *3d* series are given below :

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
1st	631	658	650	652.8	717.4	759.4	758	736.7	745.5	906.4
2nd	1235	1310	1414	1635	1509.1	1561	1646	1753	1957.9	1733.3
3rd	2389	2852	2828	2987	2248.4	2957.4	3232	3393	3554	3832.7

From these values the following points may be noted : (*i*) The ionisation potentials of *3d* series elements increase as we move across the series from left to right, although the increase is not quite regular, *e.g.*, the values for Sc, Ti, V and Cr differ very slightly. Similarly the values for Fe, Co, Ni and Cu are fairly close to one another. The value for Zn is appreciably higher due to the additional stability associated with completely-filled *3d*-level in Zn (Zn $\longrightarrow 3d^{10}\ 4s^2$). Slight variations that occur in ionisation potentials across the series are mainly due to the slight changes in atomic radii which are on account of the fact that the screening effect caused by the addition of extra electrons to *3d*-level almost compensates the effect in increase in nuclear charge, as we move from left to right in the series. (*ii*) As can be seen, second ionization energies for Cr and Cu are sufficiently higher than those of the neighouring elements on the left as well as on the right. This is because the outer electronic configuration of Cr is $3d^5$ (half-filled) and that of Cu is $3d^{10}$ (completely-filled). Thus, the second ionization of chromium means the removal of one electron from the *highly stable exactly half-filled* sub-shell. Similarly, the second ionization of copper involves the removal of one electron from the *highly stable completely-filled 3d* sub-shell. This explains why the second ionization energies of Cr and Cu are higher than those of the neighbouring elements.

7. Different Oxidation States : Variable Valency.

The term oxidation state is preferred to valency. Most of the transition metals show several oxidation states or variable valency in their compounds. Oxidation states shown by the elements of *3d*-series are : Sc (Z = 21) $\rightarrow$ (+2), +3; Ti (Z = 22) = +2, +3, +4; V (Z = 23) $\rightarrow$ +2, +3, +4, +5; Cr (Z = 24) $\rightarrow$ +2, +3, (+4), +6; Mn (Z = 25) $\rightarrow$ +2, +3, +4, (+6), +7; Fe (Z = 26) $\rightarrow$ +2, +3, (+4), (+6); Co (Z = 27) $\rightarrow$ +2, +3, (+4); Ni (Z = 28) $\rightarrow$ +2, (+3); Cu(Z = 29) $\rightarrow$ +1, +2; Zn (Z = 30) $\rightarrow$ +2. Oxidation states shown in brackets are less common oxidation states, *i.e.* these oxidation states are exhibited in a few compounds.

The cause of showing different oxidation states is that these elements have several $(n-1)d$ and *ns* electrons and that the energies of $(n-1)d$ and *ns* orbitals are fairly close to each other. Hence $(n-1)d$ electrons are as easily lost as *ns* electrons. The following points may be noted : (*i*) Among the elements of *3d* series, Mn

shows the maximum number of oxidation states because it is at Mn that the number of unpaired electrons in $3d$ orbitals is maximum, On proceeding towards right or left from Mn, the number of unpaired electrons in $3d$ orbitals decreases and hence the number of oxidation states shown by the elements lying at the right or left of Mn decreases. (*ii*) With the exception of Cr ($3d^5.4s^1$), the minimum oxidation state shown by the elements of $3d$-series is equal to the number of electrons in $4s$ orbital. (*iii*) Excepting the elements of group IB, other elements show maximum oxidation state which is never more than their group number. (*iv*) In going down a group, the higher oxidation states become more stable. For example +2, and +3 oxidation states shown by Fe are stable oxidation states while +4 and +6 are unstable ones. Similarly +2, +3, +4, and +6 are stable while +5, +7 and +8 are unstable oxidation states shown by Ru. (*v*) The relative stability of various oxidation states of a given element can be explained on the basis of the stability of d^0, d^5 and d^{10} configurations. For example : (*a*) Ti^{4+} ($3d^{10}.4s^0$) is more stable than Ti^{3+} ($3d^1.4s^0$), because of the presence of $3d^0$ orbital in Ti^{4+} ion. (*b*) Mn^{2+} ($3d^5.4s^0$) is more stable than Mn^{3+} ($3d^4.4s^0$), since Mn^{2+} ion has $3d^5$ orbital. (*c*) Ag^+ ($4d^{10}.5s^0$) is more stable than Ag^{2+} ($4d^9.5s^0$) because of the presence of $4d^{10}$ orbital in Ag^+ ion. (*vi*) Transition elements can form ionic bonds in their lower oxidation states and the ionic character of the bond decreases (or covalent character of the bond increases) with the increase of oxidation state. With the decrease of ionic character, the acidic character of oxides or chlorides increases. For example :

(*a*) With the decrease of the ionic character of M–O bond in the oxides, the acidic character of the oxides increases as shown below :

← *Oxidation states* →			
+2	+3	+4	+6
TiO	Ti_2O_3	TiO_2	—
VO	V_2O_3	—	—
CrO	Cr_2O_3	—	CrO_3
MnO	MnO_3	MnO_2	MnO_3 (unstable)
Basic	*Amphoteric*		*Acidic*

— Oxidation state increasing →

— Ionic character of M—O bond decreasing →

— Acidic character of oxides increasing →

(*b*) With the decrease of the ionic character of M—Cl bond in the chlorides, the acidic character of the chlorides increases as shown below :

← *Oxidation states* →			
+2	+3	+4	+6
$TiCl_2$	$TiCl_3$	$TiCl_4$	—
VCl_2	VCl_3	VCl_4	$VOCl_3$

— Oxidation state increasing →

— Ionic character of M—Cl bond decreasing →

— Acidic character of chlorides increasing →

8. Standard Reduction Potentials and Reducing Properties.

Standard reduction potentials (in volts) of some of the *d*-block elements are given below. These values are given in the decreasing order.

	E° (*Volts*)		E° (*Volts*)
$Hg_2^{2+} + 2e^- \longrightarrow 2Hg$;	+ 0.79	$Cr^{3+} + 3e^- \longrightarrow Cr$;	– 0.71
$Cu^{2+} + 2e^- \longrightarrow Cu$;	+ 0.34	$Zn^{2+} + 2e^- \longrightarrow Zn$;	– 0.76
$Ni^{2+} + 2e^- \longrightarrow Ni$;	– 0.24	$Mn^{2+} + 2e^- \longrightarrow Mn$;	– 1.05
$Co^{2+} + 2e^- \longrightarrow Co$;	– 0.28	$V^{2+} + 2e^- \longrightarrow V$;	– 1.20
$Cd^{2+} + 2e^- \longrightarrow Cd$;	– 0.40	$Ti^{2+} + 2e^- \longrightarrow Ti$;	– 1.60
$Fe^{2+} + 2e^- \longrightarrow Fe$;	– 0.44	$Sc^{3+} + 3e^- \longrightarrow Sc$;	– 2.08
		$La^{3+} + 3e^- \longrightarrow La$;	– 2.37

These values make the following points evident; (*i*) Excepting for Hg and Cu, these values for other elements are negative, *i.e.* less than that of hydrogen whose value is taken as zero. Their values being less than that of hydrogen, make these metals able to liberate hydrogen from dilute acids.

$$M + 2H^+ \text{ (from acid)} \longrightarrow M^{2+} + H_2\,(g) \uparrow$$

In actual practice, the rate with which most of these metals react with acid and liberate H_2 gas is very slow. Some of the metals get protected from further attack of the acids due to the formation of a thin protective layer of their oxide which prevents the acid to come in further contact with the metal, *e.g.*, although the electrode potential of Cr is much less than that of hydrogen ($E°_{Cr^{3+}/Cr} = -0.71$ volt), it gets coated with its non-reactive oxide, Cr_2O_3 which makes it so unreactive that can be used as a protective non-oxidising metal. (*ii*) In spite of the fact that all the metals of first transition series, excepting Cu, have high negative values of standard electrode potentials, these are not as good reducing agents as the metal of groups IA, IIA and IIIA. The poor reducing capacity of the transition metals is due to high heats of vaporisation, high ionisation potentials and low heats of hydration of their ions.

9. Formation of Coloured Compounds.

Normally the compounds of *s*- and *p*-block elements are colourless while those of transition metals in the solid or in solution state are usually coloured. The colours of hydrated cations of transition metals of the first transition series are : Sc^{3+}, Ti^{4+} ($3d°$, $n = 0$) → colourless; Ti^{3+} ($3d^1$, $n = 1$) → purple; V^{3+} ($3d^2$, $n = 2$) → green; V^{2+} ($3d^3$, $n = 3$) → violet; Cr^{3+} ($3d^3$, $n = 3$) → green; Cr^{2+} ($3d^4$, $n = 4$) → blue ; Mn^{3+} ($3d^4$, $n = 4$) → violet; Mn^{2+} ($3d^5$, $n = 5$) → faintly pink or faintly green; Fe^{3+} ($3d^5$, $n = 5$) → yellow; Fe^{2+} ($3d^6$, $n = 4$) → pale green or faintly green; Co ($3d^6$, $n = 4$) → blue; Co^{2+} ($3d^7$, $n = 3$) → pink; Ni^{2+} ($3d^8$, $n = 2$) → green; Cu^{2+} ($3d^9$, $n = 1$) → blue; Cu^+ ($3d^{10}$, $n = 0$) → colourless; Zn^{2+} ($3d^{10}$, $n = 0$) → colourless. Here n denotes the number of unpaired electrons in the respective cations. For simplicity water molecules associated with each cation have not been shown.

It may be seen from the colours given above that the cations (*e.g.* Sc^{3+}, Ti^{4+}, Cu^{+}, Zn^{2+}) having vacant or completely-filled *d*-orbitals (d^0 and d^{10} orbitals) are colourless while those (*e.g.* Ti^{3+}, V^{3+}, Cr^{3+} etc.) having partially-filled *d*-orbitals (d^1, d^2, d^3 etc. orbitals) are coloured. In other words, the cations having all the electrons paired in *d*-orbitals (*i.e.* completely-filled *d*-orbitals) or no electrons in *d*-orbitals (*i.e.* empty *d*-orbitals) are colourless while those having some or all the electrons unpaired in *d*-orbitals are coloured. If n is the number of unpaired electrons in *d*-orbitals, then the ions having $n = 0$ are colourless while those having $n = 1, 2$ etc. are coloured.

10. Magnetic Properties.

There are, in general, three types of magnetism : (*i*) *Paramagnetism* (*ii*) *Diamagnetism* (*iii*) *Ferromagnetism.*

(*i*) **Paramagnetism.** This property is shown by the substances which, when, placed between the magnetic poles allow the magnetic lines of force to pass through them rather than through vacuum, *i.e.* a paramagnetic bar will tend to set itself with its length parallel to the field, when it is placed between the magnetic poles. In other words a *paramagnetic substance is attracted into a magnetic field.* Paramagnetism is common among the transition metal complexes, *i.e.* most of the transition metals are paramagnetic.

Origin of paramagnetism. The paramagnetism is caused by the presence of unpaired electrons in the substance. How do the unpaired electrons render the substance paramagnetic ? We know that an electron has two types of motion : *spin motion* (*i.e.*, spinning of the electron on its axis) and *orbital motion* (*i.e.*, moving of the electron in an orbital round the nucleus). It is also known from elementary Physics that the movement of an electric charge produces a magnetic field. Consequently an electron spinning on its axis which may be regarded as a small sphere of negative charge also creates a magnetic moment which is called *spin magnetic moment* or simply *spin moment* of the electron. The orbital motion produces a magnetic moment just like an electric current travelling in a loop of wire. The magnetic moment produced in this way is called *orbital moment* of the electron. The observed magnetic moments are combination of these two moments. Both these moments arise due to the presence of unpaired electrons.

In the substances containing *one or more unpaired electrons*, the magnetic moment which is a combination of spin moment and orbital moment is sufficiently of high magnitude to overcome the small magnetic moments induced by an approaching magnetic field. Such a substance, therefore, instead of experiencing repulsion, experiences *attraction* in a magnetic field, *i.e.*, it shows *paramagnetic behaviour. The compounds having one or more unpaired electrons are paramagnetic.*

If two electrons with opposite spins are paired in the same orbital, the magnetic field caused by one electron is cancelled by that caused by the other electron, because each of the two electrons will have equal but opposite magnetic momenta, thus giving zero resultant magnetic moment. Consequently the substances having *paired electrons* will not show paramagnetism but, in fact, they will show

diamagnetism. The magnetic moment is expressed in *Bohr magneton* (BM) which is given by :

$$\boxed{1 \text{ BM} = \frac{eh}{4\pi mc}}$$

where h = Planck'a constant, e = electronic charge, c = velocity of light and m = mass of the electron.

(*ii*) **Diamagnetism.** This property is exhibited by the substances which allow the magnetic lines of force to pass through the vacuum rather than through themselves. Thus a diamagnetic substance is *repelled* by a magnetic field and hence tends to set itself at right angles to the field. *The compounds having all the electrons paired are diamagnetic, i.e. diamagnetic compounds have no unpaired electron, and hence their magnetic moment is zero.* The property of diamagnetism is produced by the orbital motion of the electrons of the atoms, ions or molecules of the sample. It is characteristic of all substances that contain paired electrons. Diamagnetism is exhibited by all substances. Even paramagnetic substances have some diamagnetic character and the net magnetic moments for paramagnetic substances are obtained after making due corrections for the diamagnetism. Diamagnetic behaviour is due to small magnetic moments which are induced by the applied magnetic field but does not exist in the absence of the field.

(*iii*) **Ferromagnetism.** In case of some transition metals (*e.g.* Fe, Co and Ni) the unpaired electron spins are more pronounced and hence such metals are much more paramagnetic than the other transition metals. Such metals are called ferromagnetic metals and the magnetic behaviour shown by these metals is known as ferromagnetism. Such metals can be magnetised.

11. Tendency to Form Complexes.

The cations of *d*-block elements have a strong tendency to form complexes with certain molecules (*e.g.* CO, NO, NH_3 etc.) or ions (*e.g.* F^-, Cl^-, CN^- etc.). The molecules or ions with which the cations attach themselves to form the complexes are called *ligands.* The molecules or ions acting as ligands have one or more lone pairs of electrons on their central atom. In the process of formation of complexes the central atom of the ligands donates readily lone pairs of electrons to the cation to form M $\leftarrow$ L coordinate bond (M = metal cation and L = ligand) The tendency of the cations of *d*-block elements to form complexes with ligands is due to two reasons: (*i*) The cations are relatively very small in size and hence have high positive charge density which makes it easy for the cations to accept the lone pairs of electrons from the ligands. (*ii*) The cations have vacant $(n-1)d$ orbitals which are of appropriate energy to accept lone pair of electrons from the ligands for bonding with them.

12. Formation of Non-stoichiometric Compounds.

Many of the compounds given by the transition metals are non-stoichiotnetric compounds, *i.e.* these compounds have indefinite or variable composition. Transition metals form non-stoichiotnetric compounds due to their variable valency and due

to the defects existing in the solid structures. Some examples of non-stoichiometric compounds given by transition metals are given below: (*i*) The formula of Fe(II) oxide is FeO which shows that it has Fe and O atoms in 1 : 1 ratio. But the analysis of this oxide has revealed that the actual formula varies between $Fe_{0.94}O$ and $Fe_{0.84}O$ and hence the oxide is a non-stoichiometric compound. In order to show the non-stoichiometric nature of the compound, it is written with a bar over its formula, *i.e.* this oxide is written as $\overline{FeO}$, (*ii*) Vanadium selenide is another non-stoichiometric compound whose composition varies between $VSe_{0.98}$ and VSe_2. (*iii*) Small nonmetallic atoms (*e.g.*, H, B, C, N etc.) are able to fit into the interstitial sites of transition metal lattices to form the compound which are called interstitial compounds. These have variable composition and cannot, therefore, be expressed by simple formulae, *i.e.*, these are also *non-stoichiometric compounds.* Interstitial compounds of transition metals, *viz.*, hydrides, borides, carbides and nitrides are usually prepared by heating the metal with hydrogen, boron, carbon (or hydrocarbon), and nitrogen (or ammonia), respectively. Interstitial compounds have the properties of alloys. They are extremely hard, possess good electrical conductivity and are with high melting point (titanium carbide melts at 3410°C, titanium nitride melts at 3200°C). Except towards strong oxidizing agents, the compounds are inert chemically.

13. Catalytic Properties.

Most of the transition metals and their compounds are used as catalysts. Transition metals show a variety of oxidation states and thereby can form intermediate products with various reactants. They are also capable of forming interstitial compounds which can absorb and activate the reacting species. Thus, they act as catalysts. Some examples of catalysts are : Ni acts as a catalyst in hydrogenation reactions; MnO_2 catalyses the decomposition of H_2O_2; $TiCl_4$ is employed as a catalyst in the manufacture of polythene ; V_2O_5 is used for catalytic oxidation of SO_2, to SO_3, etc.

14. Formation of Alloys.

Transition metals form alloys with each other. This is because they have almost similar sizes and the atoms of one metal can easily take up positions in the crystal lattice of the other. Thus, we have alloys of Cr—Ni, Cr—Ni—Fe, Cr—V—Fe, Mn—Fe, etc. Alloys are usually harder and have higher melting point than the parent metals. They are more resistant to corrosion than their constituents.

Comparison of Transition Elements with Non-transition Elements.

A comparison of important properties of transition elements (*d*-block elements) with those of non-transition elements (*s*- and *p*-block elements) is given Table 44.1. There are, however, two generalizations that will apply equally to both the transition and non-transition elements : (*i*) High oxidation states are usually stabilized in alkaline media. (*ii*) The capacity of the halogens to bring out high oxidation states varies in the order : F > Cl > Br > I.

Table 44.1. Comparison of the important properties of transition elements (*d*-block elements) with those of non-transition elements (*s*- and *p*-block elements).

Transition elements (*d*-block elements)	Non-transition elements (*s*- and *p*-block elements)
(*i*) All the transition elements are metals.	(*i*) Non-transition elements may be metals, metalloids or non-metals. The metallic character in a group increases with the increase in atomic weight.
(*ii*) The atomic radii show irregular decrease in a series of transition elements. The decrease is not pronounced.	(*ii*) The atomic radii show regular and pronounced decrease along a period of non-transition elements.
(*iii*) The ionization energies show irregular increase in a series of transition elements. The increase is not pronounced.	(*iii*) The ionization energies show regular and pronounced increase on moving across a period of non-transition elements.
(*iv*) They exhibit a variety of oxidation states in their compounds. The oxidation states differ from each other by one unit. For example : Cu^{+}, Cu^{2+} Fe^{2+}, Fe^{3+} Ti^{3+}, Ti^{4+} V^{4+}, V^{5+}	(*iv*) They usually exhibit the group valency or another valency which is less by two units than the group valency (inert pair effect). For example : Ti^{+}, Ti^{3+} Sn^{2+}, Sn^{4+} Pb^{2+}, Pb^{4+}
(*v*) Most of the transition metal ions are coloured in aqueous solution. For example : Cu^{2+}, V^{4+} — Blue Ni^{2+}, Cr^{3+} — Green Co^{2+} — Pink Fe^{3+} — Yellow	(*v*) Aqueous solutions of the ions of non-transition elements are colourless. For example : Na^{+} — Colourless Ba^{2+} — Colourless Al^{3+} — Colourless Cl^{-} — Colourless
(*vi*) They form a large number of complexes. For example : $[Ag(N\ H_3)_2]^{+}$, $[Cu(NH_3)_4]^{2+}$ $K_4[Fe(CN)_6]$	(*vi*) They do not form many complexes.
(*vii*) Transition elements or their compounds show catalytic activity. For example nickel catalyses hydrogenation reactions and V_2O_5 is used as a catalyst for the oxidation of SO_2 to SO_3.	(*vii*) They lack catalytic activity.
(*viii*) They form interstitial compounds with the non-metals like H, C and N. These compounds may have non-stoichiometric ratios, For example : $TiH_{1.7}$, $VH_{0.56}$, etc.	(*viii*) They do not form non-stoichiometric compounds.
(*ix*) Their compounds are mostly *paramagnetic.*	(*ix*) Their compounds are mostly *diamagnetic.*

4f Block Elements : Lanthanides

What are f-block Elements ?

The elements in which the extra electron (also called differentiating electron) enters $(n-2)f$ orbitals are called *f*-block elements. Since the extra electron goes to $(n-2)$ *f*-orbitals, these elements have been given the name *f*-block elements. Since $(n-2)$ *f*-orbitals lie comparatively deep within the kernel (being inner to the penultimate shell), these elements are also called ***inner-transition elements.***

Classification of f-Block Elements.

We have already said that in case of *f*-block elements, the extra electron enters $(n-2)$ *f*-orbitals. These $(n-2)$ *f*-orbitals may be either 4*f*-orbitals or 5*f*-orbitals, Depending on whether the extra electron enters 4*f* or 5*f*-orbitals, *f*-block elements have been classified into two blocks namely (*i*) 4*f*-block elements. These elements are also called by other names like *1st inner-transition series elements, lanthanides* and *lanthanones*, (*ii*) *5f-block elements.* These elements are also called by other names like *2nd inner-transition series elements, actinides* and *actinones.*

What are 4f-Block Elements ?

In the atoms of the 4*f*-block elements the extra electron enters 4*f*-orbital, *i.e.* in the atoms of the elements of this block, 4*f*-orbitals are being progressively filled. A group of 14 elements from cerium, Ce(Z = 58) to lutetium, Lu (Z = 71) constitute this series. The elements of this series are also called *lanthanides* or *lanthanones*, since they follow lanthanum, La (Z = 57) in the periodic table and show close similarities with La. Although, strictly speaking the fourteen elements from Ce(Z = 58) to Lu(Z = 71) are called lanthanides, yet, due to the similarities in properties among all the fifteen elements from La(Z = 57) to Lu (Z = 71), all these fifteen elements are considered to be the members of lanthanide series, Thus La is also studied along with lanthanides. The lanthanide elements constitute the first *inner-transition series.* Lanthanide elements lie in *7th* period (incomplete period with $n = 7$) and group III B of the periodic table.

Position of Lanthanides in the Periodic Table.

All the fifteen lanthanides have atomic weights between those of barium (atomic number, Z = 56) and hafnium (Z = 72) and, therefore, must be placed between these two elements as was also proved by Moseley.

Barium has exactly the same outer electronic configuration as calcium and strontium and resembles them very closely. In a similar way hafnium (Z = 72) is similar to zirconium (Z = 40). Therefore Ba must be placed below Sr (Group IIA) and Hf below Zr (Group IV B), thus leaving only one place between them, which lies exactly below Y (Z = 39, Group III B).

Since all the fifteen lanthanides resemble one another in many respects, these must be placed in the same group. These elements also resemble Y, because of the following additional similarities : (*a*) Owing to lanthanide contraction (to be discussed subsequently), the ionic radius of Y^{3+} ion is almost similar to that of Er^{3+}(r_{Y3+} = 0.93Å, r_{Er3+} = 0.96Å). (*b*) Y generally occurs in nature associated

with the ores of heavier lanthanides and resembles Tb(III) and Dy(III) in its compounds. It, therefore, became necessary to accommodate all the fifteen lanthanides together at one place. This has been done by placing the first element *viz.* La_{57} below Y_{39} and remaining fourteen elements (*viz.* Ce_{58}, to Lu_{71}) have been placed separately in the lower part of the periodic table as shown below in the margin.

General Characteristics of Lanthanides

1. Occurrence.

Lanthanides are not so scare in the earth's crust as the name rare earth implies. Rather, their sources are unlimited. Each lanthanide mineral contains all the lanthanides (some in traces) excepting promethium, Pm (Z = 61) which is an unstable radioactive element Lanthanide minerals can be divided into two sub-groups : (*i*) *Cerium sub-group minerals.* These minerals contain largely the lighter lanthanides with atomic numbers 57 to 62 (La to Sm). Lanthanides with atomic number 57 to 62 are also called *cerium earths. Monazite sand* and *bastanesite* are the minerals which contain cerium earths. Monazite mineral is a mixture of phosphates mainly the phosphates of rare earths (RPO_4 where R is any lanthanide). It contains 49–74% of cerium earths as oxides and 1–4% of yttrium earths (yttrium earths are lanthanides with atomic number 63 to 71 and yttrium) as oxides. It also contains 5–9% of ThO_2, 1–2% of SiO_2 and traces of uranium, Monazite sand occurs mainly in the sand beaches of Travancore (India), Brazil, Union of South Africa, U.S.A. Bastanesite mineral contains mixed fluorides and carbonates ($RFCO_3$) and contains 65–70% of cerium earths, < 1% of yttrium earths and traces of thorium. This mineral is found in California, New Mexico and Sweden. (*ii*) *Yttrium sub-group minerals.* These minerals contain largely yttrium and heavier lanthanides with atomic number 63 to 71, *i.e.* these minerals contain yttrium earths. *Euxenite* and *gadolinite* are minerals which contain yttrium earths. Euxenite mineral is represented as R(Nb, Ra) $TiO_6.xH_2O$. It may contain 13–35% of yttrium earths as oxides, 2–3% cerium earths as oxides, 20–23% of ThO_2 and 25–35% of $(Nb,Ta)O_5$. This mineral is found in Australia and Idaho. Gadolinite is represented as $R_2\ M_3^{II}\ S_2O_{19}$, where R = lanthanide atom and M = divalent atom like Fe or Be. This mineral contains 35–48% of yttrium earths as oxides, 2–17% of cerium earths, 11.6% of BeO and traces of Te. This mineral is found in Sweden, Norway and U.S.A.

II A	III B	IV B
Be_4		
Mg_{12}		
Ca_{20}	Sc_{21}	Ti_{22}
Sr_{36}	Y_{39}	Zr_{40}
Ba_{56}	La_{57}	Hf_{72}
	⋮	
	⋯⋯→	Ce_{58}.....Lu_{71}
		Lanthanides

Position of lanthanides in the periodic table.

2. Electronic Configuration.

Complete and valence-shell configurations of the atoms of lanthanides in their ground state are : La (Z = 57) → 2, 8, 18, 18, 9, 2 ($4f^0.5d^1.6s^2$), Ce (Z = 58) → 2, 8, 18, 19, 9, 2 ($4f^1.5d^1.6s^2$) *or* 2, 8, 18, 20, 8, 2 ($4f^2.5d^0.6s^2$), Pr (Z = 59) → 2, 8, 18, 21, 8, 2 ($4f^3.5d^0.6s^2$), Nd (Z = 60) → 2, 8, 18, 22, 8, 2 ($4f^2.5d^0.6s^2$), Pm (Z = 61) → 2, 8, 18, 23, 8, 2 ($4f^5.5d^0.6s^2$), Sm (Z = 62) → 2, 8, 18, 24, 8, 2 ($4f^6.5d^0.6s^2$), Eu (Z = 63) → 2, 8, 18, 25, 8, 2 ($4f^7.5d^0.6s^2$), Gd (Z = 64) → 2, 8, 18, 25, 9, 2 ($4f^7.5d^1.6s^2$), Tb (Z = 65) → 2, 8, 18, 27, 8, 2 ($4f^9.5d^0.6s^2$), Dy (Z = 66) → 2, 8, 18, 28, 8, 2 ($4f^{10}.5d^0.6s^2$), Ho (Z = 67) → 2, 8, 18, 29, 8, 2 ($4f^{11}.5d^0.6s^2$), Er (Z = 68) → 2, 8, 18, 30, 8, 2 ($4f^{12}.5d^0.6s^2$), Tm (Z = 69) → 2, 8, 18, 31, 8, 2 ($4f^{13}.5d^0.6s^2$), Yb (Z = 70) → 2, 8, 18. 32, 8, 2 ($4f^{14}.5d^0.6s^2$), Lu (Z = 71) → 2, 8, 18, 32, 9, 2 ($4f^{14}.5d^1.6s^2$). These configurations show that the atoms of lanthanides have a total of *six* shells. Out of these six shells, first three shells namely *1st*, *2nd* and *3rd* are completely filled while the remaining three shells *viz.* *4th*, *5th* and *6th* are partially filled as shown below :

$$\mathbf{2,\ 8,\ 18,\ 4s^2p^6d^{10}\ f^{0...7},\ ^{9...14},\ 5s^2p^6d^{0,1},\ 6s^2}\ \textbf{(six shells)}$$

The configuration given above clearly shows that 4*f* and 5*d* orbitals in the atoms of lanthanides are partially filled while 6*s* orbital is completely filled ($6s^2$ configuration). Thus the number of electrons in *4th* shell [*i.e.* (*n*–2)*th* shell] is increasing from 18 ($4s^2 + 4p^6 + 4d^{10}$) to 32 ($4s^2 + 4p^6 + 4d^{10} + 4f^{14}$) by adding an electron, one by one, to 4*f* orbital. Consequently the atoms of lanthanides have partly filled 4*f* orbitals, since the differentiating electron enters these orbitals. Due to the fact that the extra electron goes to 4*f* orbital, the lanthanides are also called 4*f*-block *elements*. Complete electronic configurations as given above also indicate that the valence shell configuration of these elements can be represented as :

$$\mathbf{4f^{0...7},\ ^{9...14},\ 5d^{0,1},\ 6s^2}$$

3. Oxidation States.

Important oxidation states shown by lanthanides and their valence-shell configurations (given in brackets) are given as : La (Z = 57) → +3 ($4f^0.5d^0.6s^0$); Ce (Z = 58) → +3 ($4f^1.5d^0.6s^0$), + 2 ($4f^2.5d^0.6s^0$), + 4 ($4f^0.5d^0.6s^0$); Pr (Z = 59) → +3 ($4f^2.5d^0.6s^0$), + 4 ($4f^1.5d^0.6s^0$); Nd (Z = 60) → +3 ($4f^3.5d^0.6s^0$), +2 ($4f^4.5d^0.6s^0$), + 4 ($4f^2.5d^0.6s^0$); Pm (Z = 61) → +3 ($4f^4.5d^0.6s^0$); Sm (Z = 62) → +3 ($4f^5.5d^0.6s^0$), +2 ($4f^6.5d^0.6s^0$); Eu (Z = 63) → +3 ($4f^6.5d^0.6s^0$), +2 ($4f^7.5d^0.6s^0$), Gd (Z = 64) → +3 ($4f^7.5d^0.6s^0$); Tb (Z = 65) → +3 ($4f^8.5d^0.6s^0$), +4 ($4f^7.5d^0.6s^0$); Dy (Z = 66) → +3 ($4f^9.5d^0.6s^0$), +4 ($4f^8.5d^0.6s^0$); Ho (Z = 67) → +3 ($4f^{10}.5d^0.6s^0$); Er (Z = 68) → +3 ($4f^{11}.5d^0.6s^0$); Tm (Z = 69) → +3 ($4f^{12}.5d^0.6s^0$), +2 ($4f^{13}.5d^0.6s^0$); Yb (Z = 70) → +3 ($4f^{13}.5d^0.6s^0$), +2 ($4f^{14}.5d^0.6s^0$); Lu (Z = 71) → +3 ($4f^{14}.5d^0.6s^0$). It may be seen

that +3 oxidation state is common to all the lanthanides. In addition to +3 oxidation state, some lanthanides also exhibit +2 and +4 states. In case of some lanthanides, the formation of M^{2+}, M^{3+} and M^{4+} cations can be explained on the basis of stability associated with $4f^0$, $4f^7$ and $4f^{14}$ configurations. For example : (*a*) La (Z = 57), Gd (Z = 64) and Lu (Z = 71) give La^{3+}, Gd^{3+} and Lu^{3+} cations by attaining $4f^0$, $4f^7$ and $4f^{14}$ configurations. Consequently in case of these elements any oxidation state other than +3 is not possible. (*b*) Ce (Z = 58) and Tb (Z = 65) form Ce^{4+} and Tb^{4+} cations by attaining $4f^0$ and $4f^7$ configuration. (*c*) Eu (Z = 63) and Yb (Z = 70) form Eu^{2+} and Yb^{2+} cations by attaining $4f^7$ and $4f^{14}$ configurations. Although the formation of La^{3+}, Gd^{3+}, Lu^{3+}, Ce^{4+}, Tb^{4+}, Eu^{2+} and Yb^{2+} cation can be explained on the basis of the special stability associated with $4f^0$, $4f^7$ and $4f^{14}$ configurations, yet the formation of many cations like Ce^{3+}, Ce^{2+}, Pr^{3+}, Pr^{4+} etc. can not be explained on this basis. In explaining the formation of these cations thermodynamic and kinetic factors are to be taken into consideration.

4. Radii of Tripositive Lanthanide Cations : Lanthanide Contraction.

A look at the values of the radii of tripositive lanthanide cations (M^{3+}) reveals that these values decrease as we move from La^{3+} to Lu^{3+} in the lanthanide series. *This steady decrease in the values of the radii of M^{3+} cations in the tanthanide series is called lanthanide contraction.*

———————— *Decreasing* ————————→

La^{3+} (r = 1.06 A°) > Ce^{3+} (1.03 A°) > Pr^{3+} (1.01 A°) > Nd^{3+} (0.99 A°) > Pm^{3+} (0.98 A°) > Sm^{3+} (0.96 A°) > Eu^{3+} (0.95 A°) > Gd^{3+} (0.94 A°) > Tb^{3+} (0.92 A°) > Dy^{3+} (0.91 A°) > Ho^{3+} (0.89 A°) > Er^{3+} (0.88 A°) > Tm^{3+} (0.87 A°) > Yb^{3+} (0.86 A°) > Lu^{3+} (0.85 A°).

Cause of lanthanide contraction.

We know that as we proceed from one element to the next one in the lanthanide series, the nuclear charge (*i.e.* atomic number) increases by +1 at each next element and the addition of extra electron takes place in 4*f* orbital. Again it is also known that the shielding of one electron in 4*f* orbital by the other electron residing in the same orbital is very poor. Due to the negligible amount of mutual shielding effect between the electrons residing in 4*f* orbital, the increase in nuclear charge by + 1 at each next element in the lanthanide series brings the valence shell nearer to the nucleus and hence the size of M^{3+} cations goes on decreasing as we move from one element to the next one in the series.

Consequences of lanthanide contraction.

Lanthanide contraction plays an important role in determining the chemistry of lanthanides and heavier transition elements. Some important consequences of lanthanide contraction are discussed below :

(*i*) Basic character of lanthanide hydroxides, $M(OH)_3$. There is a *decrease in basic strength of the hydroxides of lanthanides with increase in atomic number.* Thus $La(OH)_3$ is the most basic while $Lu(OH)_3$ is the least basic. Due to lanthanide contraction the decrease in size of M^{3+} cations increases the

covalent character (*i.e.* decreases the ionic character) between the M^{3+} ion and OH^- ion (according to Fajan's rules), thereby reducing the basic character of the lanthanide hydroxides.

***(ii)* Atomic radii of post-lanthanide elements.** Normally in the same sub-group the atomic (covalent) radii increase as the atomic number increases. This fact is evident when are compare these values for the elements of first and second transition series as given in Table 44.2. On the basis of this rule the atomic radii of the elements of 3*rd* transition series should be greater than those of the elements of 2*nd* transition series, but, as the table shows, although the atomic radius of La is greater than that of Y (La = 1.69 A°, Y = 1.62 A°), the atomic radii of Hf, Ta, W, Re etc. (elements of 3*rd* transition series) are not greater than those of Zr, Nb, Mo, Tc etc. respectively (elements of 2*nd* transition series). The expected increase in the atomic radii on proceeding from the elements of 2*nd* transition series to those of 3*rd* transition series is cancelled by the presence of 14 lanthanides (Ce with Z = 58 to Lu with Z = 71) between La(Z = 57) and Hf (Z = 72). Consequently the atomic radii of the elements of 3*rd* transition series become almost equal to those of the elements of 2*nd* transition series. Due to the similarity in size of the elements of the two series, the elements of 2*nd* and 3*rd* series resemble each other more closely than do the elements of 1*st* and 2*nd* transition series.

Table 44.2. Atomic (covalent) radii (in A°) of the elements preceding and following lanthanides.

III B		IVB	VB	VIB	VIIB		VIII		IB	IIB
Sc_{21}		Ti_{22}	V	Cr	Mn	Fe	Co	Ni	Cu	Zn_{30}
1.44		1.32	1.22	1.18	1.17	1.17	1.16	1.15	1.17	1.25
Y_{39}		Zr_{40}	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd_{48}
1.62		1.45	1.34	1.30	1.27	1.25	1.25	12.8	1.34	1.48
La_{57}	Ce_{55}–Lu_{71}	Hf_{72}	Ta	W	Re	OsI	r	Pt	Au	Hg_{80}
1.69	1.65 1.56	1.44	1.34	1.30	1.28	12.6	1.27	1.30	1.34	1.49

14 Lanthanides

***(iii)* High density of post-lanthanide elements.** Because of lanthanide contraction, the atomic sizes of the post-lanthanide elements become very small. Consequently the packing of atoms in their metallic crystal becomes so much compact that their densities are very high. Thus, while the densities of the elements of second transition series are only slightly higher than those of the elements of first series, the densities of the elements of third transition series are almost double to those of the elements of second transition series.

***(iv)* Occurrence of Y with heavy lanthanides.** The crystal radii of Y^{3+} and Er^{3+} are equal (Y^{3+} = 0.88 A° and Er^{3+} = 0.88 A°). This similarity in ionic size of these two cations coupled with the equality in ionic charge (= +3 in both the ions)

accounts for the invariable occurrence of Y with heavier lanthanides. The marked similarities in the crystal structure, chemical properties and solubility between yttrium compounds and the corresponding compounds of the heavier lanthanides make it difficult to separate yttrium from the heavier lanthanides. It is because of these similarities that yttrium is regarded for all practical purposes as a member of lanthanide series.

5. Colours of M^{3+} Cations.

Some of the tripositive lanthanide cations (M^{3+} cations) are coloured. Their colours are : La^{3+} ($4f^0.5d^0.6s^0$, $n = 0$) → colourless; Ce^{3+} ($4f^1.5d^0.6s^0$, $n = 1$) → colourless; Pr^{3+}($4f^2.5d^0.6s^0$, $n = 2$) → yellow green; Nd^{3+}($4f^3.5d^0.6s^0$, $n = 3$) → bright pink; Pm^{3+}($4f^4.5d^0.6s^0$, $n = 4$) → pink yellow; Sm^{3+}($4f^4.5d^0.6s^0$, $n = 5$) → yellow; Eu^{3+}($4f^6.5d^0.6s^0$, $n = 6$) → very pale pink; Gd^{3+}($4f^7.5d^0.6s^0$, $n = 7$) → colourless; Tb^{3+}($4f^8.5d^0.6s^0$, $n = 6$) → very pale pink; Dy^{3+}($4f^9.5d^0.6s^0$, $n = 5$) → yellow; Ho^{3+}($4f^{10}.5d^0.6s^0$, $n = 4$) → pink yellow; Er^{3+}($4f^{11}.5d^0.6s^0$, $n = 3$) → pink; Tm^{3+}($4f^{12}.5d^0.6s^0$, $n = 2$) → pale green; Yb^{3+}($4f^{13}.5d^0.6s^0$, $n = 1$) → colourless Lu^{3+}($4f^{14}.5d^0.6s^0$, $n = 0$) → colourless. Here n is the number of unpaired electrons in $4f$ orbitals. Following points may be noted from these colours. (*i*) M^{3+} cations having *empty, half-filled or completely filled* $4f$*-orbttal* (*i.e.*, $4f^0$, $4f^7$ and $4f^{14}$ configuration) are colourless, *e.g.*, $La^{3+}(4f^0)$, $Gd^{3+}(4f^7)$ and $Lu^{3+}(4f^{14})$ ions are colourless. The fact that the cations namely $Ce^{3+}(4f^1)$ and $Yb^{3+}(4f^{13})$ are also colourless can not be explained on the basis of the above concept. (*ii*) Pairs of M^{3+} cations having the same number of unpaired electrons in $4f$ orbitals have the same colour. The colours of following five pairs of M^{3+} cations confirm this rule. (*a*) Pr^{3+} (yellow green)—Tm^{3+} (pale green), $n = 2$. (*b*) Nd^{3+} (bright pink)—Er^{3+}(pink), $n = 3$. (*c*) Pm^{3+} (pink yellow)—Ho^{3+} (pink yellow), $n = 4$. (*d*) Sm^{3+} (yellow)—Dy^{3+} (yellow), $n = 5$. (*e*) Eu^{3+} (very pale pink)—Tb^{3+} (very pale pink), $n = 6$. Here n indicates the number of unpaired electrons in $4f$ orbitals.

6. Magnetic Properties of M^{3+} Cations.

We know that ions having unpaired electrons are paramagnetic while those having all the electrons paired are diamagnetic. Thus, since $La^{3+}(4f^0.5d^0.\ 6s^0)$ and $Lu^{3+}(4f^{14}.5d^0.6s^0)$ ions have all the electrons paired, these ions are diamagnetic. On the other hand, the remaining tripositive lanthanide ions (M^{3+} ions) are paramagnetic, since they contain 1, 2,...6 unpaired electrons.

Cause of paramagnetism. In case of M^{3+} cations, since $4f$ orbitals are quite deeply seated, these are well shielded from the ligands surrounding the M^{3+} ions by the overlapping $5s$ and $5p$ orbitals and hence the electrons residing in $4f$ orbitals are not able to interact with the surrounding ligands. Thus the orbital motion of electrons in $4f$ orbitals is not quenched as in case of d-block elements, and hence the observed paramagnetism in $4f$-blook elements is due to both factors namely orbital motion of the electron and its spinning round its axis.

7. Formation of Complexes.

Although tripositive lanthanide cations have a high charge equal to +3 on them, yet their size is so large that their charge-to-radius ratio becomes so small that these ions have very poor tendency to form complexes. Common ligands with which M^{3+} ions form stable complexes are : (*i*) *chelating oxygen containing ligands* like EDTA, citric acid, oxalic acid, acetylacetone (*ii*) *nitrogen containing ligands* like ethylenediamine, NCS^- etc.

8. Properties Dependent on Standard Reduction Potential Values.

The values of standard reduction potential (E° values) for the reduction reaction :

$$M^{3+}(aq) + 3e^- \rightleftarrows M(s)$$

increase from La to Lu, *i.e.* E° values become less negative as we move from La to Lu as shown below (values are given in volts) :

$$\longleftarrow E^\circ \text{ values become less negative} \longrightarrow$$

La = –2.52, Ce = –2.48, Pr = –2.46, Nd = –2.43, Pm = –2.42, Sm = –2.41, Eu = –2.40, Gd = –2.39, Tb = –2.39, Dy = –2.35, Ho = –2.32, Er = –2.30, Tm = –2.28, Yb = –2.27, Lu = –2.25.

These E° values explain the following properties of lanthanides :

(*a*) Reducing property. Since lanthanides have high negative E° values, these elements have a strong tendency to lose their three electrons to undergo oxidation and hence are strong reducing agents. With the increase of E° values from La to Lu, *i.e.* as E° values become less negative from La to Lu, the reducing power of these elements decreases from La to Lu.

(*b*) Electropositive character. Due to negative E° values, the lanthanides readily lose their electrons and hence show strong electropositive (or metallic) character. With the increase of E° values from La to Lu, the electropositive character of these elements decreases from La to Lu.

(*c*) Liberation of H_2 from H_2O. Due to highly electropositive character of lanthanides, these elements slowly react with cold water and rapidly with hot water to liberate H_2 from it.

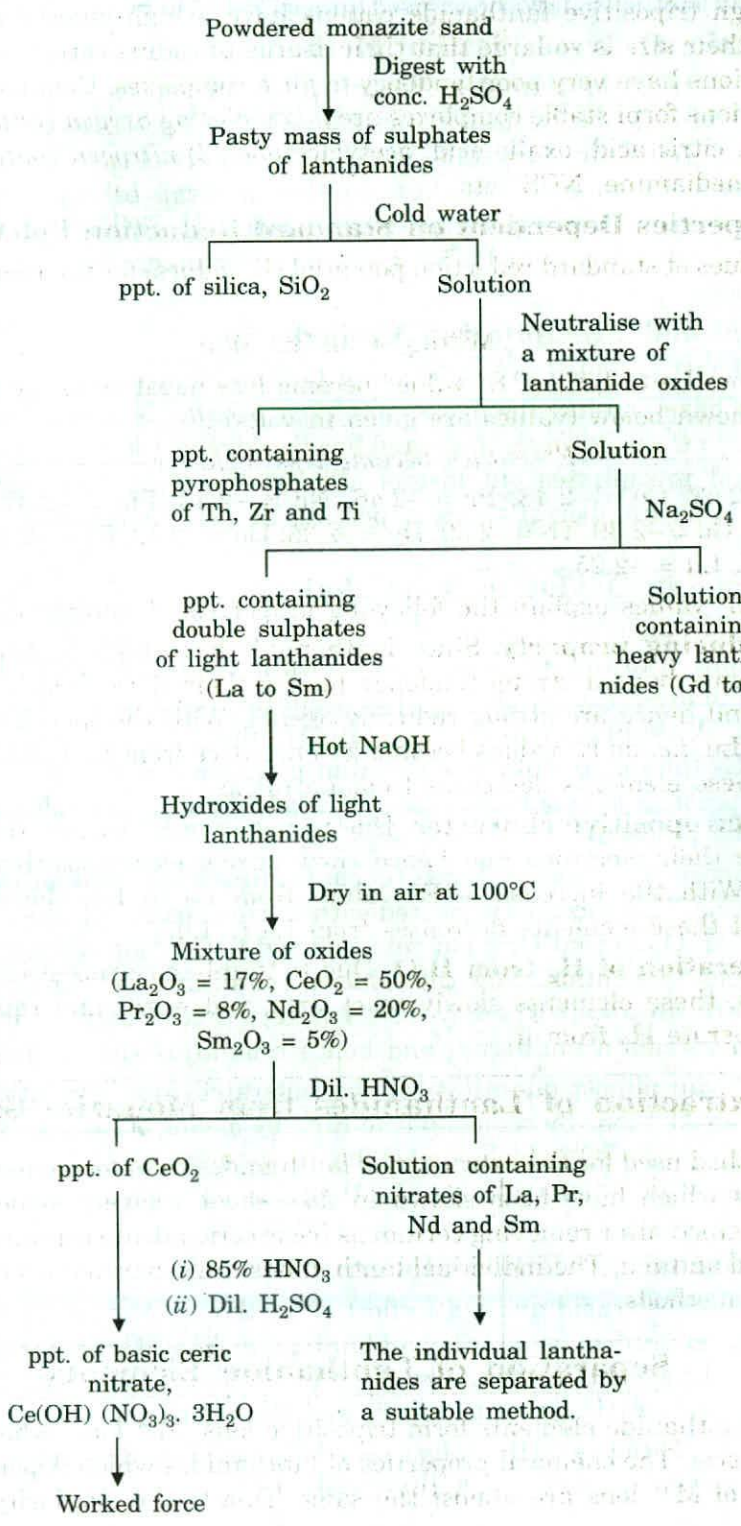
Extraction of Lanthanides from Monazite Sand

The method used for the extraction of lanthanides from monazite sand consists of the steps which have been shown in flow sheet 1 given on next page. The solution obtained after removing cerium as basic ceric nitrate contains the nitrates of La, Pr, Nd and Sm. The individual lanthanides are separated from this solution by suitable methods.

Separation of Lanthanide Elements

All the lanthanide elements form tripositive ions (M^{3+} ions) which are almost identical in size. The chemical properties of lanthanides which depend on the size and charge of M^{3+} ions are almost the same. Due to the similarity in chemical

Flow sheet 1. Extraction of lanthanides from monazite sand.



properties, it is difficult to separate the lanthanides from each other. However, the following methods have been used to separate them.

1. Fractional Crystallisation Method.

Simple salts of lanthanides like nitrates, sulphates, oxalates, bromates, perchlorates and double salts such as $2M(NO_3)_3 . 3Mg(NO_3)_2 . 24H_2O$ crystallise well and form well-defined crystals. Since the solubility of these simple and double salts decreases from La to Lu, these lanthanides can be separated from each other by repeating the fractional crystallisation a number of times. In the separation of $Nd(NO_3)_3$ from $Pr(NO_3)_3$ the use of non-aqueous solvent like ether has been made.

2. Fractional Precipitation Method.

When NaOH is added to a solution of lanthanide nitrates, $Lu(OH)_3$ which is the weakest base and has the *lowest solubility product* is precipitated first while $La(OH)_3$ which is the *strongest base* and has the *highest solubility product* remains dissolved and precipitates out last of all. By dissolving and precipitating the hydroxides for a number of times it possible to get the complete separation of lanthanides.

3. Change in Oxidation State Method.

As already mentioned, some of the lanthanides show +2 and +4 oxidation states in addition to the usual +3 state which is the common oxidation state for all the lanthanides. The properties of M^{2+} and M^{4+} ions are different from those of M^{3+} ions. A change in oxidation state results in a remarkable change in properties. By taking advantage of different properties of M^{2+}, M^{3+} and M^{4+} ions, it has been possible to separate some of the lanthanides. The following examples illustrate this procedure.

(*i*) Suppose we have a mixture containing Ce^{3+} and other tripositive lanthanide ions. This mixture is treated with a strong oxidising agent like alkaline solution of $KMnO_4$ so that Ce^{3+} ion gets oxidised to Ce^{4+} ion while other M^{3+} ions remain as such in solution. Now the solution containing Ce^{4+} and other M^{3+} ions is treated with an alkali whereby Ce^{4+} ion gets precipitated as $Ce(OH)_4$ while other M^{3+} ions remain unaffected and hence remain as such in solution.

(*ii*) Eu^{3+} can almost quantitatively be separated from a solution containing Eu^{3+} and other M^{3+} ions by reducing it to Eu^{2+} by means of Zn-amalgam and then precipitating it as $EuSO_4$ which is insoluble in water and hence can be separated. The sulphates of all other tripositive lanthanides, on the other hand, are soluble in water.

4. Ion Exchange Method–Modern Method.

This is the most rapid and most effective method. When an aqueous solution containing the mixture of usual trivalent lanthanide ions, $M^{3+}(aq)$ is passed through a column having synthetic cation-exchange resin [abbreviated as HR (solid)], the $M^{3+}(aq)$ ions replace H^+ ion of the resin and thus get fixed on it.

$$M^{3+}(aq) + 3HR\ (solid) \longrightarrow MR_3\ (solid) + 3H^+(aq)$$

Since $Lu^{3+}(aq)$ is largest in size and $La^{3+}(aq)$ is smallest, $La^{3+}(aq)$ is attached to the column with maximum and $Lu^{3+}(aq)$ with minimum firmness.

In order to recover the M^{3+} ions fixed on the resin, the column is *eluted* (*i.e.*, leached) with a citric acid–ammonium citrate solution (called **eluant** or **eluante**). During elution process NH_4^+ ions replace M^{3+} ions and M-citrate complexes are formed.

$$MR_3 + 3NH_4^+ \longrightarrow 3NH_4R + M^{3+}$$

$$M^{3+} + \text{citrate ions} \longrightarrow \text{M-citrate complex}$$

We have seen that since $La^{3+}(aq)$ is attached to the resin with maximum and $Lu^{3+}(aq)$ with minimum firmness, *Lu-citrate complex comes out of the column first and La-citrate complex comes out last.* In actual practice the process has to be repeated several times by careful control of concentration of citric acid-ammonium citrate solution.

5. Solvent Extraction Method.

This method makes the use of the difference in the value of partition coefficient of lanthanides between two solvents. $La(NO_3)_3$ and $Gd(NO_3)_3$ have been separated form each other by this method. The partition coefficient of $Gd(NO_3)_3$ between water and tributyl phosphate in kerosene is different from that of $La(NO_3)_3$ between the same solvents. This means that $Gd(NO_3)_3$ can be separated from $La(NO_3)_3$ by continuous extraction with water from a solution of these salts in tributyl phosphate in kerosene.

Production of Lanthanide Metals

The following methods may be used for this purpose :

1. Electrolysis of Fused Chlorides.

This method is similar to that used in the metallurgy of Ca by the electrolysis of $CaCl_2$.

2. Reduction of Anhydrous Chlorides with Na.

Lighter lanthanides such as La, Ce and Gd can easily be prepared by the reduction of their anhydrous chlorides with Na at 100°C.

$$LaCl_3 + 3Na \xrightarrow{100°C} La + 3NaCl$$

3. Reduction of Anhydrous Fluorides and Chlorides with Mg or Ca.

Heavier lanthanides such as Lu are prepared when anhydrous fluorides and chlorides are reduced by Ca or Mg metals at a temperature above 1000°C, since the fluorides are less volatile than the chlorides and consequently the loss caused by evaporation in case of fluorides is small.

Uses of Lanthanides and Their Compounds

(*i*) Certain alloys of the lanthanide elements, known as ***mishmetals*** containing predominantly 30–35% of Ce together with smaller quantities of other light lanthanides are used as reducing agents in metallurgical operations. Mg-alloys containing about 30% misch metal and 1% Zr are used for making parts of jet engine. (*ii*) La, Ce, Pr, Nd mixed with steel are used in cigarette lighters, toys,

flame throwing tanks. (*iii*) Nd_2O_3 and PrO_3 are used as colouring agents for glass and in the production of standard filters. Lanthanum oxides are used for polishing glass. Ceria (CeO_2) is used in gas mantles. (*iv*) Cerium phosphate is used as a catalyst in petroleum cracking. (*v*) Cerium salts are used in analysis, dyeing cotton, lead accumulators, medicines etc. (*vi*) Lanthanide compounds are used as good catalysts in a number of reactions like hydrogenation, dehydrogenation, oxidation and cracking of petroleum. (*vii*) Lanthanide compounds are filled into arc carbon electrodes to give more brilliant light.

Comparison Between d- and f-Block Elements (*particularly between 3d and 4f-block elements*).

Some of the differences are given below :

1. Entry of extra electron. In case of *d*-block elements the extra electron enters $(n-1)d$-orbitals while in case of *f*-block elements the extra electron occupies $(n-2)$ *f*-orbitals.

2. Energy of orbitals. $(n-1)$ *d*-orbitals have higher energy than $(n-2)$ *f*-orbitals.

3. Cause of paramagnetism. The maximum value of magnetic moment (μ value) for *d*-block elements is due to the presence of 5 unpaired electrons while the maximum value of μ for *f*-block elements is due to the presence of 7 unpaired electrons. Further, in case of *d*-block elements, since *d*-orbitals project out, these are not well shielded from the ligands surrounding the transition metal atoms or ions, *i.e.* the electrons residing in *d*-orbitals are able to interact with the surrounding ligands. Thus in case of transition metals, the orbital motion of the electron is quenched and hence the observed paramagnetism in these elements is only due to the spin motion of the electron. Due to the quenching of orbital motion, the value of μ is calculated from the spin-only formula, $\mu = \sqrt{n\,(n+2)}$.

Now consider the case of tripositive lanthanide ions. In case of these ions since 4 *f*-orbitals are quite deeply seated, these are well shielded from the ligands surrounding these ions by the overlapping 5*s* and 5*p* orbitals, *i.e.* the electrons residing in 4*f* orbitals are not able to interact with the surrounding ligands. Thus in case of lanthanides. the orbital motion of the electron is not quenched as in case of *d*-block elements and hence the observed paramagnetism in these elements is due to both the motions of the electron *viz.* orbital motion and spin motion. In other words, the value of μ for M^{3+} ion, cannot be calculated by using spin-only formula. Rather μ is calculated from : $\mu = g\sqrt{J\,(J+1)}$.

4. Nature of absorption bands. *d*-block elements give *broad bands* in the absorption spectra in the visible region while, excepting La^{3+}, and Lu^{3+}, all the remaining tripositive lanthanide ions give *sharp almost line-like bands* in the absorption spectra.

5. Oxidation states. *d*-block elements show much greater number of oxidation states while *f*-block elements, particularly lanthanides, show a limited number of oxidation states.

6. Formation of complex compounds. *d*-block elements form complexes more easily while *f*-block elements, particularly lanthanides, do so with great difficulty.

7. Coordination number. Because of their larger size, lanthanide ions generally have higher coordination numbers than transitional metal ions. Coordination numbers greater than 6 for transition metal ions are only formed with difficulty because of the strong ligand repulsion in the coordination spheres.

5f-block Elements : Actinides

What are 5*f*-Block Elements ?

In the atoms of 5*f*-block elements the extra electron enter 5f-orbitals, *i.e.* in the atoms of the elements of this block 5*f* orbitals are being progressively filled. A group of 14 elements from thorium, Th (Z = 90) to lawrencium, Lw (Z = 103) constitute this series. The elements of this series are also called *actinides* or *actinones*, since these elements follow actinium, Ac (Z = 89) in the periodic table and show close similarities with Ac. Although, strictly speaking, the fourteen elements from Th (Z = 90) to Lw (Z = 103) are called actinides, yet, due to the similarities in properties among all the fifteen elements from Ac (Z = 89) to Lw (Z = 103), all these fifteen elements are considered to be the members of actinide series. Thus Ac (Z = 89) is also studied along with actinide elements. The actinide elements constitute the *second inner transition series.* Actinide elements lie in *7th* period (incomplete period with $n = 7$) and IIIB group of the periodic table.

Position of Actinides in the Periodic Table.

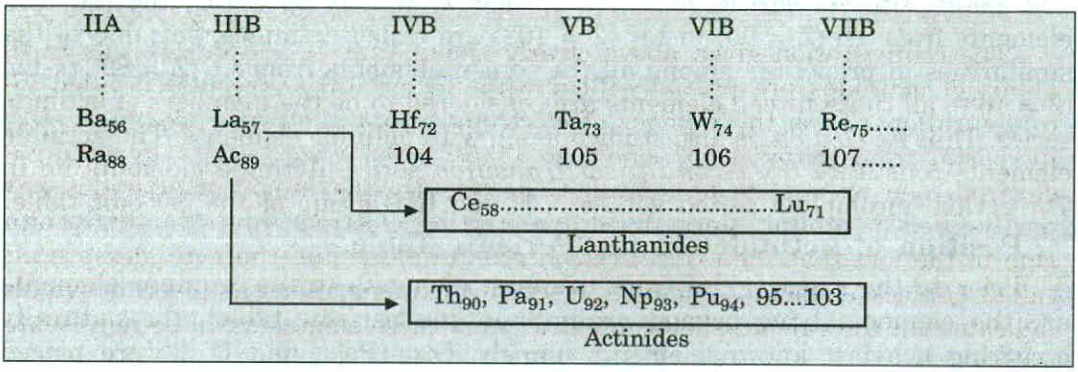
Prior to the discovery of trans-uranium elements (trans-uranium elements are the elements lying beyond uranium in the periodic table), the naturally occurring heaviest known elements namely Th_{90}, Pa_{91}, and U_{92}, were placed below Hf_{72}, Ta_{73} and W_{74} in IV B, V B and VI B groups of the periodic table, because these elements showed +4, +5 and +6 oxidation states and resembled Hf, Ta and W respectively in many of their properties. The then undiscovered trans-uranium elements with atomic numbers 93 to 100 were thus expected to occupy the positions in the periodic table below Re_{75}, Os_{76}, Ir_{77}, Pt_{78}, Au_{79}, Hg_{80}, Tl_{81}, and Pb_{82} respectively as shown below :

IV B	V B	VI B	VII B	VIII			I B	II B	III A	IVA
—	—		—	—	—		—	—	—	—
Hf_{72}	Ta_{73}	W_{74}	Re_{75}	Os_{76}	Ir_{77}	Pt_{78}	Au_{79}	Hg_{80}	Tl_{81}	Pb_{82}
Th_{90}	Pa_{91}	U_{92}	93	94	95	96	97	98	99	100

The discovery of the element neptunium (Np_{93}) came in 1940 and this discovery was followed shortly by the discovery of plutonium (Pu_{94}) in 1941. The tracer chemical experiments with Np_{93} and Pu_{94} showed that the chemical properties of these two elements very much resemble those of U_{92}, and not at all those of Re_{75} and Os_{76}. On this basis in 1914, all the three elements namely U_{92}, Np_{93} and Pu_{94} were placed under W_{74} in group VIB as shown below. It was thought that the undiscovered elements with atomic numbers 95 and 96 should be very much like U_{92}, Np_{93}, and Pu_{94} in their chemical properties, and hence the elements with atomic numbers 95 and 96 were also placed along with U_{92}, Np_{93}, and Pu_{94}, below W_{74} in group VI B as shown below :

IVB	VB	VIB
Hf_{72}	Ta_{73}	W_{74}
Th_{90}	Pa_{91}	U_{92}, Np_{93}, Pu_{94}, 95, 96

This assumption, however, proved to be wrong, since the experiments directed towards the discovery of elements with atomic numbers 95 and 96 on the pattern of discovery of Np_{93} and Pu_{94} failed. Later on, in the same year (1944) Seaborg suggested that all the elements having atomic number greater than 89 (Ac_{89}) constitute a second series of inner-transition elements. This series is similar to lanthanide series. The elements of this new series which have atomic number greater than 89 were called *actinides*. The elements of this series were placed below lanthanides out of the main body of the periodic table as shown below :



The position of actinides shown above was confirmed by the discovery of the elements from atomic numbers 95 to 103 in 1961 and by the electronic configuration of these elements.

General Characteristics of Actinides

1. Occurrence.

Excepting Ac, Tb, Pa and U which occur in nature in uranium minerals, all the remaining actinides are unstable and made artificially by nuclear transmutations, The actinide elements lying beyond U (Z = 92), *i.e.* the actinide elements with atomic numbers 93 to 103 are called *trans-uranium* or *trans-uranic elements*. All the actinides are radioactive.

2. Electronic Configurations

Complete and valence-shell configurations of the atoms of actinides in their ground state are : Ac(Z = 89) → 2, 8, 18, 32, 18, 9, $2(5f^0.6d^1.7s^2)$; Th(Z = 90) → 2, 8, 18, 32, 19, 9, $2(5f^1.6d^1.7s^2)$ *or* 2, 8, 18, 32, 18, 10, $2(5f^0.6d^2.7s^2)$; Pa(Z = 91) → 2, 8, 18, 32, 20, 9, $2(5f^2.6d^1.7s^2)$ *or* 2, 8, 18, 32, 19, 10, $2(5f^1.6d^2.7s^2)$; U(Z = 92) → 2, 8, 18, 32, 21, 9, $2(5f^3.6d^1.7s^2)$; Np(Z = 93) → 2, 8, 18, 32, 23, 8, $2(5f^5.6d^0.7s^0)$ *or* 2, 8, 18, 32, 22, 9, $2(5f^4.6d^1.7s^2)$; Pu(Z = 94) → 2, 8, 18, 32, 24, 8, $2(5f^6.6d^0.7s^2)$ *or* 2, 8, 18, 32, 23, 9, $2(5f^5.6d^1.7s^2)$; Am(Z = 95) → 2, 8, 18, 32, 25, 8, $2(5f^7.6d^0.7s^2)$;

Cm(Z = 96) → 2, 8, 18, 32, 25, 9, $2(5f^7.6d^1.7s^2)$; Bk(Z = 97) → 2, 8, 18, 32, 27, 8, $2(5f^9.6d^0.7s^2)$ *or* 2, 8, 18, 32, 25, 10, $2(5f^7.6d^2.7s^2)$; Cf(Z = 98) → 2, 8, 18, 32, 28, 8, $2(5f^{10}.6d^0.7s^2)$ *or* 2, 8, 18, 32, 27, 9, $2(5f^9.6d^1.7s^2)$; Es(Z = 99) → 2, 8, 18, 32, 29, 8, $2(5f^{11}.6d^0.7s^2)$; Fm(Z = 100) → 2, 8, 18, 32, 30, 8, $2(5f^{12}.6d^0.7s^2)$; Md(Z = 101) → 2, 8, 18, 32, 31, 8, $2(5f^{13}.6d^0.7s^2)$; No(Z = 102) → 2, 8, 18, 32, 32, 8, $2(5f^{14}.6d^0.7s^2)$; Lw(Z = 103) → 2, 8, 18, 32, 32, 9, $2(5f^{14}.6d^1.7s^2)$. These configurations show that the atoms of actinides have a total of *seven* shells. Out of these seven shells, first four shells namely 1*st*, 2*nd*, 3*rd* and 4*th* are completely-filled while the remaining three shells *viz.* 5*th*, 6*th* and 7*th* shells are partially-filled as shown below :

2, 8, 18, 32, $5s^2p^6d^{10}f^{0,\ 1.....7,\ 9.....14}$, $6s^2p^6d^{0,\ 1,\ 2}$, $7s^2$ (seven shells)

The configuration given above clearly shows that 5*f* and 6*d* orbitals in the atoms of actinides are partially-filled while 7*s* orbital is completely-filled ($7s^2$ configuration). Thus the number of electrons in 5*th* shell [*i.e.* (*n*–2)*th* shell) is increasing from 18 ($5s^2 + 5p^6 + 5d^{10}$) to 32 ($5s^2 + 5p^6 + 5d^{10} + 5f^{14}$) by adding an electron, one by one, to 5*f* orbital. Consequently the atoms of actinides have partly-filled 5*f* orbital, since the differentiating electron enters in this orbital. Due to the fact that the extra electron goes to 5*f* orbital, the actinides are also called 5*f*-block elements. Complete electronic configurations as given above also indicate that the valence-shell configuration of these elements can be represented as :

$5f^{0,\ 1.....7,\ 9.....14}$, $6d^{0,\ 1,\ 2}$, $7s^2$

3. Oxidation States.

Important oxidation states shown by actinides are (Most stable oxidation states are given in circles while the unstable ones are given in brackets) given below :

Ac(Z = 89) → + 2, (+ 3), + 4; Th(Z = 90) → + 2, (+ 3), (+ 4), + 5; Pa(Z = 91) → (+ 3), (+ 4), (+ 5) ; U(Z = 92) → (+ 3), (+ 4), + 5, (+ 6); Np(Z = 93) → + 3, (+ 4), (+ 5), (+ 6), (+ 7); Pu(Z = 94) → (+ 3), (+ 4), + 5, + 6 + 7; Am(Z = 95) → + 2, (+ 3), (+ 4), + 5, + 6; Cm(Z = 96) → (+ 3), (+ 4); Bk(Z = 97) → (+ 3); Cf(Z = 98) → (+ 3); Es(Z = 99) → (+ 3); Fm(Z = 100) → (+ 3); Md(Z = 101) → (+ 3); No(Z = 102) → (+ 3); Lw(Z = 103) → (+ 3). It may be seen from these oxidation states that +2 state is shown by two elements namely Am and Th in its few compounds like $ThBr_2$, ThI_2, ThS etc. +3 oxidation state is shown by all the actinides. +3 state becomes more and more stable as the atomic number increases. +4 oxidation state is shown by Th, Pa, U, Np, Pu, Am and Cm while +5 state is shown by Th, Pu, U, Np, Pu and Am. +6 oxidation state is exhibited by U, Np, Pu and Am while +7 oxidation state is shown by Np and Pu.

The principal cations given by actinide elements are M^{3+}, M^{4+} and oxo-cations like MO_2^+ (oxidation state of M = +5) and MO_2^{2+} (oxidation state of M = + 6). Examples of MO_2^+ ion are UO_2^+ and PuO_2^+ while those of MO_2^{2+} are UO_2^{2+} and PuO_2^{2+}. These oxo-cations are stable in acid and aqueous solutions.

U^{3+} ion in aqueous solution liberates H_2 on standing. Np^{3+} and Pu^{3+} are stable in water but are readily oxidized by air to Np^{4+} and Pu^{4+} respectively. All the remaining M^{3+} ions upto Md^{3+} are stable in aqueous solution. U^{4+} and Np^{4+} ions are stable in aqueous solution but are slowly oxidized by air to UO_2^{2+}(U = + 6) and PuO_2^{2+} (Pu = + 6) ions respectively.

4. Radii of Tripositive and Tetrapositive Actinide Cations : Actinide Contraction.

A look at the values of the radii of tripositive and tetrapositive actinide cations (M^{3+} and M^{4+} cation.) reveals that these values for both the cations decrease as we move from Ac to Cm. This steady decrease in the size of M^{3+} and M^{4+} cations in the actinide series is called *adinide contraction* which is analogous to lanthanide contraction found in lanthanides.

	——————— Decreasing ———————→
Radii of M^{3+} cations (A°) :	$Ac^{3+}(1.11) > Th^{3+}(1.08) > Pa^{3+}(1.05) > U^{3+}(1.03) > Np^{3+}(1.01) > Pu^{3+}(1.00) > Am^{3+}(0.99) > Cm^{3+}(0.98)$
	——————— Decreasing ———————→
Radii of M^{4+} cations (A°) :	$Ac^{4+}(0.99) > Th^{4+}(0.96) > Pa^{4+}(0.93) > U^{3+}(0.92) > Np^{4+}(0.91) > Pu^{4+}(0.90) > Am^{4+}(0.89) > Cm^{4+}(0.88)$

Cause of Actinide Contraction. We know that as we proceed from one element to the next one in the actinide series, the nuclear charge (*i.e.* atomic number) increases by +1 at each next element and the addition of extra electron takes place in 5*f* orbital. Again it is also known that the shielding of one electron in 5*f* orbital by the other electron residing in the same orbital is very poor. Due to the negligible amount of mutual shielding effect between the electrons residing in 5*f* orbital, the increase in nuclear charge by + 1 at each next element in the actinide series brings the valence-shell nearer to the nucleus and hence the size of M^{3+} and M^{4+} cations goes on decreasing as we move from one element to the next one in the series.

5. Colours of M^{3+} and M^{4+} Cations.

Most of the tripositive and tetrapositive actinide cations (M^{3+} and M^{4+} cation.) are coloured. The colours are given below :

M^{3+} cations : Ac^{3+} ($5f^0.6d^0.7s^0$, $n = 0$) → colourless; U^{3+} ($5f^3.6d^0.7s^0$, $n = 3$) → red; Np^{3+} ($5f^4.6d^0.7s^0$, $n = 4$) → purple; Pu^{3+} ($5f^5.6d^0.7s^0$, $n = 5$) → violet; Am^{3+} ($5f^6.6d^0.7s^0$, $n = 6$) → pink; Cm^{3+} ($5f^7.6d^0.7s^0$, $n = 7$) → colourless.

M^{4+} cations : Th^{4+} ($5f^0.6d^0.7s^0$, $n = 0$) → colourless; Pa^{4+} ($5f^1.6d^0.7s^0$, $n = 1$) → colourless; U^{4+} ($5f^2.6d^0.7s^0$, $n = 2$) → green; Np^{4+} ($5f^3.6d^0.7s^0$, $n = 3$) → yellow-green; Pu^{4+} ($5f^4.6d^0.7s^0$, $n = 4$) → orange; Am^{4+} ($5f^5.6d^0.7s^0$, $n = 5$) → red.

Here n is the number of unpaired electrons in $5f$ orbitals. These colours show that M^{3+} and M^{4+} cations having $5f^0$, $5f^1$ and $5f^7$ configuration are colourless while those containing $5f^2$, $5f^3$, $5f^4$, $5f^5$ and $5f^6$ configuration are coloured. These colours are produced when an electron jumps from one energy level to the other within $5f$ orbitals.

6. Formation of Complexes.

Most of the actinide halides form complex compounds with alkali metal halides. For example $ThCl_4$ forms complexes such as $K[ThCl_5]$, $K_2[ThCl_6]$ etc. with KCl. $ThCl_4$ and $ThBr_4$ also form complexes with pyridine. Actinides also form chelates with organic compounds like EDTA and oxine.

The degree of complex formation for the ions M^{4+}, MO_2^{2+}, M^{3+} and MO_2^{+} decreases in the order :

$$M^{4+} > MO_2^{2+} > M^{3+} > MO_2^{+}$$

The complexing power of different anions with the above cations is in the order :

Singly-charged anions : $F^- > NO_2^- > Cl^-$

Doubly-charged anions : $CO_3^{2-} > C_2O_4^{2-} > SO_4^{2-}$

7. Properties of Actinides.

The actinides are silvery white metals which are highly reactive. All the actinides are highly electropositive like lanthanides. Tripositive (*e.g.* U^{3+}, Np^{3+} etc.) and tetrapositive (*e.g.* Pa^{4+}, U^{4+} etc.) actinide cations are paramagnetic like the tripositive lanthanide cations like Ce^{3+}, Pr^{3+}, Nd^{3+} etc. When actinides combine with O_2, oxides are formed. Examples are ThO_2, PaO_2, UO_2, NpO_2 AmO_2, Cm_2O_3 etc. When H_2 acts on actinides, hydrides are formed. Examples are ThH_4, PaH_3, UH_3, PuH_2, AmH_2 etc. Chlorides, bromides and iodides are obtained when the metal is acted on by Cl_2, Br_2 and I_2 respectively.

Comparison between Lanthanides and Actinides.

(A) Similarities. (*i*) In the atoms of the elements of both the series, the extra electron enters $(n-2)f$ orbitals. (*ii*) The elements of both the series show +3 oxidation state. (*iii*) Like lanthanide contraction seen in case of lanthanides, we also have actinide contraction in actinides. Both the contractions are due to the poor shielding effect between the electrons residing in $(n-2)$ f orbitals. (*iv*) The absorption bands of the elements of both the series are so sharp that they appear to be almost line-like bands. Both the bands are produced due to the jump of an electron from one energy level to the other within $(n-2)f$ orbitals. (*v*) Elements of both the series have low electronegativities and are very reactive. (*vi*) The nitrates, perchlorates and sulphates of trivalent actinides as well as lanthanides are soluble while the hydroxides, fluorides and carbonates of both cations are insoluble. (*vii*) Most of the lanthanide and actinide cations are paramagnetic. (*viii*) In the atoms of the elements of both the series, three outermost shells are partly-filled while the remaining inner-shells are completely-filled.

(B) Dissimilarities. The elements of both the series also show some dissimilarities which are due to the difference in nature of $4f$ and $5f$ orbitals. The points showing dissimilarity are given below in a tabular form :

Lanthanides	Actinides
(*i*) Due to large energy difference between 4*f* and 5*d* orbitats, the properties of lanthanides are fairly similar.	(*i*) Due to small energy difference between 5*f* and 6*d* orbitals, the properties of actinides are considerably different from each other.
(*ii*) Binding energies of 4*f* orbitals are higher.	(*ii*) Binding energies of 5*f* orbitals are lower.
(*iii*) The additional electron enters 4*f* orbitals.	(*iii*) The addition electron enters 5*f* orbitals.
(*iv*) These elements show only +2, +3 and +4 oxidation states.	(*iv*) These elements show a variety of oxidation states like +2, +3, +, +5, +6 and +7.
(*v*) The mutual shielding effect between two electrons residing in 4*f* orbitals is greater.	(*v*) The mutual shielding effect between two electrons residing in 5*f* orbitals is poor.
(*vi*) Most of the tripositive lanthanide cations are colourless.	(*vi*) Most of the tripositive and tetrapositive actinide cations are coloured.
(*vii*) The paramagnetic character of lanthanides cart easily be explained.	(*vii*) The paramagnetic character of actinides can not be explained easily.
(*viii*) They do not form complex compounds easily. They do not form complexes with p-bonding ligands like alkyl phosphines, thioethers etc.	(*viii*) They form complex compounds comparatively more easily. They do form complexes with p-bonding ligands.
(*ix*) Except Pm, all the remaining lanthanides are non-radioactive.	(*ix*) All the actinides are radioactive.
(*x*) The compounds of lanthanides are less basic.	(*x*) The compounds of actinides are more basic.
(*xi*) Lanthanides do not form oxo-cations.	(*xi*) Some actinide form oxo-cations of MO_2^+ (*e.g.* UO_2^+, PuO_2^+) and MO_2^{2+} (*e.g.* UO_2^{2+}, PuO_2^{2+}) type.
(*xii*) The atoms of lanthanides have a total of six shells. Out of these, first three shells *viz.* 1*st*, 2*nd* and 3*rd* are completely filled while the remaining three shells namely 4*th*, 5*th* and 6*th* are partially-filled.	(*xii*) The atoms of actinides have a total of seven shells. Out of these, first tour shells *viz.* 1*st*, 2*nd*, 3*rd* and 4*th* are completely-filled while the remaining three shell. *viz.* 5*th*, 6*th* and 7*th* are partially-filled.

Conceptual Questions with Answers

Q.1 Write down the electronic configuration of (*a*) Cr^{3+} (*b*) Cu^{+} (*c*) Co^{2+} (*d*) Mn^{2+}

Ans. (*a*) $Cr^{3+} = [Ar]_{18}\ 3d^3$ (*b*) $Cu^{+} = [Ar]_{18}\ 3d^{10}$ (*c*) $Co^{2+} = [Ar]_{18}\ 3d^7$ (*d*) $Mn^{2+} = [Ar]_{18}\ 3d^5$.

Q.2 Atomic radius of Cu is greater than that of Cr but ionic radius of Cr^{2+} is greater than that of Cu^{2+}. Give suitable explanation.

Ans. In Cu, all the *d*-electrons are paired ($3d^{10}\ 4s^1$). In Cr, all the *d*-electrons are unpaired ($3d^5\ 4s^1$). Hence, *d–d* electron repulsions in Cu are much greater than those in Cr. Hence, Cu atom is larger in size than Cr. In Cu^{2+} ($3d^9$), *d–d* electron repulsions decrease due to presence of one unpaired *d*-electron. Moreover in Cu^{2+} ion the electrons are attracted by 29 protons of the nucleus whereas in Cr^{2+} ($3d^4$), four unpaired electrons are still present but they are attracted by only 24 protons of the nucleus. Thus Cu^{2+} is smaller in size than Cr^{2+}.

Q.3 Why are IEs of 5*d* elements greater than 3*d* elements ?

Ans. In 5*d* elements, after La_{57} there is lanthanide contraction. In each group the size of 5*d* elements is small while nuclear charge is greater than 3*d* elements. Hence IEs of 5*d* elements are greater than 3*d* elements.

Q.4 The valence shell E.C. of Cr atom is $3d^5\ 4s^1$. Write (*i*) the most stable oxidation state of Cr (*ii*) most oxidising state of Cr.

Ans. (*i*) The most stable oxidation state of Cr is +2 which is obtained when Cr atom loses one electron from 4*s* orbital and one electron from 3*d* orbitals.

(*ii*) Most oxidising state of an element is its highest oxidation state which it can exhibit. Obviously, since the highest oxidation state of Cr is +6, the most oxidising state of Cr is also +6. This state is obtained when all the six electrons present in the valence shell of Cr are lost. This oxidation state is shown by Cr in $K_2Cr_2O_7$ which is an oxidising sgent. During its oxidising action, $K_2Cr_2O_7$ (Cr = +6) gets reduced to Cr^{3+} (Cr = +3)

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \xrightarrow{\text{Reduction}} 2\ Cr^{3+} + 7H_2O$$

Q.5 Predict which of the following will be coloured in aqueous solution ? Ti^{3+}, V^{3+}, Sc^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+} and MnO_4^-.

Ans. Only those ions will be coloured which have incompletely filled d-orbitals. Those with fully-filled or empty d-orbitals are colourless. Thus, Ti^{3+}, V^{3+}, Mn^{2+}, Fe^{3+} and Co^{2+} are all coloured. ($Ti^{3+} = 3d^1$, $V^{3+} = 3d^2$, $Mn^{2+} = 3d^5$, $Fe^{3+} = 3d^5$, $Co^{2+} = 3d^7$). MnO_4^- is also coloured but due to charge transfer (from O to Mn) which reduces the oxidation state of Mn from +7 to +6 momentarily.

Q.6 Out of Co^{2+} and Zn^{2+} salts which is attracted in a magnetic field. Explain with reasons.

Ans. Co^{2+} and Zn^{2+} ions are $3d^7$ ($n = 3$) and $3d^{10}$ ($n = 0$) ions. Since Co^{2+} ion has unpaired electrons ($n = 3$) and Zn^{2+} ion has no unpaired electrons ($n = 0$), Co^{2+} ion is paramagnetic and Zn^{2+} ion is diamagnetic. Being paramagnetic Co^{2+}

ion is attracted in magnetic field. On the other hand, Zn^{2+} ion, being diamagnetic, is not attracted by the magnetic field.

Q.7 Why hydrated copper sulphate is blue while anhydrous copper sulphate is white ?

Ans. In hydrated copper sulphate, four water molecules are present as ligands. In the presence of these ligands *d*-orbitals are no longer degenerate in energy. Hence *d–d* transition takes palce absorbing red wavelength. The complementary colour, *viz.*, blue is reflected. In anhydrous $CuSO_4$, *d*-orbitals remain degenerate. Hence, no *d–d* transition can occur. The white light is completely reflected back. Hence,it looks white.

Q.8 Write the formulae of different oxides of manganese. What is the oxidation state of manganese in each of them ? Arrange them in order of their decreasing acidic charater.

Ans.

+2	+8/3	+3	+4	+7
MnO	Mn_3O_4	Mn_2O_3	MnO_2	Mn_2O_7
Basic	Amphotetic			Acidic

Thus, their acidic character decreases as follows :

$Mn_2O_7 > MnO_2 > Mn_2O_3 > Mn_3O_4 > MnO$.

Q.9 Why Zr and Hf or Nb and Ta exhibit similar properties ?

Or Zirconium (atomic number 40) and hafnium (atomic number 72) occur together in minerals and they exhibits similar properties. Give reasons.

Ans. Due to lanthanoid contraction, Hf (Z = 72) has size similar to that of Zr(Z = 40). Hence, their properties are similar and therefore, occur together. For the same reason, Nb and Ta have similar size and hence similar properties.

Q.10 The E° values in respect of the electrodes of chromium (Z = 24), manganese (Z = 25) and iron (Z = 26) are :

$Cr^{3+} / Cr^{2+} = -0.4V$, $Mn^{3+} / Mn^{2+} = +1.5V$, $Fe^{3+} / Fe^{2+} = +0.8V$.

On the basis of the above information compare the feasibilities of further oxidation of their +2 oxidation states.

Ans. –ve value of E° for Cr^{3+} / Cr^{2+} shows that Cr^{2+} is least stable. Greater +ve value for Mn^{3+} / Mn^{2+} than that for Fe^{3+} / Fe^{2+} shows that Mn^{2+} is more stable than Fe^{2+}. Hence, stability of +2 oxidation state is in the order :

$$Cr^{2+} < Fe^{2+} < Mn^{2+}$$

or the feasibility of oxidation of thier +2 state to +3 state is in the order :

$$Cr^{2+} > Fe^{2+} > Mn^{2+}$$

Q.11 Why Sm^{2+}, Eu^{2+} and Yb^{2+} ions in solutions are good reducing agents but an aqueous solution of Ce^{4+} is a good oxidizing agent ?

Ans. The most stable oxidation state of lanthandies is +3. Hence, ions in +2 state tend to change to +3 state by loss of electron and those in +4 state tend to change to +3 state by gain of electron.

Q.12 Expalin why lanthnoids are paramagnetic in nature ?

Ans. All lanthanoids except La^{3+} and Lu^{3+} contain unpaired electrons and hence are paramagnetic.

Q.13 The +3 oxidation state of lanthanum (Z = 57), gadolinium (Z = 64) and lutetium (Z = 71) are especially stable. Why ?

Ans. This is because they have empty, half-filled and completely filled $4f$ subshell respectively.

Q.14 Among the ionic species, Sc^{3+}, Ce^{4+} and Eu^{2+}, which one is a good oxidizing agent ? Give a suitable reason for your answer. (Atomic nos : Sc = 21, Ce = 58, Eu = 63)

Ans. The typical (stable) oxidation state of lanthanoids is +3. Ions with oxidation state +2 or +4 tend to change to +3 by loss or gain of electrons. Ce^{4+} gains electron to change to Ce^{3+}. Hence, it is a good oxidizing agent.

Q.15 Among the lanthanides, Ce (III) can be easily oxidized to Ce (IV) (At. No. of Ce = 58). Explain why ?

or Of the lanthanides, cerium (At. No. 58) forms a tetrapositive ion, Ce^{4+} in aqueous solutions. Why ?

Ans. Ce (III) having the configuration $4f^1\ 5d^0\ 6s^0$ can easily lose an electron to acquire the configuration $4f^0$ and form Ce(IV). In fact, this is the only (+ IV) lanthanide which exists in solution.

Q.16 The outer electronic configuration of two members of the lanthanoid series are as follows :

$$4f^1\ 5d^1\ 6s^2 \text{ and } 4f^7\ 5d^0\ 6s^2$$

What are their atomic number ? Predict the oxidation states exhibited by these elements in their compounds.

Ans. Complete E.C. of 1st lanthanoid = $[Xe]^{54}\ 4f^1\ 5d^1\ 6s^2$. Atomic No. = 58 (Ce)

Complete E.C. of 2nd lanthanoid = $[Xe]^{54}\ 4f^7\ 5d^0\ 6s^2$. Atomic No. = 63 (Eu)

Oxidation states of 1st lanthanoid = + 2 ($4f^2$), + 3 ($4f^1$), +4 ($4f^0$)

Oxidation states of 2nd lanthanoid = + 2 ($4f^7$) and +3 ($4f^6$)

Q.17 Which out of the two, $La(OH)_3$ and $Lu(OH)_3$, is more basic and why ?

Ans. $La(OH)_3$ is more basic than $Lu(OH)_3$. As the size of the lanthanoid ions decreases from La^{3+} to Lu^{3+}, the covalent character of the hydroxides increases (Fajan's rules). Hence, the basic strength decreases from $La(OH)_3$ to $Lu(OH)_3$.

University Questions

1. Explain, with examples, what you understand by transition (or *d*-block elements. *(Meerut 82, 84; Raj. 88; Utkal 86; Agra 84; Andhra 85; MD Rohtak 84; Punjab 86; Saugar 85)*

2. Discuss the general characteristics of *d*-block elements. *(Meerut 82, 89; Raj. 82, 83, 86, 87, 87S)*

3. What do you understand by the shielding effect of electrons? How does this effect affect the properties of transition elements. *(Raj. 78)*

4. Discuss the radii of *d*-block elements. *(Raj. 86)*

5. Discuss the trends and variation in oxidation states (valeney) of transition metals. *(Raj. 82, 86; Meerut 82; Bundelkhand 88; Utkal 86; Agra 84; Andhra 85; R.D. Rohtak 84)*

6. Discuss the trends and variations in ionisation potential of transition metals. *(Meerut 81)*

7. Discuss the tendency of transition metals to form complex compounds. Explain with examples. *(Utkal 86; Agra 84; Andhra 86; M.D. Rohtak 84)*

8. Discuss the magnetic properties of *d*-block elements. *(Raj. 86)*

9. Distinguish between transition elements and main group elements in term of their electronic configuration. *(Andhra 85; Madras 85)*

10. How do *d*-block elements differ from *f*-block elements ? *(Meerut 82)*

11. (*a*) Discuss the properties of actinide elements in respect of the following : (*i*) Electronic configuration (*ii*) Oxidation states (*iii*) Ionic radius (*iv*) Magnetic properties.

(*b*) Give an account of physico-chemical principles involved in the separation of lanthanides by the following methods : (*i*) Fractional precipitation method (*ii*) Fractional crystallisation method.

(*c*) Give an account of separation of La^{3+}, Pr^{3+}, Nd^{3+} and Sm^{3+} ions by ion exchange chromatographic method. *(Kanpur 99)*

12. What are lanthanides ? Describe ion exchange method for the separation of lanthanides. *(Himachal Pradesh 99)*

13. (*a*) Why do some lanthanides exhibit unusual oxidation states ? Discuss this on the basis of their electronic configuration.

(*b*) How do transition elements differ from inner transition elements ? Explain. *(Gorakhpur 99)*

14. What are actinides and how do they differ from lanthanides with reference to the following : (*a*) Electronic configuration (*b*) Tonic radii (*c*) Oxidation states. *(Kumaon 2000)*

15. (*a*) What are lanthanide Elements?

(*b*) Write brief notes on the oxidation states by these elements and also the changes in the magnetic properties of their compounds.

(*c*) Explain why trivalency oxidation state of the lanthanides elements is common and most stable. *(Avadh 2000)*

16. Discuss the principle and procedure of determination of magnetic moments by Gouy method. How are these helpful in deciding the structure of molecules? *(Avadh 2000)*

17. (*a*) Giving electronic configuration justify the position of *f*-block elements in the periodic table.

(*b*) Write note on "Lanthanide Contraction". (*Lucknow 2001*)

18. Arrange the following actinide ions in the increasing order of their size : Th^{3+}, Am^{3+}, Np^{3+} and U^{3+}. (*H.N. Bahuguna 2005*)

19. What are lanthanides ? Explain in detail their oxidation states and lanthanide contraction. (*Gurukul Kangri 2008*)

20. Explain lanthanide contraction. (*Agra 2008*)

21. (*a*) What are inner transition elements ? Discuss their electronic configurations and oxidation states.

(*b*) Why do actinides show higher oxidation states than lanthanides ?

(*c*) List important uses of actinides. (*M.J.P. Rohilkhand 2008*)

22. Describe general characteristics of lanthanides. (*M.J.P. Rohilkhand 2009*)

23. What are actinides ? Explain resemblances and differences of these from lanthanides. (*Meerut 2009*)

24. Discuss d-block elements in the following respects. (ii) Electronic configuration (ii) Coloured ion formation (iii) oxidation states (iv) Magnetic properties (v) Complex formation. (*Meerut 2009*)

25. Write a note on "Lanthanide Contraction". (*Meerut 2009*)

CHAPTER

45

Group Discussion of d-Block Element

Group 3 (III B) : Sc_{21}, Y_{39}, La_{57} and Ac_{89}

Group III B of the periodic table consists of four elements which are *Scandium* (Sc), *Yttrium* (Y), *Lanthanum* (La) and *Actinium* (Ac). These elements are generally called *Scandium group elements.*

Position of Scandium Group Elements in the Periodic Table

The inclusion of scandium group elements in the same group of the period table is justified by the similarity and gradation in their properties as discussed below :

The electronic configurations of these elements in the ground state given as : Sc (Z = 21) $\rightarrow$ 2, 8, 9, 2 ($3d^1.4s^2$); Y (Z = 39) $\rightarrow$ 2, 8, 18, 9, 2 ($4d^1.5s^2$); La (Z = 57) $\rightarrow$ 2, 8, 18, 18, 9, 2 ($5d^1.6s^2$); Ac (Z = 89) $\rightarrow$ 2, 8, 18, 32, 18, 9, 2, ($6d^1.7s^2$) show that the valence-shell configurations of these elements can be represented by $(n-1)d^1.ns^2$, indicating that the extra electron goes in $(n-1)d$ orbital. Thus these are *d*-block (transition) elements. All the elements have 2 electrons in the outermost shell. All the elements show +3 oxidation state in solution, *i.e.* in solution all the elements exist as M^{3+} ions. These ions are obtained by removing both *ns* and one $(n-1)d$ electrons. The salts of M^{3+} ions have *paired electrons* and hence are *colourless* and *diamagnetic.* The metals have high melting points. Due to their high electropositive character, these metals are highly reactive. For example they react with H_2O to form basic oxides, MO.OH and liberate H_2 gas. These metals react slowly with cold water and more rapidly with hot water. The oxides of these metals can be prepared by heating hydroxides or salts such as carbonate, nitrate or sulphate, while hydroxides can be prepared by treating these metals with H_2O. Oxides and hydroxides have basic character. *The basic character of the hydroxides increases with the increase in size of M^{+3} ion.* $[Sc(OH)_3 < Y(OH)_3 < La(OH)_3]$. Thus $La(OH)_3$ is the strongest base. Because of their basic character the oxides and hydroxides react with acids to form salts. Their oxides are very stable and hence cannot be reduced by thermit reaction. The size of the atoms (atomic radii) and M^{3+} ions increase as we proceed from Sc to Ac. *The tendency of M^{+3} ions to form complexes decreases with the increase of their size.* The Sc^{3+} ion which is the smallest shows some tendency to form the complexes like $[ScF_4]^-$, $[ScF_5]^{2-}$, $[ScF_6]^{3-}$ etc, while the other members do not have a strong tendency to form complexes.

Group 4 (IV B) : Ti_{22}, Zr_{40}, Hf_{72} and Ku_{104}

Group IVB of the periodic table consists of four elements which are *Titanium* (Ti), *Zirconium* (Zr), *Hafnium* (Hf) and *Kurchatovium* (Ku). These elements are generally called *titanium group elements.*

Position of Titanium Group Elements in the Periodic Table : Position of Titanium in the Periodic Table

The inclusion of titanium group elements in the same group of the periodic table is justified by the similarity and gradation in their properties as discussed below :

The electronic configurations of these elements in the ground state given as Ti (Z = 22) → 2, 8, 10, 2 ($3d^2.4s^2$); Zr (Z = 40) → 2, 8, 18, 10, 2 ($4d^2.5s^2$); Hf (Z = 72) → 2, 8, 18, 32, 10, 2 ($5d^2.6s^2$) indicate that the valence-shell configurations can be represented by $(n-1)d^2.ns^2$ showing that the extra electron goes to $(n-1)d$ orbitals. Thus these are *d*-block (transition) elements. All the elements have 2 electrons in the outer most shell. More common oxidation states are +2, +3 and +4. +2 oxidation state is very unstable and so strongly reducing that it reduces water and itself is oxidised to +3 state. +3 oxidation state is comparatively more stable and hence the compounds in this state are reducing agents. Since M^{3+} ions (+3 oxidation state) have one unpaired electron [$M^{3+} \rightarrow (n-1)d^1$], the compounds in this oxidation state are paramagnetic. Due to *d–d* transition of one $(n-1)d$ electron, the compounds of M^{3+} ions show one band in the visible spectrum and hence are purple coloured. +4 oxidation state is most common oxidation state for these elements. Compounds of M^{4+} ion have the following properties : (*i*) Since the amount of energy to remove all the four $(n-1)d^2.ns^2$ electrons to get M^{4+} ions is large, the anhydrous compounds having M^{4+} ion (*e.g.* $TiCl_4$) are covalent. (*ii*) The covalent compounds are tetrahedral. (*iii*) Since the element in +4 oxidation state has no electron (d° configuration), the compounds in this state are diamagnetic and colourless or white. Lower oxidation states undergo disproportionation into higher and more lower oxidation states. Zero, –1 and –2 oxidation states are shown in $[Ti(dipy)_3]^\circ$, $Li[Ti(dipy)_3]$. 3.5 THF and $Li_2[Ti(dipy)]$, 5 TIIF respectively. (THF tetrahydrofuran). The covalent radii increase from Ti to Zr and then decrease to Hf. Ionic radii of M^{4+} ions increase from Ti^{4+} to Hf^{4+}. No definite hydroxides, $M(OH)_4$ are known. The hydroxides are really hydrated oxides. These metals, on heating with O_2 above 800°C, give dioxides (MO_2) which are stable, non-volatile and insoluble and become refractory on heating. TiO_2 is amphoteric (though more acidic than basic). It dissolves in alkalies to form titanates and in acids to form titanyl compounds. ZrO_2 and HfO_2 are more basic and less acidic. The metals also form peroxides and proxy compounds when reacted with H_2O_2. Ti and Zr give complete series of tetrahalides. Hf gives only HfF_4 and $HfCl_4$. MX_4 tetrahalides are formed by the interaction of the metal with halogen. $TiCl_4$ is formed by heating TiO_2 with carbon and chlorine. Other tetrahalides of Ti can be prepared from $TiCl_4$ by the reaction with appropriate HX. Tetrafluorides are largely ionic while other tetrahalides are predominantly covalent volatile substances. Except tetrafluorides all other tetrahalides are readily hydrolysed by H_2O. The extent of

hydrolysis decreases from Ti to Hf. TiX_4 compounds are hydrolysed to TiO_2 while ZrX_4 and HfX_4 give $ZrOX_2$ and $HfOX_2$. Tetrahalides act as electron pair acceptor (Lewis acid) donated by the donor atoms like F^-, Cl^-, phosphines (R_3P), arsines (R_3As), R_2O, NH_3, pyridine and $(CH_3)_3$ N and form complexes or addition compounds. These elements are very hard metals, good conductors and possess high melting and boiling points. These are unreactive at ordinary temperature but combine on heating with O_2 to give dioxides (MO_2) and with halogens to give tetrahalides (MX_4). Hydrogen, nitrogen, carbon and boron give hydrides ($MH_{1.7, 2.0}$), nitrides (MN), carbides (MC) and borides (MB and MB_2) respectively. These are interstitial compounds, very hard and refractory (can withstand high temperatures). These metals are not attacked by dil. acids or alkalies. This is due to the formation of a protective oxide film. Ti dissolves slowly in hot and conc. acids and explodes in fuming HNO_3. Zr dissolves in acqua regia and to a smaller extent in hot conc. H_2SO_4. The best solvent for Ti is HF which forms hexafluoro complex with it. As a result of *lanthanide contraction* Hf has almost the same atomic (covalent) ionic radius as Zr. The similarity in size of the atoms and ions of these two elements is responsible for similarity in their properties. The chemical properties of the two elements are so similar that till recently their separation from each other was considered difficult. Now these are separated by ion exchange technique. Ti^{4+} does not form any normal salt with oxy-acids. However the normal salts of Zr^{4+} ion like $Zr(SO_4)_2$ have been obtained.

Group 5 (V B) : V_{23}, Nb_{41} and Ta_{73}

Group VB of the periodic table consists of three elements which are *Vanadium* (V), *Niobium* (Nb) and *Tentalum* (Ta).

Position of Vanadium Group Elements in the Periodic Table : Position of Vanadium in the Periodic Table

The inclusion of vanadium group elements in the same group is justified by the similarity and gradation in their properties. Some of these properties are discussed below :

The electronic configurations of these elements in the ground state given as V (Z = 23) → 2, 8, 11, 2 ($3d^2.4s^2$); Nb (Z = 41) → 2, 8, 18, 12, 1 ($4d^4.5s^1$); Ta (Z = 73) → 2, 8, 18, 32, 11, 2 ($5d^3.6s^2$) show that, excepting Nb, the valence-shell configuration of the remaining two elements can be represented as $(n–1)d^3.ns^2$. In case of Nb one electron from 5*s* orbital gets shifted to 4*d* orbital and hence the valence-shell configuration of Nb becomes $4d^4.5s^1$ instead of the expected configuration namely $4d^3.5s^2$. The valence-shell configurations also show that the extra electron goes to $(n–1)d$ orbital and hence these are *d*-block (transition) elements. It is also evident that these elements have 5 electrons in their valence-shell. They show a variety of oxidation states. The stability of +5 state increases from V to Ta. Thus V(+ 5) compounds are reduced all the way to V(+2) compounds and Nb (+5) and Ta (+5) compounds remain stable towards reduction. Consequently V(+5) compounds are good oxidising agents while those of Nb (+5) and Ta (+5), being stable, are not, Lower oxidation states become less stable on moving down from V to Ta. The ionic character of compounds of each element decreases with

the decrease of cationic size (*Fajans's rule*). Thus, since V (+2) > V (+3) > V (+4), V(+2) compounds are more ionic than those of V (+3) and (V +4). Consequently V (+4) compounds (*e.g.* VCl_4) are covalent. These metals are unreactive at ordinary temperatures. But, on heating, they show their reactivity. On heating with O_2 these elements give M_2O_5 type pentoxides. Vanadium also gives V_2O_4 in addition to V_2O_5, The basic character of M_2O_5 type oxides increases from V_2O_5 to Ta_2O_5. Thus V_2O_5 is amphoteric (but more acidic than basic) while Nb_2O_5 and Ta_2O_5 are less acidic than basic. This type of variation in the basic character of M_2O_5 oxides shows that the metallic character of the elements increases from V to Ta on descending the group. The ionic character of their compounds decreases as the oxidation state of the element increases. For example V (+2) compounds are ionic. V (+3) compounds are less ionic while V (+4) compounds (*e.g.* VCl_4) are definitely covalent. Since the compounds with lower oxidation states have incomplete *d*-orbitals, these are *coloured*, while those with higher oxidation states which have *completely-filled d-orbitals* are *colourless*. For example the pentoxides namely Nb_2O_5 and Ta_2O_5 have completely filled *d*-orbitals and are, therefore, colourless. V_2O_5 is however, red-orange. Its orange colour is considered to be due to some defects in the crystal structure of the oxide. The colour of NbX_5 is considered to be due to charge transfer. Vanadium, on heating with halogens, gives VF_5, VCl_5, VCl_4, VCl_3, VI_3 halides while Nb and Ta give only MX_5 pentahalides (M = Nb, Ta). All these halides are covalent and are, therefore, volatile and get readily hydrolysed On heating with N_2, H_2 and carbon, these elements form nitrides (MN), hydrides and carbides (MC and MC_2). Nitrides are interstitial compounds. MC type carbides are interstitial, refractory and hard while MC_2 type carbides are ionic and react with water to liberate acetylene. Hydrides are non-stoichiometric and the amount of hydrogen absorbed depends on the temperature and pressure. $VH_{0.71}$, $NbH_{0.86}$ and $TaH_{0.76}$ are the examples of non-stoichiometric hydrides. The tendency of these elements to forms the complexes decreases with the increase of atomic size. Thus vanadium which has the smallest size forms the largest number of complexes while Ta gives the smallest number. Tetraperoxy compounds of $[M(O_2)_4]^{3-}$ type (M = V, Nb and Ta) are known. In these compounds V, Nb and Ta are in +5 oxidation state. $K_3[V(O_2)_4]$ is obtained by adding alcohol to the blue solution obtained by treating V_2O_5 with KOH and H_2O_2. $K_3[V(O_2)_4]$ is isomorphous with $K_3[Cr(O_2)_4]$. $K_3[Nb(O_2)_4]$ and $K_3[Ta(O_2)_4]$ can also be prepared by similar methods. In addition to $[V(O_2)_4]^{3-}$ vanadium also gives $[HV(O)(O_2)_3]^{2-}$, $[HV(O)_2(O)_2]^{2-}$ and $[V(O)(O)_2]^{+}$ peroxy compounds.

Group 6 (VI B) : Cr_{24}, Mo_{42} and W_{74}

Group VI B of the periodic table consists of three elements which are *Chromium* (Cr). *Molybdenium* (Mo) and *Tungsten* (W). These are called *Chromium group elements.*

Position of Chromium Group Elements in the Periodic Table

The inclusion of chromium group elements in the same group is justified by the similarity and gradation in their properties. Some of these properties are discussed below :

The electronic configurations of these elements in the ground state given as : Cr (Z = 24) → 2, 8, 13, 1 ($3d^5.4s^1$); Mo (Z = 42) → 2, 8, 18, 13, 1 ($4d^5.5s^1$); W (Z = 74) → 2, 8, 1, 2, 12, 2 ($5d^4.6s^1$) show that, excepting W, the valence-shell configuration of the remaining two elements can be represented as $(n-1)d^5.ns^1$. In case of these two elements one electron from ns orbital gets shifted to $(n-1)d$ orbital and hence the observed configuration becomes $(n-1)\ d^5.ns^1$ instead of the expected configuration, $(n-1)\ d^4.ns^2$. The observed valence-shell configuration of W is the same as the expected configuration. The valence-shell configuration of all the three elements shows that the extra electron goes to $(n-1)\ d$ orbital and hence these are *d*-block (transition) elements. It is also evident that these elements have six electrons in their valence- shell. These elements show variable oxidation states. This is because of the fact that the energy of $(n-1)d$ orbitals is almost the same as that of *ns* orbitals and hence the electrons from both the orbitals can be used for bonding. Most stable oxidation state for Cr is +3 while that for Mo and W is +5. This shows that with increase of atomic number the higher oxidation state becomes more stable while the lower one becomes less stable. *The stability of the hexavalent compounds increases with the atomic number.* Chromic acid is one of the well known powerful oxidising agents; it gives out oxygen and reverts to a chromic salt in which it is positively trivalent. Molybdic acid is only a weak oxidising substance but tungstic and uranic acid are stable acids, devoid of oxidising character. In metal carbonyls like $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ these metals have *zero oxidation state.* The most stable chromium salts have the valency 2 (*chromous*) and 3 (*chromic*). These are hard silvery metals. These are harder than glass and are refractory. Ionisation energy values of these elements gradually increases from Cr to W. The density of these elements increases gradually from Cr to W. All the three metals have high melting and bonding points and these values increase with the increase in atomic number. All the three elements have almost the same electronegativity. The size of M atoms and M^{6+} ions increase from Cr to W. The size of Mo and W are almost the same because of lanthanide contraction. All the three metals form excellent alloys. For example Cr is used in making stainless steel, Mo and W, when alloyed with steel, give very hard alloys. All the three metals combine with S and N_2 and form sulphides and nitrides respectively. All the three metals combine with O_2 and form trioxides of RO_3 type in which R(R = Cr, Mo or W) is in +6 oxidation state. All the three metals form oxy-acids of H_2RO_4 type. The strength of these acids decreases from H_2CrO_4 (very strong acid) to H_2WO_4 (very weak acid). Their oxidising properties decrease from H_2CrO_4 to H_2WO_4. All the three metals form oxychlorides of RO_2Cl_2 type. These are obtained by dissolving RO_3 oxides in conc. HCl in presence of H_2SO_4 or by direct addition of Cl_2 to RO_3 oxide.

Position of Cr in the Periodic Table

A look at the position of Cr in the periodic table shows that (1) Cr lies with Mo and W in the same sub-group (2) Mn and Fe lie to its right hand side (3) S is acting as a bridge element between the elements of sub-groups VIA and VI B. Thus the position of Cr in the periodic table is justified by discussing the similarities of Cr with the above said elements. These similarities are discussed as follows :

1. Similarities of Cr with Mo and W. The similarities of Cr with Mo and W have already been discussed under "*Position of Chromium Group Elements in the Periodic Table*".

2. Similarities of Cr with Mn and Fe. The points showing the similarity between the three metals are (*i*) None of them occurs in nature in the free state. (*ii*) These are transition elements and show all the properties of transition elements. (*iii*) Their hydroxides *viz.* $Cr(OH)_3$, $Mn(OH)_2$ and $Fe(OH)_3$ are insoluble in H_2O. (*iv*) These are hard and shining metals. The melting and boiling points of all the three metals are high. (*v*) They form the oxides of MO (*e.g.* CrO, MnO, FeO) and M_2O_3 (*e.g.* Cr_2O_3 Mn_2O_3, Fe_2O_3) type. (*vi*) Oxides of Cr and Fe (Cr_2O_3 and Fe_2O_3) are isomorphons. (*vii*) CrO_3 and Mn_2O_3 are acidic in nature, since they dissolve in water, giving chromic (H_2CrO_4) and manganic (H_2MnO_4) acids. The salts of H_2CrO_4 (called chromates) and H_2MnO_4 (called manganates) are isomorphous *e.g.* K_2CrO_4 and K_2MnO_4. (*viii*) They give excellent alloys. (*ix*) Cr and Fe form isomorphous alums, *e.g.* K_2SO_4. $Fe_2(SO_4)_3$. $24H_2O$ (called *ferric alum*) and K_2SO_4. $Cr_2(SO_4)_3$ $24H_2O$ (*chrome alum*) are isomorphous. (*x*) Both Cr and Fe become passive on treatment with conc. HNO_3.

3. Similarities of Cr with S. The points showing similarities between Cr and S are : (*i*) Both show hexavalency. (*ii*) Trioxides of both (*i.e.*, CrO_3 and SO_3) are acidic and react with water to give chromic and sulphuric acid. The salts of these acids, chromates and sulphates are isomorphous. (*iii*) $BaSO_4$ and $BaCrO_4$, and $PbSO_4$ and $PbCrO_4$ are insoluble in water. (*iv*) CrO_2Cl_2 and SO_2Cl_2 both react with water to give H_2CrO_4 and H_2SO_4 respectively.

Comparison between Cr and S.

The comparison between Cr and S consists of making a discussion of the similarities and dissimilarities between Cr and S.

(*a*) **Similarities.** These have already been discussed above.

(*b*) **Dissimilarities.** (*i*) Sulphur is a *typical element* with *six* electrons in its outermost orbit ($3s^2p^4$) while chromium is a *transition element* with *one* electron in its outermost orbit ($3d^54s^1$). (*ii*) Sulphur is a typical non-metal while chromium shows *metallic behaviour.* It is hard, lustrous and has high density, melting and boiling point. (*iii*) Sulphur readily burns in air and forms SO_2 while chromium is not acted upon by air. (*iv*) Sulphur dissolves in alkalies to form thiosuiphate while chromium remains unaffected by alkalies. (*v*) Dilute acids have on action on sulphur but chromium dissolves in them to form salts. Concentrated HNO_3 oxidises sulphur to form H_2SO_4 but chromium remains passive. (*iv*) Sulphur combines with metals and non-metals to give sulphides. Chromium forms alloys with metals.

Group 7 (VII B) : Mn_{25}, Tc_{43} and Re_{75}

Group VII B of the periodic tae consists of three elements which are *Manganese* (Mn), *Technitium* (To) and *Rhenium* (Re). Of these the last two are rare metals. The elements of this group are called manganese group elements. Out of these metals Tc does not occur in nature and was the first man-made element. It is radioactive and its chemistry is not fully known.

Position of Manganese Group Elements in the Periodic Table

The inclusion of manganese group elements in the same group of the periodic table is justified by the similarity and gradation in their properties. Some of these properties re discussed below:

The electronic configurations of these elements in the ground state given as : Mn (Z = 25) → 2, 8, 13, 2 ($3d^5.4s^2$); Tc (Z = 43) → 2, 8, 18, 13, 2 ($4d^5.5s^2$) : Re (Z = 75) → 2, 8. 18, 32, 13, 2 ($5d^5.6s^2$), show that the valence-shell configurations of these elements can be represented by $(n-1)d^5.ns^2$ showing that the extra electron goes to $(n-1)d$ orbital and hence these are *d*-block (transition) elements. In accordance with their electronic configurations these metals show a maximum oxidation state of +7 in compounds like $KMnO_4$. Mn_2O_7, Re_2O_7 etc. In addition to this state, they also show lower oxidation states. The stability of higher oxidition states increases gradually from Mn to Re, *e.g.* the permanganates, MnO_4^-, decompose readily in acidic, alkaline and neutral solutions evolving O_2 and thus act as strong oxidising agents, while pertechnetates, TcO_4^- and perrhenates, ReO_4^- are more stable and hence have less oxidising power. The stability of lower oxidation states decreases from Mn to Re. All these elements show zero oxidation states in carbonyls like $Mn_2(CO)_{10}$, $Tc_2(CO)_{10}$ and $Re_2(CO)_{10}$.

Both Mn and Re form a number of oxides while the most important oxide of Tc is Tc_2O_7. The basic character of the oxides decreases gradually with the increase of oxidation state of the element. For example, the oxides *viz.* MnO and Mn_2O_3 (in which Mn is in +2 and +3 state respectively) are *basic and ionic*, MnO_2 (in which Mn is in +4 state) is *amphoteric* and *does not exist as* Mn^{4+} *ion*, MnO_3 (in which Mn is in +6 state) is an *unstable acidic oxide* and Mn_2O_7 (in which Mn is in +7 state) is *strongly acidic.* The permanganic acid, $HMnO_4$ which corresponds to Mn_2O_7 is the *strongest acid known.* This acid exists only in solution. Thus we see that *with the increase of oxidation state of Mn atom in its oxides, the character of these oxides changes from basic to amphoteric and finally to acidic.* All the three elements form the oxy-acids of HMO_4 type (M = Mn, Tc and Re), *e.g.* $HMnO_4$ (*permanganic acid*), $HTcO_4$ (*pertechnetic acid*) and $HReO_4$ (*perrhenic acid*). The salts of these acids are called permanganates (MnO_4^-), *pertechnetates* (TcO_4^-) and *perrhenats* (ReO_4^-) respectively. These salts are analogous to each other.

Position of Mn in the periodic Table

A look at the position of Mn in the periodic table shows that (1) Mn lies with Tc and Re in the same sub-group (2) Cr lies to its left hand side (3) Fe lies to its right hand side (4) Cl is acting as a bridge element between the elements of sub-groups VII A and VII B. Thus the position of Mn in the periodic table is justified by discussing the similarities of Mn with the above said elements. These similarities are discussed below :

1. Similarities of Mn with Tc and Re (*Vertical relationship*). This has already been discussed above under "*Position of manganese group elements in the periodic table*".

2. Similarities of Mn with Cr (*Horizontal relationship*). For this see "*Position of Cr in the periodic table (Group VI B)*".

3. Similarities of Mn with Fe (*Horizontal relatsonship*). For this see "*Position of Cr in the periodic table (Group VI B)*".

4. Similarities of Mn with Cl. Mn also shows some similarities with chlorine which is the bridge element. These similarities are very slight and are shown in their highest oxidation states, *e.g.* (*i*) The heptoxides of both the elements (Mn_2O_7 and Cl_2O_7) are similar to each other, *e.g.* both these oxides are acidic, volatile and explosive. (*ii*) Permanganates (MnO_4^-) and perchlorates (ClO_4^-) are isomorphous salts and have similar solubilities, *e.g.* both $AgMnO_4$ and $AgClO_4$ are sparingly soluble in water.

Groups 8, 9 and 10 (VIII) : Ferrous Metals (Fe_{26}, Co_{27}, Ni_{28}) and Platinum Metals (Ru_{44}, Rh_{45}, Pd_{46}; Os_{76}, Ir_{77}, Pt_{78})

Group VIII of the periodic table consists of nine elements which are grouped into three triads namely : (*i*) First triad which consists of iron (Fe), cobalt (Co) and nickel (Ni) (*ii*) Second triad, consisting of ruthenium (Rh), rhodium (Rh) and palladium (Pd) (*iii*) Third triad, consisting of osmium (Os), iridium (Ir) and platinum (Pt). The elements of the first triad belong to the first transition series and are called *ferrous metals* while those of second and third triads are the members of the second and third transition series respectively and are collectively known as the *platinum metals.* Ru, Rh and Pd are called *light platinum metals* while Os, Ir and Pt are known as *heavy platinum metals* on the basis of their density as compared to platinum.

Position of Ferrous Metals (Fe, Co, Ni) in the Periodic Table

We know that the elements lying to the left of Fe are Mn (Group VII B) and Cr (Group VI B), the element lying to the right of Ni is Cu (Group I B) while the elements lying below Fe, Co and Ni are Ru, Os (below Fe), Rh, Ir (below Co) and Pd, Pt (below Ni). Thus the inclusion of ferrous metals in the same group is justified by discussing the following similarities

1. Similarities between Fe, Co and Ni. The electronic configurations of these element given as : Fe (Z = 26) $\rightarrow$ 2, 8, 14, 2 ($3d^6.4s^2$); Co (Z = 27) $\rightarrow$ 2, 8, 15, 2 ($3d^7.4s^2$); Ni (Z = 28) $\rightarrow$ 2, 8, 16, 2 ($3d^8.4s^2$) show that Fe, Co and Ni have two electrons in their outermost shell (*i.e. 4th shell*) but their kernels are incomplete. As the atomic number increases from Fe to Ni, the number of electrons in the *d*-orbital of the penultimate shell (*i.e. 3rd shell*) increases by one in each succeeding element. All the ferrous metals particularly Fe and Ni occur in nature in large quantities. Their natural abundance is attributed to the high stability of their atomic nuclei. These are all greyish white hard metals of high densities. The hardness and density increases from Fe to Ni. These have fairly close melting and boiling points which are uniformly high. Very similar melting points seem to indicate that the average number of electrons per atom contributing to the metallic bonding is nearly the same per each one of them. Their oxidation potentials, particularly of Co and Ni, are very close and uniformly positive indicating that they can liberate hydrogen gas from acids very slowly. Fe reacts readily while Ni and Co react only slowly. This behaviour is in accordance with similar values of

electrode potentials of these metals. All the three metals are *ferromagnetic*, *i.e.*, these are strongly attracted by a magnet and remain magnetised even after the removal of the magnetic field. The ferromagnetic property *decreases* from Fe to Ni. At elevated temperatures called their *curie points*, the metals lose ferromagnetic property and become paramagnetic. All the metals show allotropy and exist in *two solid phases.*

Fe shows both +2 (in *ferrous salts*) and +3 (in *ferric salts*) oxidation states, cobalt mostly exhibits +2 oxidation state but also forms alums and complexes [*e.g.*, $CoCl_6^{3-}$, $Co(CN)_6^{3-}$] in which it shows +3 state while nickel usually shows +2 state. In certain complexes nickel also shows +1 state, *e.g.*, $K_2[Ni(CN)_3]$, NiCN etc. Nickel does not form Ni^{3+} ion. The removal of a 3*d*-electron from M^{2+} cations to oxidise them into M^{3+} cations becomes more and more difficult as we proceed from Fe^{2+} to Ni^{2+}, *i.e.*, the stability of M^{2+} cations is in the order : $Fe^{2+} < Co^{2+} < Ni^{2+}$ and hence the reducing properties of these ions is in the order : $Fe^{2+} > Co^{2+} > Ni^{2+}$. The increase in stability from Fe^{2+} to Ni^{2+} ions is evident from the behaviour of their M(II) oxide on heating. *e.g.*, FeO is oxidised to Fe_2O_3 simply on heating, CoO changes to Co_3O_4 but does not undergo further oxidation to Co_2O_3 while NiO is stable. *i.e.* it remains unaffected. The tendency of these elements to show + 3 state decreases sharply from Fe to Ni, *i.e.*, the stability of M cations is in the order : $Fe^{3+} > Cb^{3+} > Ni^{3+}$, indicating that the oxidising properties of Fe^{3+}, Co^{3+} and Ni^{3+} cations are in the order : $Fe^{3+} < Co^{3+} < Ni^{3+}$. The reason for this difference in the +3 state is that, while Fe ion has a half-filled 3*d*-orbital ($Fe^{3+} \rightarrow 3d^5 4s^0$) and therefore stable, Co^{3+} and Ni^{3+} have relatively unstable $3d^6$ and $3d^7$ configurations respectively ($Co^{3+} \rightarrow 3d^7 4s^0$, $Ni^{3+} \rightarrow 3d^7 4s^0$). The +4 state is relatively uncommon for these elements. While +6 oxidation state is reported for iron in ferrate ion, $[FeO_4]^{2-}$ which is unstable and oxidising agent, this state has not been reported for Co and Ni. Lower oxidation states such as zero are found in complexes having *pi*-bonding ligands such as CO. Thus in the carbonyls, $Fe(CO)_5$, $Co_2(CO)_8$ and $Ni(CO)_4$ these metals show zero oxidation state.

They are weak metals and, therefore, their salts react acidic in solution. All of them occlude hydrogen, Ni being superior to the other two in this respect. As a result of this property they are used as catalyst in certain reactions involving the addition of hydrogen. They give rise to similar *complex cyanides.* All the three elements from isomorphous vitriol type sulphates $MSO_4.7H_2O$, where M = Fe(II), Co(II) or Ni(II). For example $FeSO_4.7H_2O$ is isomorphous with $CoSO_4.7H_2O$. All these sulphates form schonite type double sulphates, $M^+_2 SO_4.M_2^{2+} SO_4. 6H_2O$. Of these Mohr's salt, $(NH_4)_2SO_4. FeSO_4.6H_2O$ is very important. These schonites are also isomorphous with each other, *e.g.*, Mohr's salt is isomorphous with nickel ammonium sulphate, $(NH_4)_2SO_4. NiSO_4.6H_2O$. Since Fe(III) and Co(III) [but not Ni(III)] are known as aquo ions, these form alum type sulphates : $M_2^+SO_4.M_2^{3+}(SO_4)_3. 24H_2O$ M^+ = Na, K, NH_4^+ etc. and M^{3+} = Fe(III) or Co(III). Under the influence of conc. HNO_3 all the three metals become passive. This tendency increases in the order : Fe < Co < Ni. All the three metals are reactive and reactivity decreases from Fe to Ni.

2. Similarities of Fe with Cr and Mn. These similarities have already been discussed under "*Position of Cr in the periodic table*".

3. Similarities between Ni and Cu. Both the metals give coloured salts. Copper salts are bluish and green, while the salts of nickel are green. The stable salts of nickel and copper (one-*ous* and the other -*ic*) are both bivalent. Both give two series of salts : *cuprous* and *cupric* ; *nickelous* and *nickelic*. Both form *isomorphous* sulphates, *e.g.* $CuSO_4.5H_2O$; $NiSO_4.7H_2O$. Both give black sulphides. Both give complex compounds, *e.g.* $[Cu(NH_3)_4]SO_4$, $K_2[Ni(CN)_4]$. The oxides of both the elements can be obtained by heating their carbonates or nitrates. Both the elements form schonite type double sulphates, $M^+_2\ SO_4\ M^{2+}SO_4.\ 6H_2O$ where $M = NH_4^+$ etc., $M' = Cu(II)$ or $Ni(II)$. Both the elements show a co-ordination number of 4. Their M^{2+} ions are almost similar in size (Cu^{2+} = 0.69A, Ni^{2+} = 0.72Å). Their hydrated salts in solution react with acid due to hydrolysis. Basic carbonates of the general formula $MCO_3.M(OH)_3$ are precipitated on treating their salt solutions with Na_2CO_3. Both of them show catalytic properties. Salts of both the metals give precipitates of their hydroxides when treated with NH_4OH. The hydroxides of both dissolve in excess of NH_4OH to form complex salts.

4. Similarities between Fe, Ru and Os. All the three metals form isomorphous complex cyanides. Ferrites. (FeO_3^{2-}) and ruthenites (RuO_3^{2-}) are similar. Ferrates, rutherates and osmates (MO_4^{2-}) are also similar.

5. Similarities between Co, Rh and Ir. These elements form similar complex cyanides, ammines, nitrites etc. The sulphates of all the elements form true alums.

6. Similarities between Ni, Pd and Pt. These elements form similar complex ammines, cyanides and nitrites. These elements are relatively inert in their respective triads. All show variable valency. All can occlude H_2 and hence act as catalysts. They give similar oxides and chlorides.

Similarities between Pt and Au

Both the metals occur native. They have high melting points and show metallic lustre. They are malleable, ductile and good conductors of heat and electricity. Both are noble metals and are not acted upon by air, water, alkalies and acids. Both have similar electronic configurations. Both form similar complex halogen acids like $HAuCl_4$, $H_2Pt\ Cl_6$. Colloidal solutions of both the metals can be prepared by Bredig's method.

Position of Cobalt in the Periodic Table

Cobalt is present in group VIII of the periodic table. To its left and right are lying Fe arid Ni respectively which belong to the same group and period. Below it are lying Rh and Ir. Thus the position of Co in the periodic table is justified by discussing the following similarities.

1. Similarities between Fe, Co and Ni. These have already been discussed under "*Position of ferrous metals in the periodic table*".

2. Similarities between Co, Rh and Ir. This has been discussed above.

Position of Nickel in the Periodic Table

Nickel is present in group VIII of the periodic table. To its left are lying Fe and Co (same group) while to its right is lying Cu (Group IB). Below it are Pd and Pt which are in the same sub-group. Thus the position of nickel in the periodic table is justified by discussing the following similarities :

1. **Similarities between Fe, Co and Ni.** This has been discussed above.
2. **Similarities between Ni, Pd and Pt.** These have been discussed above.
3. **Similarities between Ni and Cu.** See *Position of ferrous metals.*

Position of Platinum in the Periodic Table

We know that Pt is present in group VIII of the periodic Table. To its right is lying Au (Group IB) and above it are lying Ni and Pd (same group). Thus the position of Pt in the periodic table is justified by discussing the following similarities :

1. **Similarities between Pt and Au.** These have been discussed above.
2. **Similarities between Ni, Pd and Pt.** These have been discussed above.

Group 11 (IB) : Cu_{29}, Ag_{47} and Au_{79} (Coinage Metals)

Group IB of the long form of periodic table consists of three elements which are : *Copper* Cu), *Silver* (Ag) and *Gold* (Au). These are collectively known as *coinage metals* or *currency metals* because they have been used in the past for the manufacture of coins for currency. However, now their main uses are quite different. These are also called *copper group metals.*

Position of Coinage Metals in the Periodic Table

We know that Cu, Ag and Au belong to group IB and the elements lying to their left are Ni, Pd and Pt (Group VIII) while those lying to their right are Zn, Cd and Hg (Group II B).

Thus the inclusion of Cu, Ag and Au in the same sub-group is justified by discussing the following similarities :

1. Similarities between Cu, Ag and Au. On account of their great inert character, all these metals are found in the native state in nature. All are hard, malleable and ductile metals. They possess characteristic metallic lustre and take high polish. They have high density, melting points and boiling points and low atomic volume. All are good conductors of heat and electricity. Ag is the best conductor of heat and electricity. The electronic configurations of these elements given as Cu(Z = 29) $\rightarrow$ 2, 8, 18, 1 ($3d^{10}.4s^1$) Ag(Z = 47) $\rightarrow$ 2, 8, 18, 18, 1 ($4d^{10}.5s^1$); Au(Z = 79) $\rightarrow$ 2, 8, 18, 32, 18, 1 ($5d^{10}.6s^1$) show that the ultimate shell of these elements has *one* electron (s^1 electron) while the penultimate shell contains 18 (s^2 p^6 d^{10}) electrons. All the elements are weakly electropositive and hence are almost unreactive. These metals show variable valency. These metals are not able to displace H_2 from the acids, since they are less electropositive than hydrogen. Zn, Fe and Mg can displace these metals from their salt solutions. The *monovalent salts* of these metals are colourless and generally insoluble in water. For example,

cuprous chloride (CuCl) and silver chloride (AgCl) are both colourless and insoluble in water. All of them form *complex salts* and in them metal may be a part of the complex cation or of the complex anion.

2. Similarities between Cu and Zn. Both the metals show bivalency. Sulphides, phosphates and carbonates of both the metals are insoluble in H_2O while their chlorides and sulphates are soluble in H_2O. Both the metals form isomorphous salts like $CuSO_4.\ 5H_2O$; $ZnSO_4\ 7H_2O$; form double salts like $MSO_4.(NH_4)_2SO_4.6H_2O$ and complex compounds.

3. Similarities between Cu and Ni. See *Position of ferrous metals.*

4. Similarities between Ag and Cd. Both are white metals. Both form complexes like $[Ag(NH_3)_2]^+$, $[Cd(NH_3)_4]^{2+}$. Their oxides are coloured and get reduced when heated with carbon.

5. Similarities between Ag and Pd. Both are metals and are white in colour. Both are noble metals. Both act as catalysts in their finely-divided state. Both the metals form complex compounds.

Group 12 (II B) : Zn_{30}, Cd_{80} and Hg_{48}

Group II B of the long form of periodic table consists of three elements namely *zinc* (Zn), *cadmium* (Cd) and *mercury* (Hg). These elements are collectively known as *zinc group elements.*

Position of Zinc Group Elements in the Periodic Table

The inclusion of Zn, Cd and Hg in the same sub-group II B of the periodic table is justified by the similarities in their properties and gradation in them with the rise of atomic number from Zn to Hg as shown below :

The electronic configurations of these elements given as : Zn(Z = 30) $\rightarrow$ 2, 8, 18, 2 ($3d^{10}.4s^2$); Cd(Z = 48) $\rightarrow$ 2, 8, 18, 18, 2 ($4d^{10}.5s^2$) ; Hg(Z = 80) $\rightarrow$ 2, 8, 18, 32, 18, 2 ($5d^{10}.6s^2$) show that the ultimate shell has two electrons (s^2 electrons) while the penultimate shell contains 18 electrons ($s^2p^6d^{10}$ electrons). Thus the valence-shell configuration can he represented as $(n-1)d^{10}ns^2$. Thus *these are transitional elements*, but they do not show many properties which are shown by transition elements, *e.g.*, (*i*) They do not show variable valency (*ii*) Many of their compounds are white. (*iii*) Their melting and boiling points are very low.

These elements do not occur free in nature. Important ore of the metals is sulphide. We have seen that the valence-shell configuration of these elements can be represented as $(n-1)d^{10}.ns^2$. When s^2 electrons are lost by these elements, M^{2+} ion produced possesses $(n-1)d^{10}$ configuration. This configuration is stable and hence cannot lose any more electrons. Thus all the elements show +2 oxidation state. It may be noted that Hg forms two series of salts–mercurous salts containing Hg_2^{2+} ion and *mercuric* salts containing Hg^{2+} ion. Both these ions are in +2 oxidation state. These are greyish white lustrous metals, malleable end ductile. The malleability and ductility gradually decrease as the atomic number increases from Zn to Gd to Hg. Except Hg which is a liquid, other two elements are moderately hard. The hardness of Cd and Zn is in the order : Cd < Zn. All the

three metals are good conductors of electricity. The atomic radii of these elements are fairly large. Atomic and ionic radii both increase with the increase of atomic number from Zn to Cd to Hg. This accounts for the covalent character in them. The atomic volume increases from Zn to Hg due to an increase in the atomic radii in the same direction. All these elements have high values of density which gradually increases from Zn to Hg. These elements have very low melting and boiling points as compared to other elements because electrons from $(n–1)d$ orbital are not available for bonding. Excepting Hg, both the metals have higher melting and boiling points than the alkali metals present in the same period.

These metals have fairly high values of ionisation energy which indicate that these metals should be less reactive. In fact, they are even more reactive than the coinage metals (Cu, Ag and Au). This is due to their high values of reduction electrode potential for M^{2+}/M couple. It can also be noted that ionisation potential values do not show regular trends. These metals have low electronegativity values and these values decrease from Zn to Cd to Hg. These metals are not very reactive and their chemical reactivity decreases from zinc to mercury with the decrease in standard electrode potential which is negative in the case of mercury. Accordingly, zinc and cadmium dissolve in dilute mineral acids with the evolution of H_2 while Hg does not.

The action of air on these metals increases from Zn to Hg. For example in air, zinc is slowly coated with a bluish white film of its oxide which prevents further action while cadmium is much less affected and mercury is not affected at all. They *do not react with cold water.* Zinc and cadmium slightly decompose boiling water and decompose steam at red heat while mercury does not react with water at any temperature.

Metallic zinc and cadmium dissolve readily in dilute mineral acids forming corresponding salts with the liberation of H_2 (oxides of nitrogen or NH_3 in case of HNO_3). Hg remains unaffected by dilute acids. It dissolves in cold HNO_3 whether dilute or concentrated evolving respectively nitric oxide and nitrogen dioxide. It also remains unaffected by cold and concentrated H_2SO_4 but dissolves in boiling H_2SO_4 forming $HgSO_4$ and evolving SO_2.

Metallic zinc dissolves in caustic alkalies forming zincate (ZnO_2^{2-}) with the evolution of H_2 while Cd and Hg remain unaffected. When a caustic alkali is added to solutions of zinc, cadmium and mercuric salts, Zn^{2+} and Cd^{2+} ions are preciptated as their hydroxides while Hg^{2+} is precipitated as HgO. (The hydroxide of Hg is unknown)

All the three elements form stable complexes readily. The important *ligands* (*i.e.* lone pair donors) are cyanide ions, ammonia amines and chloride ions. The complexes of Hg^{2+} are much more stable than those of Zn^{2+} and Cd^{2+}. The co-ordination number in case of zinc and cadmium ions is 4 whereas in the case of Hg_2^{2+} ion, it is 4 as well as 2.

Their halides may be prepared by the direct combination of elements and have very low melting points and are easily volatile. The chlorides are freely soluble in organic solvents. The nature of the bond in the halides depends on the

polarising power of M^{2+} cation (M^{2+} = Zn^{2+}, Cd^{2+} or Hg^{2+}) and the polarisability of the halide anion. It may be noted that the polarising power of M^{2+} cation increases as $Zn^{2+} < Cd^{2+} < Hg^{2+}$ while the polarisability of halide ions increases as $F^- < Cl^- < Br^- < I^-$. Therefore CdI_2 is much less ionic than CdF_2. Similarly HgF_2 is ionic while $HgCl_2$ is covalent.

University Questions

1. Give reasons for the following :

(*i*) The salts of scandium group elements are colourless and diamagnetic.

(*ii*) Scandium group elements undergo hydrolysis readily.

(*iii*) Scandium forms complexes easily.

(*iv*) Sc^{3+} ion has greater polarising power.

2. Taking La and Ac as examples, compare and contrast the properties of *d*-block elements with *f*-block elements. (*Delhi Hons. 85*)

3. Lanthanium belongs to *f*-block although it has no electron in 5*f* orbital. Comment. (*Bombay 84*)

4. Discuss briefly the general characteristics of the elements of titanium group under the following heads : (*i*) oxidation states (*ii*) reactivity and passive behaviour (*iii*) nature of oxides (*iv*) formation of complexes. (*Bharathiar 86*)

5. Discuss the position of V, Nb and Ta in the periodic table. (*Delhi 85*)

6. How do the following change when we move from V to Ta ma Nb?

(*i*) Stability of various oxidation states shown by V, Nb and Ta.

(*ii*) Ionic character of the compounds of V, Nb and Ta with change in their oxidation states.

(*iii*) Basic character of the oxides *viz.* V_2O_5, Nb_2O_5 and Ta_2O_5. (*Delhi Hons. 86*)

7. Give the reason for the following :

(*i*) Vanadium has a greater tendency to form complexes than do niobium and tantalum.

(*ii*) The compounds of V B group elements in their lower oxidation states are coloured while those in higher oxidation states are colourless. (*Banaras 84; Lucknow 86*)

8. Give a comparative account of the general chemistry of Cr, Mo and W. Also discuss the position of these elements in the periodic table. (*Allahabad 88*)

9. Discuss the position of Mn in the periodic table. (*Madras 86; Bharathiar 86; M.D. Rohtak 84*)

10. Indicate the resemblance in properties between (*i*) Mn and Cr (*ii*) Mn and Fe. (*Madras 86*)

11. Give reason for the following :

(*i*) The aqueous solution of Mn^{2+} has only a pale-pink colour. (*Madras 85*)

(*ii*) Mn with five unpaired electrons is less ferromagnetic than Fe with four unpaired electrons. (*Delhi Hons. 87*)

(*iii*) Mn is an example of an element exhibiting a high degree of paramagnetic character. (*Andhra 85*)

12. Make a comparative study of Fe, Co and Ni and their compounds. (*Madras 86; Bharathiar 86; Madurai 86*)

13. Give the reasons for the following :

(*i*) Coinage metals show variable valency. (*Madras 85*)

(*ii*) The first iomisation potential of copper is higher than those of alkali metals but second and third ionisation potentials are lower. (*Punjab 85*)

14. Discuss the position of Cu, Ag and Au in the periodic table. (*Delhi 85*)

15. Why do you write murcurous ion as Hg_2^{2+} and cuprous ion as Cu^+ ? (*Delhi 85*)

16. Discuss the position of Zn in the periodic table with reference to electronic structure and characteristics of its oxide and chloride. (*Madras 86*)

17. Discuss the position of chromium or copper family elements in the periodic table. (*Kanpur 2000*)

CHAPTER

46 Extraction, Properties and Uses of Some d- and f-Block Elements

Titanium (Ti_{22})

Occurrence

Titanium is the ninth most abundant element in the earth's crust. Its main ores are : (*i*) *Rutile*, TiO_2 which is one of the three forms of TiO_2, and (*ii*) *Ilmenite*, $FeTiO_3$.

Extraction of Titanium Metal From Rutile Ore, TiO_2

Since titanium has high melting point and it reacts quite readily with air, O_2, N_2, H_2 and carbon at elevated temperatures, the extraction of the metal is a difficult task. The extraction of the metal from the rutile mineral consists of the following steps :

1. Conversion of rutile ore into $TiCl_4$. Rutile (TiO_2) mineral is heated with carbon in a current of Cl_2.

$$\underset{\text{Rutile ore}}{TiO_2} + C + 2Cl_2 \longrightarrow TiCl_4 + CO_2$$

2. Reduction of $TiCl_4$ to Ti metal. $TiCl_4$ obtained as above is reduced to Ti metal by any of the following methods :

(*a*) Kroll process. In this process vapours of $TiCl_4$ are passed over molten magnesium, when $TiCl_4$ is reduced to spongy Ti metal.

$$TiCl_4 + 2Mg \xrightarrow{830°C} \underset{\text{Spongy}}{Ti} + 2MgCl_2$$

The spongy metal is heated n an inert atmosphere of Ar to get a compact mass.

(*b*) I.C.I. process. In this process $TiCl_4$ is reduced by heating it with Na in an atmosphere of Ar.

$$TiCl_4 + 4Na \xrightarrow{\text{Heat}} Ti + 4NaCl$$

Extraction of Titanium Metal From Ilmenite Ore, $FeTiO_3$

The extraction of titanium metal from ilmenite ore consists of the following steps :

1. Conversion of ilmenite ore, $FeTiO_3$ into TiO_2. TiO_2 can be obtained from the ilmenite ore by the following processes :

(*a*) When ilmenite ore is heated with HCl in a current of Cl_2, TiO_2 is obtained.

$$\underset{\text{Ilmenite}}{2FeTiO_3} + 4HCl + Cl_2 \xrightarrow{\Delta} 2FeCl_3 + 2TiO_2 + 2H_2O$$

(*b*) The powdered ilmenite ore is fused with Na_2S. The product obtained consists of FeS, TiO_2 and Na_2O.

$$\underset{\text{Ilmenite}}{FeTiO_3} + Na_2S \xrightarrow{\text{Fuse}} \underbrace{FeS + TiO_2}_{\text{Insoluble}} + \underset{\text{Soluble}}{2Na_2O}$$

Now when the product consisting of FeS, TiO_2 and Na_2O is extracted with H_2O, FeS and TiO_2 remain insoluble and Na_2O goes into solution. The insoluble portion containing FeS and TiO_2 is treated with H_2SO_3 in presence of atmospheric O_2 when FeS is converted into soluble FeS_3O_3 but TiO_2 remains unaffected.

$$FeS + H_2SO_3 + \tfrac{1}{2}O_2 \text{ (From air)} \longrightarrow \underset{\text{Soluble}}{FeS_2O_3} + H_2O$$

$$TiO_2 + H_2SO_3 + \tfrac{1}{2}O_2 \text{ (From air)} \longrightarrow \text{No reaction}$$

(*c*) When ilmenite ore is mixed with carbon and heated in a current of Cl_2 at 360° a mass is obtained which consists of $FeCl_3$ and $TiCl_4$. Now when this mass is heated at 550°C, volatile $TiCl_4$ distils over. $TiCl_4$ thus obtained is hydrolysed by H_2O to get TiO_2.

$$\underset{\text{Ilmenite}}{2FeTiO_3} + 2C + 7Cl_2 \xrightarrow{350^\circ} \underbrace{2FeCl_3 + 2TiCl_4}_{\downarrow\ 550^\circ C} + 3CO_2\uparrow$$

$TiCl_4$ distils over

$$TiCl_4 + 2H_2O \xrightarrow{\text{Hydrolysis}} TiO_2 + 4HCl$$

2. Reduction of TiO_2 to Ti metal. TiO_2 obtained as above is reduced to titanium metal by any of the following methods :

(*a*) By alumino-thermic process. In this method TiO_2 is mixed with Al and the mixture is ignited with a suitable fuse.

$$3TiO_2 + 4Al \longrightarrow 2Al_2O_3 + 3Ti$$

(*b*) By heating with carbon. TiO_2 can also be reduced to free Ti metal by heating it with carbon.

$$TiO_2 + C \longrightarrow Ti + CO_2\uparrow$$

Purification of Titanium Metal

Titanium metal obtained either from rutile or from ilmenite contains many impurities. Impure metal can be purified by ***Van Arkel process*** in which impure titanium is heated with a limited amount of I_2 in an evacuated glass apparatus. TiI_4 vapours formed are allowed to diffuse on to a tungsten filament at a very

high temperature. The vapours of TiI_4 decompose and the pure Ti metal gets deposited on the W-filarnent.

$$\text{Impure Ti metal} + 2I_2 \xrightarrow[150\text{–}250^\circ]{} TiI_4(g) \xrightarrow[\text{filament}]{1800^\circ,\ \text{Tungsten}} \underset{\text{(gets deposited on W-filament)}}{\text{Pure Ti metal}} + 2I_2(g)\uparrow$$

Properties

Metallic titanium has a silvery lusture and when polished resembles steel appearance. Amorphous form is a dark grey powder resembling iron (reduced) in appearance. It is brittle at ordinary temperature but at low red heat it is readily malleable. The pure metal is very ductile. Its m.pt. and b.pt. are 1850°C and 3000°C. The fused metal is very hard and crystalline and scratches quartz. When rubbed against steel, it gives bright sparks. Titanium metal is stable in air at room temperature, but, when heated. it reacts with O_2 and N_2 present in air to form TiO_2 and TiN. Hot titanium metal decomposes steam to form TiO_2 with the evolution of H_2. With acids like H_2SO_4, HF, HNO_3, CH_3COOH etc. Ti (*III*) salts are formed with the evolution of H_2. With halogens, the metal gives tetrahalides. The metal combines with non-metals like H_2, S, C, Si etc. to form TiH_2, TiS, TiC, TiSi etc.

Uses of Titanium Metal and its Alloys

(*i*) Due to the strength, lightness, corrosion, resistance and low thermal expansion of Ti metal, it is used in high speed air- craft, naval and military projects and also in chemical industry. (*ii*) It is used to remove the last traces of gases like O_2, H_2 and N_2 from evacuated vessels. (*iii*) A titanium cathode is used in special photoelectric cell. (*iv*) Pure Ti metal is used in making incandescent filament. (*v*) A number of titanium alloys have been found to be very useful in industry. For example : (*a*) Ferrotitanium alloy is used in steel industry as a scavanger to remove adsorbed O_2, H_2 and N_2, and as a cleansing and deoxidising agent in the metallurgical operations. Ferrotitanium is obtained in the electric furnace by reducing ilmenite ore, $FeTiO_3$ with carbon or Al metal.

$$\underset{\text{Ilmenite}}{FeTiO_3} + 3C \text{ (or } 2Al) \longrightarrow \underbrace{Fe + Ti}_{\text{Ferrotitanium alloy}} + 3CO \text{ (or } Al_2O_3)$$

(*b*) The alloys of Ti with Cr, Fe and Mo are used for making rails, gears, propellers, car wheels etc. (*c*) The alloys of Ti with Co and Ni are used as filaments in vacuum tubes in place of Pt—Ir alloys which are very costly.

Vanadium (V_{23})

Occurence

Compounds of vanadium are abundantly distributed in the earth's crust. Some of the prominent minerals are : (*i*) *Vanadinite*, $3Pb_3(VO_4)_2 . PbCl_2$ or $2Pb_5(VO_4)_3Cl$

(*Lead chloro orthotvanadate*) (*ii*) *Carnotite*, $K_2O.2UO_3.V_2O_5.3H_2O$ or $K_2(UO_2)_2(VO_4)_2.3H_2O$ (*Potassium uranyl orthovanadate*) (*iii*) *Patronite*, $V_2S_5.3CuS_2$. Vanadium is also found in small amounts in clays, rocks, coal and crude oil.

Extraction

The extraction of vanadium metal from its ores consists of the following steps :

1. Preparation of ammonium metavanadate, NH_4VO_3. Ammonium metavanadate can be obtained either from carnotite or vanadinite ore as shown below :

(*a*) From carnotite ore, $K_2(UO_2)_2(VO_4)_2.3H_2O$. Carnotite ore is boiled with Na_2CO_3 solution and concentrated. On cooling, the crystals of sodium uranyl carbonate, $Na_4(UO_2)(CO_3)_3$ are obtained and sodium orthovanadate, Na_3VO_4 is left in solution. The solution containing Na_3VO_4 is treated with NH_4Cl when ammonium metavanadate, NH_4VO_3 is precipitated.

$$\underset{\text{Carnotite ore}}{K_2(UO_2)_2(VO_4)_2} + 7Na_2CO_3 \longrightarrow \underset{\text{Sod. uranyl carbonate (crystals) (Solution)}}{2Na_4(UO_2)(CO_3)_3} + \underset{\text{Sod. ortho vanadate (Insoluble)}}{2Na_3VO_4} + K_2CO_3$$

$$\underset{\text{(In solution)}}{Na_3VO_4} + 3NH_4Cl \longrightarrow \underset{\text{Ammonium metavanadate (ppt)}}{NH_4VO_3} + 3NaCl + H_2O + 2NH_3\uparrow$$

(*b*) From vanodinite ore, $Pb_5(VO_4)_3Cl$. Powdered vanadinite ore is treated with conc. HCl when $PbCl_2$ is obtained as precipitate and a complex salt, $[V(OH)_4]Cl$ goes into solution. When the solution containing $[V(OH)_4]Cl$ is boiled with NH_4Cl, ammonium metavanadate, NH_4VO_3 is obtained as precipitate.

$$\underset{\text{Vanadinite ore}}{Pb_5(VO_4)_3Cl} + 12HCl \longrightarrow \underset{\text{ppt.}}{5PbCl_2} + \underset{\text{In solution}}{3[V(OH)_4]Cl}$$

$$\underset{\text{(In solution)}}{[V(OH_4)]Cl} + NH_4Cl \longrightarrow \underset{\text{Ammonium motavenadale (ppt)}}{NH_4VO_3} + 2HCl + H_2O$$

2. Conversion of NH_4VO_3 to V_2O_3. When NH_4VO_3 obtained from carnotite or vanadinite as shown above is ignited, vanadium pentoxide (V_2O_5) is obtained.

$$\underset{\text{Ammonium megavanadate}}{2NH_4VO_4} \xrightarrow{\text{Ignite}} V_2O_5 + 2NH_3 + H_2O$$

3. Reduction of V_2O_5 to vanadium metal. Vanadium metal can be obtained by reducing V_2O_5

(*a*) with Ca and $CaCl_2$ (used as a flux) in a steel bomb at 900–950°C (*Marden and Rich process*)

$$V_2O_5 + 5Ca + 5CaCl_2 \longrightarrow 2V + 5(CaO.CaCl_2)$$

(*b*) with Al (*Alumino-thermic process*)

$$3V_2O_5 + 10Al \longrightarrow 5Al_2O_3 + 6V$$

(*c*) with mishmetal (*Thermite process*). Mischmetal is an alloy of certain rare earth metals like Ce, La, Nd, Pr etc obtained from the residues left after the extraction of Th.

4. Purification of vanadium metal. Vanadium metal obtained as above is impure, since it contains some impurities associated with it. The impure metal is purified by *Van Arkel method* in which the impure vanadium metal is heated with a limited amount of I_2 in a evacuated glass apparatus. VI_4 vapours so formed are allowed to diffuse on a tungsten filament at a very high temperature. The vapours of VI_4 decompose and the pure vanadium metal gets deposited on the filament.

$$\text{Impure V metal} + 2I_2 \longrightarrow VI_4(g) \xrightarrow{\text{W-filament}} \underset{\text{Pure metal}}{V(s)} + 2I_2(g) \uparrow$$

Properties of Vanadium Metal

It is a steel-grey hard metal which melts above 1700°C and boils at 3400°C. When pure, it is malleable as well as ductile. When heated in air, the metal is converted into V_2O_5. When heated upto 1400°C, it forms VH_2. When treated with excess of dry Cl_2, VCl_4 is formed. Bromine water has no action on vanadium metal. HCl and H_2SO_4 both have no action on the metal. However, with hot and conc. H_2SO_4 it gives SO_2. With HF it gives H_2. It is easily attacked by HNO_3 and forms $V(NO_3)_3$. Aquea regia attacks the metal very vigorously. Fused alkalies give orthovanadates (Na_3VO_4), with the liberation of H_2.

$$2V + 6NaOH + 2H_2O \longrightarrow 2Na_3VO_4 + 5H_2$$

Oxidising agents like chloric acid, perchloric acid, bromic acid, $KClO_3$, bromate, iodate and perchiorate convert vanadium into V_2O_5. Vanadium metal reduces the solution of $AgNO_3$, $AuCl_3$, $PtCl_4$ and $IrCl_4$. It combines with non-metals like N_2, C, S anti Si to form nitride, carbide, sulphide and silide respectively. Vanadium combines with a number of metals like Fe, Cu, Co, Ni and Al and forms alloys. For example :

(*a*) *Ferro-vanadium alloy* is obtained by heating V_2O_5 with iron ore (Fe_2O_3) and coke in presence of a flux (lime or fluorspar) in an electric furnace.

$$V_2O_5 + 5C \longrightarrow 2V + 5CO \uparrow$$

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO \uparrow$$

This alloy contains 40–80% vanadium.

(*b*) *Nickel-vanadium alloy* is obtained by heating a mixture of V_2O_5 and NiO.

(*c*) *Alumino-vanadium alloy* is prepared by adding Al and then thermite mixture of V_2O_5 and aluminium soot in the electric furnace having melting fluorspar.

Uses of Vanadium.

The most important use of vanadium is in the form of its alloys. For example, ferro-vanadium alloy is used as a scavanger by removing efficiently N_2 and O_2 in the manufacture of special steels. The presence of a small amount of vanadium (0.1 to 0.3%) increases the toughness, tensite strength and resistance to shock which are valuable characteristics for the manufacture of machinery parts subjected to vibration. Thus ferrovanadium is used in the construction of motor parts. Aluminovanadium alloy is used in the manufacture of aircraft parts. The addition of 0.2% vanadium in glass manufacture is recommended for cutting of all the wave lengths below 3580°A which are harmful for the eyes and fade fabrics.

Chromium (Cr_{24})

Occurrence

Metallic chromium does not occur in the native state. The ores of chromium are : (*i*) *chromite* or *chrome ore*, $FeO.Cr_2O_3$ (*ii*) *chrome-ochre*, Cr_2O_3 (*iii*) *crocosite*, $PbCrO_4$. Chromite ore is the most common and is the industrial source of the metal. In India the chromite ore occurs in Singhblum district of Bihar, Mysore, Orissa, Madras and Bombay.

Extraction of Chromium Metal from Chromite Ore, $FeO.Cr_2O_3$

The extraction of Cr metal from chromite ore consists of the following steps :

1. Concentration of the chromite ore. The ore is first crushed and then concentrated by *Wilfley table method* (*Gravity separation method*). In this method the crushed ore is collected in the form of a heap on a sloping floor. A stream of water is allowed to flow through the heap. By this operation the lighter impurities of earthy matter go with water flowing down the slope while the heavier impurities remain with the ore in the heap.

2. Conversion of the concentrated chromite ore into Na_2CrO_4 : Roasting of the concentrated ore. The concentrated ore is mixed with excess of Na_2CO_3 and roasted in a reverberatory furnace at 900–100°C in the presence of free supply of air. By this operation the chromite ore, $FeO.Cr_2O_3$ is converted into soluble sodium chromate, Na_2CrO_4.

$$\underset{\text{Chromite ore}}{4(FeO.Cr_2O_3)} + 8Na_2CO_3 + 7O_2\ (\text{From air}) \xrightarrow{900\text{–}100^\circ C} \underbrace{\underset{\text{Soluble}}{8Na_2CrO_4} + \underset{\text{Insoluble}}{2Fe_2O_3}}_{\text{Roasted mass}} + 8CO_2\uparrow$$

The roasted mass containing Na_2CrO_4 and Fe_2O_3 is extracted with water when Na_2CrO_4 goes into solution while Fe_2O_3 is left behind as a residue.

In the process of roasting, a small amount of lime (CaO) is also added with the mixture of the ore and Na_2CO_3. The addition of CaO makes the mass porous so that the process of roasting is facilitated.

3. Conversion of Na_2CrO_4 into $Na_2Cr_2O_7$. The solution containing Na_2CrO_4 is treated with a calculated quantity of H_2SO_4 whereby Na_2CrO_4 is converted into sodium dichromate, $Na_2Cr_2O_7$ and less soluble Na_2SO_4 is also obtained.

$$2Na_2CrO_4 + H_2SO_4 \longrightarrow \underset{\text{More soluble}}{Na_2Cr_2O_7} + \underset{\text{Less soluble}}{Na_2SO_4} + H_2O$$

The solution containing $Na_2Cr_2O_7$ (more soluble) and Na_2SO_4 (less soluble) is concentrated when the less soluble Na_2SO_4 crystalises out leaving behind more soluble $Na_2Cr_2O_7$ in solution. The solution containing $Na_2Cr_2O_7$ is further concentrated when crystals of $Na_2Cr_2O_7$ are obtained.

4. Conversion of $Na_2Cr_2O_7$ into Cr_2O_3. $Na_2Cr_2O_7$ obtained as above can be converted into Cr_2O_3 by the following methods :

(*a*) $Na_2Cr_2O_7$ is heated with carbon to get sodium chromite, $Na_2Cr_2O_4$ which, on being treated with H_2O, gives the precipitate of chromic oxide, Cr_2O_3.

$$Na_2Cr_2O_7 + 3C \xrightarrow{\Delta} \underset{\text{Sod. chromite}}{Na_2Cr_2O_4} + 3CO \uparrow$$

$$\underset{\text{Sod. chromite}}{Na_2Cr_2O_4} + H_2O \longrightarrow \underset{\text{ppt.}}{Cr_2O_3} + 2NaOH$$

(*b*) $Na_2Cr_2O_7$ is heated with NH_4Cl when the precipitate of Cr_2O_3 is obtained.

$$Na_2Cr_2O_7 + 2NH_4Cl \xrightarrow{\Delta} \underset{\text{ppt.}}{Cr_2O_3} + 2NaCl + 4H_2O + N_2 \uparrow$$

5. Reduction of Cr_2O_3 to chromium metal. Cr_2O_3 obtained as above is reduced to Cr metal

(*i*) by heating Cr_2O_3 with Al powder (Alumino-thermite process)

(*ii*) by heating Cr_2O_3 with a calculated quantity of silicon in presence of CaO which forms a slag of $CaSiO_3$ with SiO_2

$$2Cr_2O_3 + 3Si \longrightarrow 4Cr + 3SiO_2; \qquad SiO_2 + CaO \longrightarrow \underset{\text{Slag}}{CaSiO_3}$$

(*iii*) by passing H_2 over Cr_2O_3 (industrial method) (*iv*) by heating Cr_2O_3 with sugar charcoal (Daville's process).

Properties

The metal is silver white and crystalline. It is malleable and can take a very high polish producing a brilliant surface which is not tarnished even after long exposures to the atmosphere. Its sp. gr. is 7.14, m.pt. = 1830°C and b.pt. = 2200°C. It is extremely hard. Air and water have no action on chromium at the ordinary temperature. Heated in air, it is superficially oxidised to Cr_2O_3 but it burns in the oxy-hydrogen flame forming Cr_2O_3. It decomposes steam. Chromium dissolves in dilute hydrochloric acid forming chromous and ohromic chloride and liberating hydrogen. With dilute sulphuric acid, chromous sulphate and hydrogen are produced. Hot concentrated sulphuric acid produces sulphur dioxide forming chromic sulphate. It is insoluble in dilute nitric acid. Concentrated HNO_3 makes it *passive i.e.*, after immersion in it, it no longer reacts with hydrochloric or sulphuric acid. When heated with NH_3 or N_2, the metal gives the nitride, CrN. The metal reacts directly with halogens, sulphur and carbon etc.

Alloys of Chromium

Chromium combines with a number of metals and forms alloys which are very useful. Its important alloys are given in the Table 46.1.

Table 46.1. Alloys of chromium.

Name of the alloy	Composition	Properties and Uses
(*i*) Ferrochrome	Cr = 65%, Fe = 35%. It is prepared by heating the chrommite ore, $FeO.Cr_2O_3$ with carbon in an electric furnace. $\xrightarrow{\Delta} \underbrace{Fe + 2Cr}_{\text{Ferrochrome}} + 4CO\uparrow$	It is used in the manufacture of chrome-steel. Chrome-steel is drill proof and is, there-fore, used in the manufacture of burglar-proof safes.
(*ii*) Stainless steel	Cr = 11–13%, C = 0.1–0.4%.	It is used for cutlery and house hold wares.
(*iii*) Chromium-vanadium steel		It is very hard and strong and is used for gears, locomotive wheels, oxide and bearings etc.
(*iv*) Nichrome	Cr = 15%, Ni = 60%, Fe = 25%	It is resistant to atmospheric corrosion and can withstand high temperature. It is used in resistance wires for electrical heating.
(*v*) Stellite	Cr = 20–35%, Co = 40–80%, Ni = 0.25%, C = 0.75–2.5%.	It is extremely hard, bright and very resistant to corrosion and is used in cutlery, surgical instruments, cutting and high speed tools etc.
(*vi*) Chrome-nickel steel		It is used for armour pintes.

Uses of Chromium

(*i*) The metal is used in the preparation of various types of alloys which have been put to many uses as shown in the above table. (*ii*) The metal is also used in *chrome plating*, since even very thin layer imparts remarkable resistance to corrosion and has great protective power. Generally iron articles on which chromium plating is desired are first coated with layer of Cr or Ni before chrome plating is done.

Molybdenum (Mo_{42})

Occurrence

The chief ores of molybdenum are *molybdenite*, MoS_2; *wulf-fenite*, $PbMoO_4$; and *molybdite*, also known as *molybdic ochre*, $Fe_2O_3.3MoO_3\ 7\frac{1}{2}H_2O$.

Extraction of Molybdenum From Melybdenite Ore MoS_2

The extraction of molybdenum from molybdenite ore consists of the following steps :

1. Concentration of the ore. Molybdenite ore is crushed in jaw-crushes and powdered in ball mills. Now the powdered ore is concentrated by froth floatation process.

2. Conversion of molybdenite ore, MoS_2 into MoO_3 : Roasting. Concentrated molybdenite ore is roasted in a reverberatory furnace in a plenty supply of air to get the crude MoO_3.

$$\underset{\text{Molybdenite}}{2MoS_2} + 7O_2 \xrightarrow{\text{Roasting}} 2MoO_3 \text{ (Impure)} + 4SO_2$$

The crude MoO_3 obtained as above is extracted with hot conc. NH_4OH to get the crystals of ammonium molybdate, $(NH_4)_2MoO_4$.

$$MoO_3 \text{ (Impure)} + 2NH_4OH \longrightarrow (NH_4)_2MoO_4 + H_2O$$

Now the crystals of $(NH_4)_2\ MoO_4$, on heating, give relatively pure MoO_3.

$$(NH_4)_2MoO_4 \xrightarrow{\Delta} MoO_3 + 2NH_3 + H_2O$$

3. Reduction of MoO_3 into Mo metal. MoO_3 obtained as above is reduced to Mo metal either by H_2, carbon or Al (*Alumino-thermic process*). Mo metal obtained by the second method is contaminated with some carbide of molybdenum.

$$MoO_3 + 3H_2 \longrightarrow Mo + 3H_2O;\ MoO_3 + 3C \longrightarrow Mo + 3CO$$
$$MoO_3 + 2Al \longrightarrow Mo + Al_2O_3.$$

4. Purification of Mo metal. Mo metal obtained as above is contaminated with impurities. In order to remove impurities, crude Mo metal obtained as above is heated with CO at 200°C under pressure of about 200 atmospheres when $Mo(CO)_6$ is formed.

$$Mo \text{ (Impure)} + 6CO \longrightarrow Mo(CO)_6$$

$Mo(CO)_6$, on being heated at 360–410°C, gets decomposed to form pure Mo metal.

$$Mo(CO)_6 \xrightarrow{\Delta} Mo \text{ (pure)} + 6CO \uparrow$$

Preparation of Pure Molybdenum Metal

Thermal decomposition of molyodenum pentachloride on an electrically heated molybdenum filament gives pure metal.

$$2MoCl_5 \xrightarrow[\text{filament}]{\text{Molybdenum}} 2Mo \text{ (pure) } 5Cl_2$$

Properties

Massive Mo has typical silver white appearance and metallic properties. Mo has density 10.2 and high m.pt. (= 2600°C). The metal is extremely resistant to the action of dil. or conc. acids except moderately conc. HNO_3 and hot conc. H_2SO_4 which oxidises it. Mo remains unaffected by solutions of alkalies but is rapidly attacked by fused alkalies in presence of oxidising agents like $NaNO_3$. The metal does not combine at ordinary temperature with non-metals but at elevated temperature it readily combines with O_2, S, C, N_2 and halogens to form MoO_3, MoS_2, MoC, MoN, MoF_6, $MoCl_5$ etc.

Uses of Molybdenum and its Compounds

(*i*) Molybdenum finds most important use in the production of alloy steels and high speed tools. (*ii*) Molybdenum is used in thermo-couples for high temperature measurement, (*iii*) Both in radio valves and bulbs molybdenum is used as filament support. (*iv*) Mo is used in the manufacture of standard weights. (*v*) In potteries, Mo-compounds are used as blue pigments. (*vi*) Molybdenum compounds are used for dyeing silk and wool and for colouring leather and rubber. (*vii*) $(NH_4)_2\ MoO_4$ is used to detect and estimate phosphate and arsenic in chemical analysis.

Tungsten (W_{74})

Occurrence

Tungsten is a rare element, found combined in minerals which are usually associated with tin ores. The chief minerals are *wolframite* (Fe, Mn) WO_4, *scheelite*, $CaWO_4$ and *hubnerite*, $MnWO_3$, all the three containing 70 to 80 per cent of WO_3.

Extraction of Tungsten From Wolframite Ore, (Fe, Mn) WO_4

The extraction of tungsten metal from wolframite involves the following steps :

1. Concentration of the ore. The powdered wolframite ore is concentrated by electromagnetic separation method to remove the non-magnetic impurities.

2. Conversion of wolframite ore into WO_3. The concentrated wolframite ore is fused with Na_2CO_3 in air. This operation gives a fused mass consisting of sodium tungstate, Na_2WO_4 (soluble) and a mixture of Fe_2O_3 and MnO_2 (insoluble).

$$\underbrace{4[(Fe,\ Mn)WO_4] \text{ or } (4FeWO_4 + 4MnWO_4)}_{\text{Wolframite ore}} + 8Na_2CO_3 + 3O_2 \text{ (from air)} \xrightarrow{\text{Fusion}} \underbrace{\underbrace{8Na_2WO_4}_{\text{Soluble}} + \underbrace{2Fe_2O_3 + 4MnO_2}_{\text{Insoluble}}}_{\text{Fused mass}} + 8CO_2 \uparrow$$

Now the fused mass is leached with water so that Na_2WO_4 goes into solution and the mixture of Fe_2O_3 and MnO_2 is left as residue. The solution containing Na_2WO_4, on being acidified with HCl, gives a precipitate of tungstic acid, H_2WO_4 which on ignition gives WO_3.

$$Na_2WO_4 + 2HCl \longrightarrow \underset{\text{ppt.}}{H_2WO_4 \downarrow} + 2NaCl$$

$$H_2WO_4 \xrightarrow{\text{Ignition}} WO_3 + H_2O$$

3. Reduction of WO_3 into W metal. WO_3 obtained as above is reduced to W metal by either of the following methods.

$$WO_3 + 3H_2 \xrightarrow{1200^\circ\ C} W + 3H_2O; \quad WO_3 + 3C \xrightarrow{\text{White heat}} W + 3CO$$

$$WO_3 + 2Al \longrightarrow Al_2O_3 + W$$

Preparation of Pure Tungsten Metal

Pure tungsten metal can be obtained :

(*i*) by heating the tungstic acid, H_2WO_4 in a current of H_2.

(*ii*) by the thermal decomposition of WCl_6 vapour on a tungsten electric arc.

$$H_2WO_4 + 3H_2 \longrightarrow W \text{ (pure)} + 4H_2O \; ; \; WCl_6 \longrightarrow W \text{ (pure)} + 3Cl_2$$

Properties

Massive tungsten possesses typical white appearance and the metallic properties. Its density and m.pt. are 19.9 and 3400°C respectively. The metal is not acted upon by dil. and conc. acids and solutions of alkalies. It is, however, readily attacked by fused alkalies in presence of oxidising agents like KNO_3. The metal does not combine with elements at ordinary temperature but at high temperatures it interacts with O_2, S, N_2, halogens, C and H_2.

$$2W + 3O_2 \longrightarrow 2WO_3; \quad W + 2S \longrightarrow WS_2; \; W + C \longrightarrow WC$$

$$2W + C \longrightarrow W_2C; \quad 4W + N_2 \longrightarrow 2W_2N; \; 2W + N_2 \longrightarrow 2WN$$

$$W + 3X_2 \longrightarrow WX_6 (X = F, Cl, Br) \; ; \; W + I_2 \longrightarrow WI_2.$$

Uses to Tungsten and Its Compounds

The metal is used in making high speed tool steels, alloy steels, filaments of electric lamps, pen-points, strings of musical instruments, contact points, telegraphic keys, gramophone needles, voltage regulators etc. Surgical instruments are manufactured from its alloy namely "stellite" which contains W along with Co and Cr.

Manganese (Mn_{25})

Occurrence

Manganese does not occur in the free state in nature. The chief ores of manganese are oxide ores which are : (*i*) *Pyrolusite,* MnO_2. This ore contains 60–63% manganese and is black in colour. It is found mainly in India, Russia, South Africa, U.S.A. and Germany. (*ii*) *Braunite,* Mn_2O_3. This ore contains 60–70% manganese and is brownish-black in colour. (*iii*) *Hausmannite,* Mn_3O_4 which contains 72.1% manganese and is brownish black. (*iv*) *Manganite,* $Mn_2O_3.H_2O$ which contains 62.4% manganese and is grey or black. Other less important ores of manganese are *manganese blende* (*MnS*), *rhodonite* ($MnSiO_3$) and *rhodothrosite* ($MnCO_3$). Manganese is commonly associated with iron ores. Its estimated abundance is 0.01% of the earth's crust. Traces of Mn occur in water, plants, animals and in many amethyst coloured minerals.

Occurrence in India

India is the biggest producer of manganese ores in the world. Pyrolusite, MnO_2 which is the most important ore is found in India at Panch Mahal (Bombay), Karnatak, Singbhum (Bihar), Madhya Pradesh, Orissa, Mysore and Rajasthan.

Extraction of Mn From Oxide Ore

Manganese may be extracted from its oxide ores like *pyrolusite* (MnO_2) and *hausmannite* (Mn_3O_4) by any of the following methods :

1. Carbon-reduction process. When any oxide ore of Mn is heated with carbon, the reduction of the oxide ore stops at the stage of manganese monoxide, MnO. The reduction of MnO to the metallic manganese requires a very high temperature. The molten metal at such a high temperature of the furnace dissolves much carbon and other impurities. High grade oxide ores (*e.g.* MnO_2 and Mn_3O_4) are, therefore, mixed with charcoal and a little borax and heated to a white heat in an electric furnace when the oxide ores are reduced to metallic manganese.

$$MnO_2 + 2C \xrightarrow{\text{Heat to white heat}} Mn + 2CO$$

$$Mn_3O_4 + 4C \xrightarrow{\text{Heat to white heat}} 3Mn + 4CO$$

Mn obtained by this method is not pure, since it is contaminated with carbon. For obtaing pure metal, less than the theoretical amount of carbon is used in this method.

2. Alumino-thermic process. The reaction between the pyrolusite ore (MnO_2) and aluminium is an explosive reaction. Hence MnO_2 is first converted into Mn_3O_4 by heating it to redness and then reduced to Mn by metallic aluminium.

$$3MnO_2 \xrightarrow{\text{Heat of redness}} Mn_3O_4 + O_2$$

$$3Mn_3O_4 + 8Al \longrightarrow 9Mn + 4Al_2O_3 + \text{Heat evolved}$$

The heat produced in the reaction makes the reaction proceed very rapidly and vigorously and Mn melts and collects as a liquid at the bottom of the crucible and alumina (Al_2O_3) remains on the surface as a slag which solidifies to form artificial corundum. Mn in the molten state is prevented from being oxidised by the layer of Al_2O_3. Molten Mn may be allowed to flow out through the tapping plug. Molten manganese obtained by this method is fairly pure.

3. Elcctrolytic method : Production of pure manganese. In this method, the oxide ores of Mn namely MnO_2 and Mn_3O_4 are converted into $MnSO_4$ and the oxide, MnO_2 is converted into $MnCl_2$. These conversions are made as follows :

(*i*) $MnO_2 + 2CO \xrightarrow{\text{Reduction}} 2MnO + 2CO_2 \uparrow$

MnO thus obtained is treated with H_2SO_4 to get $MnSO_4$.

$$MnO + H_2SO_4 \longrightarrow MnSO_4 + H_2O$$

(*ii*) $Mn_3O_4 + H_2SO_4 \longrightarrow \underset{\text{Solution}}{2MnSO_4} + \underset{\text{Residue}}{MnO_2.H_2O}$

(*iii*) $MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2 \uparrow$

Concentrated solution of $MnSO_4$ or $MnCl_2$ obtained as above is prepared and electrolysed, using a mercury cathode, and carbon as anode. Mn is liberated on the cathode and forms an amalgam with Hg. The amalgam thus obtained is distilled in vacuum at 250° to remove Hg.

Properties

In the solid state Mn exists in three allotropic modifications which are α, β and γ. The α-form is stable upto 742°C and has a complex cubic structure. It is hard and brittle metal which scratches glass. α-form is a silvery white metal in the pure state and grey when impure. It melts at 1260°C, boils at 1900° and its specific gravity is 7.39. The metal becomes very hard if traces of carbon or silicon are present in it as impurity. Mn is not magnetic at any temperature but its compounds like carbides and nitrides are magnetic. β-form is stable between 742° and 1100°C. Like α-form it has also a complex cubic structure and is hard and brittle metal which scratches glass. γ-form is stable above 1100°C and forms face-centred cubic tetragonal crystals. It is ductile and tends to pass into α-form under the ordinary conditions. It is flexible and soft with a density of 720. Mn is superficially oxidised when exposed in air but is readily oxidised on heating in air. The finely divided metal burns in air (*pyrophoric*). Pure Mn decomposes cold water slowly but hot water rapidly, forming $Mn(OH)_2$ and evolving H_2. Mn has a tendency to form Mn^{2+} ions and the oxidation potential is equal to +1.18 volts. Thus Mn can be oxidised to Mn^{2+} ions by H^+ ions from the dilute acids or Mn can displace H_2 from acids. Mn dissolves in conc. H_2SO_4 with the evolution of SO_2 and in HNO_3 evolving NO. It combines with carbon at a temperature of electric arc (1300°C) to form Mn_3C. When heated to 1200°C in an atmosphere of *nitrogen*, it forms Mn_3N_2. When heated with halogens, it forms halides. With *sulphur* it gives sulphide.

It gives Mn_3N_2 with NH_3 and at 330° it gives carbonyl, $Mn_2(CO)_{10}$ with CO. Because of its position in electrochemical series, the metal can displace As, Sb, Bi, Sn, Pb, Cu, Fe, Ni, Co, Cd and Zn from the solutions of the salts of these elements. This property is used for cathodic protection and prevention of corrosion in steel equipment.

Uses

Manganese, in the form of pure metal, is used only for special purposes. It is generally used in the form of its alloys with other metals. Thus, about 80% of Mn produced is used in the manufacture of its alloys which are more useful than Mn itself. Its important alloys are : (*i*) Ferro-manganese and spiegeleisen are the alloys of Mn with Fe and carbon These are obtained by strongly heating a mixture of MnO_2, iron oxide (*e.g.* Fe_2O_3) and a calculated quantity of carbon in a blast furnace. For example ferro-manganese is obtained as follows :

$$3MnO_2 \longrightarrow Mn_3O_4 + O_2 \uparrow$$
$$Mn_3O_4 + 4C \longrightarrow 3Mn + 4CO \uparrow$$
$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO \uparrow$$

The approximate composition of these alloys is : *Ferromanganese*— Mn = 70–80%, C = 0.2–0.3%, rest is Fe; *Spiegeleisen*— Mn = 20–30%, C = 5%, rest is Fe. These alloys are used in the manufacture of steel by the Bessemer process. When Mn, in the form of these alloys, is added to steel in small amounts, it acts as *scavenger* (cleaning agent), *i.e.* it removes dissolved O_2, N_2, P and S in the form of oxide, nitride, phosphide and sulphide of Mn which can easily be removed.

The removal of dissolved O_2, N_2, P and S gives us steel of greater strength. (*ii*) When Mn, in the form of ferro-manganese and spiegeleisen, is added to steel in large amounts upto 14%, we get steel of special hardness and toughness. This steel which contains 14% Mn is called *manganese steel* and is used for making rock crushes, steel halmets etc. (*iii*) Manganese is an alloy of Mn with Cu, Ni and Fe. Its approximate composition is : Mn = 10–14%, Cu = 83–85%, Ni = 3–4% and Fe = 0.4%. It has a very low coefficient of resistance (*i.e.* high specific resistance and hence is used in electrical instruments for making resistance wires. (*iv*) Manganese bronze is an alloy of Mn with Cu Zn and Fe. Its approximate composition is : Mn = 0.5%h Cu = 60–65%, Zn = 35–40% and Fe = 0.5–1%. It contains no tin and hence the name bronze is misnomer. It is really manganese brass and not manganese bronze. It is resistant towards water and is, therefore, used in making parts required in shipping industry.

Iron (Fe_{26})

Occurrence of Iron

Iron is the fourth most abundant element and second most abundant metal—the first three elements being oxygen, silicon and aluminium. Iron rarely occurs in the free state, since it is highly reactive.

The most important ores of iron are : (*i*) *Magnetite*, Fe_3O_4 which contains 70% or even more of Fe (*ii*) *Haematite*, Fe_2O_3. (*iii*) *Limonite* or *hydrated oxide*, $Fe_2O_3 \cdot 3H_2O$. (*iv*) *Copper-iron pyrites*, $CuFeS_2$. India possesses about one fourth of the total world reserve of iron ore, compaired to U.S.A. (14%) and U.S.S.R. (24.7%). Huge deposits of iron are found in Singhbhum and Bonai. The iron ores of these places are of highest quality. Iron ores are widely distributed in Madhya Pradesh (Durg, Bastar, Katni, Bijori). Important deposits have been found in Maharashtra (Chanda, Loharu, Akola, Ratanpur, Ratangiri), Mysore (Hospet, Bellary districts), Orissa (Cuttack, Koraput, Sambalpur, Mayurbhanj, Brrybil-Koira Valley). Small deposits of iron ore have also been located in Kerala, Himachal Pradesh (Mandi district), Assam (Kashi Hills), Punjab (Mahendragarh), Rajasthan (Alwar, Bundi, Udaipur and Jaipur), Uttar Pradesh and West Bengal.

Passivity of Iron

When a piece of iron is brought in contact with dilute sulphuric acid, a vigorous reaction begins and hydrogen gas starts coming out. The same piece of iron will displace copper from a solution of copper sulphate. It is not iced, however, that if the iron piece be kept for sometime in cone. HNO_3, then washed free from nitric acid and allowed to react in the above manner it can neither liberate hydrogen from H_2SO_4 nor precipitate copper from copper sulphate solution. In other words, by treatment with nitric acid iron has so changed that it would not behave in the same manner as any other untreated piece of iron would do. *Iron in this form is said to be passive, i.e. it shows lesser reactivity than it would normally show.* Iron can also be made passive (*i.e.* can be passivated) (*i*) by dipping it in a solution of other oxidising agents like H_2CrO_4, acidified $KMnO_4$, H_2O_2 (*ii*) by treating it with dry NO_2 (*iii*) by subjecting it to anodic oxidation, *i.e.* in electroplating or electrolysis, the anodes sometimes become passive, if a high current density is employed.

Degree of Passivity

Passivity is not an absolute property and a metal exhibits variable degree of passivity depending on the chemical conditions. For example :

(*i*) Oxidising conditions tend to promote passivity while reducing conditions tend to decrease it.

(*ii*) Fe coupled with Pt is more easily passivated than iron alone while Fe coupled with Zn cannot be passivated.

Theories of Passivity

(*i*) Smith and Russet's theory. According to Smith and Russel (1926) the passivity is due to the change in electron configuration of atoms on the surface of the metal.

(*ii*) Oxide film theory. *Faraday* suggested that the passivity of iron is due to the formation of an extremely thin and impervious film on the surface of iron. This film is usually of ferroso-ferric oxide, Fe_3O_4. This theory is confirmed by the fact that if the oxide film on the surface is removed by scratching or by heating it in a reducing atmosphere of H_2 or CO or by dissolving it in iodine solution, iron again becomes active and begins to give its usual reactions. *Evans* strongly supported this theory in 1927 by his researches on the subject of passivity.

Rusting or Corrosion of Iron

When a piece of iron is left exposed to ordinary moist air, it is found covered with a reddish-brown coating which can easily be detached and is called *rust. The process of formation of rust is called rusting.* Partington suggests that rust is chiefly *hydrated ferric oxide*, $2Fe_2O_3.3H_2O$. Some authorities believe that rust is an indefinite mixture which varies in its composition according to its age. Analysis shows that it is probably a mixture of *ferric oxide, hydrated ferrous and ferric oxides and basic ferrous and ferric carbonates.* If the rust is long exposed to the air, the amounts of ferrous compounds becomes very small and ultimately hydrated ferric oxide predominates.

Conditions Required for Rusting

Conditions essentially required for the rusting of iron are : (*i*) *Presence of moisture* (*ii*) *Presence of a weakly acidic atmosphere* (*iii*) *Presence of impurity in the iron.*

Theories of Rusting

A number of theories have been put forward to explain the phenomena of rusting, But the following theories are mentioned here,

(*i*) Acid theory (Carbonate formation theory). According to this theory put forward by *Calvert* and *Crum Brown* in 1888, iron reacts with H_2CO_3 formed by the dissolution of CO_2 in H_2O to form $FeCO_3$ which is then hydrolysed in presence of dissolved oxygen to give a precipitate of $Fe(OH)_3$ and an acidic solution of H_2CO_3 which continues to attack iron.

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

$$H_2CO_3 + Fe \longrightarrow FeCO_3 + H_2$$

$$FeCO_3 + 10H_2O + O_2 \longrightarrow \underset{\text{ppt.}}{4Fe(OH)_3} + 4H_2CO_3$$

This theory fails to explain rusting in the absence of CO_2 and even in alkaline solutions. Alkalies prevent rusting, since they neutralise the CO_2 present.

***(ii)* Electrochemical theory.** According to this theory rusting is an electrochemical phenomena and takes place due to local action. Iron contains a number of impurities of lower oxidation potential and hence a kind of tiny voltaic cell (or an *electronic couple* or a *corrosion couple*) is set up between the impurities and iron itself in contact with H_2O containing dissolved O_2 and CO_2 in which iron acts as an anode.

Reactions : The surface of the moist iron is covered with water film which contains dissolved O_2 and CO_2. CO_2 reacts with H_2O to give H_2CO_3. Thus the surface of Fe is covered with a solution of an electrolyte *viz.* H_2CO_3 and a depoliser *viz.*, dissolved O_2. H_2O and H_2CO_3 give H^+, HCO_3^- and OH^- ions as follows :

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

At cathode : $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$

At anode : $H_2O \rightleftharpoons H^+ + OH^-$

H^+ ions originated from H_2CO_3 and H_2O go to the cathode where these are converted into H_2 molecules. These molecules of hydrogen are oxidized to H_2O by the dissolved O_2 which acts as a depolariser.

$$2H^+ + 2e^- \longrightarrow H_2;\ 2H_2 + O_2 \longrightarrow 2H_2O$$

HCO_3^- and OH^- ions obtained from H_2CO_3 and H_2O respectively migrate to the anode where OH^- ions combine with Fe^{3+} ions (formed at the anode from Fe^{2+} ions–see below) to form $Fe(OH)_3$—a powdery deposit of rust.

$$Fe^{3+} + 3OH^- \longrightarrow \underset{\text{deposit of rust}}{Fe(OH)_3}$$

Fe^{3+} ions are formed at the anode as follows : Fe atoms at the anode are oxidised to Fe^{2+} ions by losing two electrons and these Fe^{2+} ions pass into solution and then are oxidised to Fe^{3+} ions by the dissolved O_2

$Fe \longrightarrow Fe^{2+} + 2e^-$ (*Oxidation of Fe atoms to Fe^{2+} ions*)

$Fe^{2+} + H_2O + O_2$ (*Dissolved oxygen*) $\longrightarrow 4Fe^{3+} + 4OH^-$ (*Oxidation of Fe^{2+} ions to Fe^{3+} ions*).

Protection of Iron From Rusting

The protection of iron and steel from rusting may be brought about :

***(i)* By coating iron with an impervious film of oils, paints (specially aluminium paints, red oxide), coal tar, grease, pitch etc.** which does not allow iron to come in contact with air and moisture and thus protects iron from rusting.

***(ii)* By blowing steam over red-hot iron.** An adherent film of Fe_3O_4 gets deposited on the surface of iron (Russian iron) and thus iron is protected from rusting (*Barf process*).

***(iii)* By alloying iron water with Ni, Cr, Si etc.** The alloys obtained by alloying iron water with Ni, Cr, Si etc have excellent resistance towards rusting due to homogenous make up and formation of a film of the oxide on the surface.

***(iv)* By metallic coatings.** In this method the surface of iron is covered with a layer of a metal more active than iron, *e.g.* Zn, Sn, Al, Cr etc. The zinc coating is usually obtained by galvanising which is carried out by dipping iron into a bath of molten zinc. The zinc coating of the galvanised iron does not allow iron to come in contact with air and moisture and thus protects it from rusting. Even when the zinc coating is partially removed from the surface of iron, iron does not get rusted. In this case both the metals *viz.* Fe and Zn come in contact with air. But, because Zn has higher oxidation potential, it gets oxidised to Zn^{2+} in preference to Fe, *i.e.*, reaction (*a*) takes place while the reaction (*b*) which is necessary for rusting does not take place.

(*a*) $Zn \longrightarrow Zn^{2+} + 2e^-$ (*Takes place*)

(*b*) $Fe \longrightarrow Fe^{2+} + 2e^-$ (*Does not take place*)

In other words it is the zinc and not iron that goes into solution.

***(v)* By other coatings.** Some other types of coating like phosphate coatings and concrete coatings are also effective in protecting iron from rusting.

***(iv)* By using corrosion inhibitors.** *The substances that bring about chemical alteration of the metal surface so as to make the same rustproof are called corrosion inhibitors.* The most commonly used inhibitor of this class is K_2CrO_4. In a sulution of this salt iron will remain free from corrosion indefinitely.

Commercial Forms of Iron

Iron is worked for the following three varieties of iron which *differ in their carbon content.*

1. Wrought iron or malleable iron. It is the purest form of commercial iron and contains the *lowest percentage* of carbon, *viz.*, 0.12–0.25% and some impurities like S, P, Si and Mn (not more than 0.3%).

2. Steel. It contains 0.25–2.5% of carbon and traces of S, P, Si and Mn.

3. Cast iron or pig iron. This is the *least pure* form of commercial iron and contains the *highest percentage* of carbon *viz.*, 2.5–4.5% and traces of impurities like S, P, Mn and Si.

Thus we see that the *amount of carbon in steel is midway between that in wrought iron and in cast iron.* First the cast iron is manufactured from iron ores and then both wrought iron and steel are obtained from cast iron.

Cast Iron

This is the *least pure* form of commercial iron and contains the highest percentage of carbon *viz.* 2.5 to 4.5% and traces of impurities like S, P, Mn and Si The average composition of cast iron is : iron = 93–95% *phosphorous* = 0.4–1%; *carbon* = 2.5–4.5%; *sulphur* = 01.–0.3%; *silicon* = 0.6–2.8% ; *manganese* = 0.3–1.2%. There are two varieties of cast iron namely (*i*) *White cast iron* which contains carbon mostly as *iron carbide,* Fe_3C and very small amount of graphite. It is

obtained by cooling the molten pig iron quickly. (*ii*) *Grey cast iron* which contains carbon mostly as graphite and very small amount of Fe_3C. It is obtained by cooling the molten pig iron slowly.

Manufacture of Cast Iron From Haematite Ore, Fe_2O_3

The manufacture of cast iron from haematite ore involves the following steps :

1. Concentration of the ore. The ore is first crushed to small pieces of 3–5 cm size, screened and sifted. This removes most of the gangue. In a few cases the ore is washed with water to remove silicious impurities. The ore is thus concentrated.

2. Roasting or calcination of the concentrated ore. The concentrated ore is roasted with a little of coal in shallow kilns in the excess of air whereby the following reactions take place.

$$2Fe_2O_3.3H_2O \longrightarrow 2Fe_2O_3 + 3H_2O \uparrow$$
$$FeCO_3 \longrightarrow FeO + CO_2 \uparrow$$
$$4FeO + O_2 \longrightarrow 2Fe_2O_3$$

These reactions result in the following : (*a*) *Moisture and CO_2 are removed.* (*b*) *Sulphur, arsenic and phosphorus ore oxidised to their oxides and are thus removed.* (*c*) FeO is converted into Fe_2O_3 which does not form stag of $FeSiO_3$ with silica (SiO_2) during smelting while FeO forms such slag. *Thus the loss of iron is prevented.* (*d*) In addition to the above chemical reactions, *the entire mass becomes porous and thus the reduction of Fe_2O_3 to spongy iron is facilitated.*

3. Smelting in the blast furnace. The roased ore is mixed with limestone and desulphurised coke in the ratio of 8 : 1: 4 and smelted in a blast furnace.

Construction of the Blast Furnace. (Fig. 46.1). It. is a tall, cylindrical furnace the dimension and construction of which varies from place to place. It is from 80 to 120 feet in diameter. Following are its main parts :

(*a*) *A double cup and cone arrangement.* At the top, the furnace carries a hopper which rests over a funnel-shape double cup and cone arrangement. This arrangement gets lowered by a lever arrangement worked out by chains and wheels (not fully shown in Fig. 46.1). By lowering it, a fresh charge is introduced into the furnace. This arrangement prevents the exit of gases during the charging of the furnace. The charge is fed at the cup and when it is full, the cone is depressed so that the charge automatically goes down into the furnace and subsequently the throat of the furnace is automatically closed.

(*b*) *Body, bosh and tuyers.* The furnace has a *shaft* which is about 100 feet high made of steel plates and is formed by joining two cones: the upper one is called *body* and the lower one is called *bosh.* The upper one is longer than the lower one. The furnace is lined inside with a casting of ordinary bricks and then there is a lining of fire bricks 1.5 feet thick to withstand high temperature of the furnace. At the upper part of the furnace there is a hole through which the hot burnt mixture of waste gases escapes. This mixture of waste gases is called *furnace gas.*

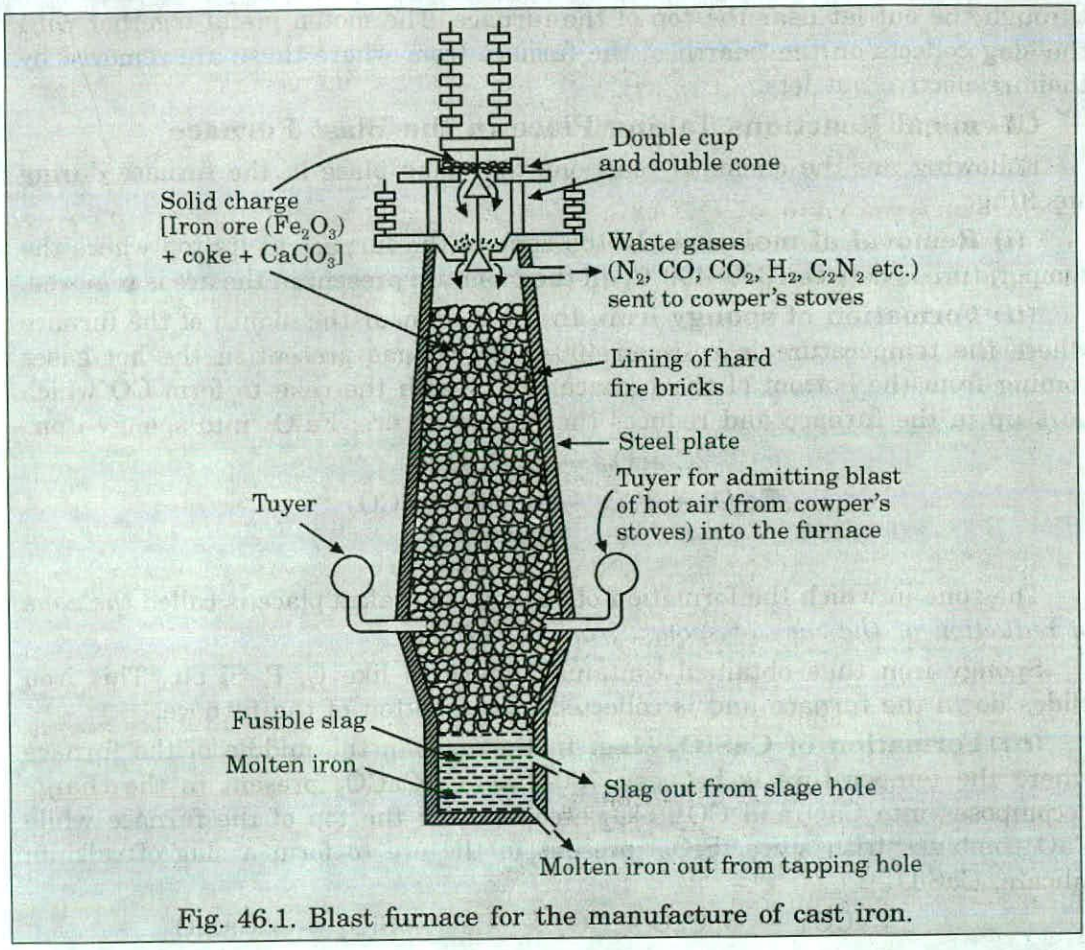


Fig. 46.1. Blast furnace for the manufacture of cast iron.

Between 6 and 8 feet from the base of the furnace there are openings for the insertion of the water-cooled pipes called *tuyers* through which a blast of hot air is sent upwards in the furnace.

(*c*) *Hearth or crucible.* The furnace narrows down below the bosh to an internal width of 8 feet at the base which is called *hearth* or *crucible* of the furnace. The hearth serves as a large crucible to hold the molten iron and is provided with two holes—one is for flowing away the lighter slag (called *slag notch* or *slag hole*) and the other taps out the molten metal (called *metal hole*).

Functioning of the Furnace. The charge consisting of roasted ore (8 parts), limestone (1 part) and desulphurised coke (4 parts) is carried to the top of the furnace. By lowering the cup and cone arrangement the charge in introduced into the furnace. At the same time the furnace is lit and a blast of hot air is sent upwards through the *tuyers*. The blast of hot air for this purpose is obtained by heating air in a series of *cowper stoves* or *preheaters* and is conveyed through a steel pipe lined with fire-bricks to the tuyers from where it is discharged into the furnace. As the charge moves down the furnace, it meets high temperature and various gases are liberated as a result of the chemical reaction between the charge and the air blast rising from the below. The waste gases leave the furnace

through the out let near the top of the furnace. The moten metal together with the slag collects on the hearth of the furnace from where these are removed by their respective out lets.

Chemical Reactions Taking Place in the Blast Furnace

Following are the chemical reactions that take place in the furnace during smelting.

***(i)* Removal of moisture.** In the zone of the furnace at its top where the temperature is between 300–400°C, all the moisture present in the are is removed.

***(ii)* Formation of spongy iron.** In the zone near the mouth of the furnace where the temperature is between 400–700°, O_2 gas present in the hot gases coming from the bottom of the furnace reacts with the coke to form CO which goes up in the furnace and reduces the haematite öre, Fe_2O_3 into spongy iron.

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

$$Fe_2O_3 + 3CO \longrightarrow \underset{\text{Spongy iron}}{2Fe} + 3CO_2$$

The zone in which the formation of spongy iron takes place is called *the zone of reduction or the zone of spongy iron formation.*

Spongy iron thus obtained contains impurities like C, P, Si etc. This iron slides down the furnace and is collected at the botton of the furnace.

***(iii)* Formation of $CaSiO_3$ slag.** In the zone in the middle of the furnace where the temperature is between 700–1000°C, $CaCO_3$ present in the charge decomposes into CaO and CO_2. CO_2 escapes from the top of the furnace while CaO combines with silica (SiO_2) present in the ore to form a slag of calcium silicate, $CaSiO_3$.

$$CaCO_3 \longrightarrow CaO + CO_2 \uparrow ; CaO + SiO_2 \longrightarrow \underset{\text{Slag}}{CaSiO_3}$$

This slag sinks down and floats over the molten iron collected at the bottom of the furnace. The slag floating over the molten iron protects iron from oxidation. The molten iron and fusible slag are removed from their respective holes. The molten metal is run into moulds and allowed to solidify. It is called *pig iron.* It is remelted in a vertical furnace called *cupola* and can be cast or poured into moulds and hence is known as *cast iron.*

The zone in which the decomposition of $CaCO_3$ and formation of $CaSiO_3$ slag takes place is called *the zone of slag fonnation.*

***(iv)* Reduction of oxides.** In the zone near the tuyers, where the temperature is between 1240–1500°C the more stable oxides like P_4O_{10}, SiO_2 and MnO_2 are reduced by red-hot coke to the free elements.

$$P_4O_{10} + 10C \longrightarrow 4P + 10CO \uparrow$$

$$SiO + 2C \longrightarrow Si + 2CO \uparrow$$

$$MnO_2 + 2C \longrightarrow Mn + 2CO \uparrow$$

Si and Mn go into the molten iron as such while P combines with Fe to form iron sulphide, Fe_3P.

By-Products of Blast Furnace

Following are the by-products obtained from the blast furnace.

(*i*) Pig iron. The molten iron produced in the blast furnace is withdrawn through a hole (*slag hole*) into a large ladle lined with fire-bricks which is packed with hundreds of tons of the metal. The molten metal is cast into small semicylindrical moulds called *pigs* and hence the name *pig iron* for the product.

(*ii*) Blast furnace gas. The mixture of waste gases coming out of the hole near the mouth of the furnace is called *blast furnace gas* which contains N_2 (58%), CO(25%), CO_2(10.5%) and H_2, C_2N_2, hydro-carbons etc. (about 6.5%). The furnace gas is first made free from dust particles by passing it through a dust *chamber* and *water scrubber* and then brought to the bottom of one of the two *cowper stoves* and *iron tower* packed with a checker. Checker is a work of firebricks with a channel on one side to act as combustion chamber. Here the furnace gas is burnt with excess of air and the heat of combustion thus obtained heats up this stove. When this stove has been heated up in this manner, the furnace gas is directed to the second stove to heat it up and at the same time the blast of dry air to be used in the furnace is passed into the first stove which heats up the blast of air which is then sent to the furnace through the tuyers. The stove gets cooled and is reheated by burning the furnace gas with excess of air as before. In the meanwhile the second stove has been heated to raise the temperature of fresh blast of air. Thus the two stoves are used alternatively, one for generating heat by burning the furnace gas with excess of air and the other for heating the blast of air to be used in the furnace. This economises fuel to a very large extent. *Thus the cowper stoves serve as heat-generators and fuel-economisers.*

(*iii*) Slag. The fusible slag which is withdrawn from the furnace through the slag hole is granulated by running it into water. It is then. (*a*) used as ballast for rail roads. (*b*) mixed with tar for road-making. (*c*) used in cement manufacture. For this purpose it is burnt with lime and then finely powdered.

Properties and Uses of Cast Iron

It is the most impure form of commercial iron and contains the highest percentage of carbon and traces of impurities of S P, Mn and Si. The impurities present in cast iron have remarkable influence on its properties. Cast iron melts at about 1250°C whereas pure iron melts at 1530°C. The presence of carbon and silicon increases the hardness and strength of the material. Phophorus increases the fluidity of iron when molten while sulphur makes it brittle when cold. Such an iron is called *cold short.* Sulphur increases the brittleness when red hot. Such a specimen is called red short. Cast iron is very hard and cannot be welded. It is so brittle that it cannot be used for making parts of machinery that are subjected to great stress. It expands on solidification and is used for casting various articles such as stoves, pipes, radiators, railway sleepers, gutter pipes, toys etc. A large quantity of cast iron is used in the manufacture of wrought iron and steel.

Wrought Iron

It is the *purest* from of commercial iron and contains the *lowest percentage* of carbon *viz.* 0.12 to 0.25% and 0.3% of impurities like S, P, Si and Mn.

Manufacture of Wrought Iron From Cast Iron

It is manufactured from cast iron by *pudlling i.e.* by heating cast iron in a special type of reverberatory furnace called *puddling furnace* (Fig. 46.2).

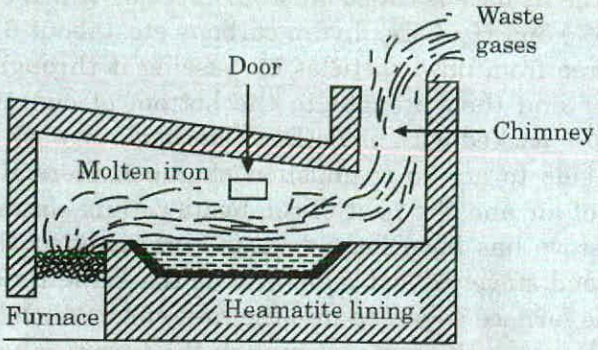


Fig. 46.2. Puddling furnace for the manufacture of wrought iron.

This furnace has a low roof to deflect the hot gases and flames downwards and to melt cast iron. The hearth of furnace is lined with haematite (Fe_2O_3). The cast iron is piled on the hearth, melted by the hot gases and stirred or puddled with long iron rods called *rabbles* through the door to bring it in thorough contact with the lining of the hearth. The heamatite (Fe_2O_3) lining supplies oxygen necessary for the oxidation of carbon, sulphur, silicon, manganese and phosphorus present in the cast iron. Oxides of carbon and sulphur, being volatile, escape while those of manganese, silicon and phoaphorus form slags. Thus :

$$3C + Fe_2O_3 \longrightarrow 2Fe + 3CO \uparrow$$

$$3S + 2Fe_2O_3 \longrightarrow 4Fe + 3SO_2 \uparrow$$

$$3Si + 2Fe_2O_3 \longrightarrow 4Fe + 3SiO_2$$

$$2Mn + O_2 \longrightarrow 2MnO;\ MnO + SiO_2 \longrightarrow \underset{\text{Slag}}{MnSiO_3}$$

$$4P + 5O_2 \longrightarrow 2P_2O_5;\ Fe_2O_3 + P_2O_5 \longrightarrow \underset{\text{Slag}}{2FePO_4}$$

With the removal of impurities, the melting point of the metal rises and it becomes a semi-solid mass. As this stage, it is taken out in the form of balls or blooms on the ends of rabbles. While still hot, these balls are subjected to hammering to squeeze out as much of slag as possible. The products so obtained is known as *wrought iron.*

Properties and Uses of Wrought Iron

It is the purest form of iron containing the lowest percentage of carbon, *viz.*, 0.12–0.25% and other impurities of S, P, Si and Mn (not more than 0.3%). It is

grey and extremely tough and hence is used in the manufacture of articles which are to stand severe and sudden stresses such as archers, wires, bolts, chains and agricultural implements. Its tough nature and resistance towards rusting and corrosion is due to the presence of slag in it. Its melting point is 1500°C. The most valuable property of wrought iron is that it is brittle and can be easily welded and worked under the hammer, so as to assume any desired shape. For most purposes, however, the use of mild steel (*i.e.* steel containing a low proportion of carbon) has replaced that of wrought iron.

Steel

What is Steel ?

Steel is an alloy of iron (as ferrite) containing 0.25 to 2.5% of carbon (as cementite, Fe_3C) and traces of S, P, Si and Mn. Thus we see that the percentage of carbon in steel is intermediate between that in wrought iron and in cast iron. S and P are objectionable impurities. The percentage of S and P is usually below 0.05%, depending on the method used for the manufacture of steel. Si is usually between 0.15 to 0.35% and is present as *iron silicide*, FeSi which is soluble in ferrite. High content of Si gives a fibrous structure to steel. Mn is added to steel during its manufacture to serve as a deoxidiser and to neutralise the harmful effect of sulphur by forming MnS which is inert, while FeS makes steel brittle in hot working.

Varieties of Steel

There are many varities of steel depending on the amount of carbon present in it.

1. Mild and quenched steels. Mild steel is a veriety which contains *lower percentage* of carbon. It possesses the properties of wrought iron along with elasticity and hardness of steel. If mild steel is heated to a high temperature (*i.e.* to bright redness) and then suddenly cooled by plunging it in oil or water, it becomes as hard and brittle as glees. This is called *quenched steel* and process is called *quenching* or *hardening*.

2. Hard steel. This variety contains *higher percentage* of carbon. It is hard and brittle like glass.

3. Special steels or alloy steels. Addition of small amounts of nickel, cobalt, chromium, tungsten, molybdenum, manganese and silicon confer special properties on steels considerably altering its hardness, tenacity, resistance to corrosion and coefficient of expansion. Such products are called *special steels or alloy steels* and find extensive use in industry.

Some of the alloy steels along with their composition, properties and uses are listed in Table 46.2 given below :

Table. 46.2 Some important alloy steels

Name of the alloy steel	Metal added	Proprties	Uses
(*i*) Manganese steel	1.2–1.5% Mn	Hard, tough, resistant to wear	Rock crushing machinery, safes, helmets etc.
(*ii*) Nickel steel	2.5–5% Ni	Hard, tough, rustless	Armour plate, cables, propeller shafts automobile parts, heavy guns.
(*iii*) Invar	3.6% Ni	Same coef. of expension as glass	Pendulum, messuring tapes, instruments.
(*iv*) Chrome steel	1.5–2% Cr	Extremely hard	Cutting tools crushing machinery
(*v*) Stainless steel	13–14% Cr 1% Ni	Resists corrosion	Cutery, food processing machenery
(*vi*) Tungsten steel	14–20% W	Hard and strong	High speed tools
(*vii*) Chrome-vanadium steel	1% Cr, 0.15% V	High tensile strength	For making spring shafts, axles etc.

4. Steel containing S and P. Iron or steel containing excess of S is brittle when hot (*hot short*) and that containing excess of P is also brittle when cold (*cold short*).

Manufacture of Steel

We have already seen that the amount of carbon in steel is mid-way between that in cast iron and in wrought iron. So the steel can be obtained either by removing a part of carbon form cast iron or by adding some carbon to wrought iron. The following methods are in use for the manufacture of steel : (*i*) *Cementation process* (*From wrought iron*). (*ii*) *Crucible process* (*From wrought iron*). (*iii*) *Bessemer's process* (*From cast iron*). (*iv*) *Open-hearth process* (*From cast iron and wrought iron or mild steel scrap*). (*v*) *Electrical process* (*From pure ore and carbon*).

Here we shall discuss *Bessemer's process, open hearth process, Duplex process and electrical process.*

1. Bessemer's Process.

This process was discovered by Sir Henry Bessemer of England in 1856 and hence the name of the process. The furnace used in this process is called *Bessemer's convertor* which is a pear-shaped vessed made of riveted steel plates. The convertor is provided at the botton with a number of holes through which a hot blast of air can be admitted. The convertor is mounted on trunnions or pivots so that it can be tilted in any position. A schemetic diagram of Bessemer's convertor used for the manufacture of steel from cast iron is shown in Fig. 46.3.

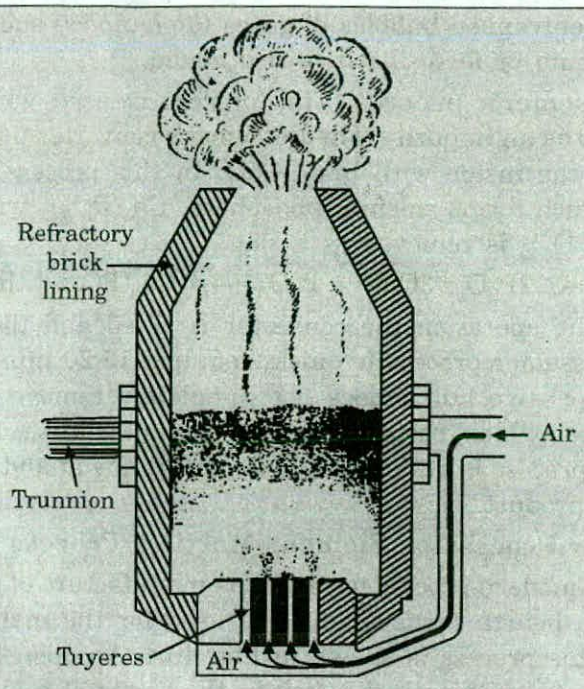


Fig. 46.3. Bessemer's converter used for the manufacture of steel from cast iron.

Depending on the nature of the impurities present in the cast iron being used for the manufacture of steel, Bessemer's process is of two types :

(*i*) Acidic Bessemer's process. This process is used when the cast iron being used for the manufacture of steel contains Si and Mn as impurities. The Bessemer's converter used in this process should be lined on the inside with silica, SiO_2. To start with, the converter is brought in the horizontal position and then cast iron (which is free from P and S) from the blast furnace is put into it. Now it is brought back into the vertical position and a blast of air is admitted into it. Si and Mn present as impurities in cast iron are oxidised to SiO_2 and MnO respectively. These two oxides combine together to form manganese silicate, $MnSiO_2$ which is removed as slag.

$$Si + O_2 \longrightarrow SiO_2;\ 2Mn + O_2 \longrightarrow 2MnO$$

$$SiO_2 + MnO \longrightarrow MnSiO_3 \text{ (Removed as slag)}$$

Later on, carbon is oxidized to carbon monoxide which burns with a blue flame at the mouth of the converter. *When the flame dies out, it indicates the complete oxidation of impurities.* At this stage, *spiegeleisen* (an alloy of iron, mananese and carbon) is added and the blast of air continued for a moment to ensure thorough mixing. Manganese and carbon serve, in the first instance, as *deoxidizers* and reduce any FeO that may be present. The excess of these elements then dissolves in the molten metal, the carbon being the necessary component of steel while manganese serves to make it harder and to increase its tensile strength.

In order to remove entrapped bubbles of gases (*blow holes*) such as O_2, N_2, CO_2 etc., a little aluminium or ferrosilicon is also added.

***(ii)* Basic Bessemer's process.** This process is used when the cast iron contains phosphours as an impurity. The Bessemer's converter used in this process should be lined on the inside with lime, CaO. In this process phosphorus gets oxidised to P_2O_5 which forms calcium phosphate, $Ca_3(PO_4)_2$ with CaO lining of the convertor. $Ca_3(PO_4)_2$ is removed as a slag.

$$4P + 5O_2 \longrightarrow 2P_2O_5;\ 3CaO + P_2O_5 \longrightarrow Ca_3(PO_4)_2 \text{ (Removed as slag)}$$

At the end of the operation the converter is tilted and the molten steel is poured out. The Bessemer process is quick (requires 15.20 minutes to complete) and relatively inexpensive but it does not completely remove acidic impurities and produces a steel which rusts easily and cannot withstand too much and sudden strain. The process is also too rapid to permit any analytical control of the composition of the product.

2. Open-hearth Process or Siemens-Martin's Process

This is the most modern process used for the manufacture of steel. A schemetic diagram of an open hearth furnace which is used for the manufacture of steel from cast iron by this process is shown in Fig. 46.4. An open hearth furnace is like a reverberatory furnace with the dish in the shape of a large oval dish. An open hearth is of two types : (*i*) furnace whose hearth is lined with a basic lining like dolomite, CaO.MgO. Such a furnace is used when the impurities present in the cast iron are of P. A furnace with a basic lining is used in the manufacture of steel (*ii*) furnace whose hearth is lined with an *acidic lining* like silica, SiO_2. Such a furnace is used when the impurities are of Mn, Si etc. An open hearth furnace utilises the heat from the waste gases obtained from the blast furnace. Hot waste gases obtained from the blast furnace are passed through a brick-work chamber which gets heated and the gases going out of this chamber are at a much lower temperature. After some time fuel gases are passed into this hot chamber and the fuel gases are made to heat another brick work chamber. The fuel gas preheated in the hot chamber burns and thus supplies more heat. After some time the direction of the gases is reversed so that the incoming gases are always preheated. Thus we see that an open hearth furnace works on the *regenerative principal of heat economy* and hence this furnace is also called *regenerative furnace.* In order to manufacture steel, the charge consisting of a mixture of *pig iron* (*or cast iron*), *scrap iron* and *haematite ore* (Fe_2O_3) is melted on the hearth of the furnace by forcing pre-heated air and burning gaseous fuels. The reactions taking place in the furnace can be shown as follows :

$$2Fe_2O_3 + 3S \longrightarrow 4Fe + 3SO_2 \uparrow \text{ (Sulphur removed)}$$

$$2Fe_2O_3 + 3C \longrightarrow 4Fe + 3CO_2 \uparrow \text{ (Carbon removed)}$$

$$5Fe_2O_3 + 6P \longrightarrow 10Fe + 3P_2O_5$$

$$2Fe_2O_3 + 3Si \longrightarrow 4Fe + 3SiO_2$$

$$Fe_2O_3 + 3Mn \longrightarrow 2Fe + 3MnO$$

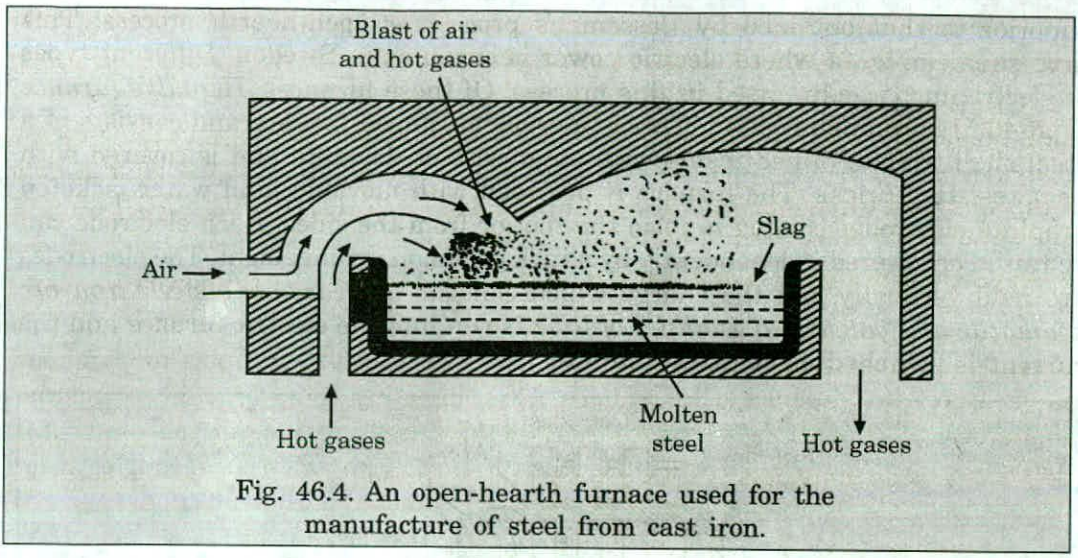


Fig. 46.4. An open-hearth furnace used for the manufacture of steel from cast iron.

SO_2 and CO_2 formed go out of the furnace while the oxides namely P_2O_5 and SiO_2 form $Ca_3(PO_4)_3$ and $CaSiO_3$ slags with CaO lining of the furnace. Similarly MnO also forms $MnSiO_3$ slag with SiO_2 lining of the furnace. Thus the impurities of P, Si and Mn are removed as slags.

$$P_2O_5 + 3CaO \longrightarrow \underset{\text{Slag}}{Ca_3(PO_4)_2} \ (\textit{Phosphorus removed})$$

$$SiO_2 + CaO \longrightarrow \underset{\text{Slag}}{CaSiO_3} \ (\textit{Silicon removed})$$

$$MnO + SiO_2 \longrightarrow \underset{\text{Slag}}{MnSiO_3} \ (\textit{Manganese removed})$$

Open-hearth process has the following advantages over Beasemer's process. (*i*) Better quality of steel of the desired composition is obtained by this process, since the composition of the product can be controlled, *i.e.* the process can be stopped when the analysis of the *sample of the charge* product meets our requirement. (*ii*) Scrap iron, iron ore and pig iron (or cast iron) of low grade can be directly utilised in this process. In other words in this process pig iron of any composition can be used. (*iii*) The temperature can be easily controlled, since heat is supplied from external source. (*iv*) Loss of iron as slag is very little (about 4% against 15% in Bessemer's process), since no blast of air is passed.

3. Duplex Process

Naw-a-days Duplex process is being used for the manufacture of large quantities of steel. This process is a combination of Bessemer's process and open-hearth process. In this process the molten pig iron is first treated in an acid Bessemer's converter to remove Si, Mn and a part of C. The molten pig iron is then transferred to open-hearth furnace with a basic lining to remove P and remaining C and is finished off as usual. Tata Iron and Steel Works are using Duplex process for the manufacture of steel.

4. Electrical Process.

Steel obtained by this process is free from sulphur, phosphorus and gas bubbles and contains fewer solid, non-matallic impurities (known as *sonims*) and hence is

superior to that obtained by Bessemer's process or open-hearth process. This process is employed where electric power is cheap as in Sweden. Different types of electric furnaces are used in this process. Of these furnaces, *Heroult's furnace* (Fig. 46.5) is commonly used. This is a crucible shaped furnace and consists of a steel shell which is lined inside with magnesite or dolomite and is covered with heat resisting bricks. The furnace is provided with movable kind water jacketed graphite electrodes coming in form the roof or from the sides. Each electrode can be raised or lowered independently by a rack or pinion arrangement. The electrodes are held vertically and the charge which consists of *Beasemer's steel, iron ore heamatite and calculated quantity of lime* is run into the electric furnace and the current is switched on to strike the arc.

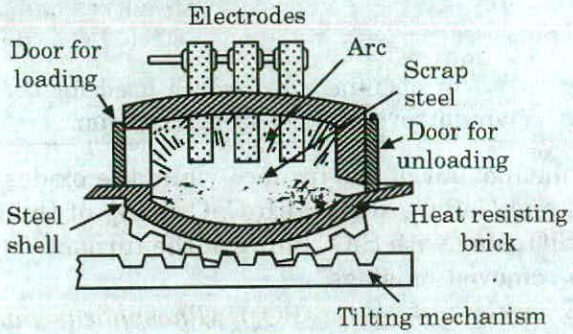


Fig. 46.5. Heroult's furnace for the manufacture of steel.

Since high temperatures are possible in electric furnaces, alloy steels with high melting points are manufactured in electric furnaces.

Reactions. The process involves the following two reactions :

(i) Oxidation and formation of slag. At the temperature of the electric arc, the charge melts and vigorous reaction starts. In this reaction Si, Mn, C and P are oxidised to SiO_2, MnO, CO and P_4O_{10} respectively and $CaCO_3$ gets decomposed.

(*a*) $3Si + 2Fe_2O_3 \longrightarrow 4Fe + 3SiO_2$
(Iron ore)

(*b*) $3Mn + Fe_2O_3 \longrightarrow 2Fe + 3MnO$

(*c*) $C + O_2 \longrightarrow CO_2$, $CO_2 + O \longrightarrow 2CO$

(*d*) $P_4 + 5O_2 \longrightarrow 2P_4O_{10}$

(*e*) $CaCO_3 \longrightarrow CaO + CO_2$

The oxides *viz.* SiO_2, MnO, CO and P_4O_{10} are removed as slags.

(*a*) $SiO_2 + CaO \longrightarrow \underset{\text{Slag}}{CaSiO_2}$

(*b*) $MnO + SiO_2 \longrightarrow \underset{\text{Slag}}{MnSiO_3}$

(*c*) $Fe_2O_3 + CO \longrightarrow CO_2 + 2FeO$; $FeO + SiO_2 \longrightarrow \underset{\text{Slag}}{FeSiO_3}$

(*d*) $P_4O_{10} + 6CaO \longrightarrow \underset{\text{Slag}}{2Ca_3(PO_4)_2}$

The slag being lighter floats over the metallic portion. As soon as the oxidation and formation of slag in complete, the furnace is carefully tilted and the slag is poured out of it.

***(ii)* Deoxidation and desulphurisation.** After the slag is poured out of the furnace, charge consisting of *lime, sand, fluorspar* and some *coke* and *ferro silicon* is added to the furnace. Any FeO present in the steel is removed as Fe by reducing it with the added coke.

$$FeO + C \longrightarrow Fe + CO \text{ (}\textit{Removal of FeO}\text{)}$$

Sulphur present as FeS is removed as CaS by treating it with

$$FeS + CaO \longrightarrow Fe + CaS \text{ (}\textit{Removal of S}\text{)}$$

FeO thus produced is at once reduced to Fe as before while CaS goes into the slag. When desulphurization (*i.e.* removad of sulphur) is complete, the steel is poured out into moulds.

This method is also used for the manufacture of *alloy steels, tool steels, stainless and many special quality steel.*

Properties of Steel.

1. Composition. Steel is an alloy of iron containing 0.25 to 2.5% of carbon and traces of S, P, Si and Mn. Thus we see that percentage of carbon in steel is intermediate between that in wrought iron and in cast iron.

2. Mechanical properties. Steel combines the useful properties of cast iron and wrought iron, being both *hard* and *elastic* and provided the proportion of carbon is not high, it can be *forged* and *welded.*

3. Action of heat : Annealing, hardening or quenching and tempering of steel. A characteristic behaviour of steel which distinguishes it from other commercial forms of iron is that its hardness and elasticity can be varied by heating the steel at different temperatures and then allowing it to cool in different ways. For example :

(*i*) When steel is heated to bright redness (200–350°C) and then cooled very slowly, it becomes soft, weak and ductile. The process of heating and cooling the steel in this way is called *annealng of the steel* and the steel obtained by this process is called *annealed steel.* Annealed steel is used in fabrication process.

(*ii*) When steel is heated to bright redness and then cooled suddenly by plunging it into water or oil, steel becomes as hard and brittle as glass. The process of heating and cooling the steel in this way is called *quenching or hardening of steel* and the steel obtained by this process is called *hardened or quenched steel.*

(*iii*) When the hardened or quenched steel obtained as above is heated to a temperature much below redness and then cooled slowly, steel becomes neither very hard nor very brittle. The process of heating and cooling the hardened steel in this way is called *tempering of steel* and the steel obtained by this process is called *tempered steel.* In the process of tempering, a thin film of the oxide is formed on the surface of the hardened steel. The colour of the oxide film depends on the temperature at which the hardened steel is heated as shown below :

Temperature range (°C) :	200–230	225–270	300
Colour of the oxide film :	yellow	brown	blue

Steel required for cutting blades and tools is tempered yellow while that required for springs, saws etc. is tempered blue.

4. Action of charcoal : Case hardening of steel. When mild steel is heated with charcoal and then plunged (quenched) into oil, a thin coating of hardened or quenched steel is produced on the surface of the mild steel. The process of producing a thin coating of hardened steel on the surface of a mild steel in this way is called *case hardening* and the steel obtained by this process is called *case-hardened steel.* The case-hardened steel becomes resistant to wear and tear and hence is largely used for the manufacture of armour plates, locomotive axles etc.

5. Action of dry NH_3 : Nitriding of steel. When steel is heated in an atmosphere of dry NH_3 in sealed boxes for about 3–4 days, hard coating of iron nitride is produced on the surface of the steel. The process of producing a hard coating of iron nitride on the surface of steel in this way is called *nitriding of the steel.*

Uses of Steel

(*i*) Steel is employed for numerous purposes. It is used for making girders, armour plates, machinery, knives, razors, swords, tools, springs, dies, etc. (*ii*) It is also used for making bar magnets and magnetic needles.

Comparison of Cast Iron, Wrought Iron and Steel

Comparison of cast iron, wrought iron and steel is given in Table 46.3.

Table 46.3. Comparison, of cast, wrought iron and steel.

Property and uses	Cost iron	Wrought iron	Steel
1. Chemical composition	Iron = 93–95% Carbon = 2.5–4.5% Impurities = 0.1 to 2.8% (P, Si, S, Mn)	Iron = 98.5–98.8% Carbon = 0.12–0.25% Impurities : not more than 0.3%	Iron = 98.5–99.5% Carbon = 0.25–2.5%
2. Melting point	Lowest about 1200°C	Highest, about 1500°C	Between 1300–1400°C
3. Hardness	Very hard	Soft	Medium hardness.
4. Behaviour when struck	Brittle	Malleable	Malleable also brittle
5. Magnetisation	Cannot be permanently magnetised.	Magnetisation not permanent but it is easy	Can be permanently magnetised
6. Tempering and welding	Can neither be tempered nor welded.	Cannot be tempered but can be welded.	Can be tempered and welded; can be brought in any state of hardness and malleability by proper tempering.
7. Structure	Crystalline	Fibrous	Granular
8. Uses	Uses for the manufacture of wrought iron and steel.	Used for making electric wires, pipes, sheets, rods etc.	Used for the manufacture of utensils, magnets, knives, engines, surgical instruments, springs, cranes and other important materials.

Prospects of Iron and Steel Industry in India

Although India has very large iron ore reserves in the world, yet it produces only 1% of the total steel production of the world. The main reasons for the poor development of iron and steel industry in India are the lack of technical knowledge and huge capital needed, in putting up steel plants. Major plants set up in private sector and producing iron and steel are *Tata Iron and Steel Company, Jamshedpur; India Iron and Steel Company, Hirapur (Asansol)*; and *Mysore Iron and Steel Works, Bhadravati.* Steel plants set up in public sector are *Hindustan Steel Ltd, Bhilai* (in collaboration with U.S.S.R); *Hindustan Steel Ltd, Durgapur* (in collaboration with U.K.) and *Hindustan Steel Ltd, Rourkela* (in collaboration with West Germany). Other plants have been set up at *Bokaro (Orissa)* and *Salem (Tamil Nadu)*. Plants are being set up at *Visakhapatnam (Andhra Pradesh)* and *Vijayanagar (Karnataka)*. We hope that a time will come soon when India would become one of the biggest producers of steel in Asia and would export steel to other countries.

Cobalt (Co_{27})

Occurrence

Cobalt does not occur free in nature. It constitutes about 0.001% of the earth's crust. Cobalt occurs mainly as *arsenide* and *sulphide* ores with which other metals like Fe, Ni and Ag are also associated. Its principal ores are : *smaltite* or *speiss cobalt*, (Ni, Co, Fe)As_2; *cobaltite* or *cobalt glance*, (Co, Fe, As) S; *crythrite* or *cobalt bloom*, $Co_3(AsO_4)2.8H_2O$ and *linnacite*, $(Fe, Co, Ni)_3 S_4$. All these ores are associated with Fe, Ni, Cu and sometimes with traces of Ag. Many cobalt ores also contain profitable amounts of Ag. Small amounts of Co are also present in the ores of some other metals and are obtained from them as by-product. *e.g.* Co is also obtained as by-product during the refining of Cu, Ni, Fe and Pb. Cobalt is also present in vitamin-12 and its presence in this vitamin is of physiological interest. Cobalt ores are found in Canada, Northern Rhodesia and Belgian Congo. In India cobalt ores are found in Rajasthan.

Extraction

Due to the presence of several other metals in the ores of cobalt, the extraction of cobalt is a very complex process. Cobalt ores are generally worked for the manufacture of cobalt salts and not for the free metal. The extraction of cobalt from cobaltite ore, (Co, Fe, As) S involves the following steps :

1. Concentration. The ore is crushed and finely powdered and then concentrated by the froath-flotation process.

2. Roasting. The concentrated ore contains Fe, Co, Ni, Ag. As and S as the chief constituents. It is roasted in a free supply of air which removes S as SO_2 and As as As_2O_3 and FeS is oxidised to FeO.

$$S + O_2 \longrightarrow SO_2;\ 4As + 3O_2 \longrightarrow 2As_2O_3 \uparrow$$

$$2FeS + O_2 \longrightarrow 2FeO + 2S$$

As_2O_3 is condensed and used as a source of As.

3. Smelting. The roasted mass is smelted in a small furnace with a fuel *e.g.* coke and fluxing material (*e.g.* sand, SiO_2 and lime stone, $CaCO_3$). Here FeO produced during roasting and CaO produced from $CaCO_3$ combine with SiO_2 to form a fusible slag at the top of the molten mass.

$$CaCO_3 \longrightarrow CaO + CO_2$$
$$\left.\begin{aligned} CaO + SiO_2 &\longrightarrow CaSiO_3 \\ FeO + SiO_2 &\longrightarrow FeSiO_3 \end{aligned}\right\} \text{slag}$$

The molten mass obtained at the end of smelting separates into the following three layers which contain different materials : (*i*) *Slag.* This is the top layer and consists of earthy matter present in the ore and slag of $FeSiO_3$ and $CaSiO_3$ formed during smelting. This is rejected. (*ii*) *Speiss.* This is the middle layer and consists of fused arsenides of Co, Ni, Fe and Cu and some As and S. (*iii*) *Bullion.* This is the bottom layer and consists of easily reducible and impure metals, mainly Ag and Cu. It is used for the recovery of 99% pure Ag.

4. Roasting the speiss with NaCl. The speiss is finely ground and roasted is air in a reverberatory furnace to convert As and S, if any, into As_2O_3 and SO_2 which are driven off. It is then mixed with NaCl and then roasted whereby the metals *viz.* Co, Ni, Fe and Cu are converted into their chlorides.

5. Separation of Co, Ni, Fe and Cu. The roasted speiss is extracted with H_2O to get the aqueous solution of the chlorides. This aqueous solution is then treated with lime atone ($CaCO_3$) to precipitate Fe as $FeCO_3$ and the filtrate (after filtration) with Na_2CO_3 to precipitate Cu as $CuCO_3$. By this treatment the chlorides of Co and Ni remain unaffected and hence remain in solution. Ag (in the form of AgCl), if present, is extracted by using a dil. solution of NaCN (*Cyanide process*).

6. Separation of Ni from Co. The solution containing the chlorides of Ni and Co is cautiously treated with lime, $Ca(OH)_2$ and bleaching powder, $CaOCl_2$ whereby $CoCl_2$ is converted into a precipitate of $Co(OH)_3$ and $NiCl_2$ remains in solution.

$$CoCl_2 + \underset{\text{Lime}}{Ca(OH)_2} \longrightarrow Co(OH)_2 + CaCl_2$$

$$2Co(OH)_2 + H_2O + \underset{\substack{\text{Bleaching}\\\text{powder}}}{CaOCl_2} \longrightarrow \underset{\text{ppt.}}{2Co(OH)_3} + CaCl_2$$

$NiCl_2$ that remains in solution can be converted into basic carbonate, if necessary.

7. Formation of Co_3O_4. The precipitate of $Co(OH)_3$ obtained as above is dried and ignited, when cobalto-cobaltic oxide, Co_3O_4 is obtained.

$$12Co(OH_3) \xrightarrow{\text{Ignite}} 4Co_3O_4 + 18H_2O + O_2$$

8. Reduction of Co_3O_4 to Co. Generally Co_3O_4 is used as such for the manufacture of cobalt compounds. In case cobalt metal is needed, it may be obtained by reducing Co_3O_4 by heating it with coke in an oil-fired furnace or with aluminium (*Alumino thermic process*).

$$Co_3O_4 + 4C \longrightarrow 3Co + 4CO$$

$$3Co_3O_4 + 8Al \longrightarrow 9Co + 4Al_2O_3$$

Preparation of Pure Cobalt

Pure cobalt can be prepared by electrolysing the solution of $CoSO_4$ containing $(NH_4)_2SO_4$ and NH_3 using platinum electrodes.

Properties

Cobalt is similar to iron in appearance but is harder, malleable and tough. It is a white metal, and is feebly magnetic. It melts at 1480°C. Cobalt absorbs upto a hundred times its volume of hydrogen, thus showing, analogy to nickel or palladium. Cobalt is not affected by dry or moist air at ordinary temperature. It gets slowly oxidised when red hot. Dilute hydrochloric and sulphuric acids have only a slow action on this metal. The metal is, however, readily soluble in nitric acid forming cobalt nitrate and liberating oxides of nitrogen. Red hot cobalt decomposes steam. Heated in ammonia, it forms the nitride Co_4N_2.

Uses

Cobalt is used in electroplating and in the formation of alloys (*e.g.*, alloys for high speed tools). *Cochrome* is an alloy similar to *nichrome* and contains Co 60%, Cr 15%, and Fe 25%. *Stellite*, an alloy of cobalt, chromium and tungsten is used for making surgical instruments.

Nickel (Ni_{28})

Occurrence

Nickel constitutes about 0.02% of the earth's crust. Metallic nickel is formed only in some of the meteorites. Chief ores of Ni are (*i*) *Pentlandite*, (Ni, Cu, Fe) S. It contains about 3% of Ni and is a mixture of sulphides of Fe, Cu and Ni. It is the main source of nickel. It is found in New Sudbury district of the province of Ontario in Canada. For this reason, this ore s also called *Sudbury ore.* (*ii*) *Nickel glance, NiAsS.* (*iii*) *Garnierite,* (Ni, Mg) $SiO_3.xH_2O$. It contains 5–8% of Ni and is found in New Caledonia (Australia), Cuba, Brazil, Russia etc. (*iv*) *Smaltite*, (Ni, Ce, Fe) As_2. (*v*) *Kupfer nickel* or *niccolite*, *NiAs* (*vi*) *White nickel ore*, Ni As_2. The arsenide ores are found in Norway, Canada, Spain and U.S.A. Nickel ores are not found in India but small amounts of the metal are recovered from the copper ores found in Khetri and other places in Rajsthan and from gold bearing rocks of Kolar and Travancore.

Extraction of Nickel from Pentlandite ore, (Ni, Cu, Fe)S

The extraction of nickel from *pentlandite ore* (Ni, Cu, Fe) S consists of the following operations.

1. Concentration of the ore. The ore is crushed, finely powdered and then concentrated by the *froth flotation process.* The concentrated ore consist of FeS, NiS and CuS, and some impurities like sulphur etc.

2. Roasting. The concentrated ore is roasted in a free supply of air in tall furnaces (about 30 feet high and 22 feet wide) for 8–10 weeks. This operation results in that : (*a*) Excess of free sulphur is oxidised to SO_2. (*b*) Most of FeS is

oxidised to FeO; some FeS remains unaffected. (*c*) Moisture is removed. During roasting NiS and CuS remain unaffected and the roasted mass thus obtained contains NiS, CuS and a little of free sulphnr and FeS. The roasting operation once started is maintained by the heat liberated by the burning of sulphur.

3. Smelting. The roasted mass containing NiS, CuS and a little of free sulpur and FeS is mixed with coke and fluxing material (*e.g.* silica, SiO_2 and limestone, $CaCO_3$) and then smelted in a blast furnace so that most of the remaining FeS and free sulphur are oxidised to FeO and SO_2 respectively. FeO produced during roasting and smelting combine with silica to form ferruos silicate, $FeSiO_3$.

$$FeO + SiO_2 \longrightarrow FeSiO_3 \text{ (}\textit{Fusible slag}\text{)}$$

At the same time lime, CaO obtained from the decomposition of $CaCO_3$ also combines with silica to form calcium silicate, $CaSiO_3$

$$CaO + SiO_2 \longrightarrow CaSiO_3 \text{ (}\textit{Fusible slag}\text{)}$$

$CaSiO_3$ and $FeSiO_3$ both form a fusible slag which, being lighter, floats on the molten mass which consists of NiS, CuS and a little of free sulphur and FeS. The slag is continuously removed.

4. Besemerisation. The molten mass obtained at the end of smelting operation is mixed with silica and then introduced into a Bessemer type converter with a basic lining and fitted with tuyers to admit hot air under pressure. A blast of hot air is admitted into the converter under pressure through the layers. This hot air oxidises almost all the remaining sulphur and FeS into SO_2 and FeO respectively. FeO combines with SiO_2 to form the slag of $FeSiO_3$ as mentioned above. This slag is continuously removed. The resulting mass obtained at this stage is called *bessemerised NiS–CuS matte* or simply *matte* which consists almost entirely of the sulphides of Ni and Cu. The composition of the matte is as Ni = 55%, Cu = 25–30%, S = 14–17% and Fe = 0.1–0.5%.

5. Recovery of nickel from NiS–CuS bessemerieed matte : Refining of nickel. The process of recovering Ni metal from the bessemerised NiS—CuS matte obtained as above is termed as *refining of matte or refining of nickel.* Refining of nickel is generally done by Mond's process in which the matte is roasted in presence of O_2 so that NiS and CuS are converted into NiO and CuO respectively. The residue consisting of oxide mixture of NiO and CuO is treated with dil. H_2SO_4 at 80°C which converts CuO into $CuSO_4$ (soluble) while NiO remains unaffected (as residue). The residue of NiO is treated with water gas (CO + H_2) when NiO is reduced to crude nickel.

$$2NiO + \underbrace{H_2 + CO}_{\text{Water gas}} \longrightarrow \underset{\substack{\text{Crude}\\ \text{nickle}}}{2Ni} + H_2O + CO_2$$

Crude nickel is treated with CO so that Ni is converted into the vapours of nickel tetracerhonyl, $Ni(CO)_4$ which, on being heated to 180°C, decomposes into 99.9% pure nickel.

$$Ni(CO)_4 \xrightarrow{180^\circ} Ni(pure) + 4CO \uparrow$$

Properties

Nickel is a soft silvery white metal, quite malleable and ductile. It is slightly magnetic and possesses a high melting and boiling point (m. pt. = 1420°C, b. pt. = 2900°C). Like iron and cobalt, it absorbs a large volume of hydrogen gas (one volume of the metal absorbing 17 volumes of the gas). The action of air on the metal is slow at the ordinary temperature, but it vigorously burns in oxygen. It is attacked by chlorine, when nickel chloride, $NiCl_2$ is formed. Nickel decomposes steam at a red heat, forming NiO and H_2 Dilute hydrochloric and sulphuric acid solutions have a very slow action on this metal. But it readily dissolves in nitric acid and aqua regia.

$$3Ni + 8HNO_3 \longrightarrow 3Ni(NO_3)_2 + 2NO + H_2O$$

When a nickel sample is kept for some time under the surface of fuming nitric acid, the metal becomes *passive.*

The metal remains unaffected by caustic alkalies, even by fused alkalies. Nickel crucibles are, therefore, commonly used for alkali fusion in qualitative experiments. When CO gas is passed over nickel kept at about 50°C, a volatile colourless liquid, nickel tetracarbonyl, $Ni(CO)_4$ is formed The formation of $Ni(CO)_4$ finds an industrial application in the purification (or extraction) of nickel by Mond's process.

Uses

(*i*) Due to high melting point, great resistance to corrosion, acids and alkalies, nickel is largely used in making crucibles, dishes and other chemical wares and also in electrical industry, (*ii*) It is used for nickel plating in which $NiSO_4.7H_2O$ or $NiSO_4.(NH_4)_2SO_4.6H_2O$ solution is used as an electrolyte. (*iii*) Finely divided nickel is used as a catalyst in the hydrogenation of oils and fats (*iv*) Nickel metal combines with many other metals and forms alloys which find a number of applications. Some important alloys of Ni and their uses are given in Table 46.4.

Table 46.4. Some important alloys of nickel and their uses.

Alloy	Approx. composition	Properties and uses
1. Inwar	Ni = 30%, C = 0.3%, rest iron	Coeffeciant of expansion is almost equal to zero, used in pendulums and scientific instruments.
2. Platinite	Ni = 46%, Fe = 54%	Same coeffecient of expansion as that of glass and platinum, used in electric bulbs and radio valves.
3. Cupro nickel	Ni = 25%, Cu = 75%	Coinage
4. Coustantan	Ni = 40%, Cu = 60%	Electrical resistance
5. Platinoid	Ni = 14%, Cu = 60%, Zn = 24%, W = 2%	Used for thermnocouples and resistance coils.
6. Permalloy	Ni = 21.5%, Fe = 78.5%	Has unusual magnetic properties, used in telephony and telegraphy.

Platinum (Pt_{78})

Occurrence

Platinum usually occurs in the native form along with Cu, Au, Fe and other Pt-metals (Os, Ir, Rh, Pd) in sands and gravels. The main deposits of native Pt are found in Russia (Ural mountains), Columbia and South Africa. In the combined state it is found in a few minerals like *sperrylite*, $PtAs_2$; *cooperite*, $Pt(AsS)_2$ and *braggite*, (Pt, Pd, Ni) S. Sperrylite is found in Sudbury district of Canada and Transvaal (South Africa).

Extraction

Platinum is generally extracted from Sudbery nickel ore. The ore is concentrated to remove the sulphides of Fe, Ni and Cu and then it is digested with dil. aqua regia under pressure. The solution thus obtained contains $PdCl_2$ and $PtCl_4$. This solution is treated with NH_4Cl when $PtCl_4$ is converted into a yellow precipitate of $(NH_4)_2[PtCl_6]$ while $PdCl_2$ remains unaffected in solution. The yellow precipitate of $(NH_4)_2[PtCl_6]$, on heating, gives spongy platinum metal.

$$2NH_4Cl + PtCl_4 \longrightarrow (NH_4)_2[Pt(Cl_6] \xrightarrow{\text{Heat}} Pt + 2NH_4Cl + 2Cl_2$$

Properties

In colour it appears as white as tin. With the exception of gold and silver it is the most malleable of the metals. It joins well with glass because its coefficient of expansion is the same as that of glass. At red heat temperature, it easily allows hydrogen to pass through it. The pure metal is not attacked by hot concentrated sulphuric acid. It, however, dissolves in hot *aqua regia*. The alloy of lead and platinum dissolves in nitric acid forming *platinum nitrate*.

Various Types of Platinum

Platinum may be obtained in various forms to be used in different industries.

1. Spongy platinum. When the double salt ammonium platinochloride $(NH_4)_2PtCl_6$ is very *gently heated*, a sort of grey porous form with a large surface is obtained which is known as spongy platinum. It has great surface activity and is, therefore. used for absorption of gases.

2. Platinum black. (*a*) When an alloy of platinum with metals like copper or zinc is treated with nitric acid, the nascent hydrogen reduces the platinum salt and falls back as a black powder. (*b*) It is best obtained by reducing platinic chloride with formaldehyde, or reducing neutral chloroplatinate with sodium formate. The platinum black absorbs much more hydrogen than the spongy platinum (160 volumes), the maximum absorption is at 0°C; and, therefore, it is commercially used in reduction processes. It also serves as a good catalyst. Alcohol is oxidised by it on account of its occluded oxygen. In its presence, a mixture of hydrogen and oxygen explodes.

3. Platinised asbestos. When asbestos, soaked with platinic chloride, a little hydrochloric and some ammonium chloride, is heated in a crucible, or, if reduced with sodium formate, platinum precipitates out in the fibres of the asbestos. This is now known as platinised asbestos and finds extensive uses as a catalyst.

4. Colloidal platinum. It is obtained either by Bredig's method by passing an electric arc between two platinum terminals dipped in water; or it may be prepared by reducing platinic chloride with hydrasine hydrate in presence of some protective colloid (*e.g.*, sodium lysalbate). The colloidal solution is also a catalyst; it decomposes hydrogen peroxide, catalytically.

Uses of Platinum

1. In scientific instruments and laboratory apparatus. Due to its remarkable properties like high melting point and corrosion resistance, platinum is largely used to manufacture scientific instruments and laboratory apparatus such as crucibles, dishes, basins etc. Pt is also used for contacts in electrical apparatus and for making electrodes.

2. As a catalyst. Pt is also used as a catalyst in a number of inorganic and organic reactions. Some important applications of platinum as catalyst are given below. (*a*) *Manufacture of* H_2SO_4. SO_3 and O_2 combine to form SO_3 in the presence of platinised asbestos in the manufacture of H_2SO_4 by contact process. (*b*) *Manufacture of* HNO_3. NH_3 is oxidised to NO in the presence of platinum gauge in the manufacture of HNO_3 by *Ostwald's process.* (*a*) *Preparation of formaldehyde.* Vapours of CH_3OH and O_2 are passed on platinum black to get HCHO. (*d*) *Synthesis of HBr and HI*, Mixture of H_2 and halogens is passed over red hot finely divided platinum. (*e*) *In hydrogenation and dehydrogenation industries.* Since finely divided platinum has the valuable property of absorbing several hundred times its own volume of hydrogen gas, the metal is widely used for many hydrogenation and dehydrogenation reactions. Large quantities of the metal are also used in the petroleum industry synthetic fibre industry and glass industry.

3. In jewellery. Pt is also used in jewellery as a setting for diamonds. For this purpose the metal is alloyed with metals like Ir, Ru or Cu. Pt—Ir alloy is also used in pen points, standard weights, coins etc.

4. In dentity. The metal is used for making artificial teeth, pins dental filling and support for dentures.

5. Other uses. Pt-salts are used in printing and toning in photography Pt wire is also used in the qualitative analysis in chemistry. In the medical fields many instruments like X-ray tubes, radium applicators, lypodermic needles require platinum.

Copper (Cu_{29})

Occurrence

Copper is found in both the native and combined forms. The native copper is remarkably pure (99.9%) and is only a minor source of copper. Native copper is found in U.S.A. Mexico, Russia and China. In the combined form it is found as (*i*) *Oxide ore.* Example is *Cuprite* or *Ruby Copper*, Cu_2O containing about 88% copper, (*ii*) *Carbonate ores.* Examples are (*a*) *Malachit* (*green*), $CuCO_3.Cu(OH)_2$ or $CuCO_3.CuO.H_2O$ containing about 57% of copper (*b*) *Azurite* (blue), $2CuCO_3.Cu(OH)_2$ containing about 65% copper (*iii*) *Sulphide ores.* Examples are

(*a*) *Chalcocite* or *copper glance* Cu_2S containing about 80% copper (*b*) *Copper pyrites* or *Chalcopyrites*, $CuFeS_2$ ($Cu_2S + Fe_2S_3$) containing about 34% copper. Out of the ores mentioned above, copper pyrites is the principle ore of copper which is found in India mainly in Singbhum district (Bihar), Dharwar and Matigara.

Extraction of Cu from Oxide and Carbonate Ores

The ore is crushed, concentrated by gravity process and roasted. The carbonate ore [*e.g.* malachite, $CuCO_3.Cu(OH)_2$] decomposes to form the oxide and the impurities either volatilize or are oxidised.

$$\underset{\text{Malachite}}{CuCO_3.Cu(OH)_2} \longrightarrow 2CuO + CO_2 + H_2O$$

The oxide so formed is reduced to copper with carbon in reverberatory furnace.

$$CuO + C \longrightarrow Cu + CO$$

The oxide ore *viz.* cuprite, Cu_2O is directly reduced by carbon to metallic copper.

$$\underset{\text{Cuprite}}{Cu_2O} + C \longrightarrow 2Cu + CO$$

Extraction of Cu from Sulphide Ore viz., Copper Pyrites, ($CuFeS_2$) by Dry Process

Copper is extracted form copper pyrites by *dry process* which is also called thermal or smelting process. In this process the crushed copper pyrites ($CuFeS_2$) is concentrated by froth flotation process so that the silicious impurities are removed. The concentrated ore is then heated strongly in a current of air on the hearth of a reverberatory furnace. In this operation (*i*) a considerable portion of S, As and Sb present as impurities are oxidized to their oxides which are then removed. (*ii*) $CuFeS_2$ is converted into a mixture of Cu_2S and FeS ($2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2$) (*iii*) Cu_2S and FeS are furher *partially* oxidised to Cu_2O and FeO respectively.

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2;\ 2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$$

The roasted ore is transferred to a small blast furnace and heated there with coke and sand (silica, SiO_2) in the presence of excess of air. Here FeO combines with SiO_2 to form the slag of iron silicate, $FeSiO_3$ which is removed. The unreacted FeS reacts with Cu_2O and form Cu_2S and FeO [$FeS + Cu_2O \longrightarrow Cu_2S + FeO$]. The molten mass obtained at the end of this operation consists of Cu_2S, FeS and SiO_2. This mass is called **matte or course metal.** Now the moten matte is introduced in a Bessemer convertor and heated in a blast of air blown through tuyers. CuS and FeS which have not been completely oxidised in the reverberatory furnace are oxidised here into Cu_2O and FeO.FeO thus formed forms a slag of $FeSiO_3$ with SiO_2 When the whole of iron has been removed, cuprous oxide reacts with cuprous sulphide to form copper [$Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2$]. The molten mass is poured off from the converter, and allowed to cool when it slowly gives up the dissolved SO_2 and produces blisters on the surface of solidified copper. The copper so produced is called **Blister copper.** It contains about 2%

impurities consisting of Ag, Au, Au, Ni, Zn, Pb, Sn, As and S. It is purified either by poling method or by electrolytic method. In poling method the blister copper is melted on the hearth of a reverberatory furnace when oxygen present in the metal as Cu_2O oxidises impurities *e.g.* iron to FeO which forms a slag with silica lining of the furnace, while oxides of others either pass out of as gases or form a scum which can be removed. Excess of Cu_2O renders copper brittle and removed by covering the surface of fused metal with powdered anthracite and stirring with poles of green wood when reducing gases bubble up through the metal and the oxide is reduced. The copper is 99.5% pure. In electrolytic method a large piece of impure copper (blister copper) is made anode in the electrolytic cell and a thin piece of very pure copper is made the cathode. An acidified solution of $CuSO_4$ is used as an electrolyte. On passing an electric current of low voltage through the electrolytic solution Cu^{2+} ions obtained from $CuSO_4$ solution go to the cathode where they are reduced to the free metal which gets deposited on the cathode. As the process goes on anode becomes thinner and the cathode becomes thicker. The impurities like Ag, Au, So, Te etc. settle down at the bottom of the electrolytic cell as **anode mud.**

Uses

Copper is one of the most important technical metals. Its chief uses are (*i*) It is used for making electric cables and other electrical appliance. (*ii*) Copper sheets are used for making utensils. (*iii*) Copper forms a number of alloys like brass, bronze etc. Its alloys find various uses in arts and industry. (*iv*) It is used for the preparation of various salts which are used as insecticides, pesticides pigment etc. (*v*) it is used in electroplating, electrotyping and in making coins.

Alloys of Copper

Copper forms a large number of alloys which are very useful. Some of these are given in Table 46.5.

Silver (Ag_{47})

Occurrence

Native silver is found in large quantity in Mexico and Norway usually associated with Cu and Ag. The principal ores of Ag are : (1) *sulphides, e.g. argentite or silver glance*, Ag_2S; *silver-copper glannce*, $(Cu, Ag)_2S$; *ruby silver*, $3Ag_2S.Sb_2S_3$. (2) *halides, e.g., horn silver*, AgCl; *bromyrite* AgBr. Most Cu and Pb ores also contain small amount of Ag and constitutes one of the important sources of Ag. U.S.A., Mexico Peru. Canada, Bolivia, New South Wales, Barma and Japan are the major silver producing countries of the world. In fact, there are no silver ores in India, the metal being obtained entirely as by-product in the mining of gold and lead. A small amount of silver is also obtained from gold ores of Kolar fields in Mysore and Anantapur mines at Madras. The lead and zinc ore of Zewar mines in Rajasthan also contains silver which is being smelted (Since 1954) at Tundoo (Bihar) by the Metal Corporation of India.

Table 46.5. Some alloys of copper

Name	Composition	Important properties	Uses
1. Brass	Cu = 60–80% Zn = 20–40%	Harder, palar and more brittle with more zinc, can be moulded, malleable and ductile. High tensile strength.	Domestic utensils, condensers, tubes, casting cart ridges.
2. Bronze	Cu = 75–90% Sn = 10–75%	Hard, brittle tenacious, durable resistant to corrosion, takes high polish.	Statues, coins, utensils, bells, machine parts, propellers, blades.
3. Aluminium bronze	Cu = 90% Al = 10%	Light, strong, tenacious, resistant to corrosion, golden yellow.	Utensils, coins, frames, statues, jewellery, bearings and castings.
4. Phosphorus bronze	Cu = 85% Sn = 13% P = 2%	Very hard, tough, elastic, resistant to corrosion,	Suspension wire instrument, gears, aerials, ships, propellers.
5. Silica bronze	CU = 97% Sn = 2% Si = 1%	Very hard, tensile, tough, non-corrosive, good conductor.	Telephone and telegraph wires, suspension wires.
6. German silver or nickel silver	Cu = 50% Zn = 30% Ni = 20%	White shining, malleable and ductile, tough, resistance to corrosion.	Utensils, plates, ornament.
7. Gun metal	Cu = 88% Sn = 10% Zn = 2%	Strength increases with the increase of the percentage of Sn, very hard and strong, resistant to corrosion.	For making cannons, guns, machine parts.
8. Monel metal	Cu = 30% Ni = 67% Fe + Mn = 3%	Very resistant to chemical action high tensile strength.	Alkali industry resistance wires, domestic wires, values, automobile engine parts.

Extraction of Silver from Argentite (Ag_2S) and Horn Silver (AgCl) by Cyanide Process

Cyanide process is also called **Mac-Arthur and Forest's cyanide process.** In this press the finely powdered ore is concentrated by froth flotation process and then is treated with a dilute aqueous solution of NaCN and a current of air is passed into the solution so that Ag present in the ore is converted into soluble sodium argento cyanide complex, $Na[Ag(CN)_2]$.

$$\underset{\text{Argentite ore}}{Ag_2S} + 4NaCn\ (\text{solution}) \rightleftharpoons \underset{\text{Sod. argento cyanide (soluble)}}{2Na[Ag(CN)_2]} + Na_2S$$

The current of air passed into the solution oxidises. Na_2S formed in the above reaction into $Na_2S_2O_3$, Na_2SO_4 and S and thus enables the above reversible reaction to proceed into the forward direction.

$$2Na_2S + 2O_2 + H_2O \longrightarrow Na_2S_2O_3 + 2NaOH$$

$$4Na_2S + 5O_2 + 2H_2O \longrightarrow 2Na_2SO_4 + 4NaOH + 2S$$

Horn silver ore, AgCl is also converted into soluble $Na[Ag(CN)_2]$ by NaCN.

$$\underset{\text{Horn silver ore}}{AgCl} + 2NaCN\ (\text{solution}) \longrightarrow Na[Ag(CN)_2] + NaCl$$

The solution containing $Na[Ag(CN)_2]$ is treated with Zn dust so that Ag gets precipitated.

$$2Na[Ag(CN)_2] + Zn\ (\text{dust}) \longrightarrow Na_2[Zn(CN)_4] + \underset{\text{ppt.}}{2Ag}$$

Ag obtained as above contains a number of impurities and hence is required to be purified. It is purified by electrolytic method. The cathode consists of a pure silver plate and the anode is a block of *impure* Ag. A solution of 6% $AgNO_3$ with 1% HNO_3 is used as the electrolyte. On passing the current, silver along with some impurities dissolves at the anode while only Ag gets deposited on the cathode. Zn and Cu remain in solution while Au, if any, settles down as anode mud.

To Get Silver From Commercial Lead (Argentiferous Lead) by Parke's Process : Desileverisation of Lead

Lead extracted from galena ore, PbS either by air-reduction process or by carbon-reduction process contains the impurities of Cu, Ag, Bi, As, Fe, Zn, Sn etc. and is called *commercial lead* or *argentiferous lead.* This commercial lead contains Ag upto 2%. Ag can be obtained from this commercial lead by *Parke's process.* To get Ag from this commercial lead is called *desilverisation of lead.* In Parke's process commercial lead is mixed with a little quantity of Zn and the mixture is melted in iron pots. In this operation Ag forms Zn—Ag alloy with Zn while Pb is obtained in the molten condition. On cooling, Zn—Ag alloy solidifies while Pb still remains in the molten state. Zn—Ag alloy is strongly heated in fire-clay retorts to distil off Zn as its vapours and Ag is obtained in the free state. Ag obtained by this method contains some quantity of Pb as impurity which can be removed by cupellation process. In cupellation process the molten impure Ag metal is taken in a cupel (boat shaped dish made of bone ash or cement) which is placed on the bead of a reverberatory furnace provided with a number of openings in the sides so that air freely circulates through it. Now the cupel is heated and a blast of air is passed over the molten metal. Lead present in impure Ag metal is oxidised to litharge, PbO which is carried away by the blast of air along with waste gases and pure Ag is left in the cupel.

To Get Silver From Silver Coins or Silver Ornaments

Silver coins or silver ornaments are Ag—Cu alloys. Ag can be obtained from such an alloy by dissolving the alloy in HNO_3 when a solution containing the mixture of $AgNO_3$ and $Cu(NO_3)_2$ is obtained. After boiling off the excess of nitric acid, the solution is treated with hydrochloric acid when a precipitate of silver chloride is obtained. This is separated and converted into silver by any of the following three methods : (*i*) By reduction with nascent hydrogen [$AgCl + H \longrightarrow Ag + HCl$] (*ii*) By fusion with sodium carbonate [$4AgCl + 2Na_2CO_3 \longrightarrow 4Ag +$

$4NaCl + 2CO_2 + O_2$] (*iii*) By boiling with caustic soda and glucose, $C_6H_{12}O_6$ [$2AgCl + 2NaOH \longrightarrow Ag_2O + 2NaCl + H_2O$; $Ag_2O + C_6H_{12}O_6 \longrightarrow 2Ag + C_6H_{12}O_7$]. The silver thus obtained is purified by fusion with borax and nitre followed by electrolytic purification.

Uses

Silver alloyed with copper is used in making coins and jewellery. Silver leaf is used in medicine while silver amalgam is employed in silvering mirrors and hi filling teeth. Salts of silver are used in photography and silverplating.

Gold (Au_{79})

Occurrence

Gold is found mostly in the *free state* in quartz veins mixed or alloyed with silver with traces of platinum, iron or bismuth as impurities. Such quartz is known as *auriferous quartz*. It is also present in the sands of those rivers which pass over auriferous rocks. In the combined state it is found as a telluride in *sylvanite* (Ag, Au) Te_2. In quantities too small to be profitably extracted, it is found in sea water. India produces about 2% of the world's gold production and Mysore is the richest centre, the *Kolar gold fields* there producing 99.97% of our gold output. Alluvial gold washing is carried out in small scale in Bihar, Assam and Orissa.

Extraction of Au From Alluvial Sands

From alluvial sands, gold is recovered by making use of its high specific gravity (= 19.3). The primitive method was known as *pan washing*. In big pans made of iron or zinc the gold-bearing sand is agitated with water by giving a rotatory motion to the pan when the heavier gold particles settle down while the sand is washed away. This has now been replaced by *placer mining* in which the gold-bearing sand is introduced in a sluice way system and powerful streams of water passed over it. *A sluice way system* is an inclined channel provided with a series of sluices *i.e.*, troughs and cross wire strips called *riffles*. The gold particles are retained in the sluices while the sand is carried away by the water. Whenever loose gold-bearing deposits occur near the edge of a river, the process of *hydraulic mining* is employed. Water under high pressure is forced on the deposit and the auriferous sand which flows down with the water stream is washed into sluices as in placer mining.

Extraction of Au From Auriferous Quartz

The original pieces of auriferous quartz are crushed and broken into pieces in jaw or gyratory crushers. These pieces are now fed in a battery of stamp mills working in series. The powdered ore is washed out of stamp mill by a current of water. Only those particles which are fine enough can pass through the screen. Now the crushed ore is treated by any of the three processes namely :

(*a*) Amalgamation process. This process which is in common use in the South Indian gold fields consists in passing the gold paste over amalgamated

copper plates placed just in front of mortar boxes. The gold combines with mercury to form amalgam. This is periodically removed from the mill plates, squeezed to remove superfluous mercury and then distilled when the mercury passes over leaving gold behind. This process can remove 70–80% of the gold. The residual ore called "*tailings*" is subjected to the above process again in order to recover more gold from it.

(*b*) Plattner's Chlorination Process. The powdered ore is roasted in order to remove sulphur and arsenic and is then placed in wooden vats with false perforated bottoms moistened with water and is treated with chlorine. The gold chloride formed is leached with water and gold recovered from the solution by the addition of ferrous sulphate, $[AuCl_3 + 3FeSO_4 = Au + Fe_2(SO_4)_3 + FeCl_3]$

(*c*) Mac-Arthur and Forrest's cyanide process. Tailings from the amalgamation process or powdered ore from stamp mill is placed in large vats made of wood or cement provided with perforated false bottoms covered with coconut mattings. It is then treated with 0.1% solution of NaCN in the presence of excess of air which is passed in from the bottom of the tank when the following reactions occur :

$$4Au + 8NaCN + 2H_2O + O_2 \longrightarrow 4Na[Au(CN)_2] + 4NaOH$$

The gold goes in solution in the form of a double cyanide of sodium and gold. From this solution gold is recovered either by the addition of zinc or by electrolysis.

$$2Na[Au(CN)_2] + Zn = 2NaCN + Zn(CN)_2 + \underset{\text{ppt.}}{2Au}$$

The precipitated gold is treated with dilute sulphuric acid to remove the excess of zinc and changed into compact mass by fusion.

Refining of Gold

The gold obtained by any of the above processes usually contains traces of Fe, Sb, Cu, Pb and other base metals as impurities. These impurities can be removed by any of the processes mentioned as : (*1*) *Fusion process.* The impure metal is fused with borax and nitre in a crucible, the base metals in the process are oxidised and form a scum at the molten surface, and are removed. (*2*) *Parting process.* The refined metal obtained by fusion, may contain silver as an impurity. This can be removed by treatment with concentrated sulphuric acid. It is found, however, that if the percentage of gold in the impure sample is more than 30%, the sample is not attacked by the acid. More silver is, therefore, added to the sample till an alloy containing one quarter of its weight of gold, *i.e.* 25% is obtained (process called *quartation*). This is treated with sulphuric acid when the silver dissolves to form silver sulphate leaving gold behind. Silver is recovered from this solution by introducing coper plates in it. (*3*) *Electrolyc refining.* Gold may be refined still further by electrolytic process using 4% gold chloride solution acidified with 10% hydrochloric acid as the electrolyte. Impure gold is made the anode while the cathode is a plate of pure gold.

Properties.

(*a*) **Physical.** Gold is a lustrous yellow metal which melts at 1063°C to a green liquid and boils at 2610°C. Its specific gravity is 19.3. It is the most malleable

and ductile of all metals and is a good conductor of heat and electricity. With mercury, it forms an amalgam.

(*b*) **Chemical.** It is not affected by dry or moist air or oxygen. It is unaffected by water or steam. Alkalis have no action on gold. Single dilute or concentrated acids except selenic acid have no action on it. It dissolves, however, in aqua regia forming chlorauric acid, $HAuCl_4$

$$2Au + 2HNO_3 + HCl \longrightarrow 2HAuCl_4 + 3NOCl + 6H_2O$$

At 200°C, it is readily attacked by chlorine forming auric chloride. It dissolves in alkali cyanide solution in presence of oxygen of air.

$$4Au + 8KCN + 2H_2O + O_2 \longrightarrow 4K[Au(CN)_2] + 4KOH$$

Uses

(*i*) In coinage, jewellery and ornamental vessels. (*ii*) In gold plating. (*iii*) Gold leaf is used for decorations, lettering and in medicine as tonic. (*iv*) "Purple of Cassius" which is a combination of gold with colloidal stannic acid is used for making ruby red glass and high class pottery.

Fineness of Gold

Gold content of an alloy of gold is termed its fineness and is generally expressed in carats. Pure gold is 24 carats. Ornaments available these days are made of 18 carat gold, which is an alloy containing 18 parts by weight of gold alloyed with 6 parts by weight of another metal generally copper.

Colloidal Gold

Colloidal gold is obtained by two methods.

1. Bredig's arc method. It is a dispersion process in which an electric arc is struck between two gold electrodes dipped under cold water. As a result of sparking the gold particles disintegrate forming a colloidal solution. A trace of KOH is added to cold water and helps to stabilise the colloidal solution.

2. Reduction process. Gold salt solutions when reduced with ferrous sulphate or stannous chloride, produce colloidal gold solution by reduction.

$$2AuCl_3 + 3SnCl_2 \longrightarrow 3SnCl_4 + 2Au$$

$$2AuCl_3 + 3FeSO_4 \longrightarrow Fe_2(SO_4)_3 + FeCl_3 + Au$$

Purple of Cassius

It is only form of colloidal gold prepared by mixing very dilute solution of gold chloride with stannous chloride solution.

$$2AuCl_3 + 3SnCl_2 \longrightarrow \underset{\text{ppt.}}{2Au} + 3SnCl_4$$

The gold thus precipitated is absorbed by stannic hydroxide formed by the hydrolysis of $SnCl_4$.

$$SnCl_4 + 4H_2O \longrightarrow Sn(OH)_4 + 4HCl$$

It is purple or red in colour and after the name of Cassius who discovered it, it is called Purple of Cassius. According to Moissan this is a colloidal form of stannic oxide with absorbed colloidal gold.

$$2AuCl_3 + 2SnCl_2 + 6H_2O \longrightarrow 2Au + 3SnO_2 + 12HCl$$

It is used in making ruby-red glass and high class pottery.

Zinc (Zn_{30})

Occurrence

Zinc is not found native. In the form of minerals, it occurs as *zinc blende ZnS, calamine $ZnCO_3$, zincite ZnO and franklinite* $ZnO.Fe_2O_3$. In India zinc is found in Rajasthan. A belt of zinc ore covers an area of about thirty square miles in the Zawar and Udaipur region of Rajasthan. It has also been located in certain parts of Kashmir.

Extraction of Zn by Reduction Process

If the ore contains iron oxide as an impurity, the latter is removed magnetically. The silicious impurities are removed by gravity separation and in case of zinc blende, the concentration is done by froth floatation process. The concentrated ore is heated in excess of air when zinc sulphide is oxidised to zinc oxide.

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$

Some of the ore is converted to zinc sulphate as well.

$$ZnS + 2O_2 \longrightarrow ZnSO_4$$

To avoid this, the roasting is done at a high temperature (900°C) in a regulated supply of air. At this temperature the sulphate is decomposed.

$$ZnSO_4 \longrightarrow 2ZnO + 2SO_2 + O_2$$

If *calamine* is the ore, it decomposes into oxide and CO_2.

$$ZnCO_3 \longrightarrow ZnO + CO_2$$

ZnO obtained as above is reduced to Zn metal by any of the following processes.

(*a*) Belgian process. The roasted ore is heated with coke to about 1100°C in small fire clay retorts. The heating is often done by producer gas. Each retort is provided with a clay pipe which serves as a condenser and an earthenware pot in which is collected the condensed metal. Zinc, being fairly volatile, is distilled in the retort and collected in the pot. The chemical reactions involved in this process are :

$$ZnO + C \longrightarrow Zn + CO$$

$$ZnO + CO \longrightarrow Zn + CO_2 \; ; \; CO_2 \rightleftharpoons 2CO$$

There are a number of such retorts which are arranged in three or four rows one above the other. The lowermost is supported on the hearth.

(*b*) New Jersy or Vertical Retort Process. It is a modern process and is much more economical than the Belgian process. It is a continuous process and yields metal of much greater purity (95–99%). Powdered ZnO and coal (called charge) is made into small brickets (small blocks) with the help of molasses which bends the particles together. These brickets are fed into the tall vertical retort from the top. The retort is lined on the inside with fire clay bricks. The retort is heated externally by means of a heating jacket in which producer gas is burnt. The vapours of zinc metal obtained by the reduction of zinc oxide with carbon rise

to the top and are condensed in the condenser. The crude metal obtained is called **spelter.**

Zinc metal obtained above contains iron, cadmium, antimony and arsenic as the main impurities. The crude metal is *redistilled* in silica retorts. More volatile cadmium, arsenic and antimony are distilled first. Zinc is distilled as a next fraction and is collected in a separate receiver. The non-volatile impurities remain in the retort. Very pure zinc is obtained by *electro refining* in which $ZnSO_4$ serves as an electrolyte, crude zinc is made the anode and cathode is a plate of pure zinc metal.

Extraction of Zn by Electrolytic Process

The zinc smelter at Debari (Rajasthan) utilises this process. The concentrated ore is roasted under controlled temperature conditions.

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$

The sulphur dioxide evolved is purified and converted into sulphuric acid. The roasted ore is dissolved out with dilute sulphuric acid as also with spent electrolyte. The zinc goes into solution as zinc sulphate, Other soluble sulphates are also dissolved. [$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O$]. The filtered extract is first treated with milk of lime to precipitate iron, aluminium, silica, arsenic and antimony. The filtrate is warmed to 75°C and treated with zinc dust to remove copper and cadmium. [$CdSO_4 + Zn \rightarrow ZnSO_4 + Cd$]. The filterate is then electrolysed in cells having pure lead inert anodes and aluminium cathodes. The zinc is deposited on the cathode while sulphuric acid is regenerated. The zinc is removed from the cathodes by melting (m. pt. of Zn 420°C; Al 660°C) and made into ingots. The purity of the metal is 99.96%.

Properties

Zinc is a bluish white metal brittle at ordinary temperature but malleable and ductile between 100° and 150°C. At 200°C, it becomes brittle again. It has a sp. gra. = 6.9, m.pt. = 420°C, and b. pt. = 930°C. *Granulated zinc* is obtained by pouring molten zinc in a thin steam in cold water. Zinc is not affected in dry air but in moist air a protective coating of basic carbonate is formed on its surface. When strongly heated in air it burns with a greenish blue flame forming clouds of light zinc oxide (*Philosopher's wool*).

$$2Zn + O_2 \longrightarrow 2ZnO$$

Pure zinc is not dissolved by water. Boiling water is slowly decomposed by impure zinc, *e.g.*, zinc-copper couple. It decomposes steam.

$$Zn + H_2O \longrightarrow ZnO + H_2$$

Pure zinc is attacked very slowly by acids but the presence of impurities accelerates the rate of reaction due to the formation of electro-chemical couples. It dissolves readily in dilute and concentrated hydrochloric acid.

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$

Dilute sulphuric acid produces hydrogen.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

Hot and concentrated sulphuric acid produces sulphur dioxide.

$$Zn + 2H_2SO_4 \longrightarrow ZnSO_4 + SO_2 + 2H_2O$$

Dilute nitric acid gives nitrous oxide or ammonium nitrate according to the strength of the acid, very dilute acid giving ammonium nitrate.

$$4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + 5H_2O + N_2O$$

$$4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

With concentrated acid, nitrogen peroxide is produced.

$$Zn + 4HNO_3 \longrightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2$$

Zinc dissolves in hot solutions of caustic alkalies forming zincates and liberating hydrogen.

$$Zn + 2NaOH \longrightarrow \underset{\text{Sodium zincate}}{Na_2ZnO_2} + H_2$$

It displaces less electro-positive metals like copper, silver, gold end lead from their salt solutions.

$$CuSO_4 + Zn \longrightarrow ZnSO_4 + Cu$$

$$2Na[Ag(CN)_2] + Zn \longrightarrow \underset{\text{ppt.}}{2Ag} + Na_2[Zn(CN)_4]$$

Zinc decomposes ammonia at red heat.

$$3Zn + 2NH_3 \longrightarrow Zn_3N_2 + 3H_2$$

Uses

The most important use of zinc is for the **galvanising (or galvanisation)** of iron. (*Galvanising is the process of depositing a thin layer of zinc over the surface of iron*). It is used in the desilverisation of lead and the extraction of gold and silver. Granulated zinc is used in the laboratory. It is also employed as cathode plate in dry cells and in photo-engraving and printing plates. Its alloys with copper find extensive application in industry and arts.

Alloys of zinc

As already said, zinc metal combines with copper and forms many useful alloys. Some useful alloys of Zn with Cu are given below :

1. *Brass.* For this see "*Alloys of copper*"
2. *Muntz metal.* It is an alloy containing Zn = 60% and Cu = 40%.
3. *German silver.* For this see "*Alloys of copper*"
4. *Die casting metal.* Zinc alloyed with 4% Al, upto 3.5% Cu and 0.05% Mn is used for the production of die castings.

Mercury (Hg_{80})

Occurrence

The principal ore of mercury is *cinnabar*, HgS. Mercury also occurs as *tremannite*, HgSe; *calomel*, Hg_2Cl_2. Small drops of metallic mercury are also

found distributed throughout the rock. The principal sources of world supply of mercury are Spain, Italy, California, Russia, Mexico, China and Japan.

Extraction of Mercury From Cinnabar Ore, HgS

Hg is extracted from cinnabar ore by using the following two processes.

1. Old process (Idrian process). This process is only used in Spain. The ore is crushed and finally powdered and then concentrated by the froth floatation process. The concentrated ore is placed on the perforated arches constructed over one another in the central chamber. The larger lumps of the concentrated ore are placed on the lowest arch and finer ones, on the uppermost. Now the concentrated ore is heated by the flames of the furnace rising from below. HgS is oxidised to HgO and SO_2, the former decomposes at about 300°C to give Hg and O_2.

$$2HgS + 3O_2 \longrightarrow 2HgO + 2SO_2 \; ; \; 2HgO \xrightarrow{300^\circ} 2Hg + O_2$$

Mercury vapours and SO_2 are passed into a series of condensing (cooling) chambers on both sides of the furnace. Hg vapours get condensed at the botton of the chamber while SO_2 etc. escape out through the chimney.

2. Modern process. In this process HgS ore is mixed with charcoal and is charged into a shaft furnace from the top fitted with cup and cone arrangement. The charge (*i.e.* HgS + charcoal) is heated on the sloping bars of iron in a current of air drawn through the furnace. Gases coming out of the furnace are Hg vapours, SO_2 and CO.

$$2HgS + 3O_2 \longrightarrow 2HgO + 2SO_2$$

$$2HgO + 2Hg \text{ (vapours)} + O_2 \; ; \; HgO + C \longrightarrow Hg \text{ (vapours)} + CO\uparrow$$

The gases of Hg vapours, SO_2 and CO are passed in Y-shaped tubes cooled in water when vapours of Hg get condensed. The advantages of this process over the old one are : (*i*) it is a continuous process (*ii*) loss of Hg vapours is negligible, and (*iii*) it can be used for the extraction of Hg from all grades of HgS ore.

Purification of Mercury

Mercury obtained by any of the above methods is usually contaminated with metallic impurities like Zn, Sn, Pb, Bi etc. Some of these impurities get oxidised in air and form a black scum of their oxides on the surface of Hg. The suspended impurities can be removed by filtering impure Hg through chamois leather and filtered matter is obtained. Hg can further be purified by treating the filtered matter with dil. HNO_2. In this method the filtered matter is dropped in a long tube containing dil. HNO_3. The base metal impurities like Pb etc. react with $Hg_2(NO_3)_2$ (which is formed by the action of Hg on HNO_3) to give their nitrates which go into the solution and pure Hg is obtained at the other end. Finally the metal is purified by distillation in vacuum.

$$\text{Pb (base metal impurity)} + Hg_2(NO_3)_2 \longrightarrow \underset{\text{Soluble}}{Pb(NO_3)_2} + 2Hg$$

Uses of Mercury

(1) Because of its high boiling point and low freezing point it is used as a barometric and thermometric liquid. (2) In the extraction of gold and silver by

amalgamation process. (3) Compounds of mercury are used in medicine. (4) In the manufacture of caustic soda by Castner-Kellner process or Solvay-Kellner process. (5) Mercury vapour lamp is used as a source of ultraviolet rays. (6) Sodium and aluminium amalgams are used as reducing agents. Tin amalgam is used as a dental filling.

Amalgams

Mercury dissolves nearly in all the metals forming alloys which are called *amalgans*. As a rule, amalgams are the solutions in mercury of the compounds of metals and mercury. Sodium amalgam is formed by dissolving clean pieces of sodium in mercury. The metal dissolves with a bright flash and a solid compound Na—Hg is formed. Sodium amalgam is a useful reducing agent, evolving hydrogen in presence of water. When Na—Hg amalgam is placed in a concentrated solution of NH_4Cl, HgS swells up into a buttery mass thirty times its original volume which is known as ***ammonium amalgam*** which at higher temperature decomposes to give Hg, N_2 and NH_3. ***Iron amalgam,*** Fe—Hg is prepared by placing Na—Hg or Zn—Hg amalgam in solution of $FeSO_4$.

$$FeSO_4 + 2Na\text{–}Hg \longrightarrow Na_2SO_4 + \underset{\text{Iron amalgam}}{Fe\text{–}Hg}$$

Copper amalgam, Cu—Hg is formed by dipping the Cu metal in a solution of $HgNO_3$ or $HgCl_2$.

$HgCl_2 + Cu \longrightarrow Hg + CuCl_2$; $Cu + Hg \longrightarrow Cu\text{–}Hg$ (*copper amalgam*)

Cu—Hg amalgam is used in filling teeth.

Thorium (Th_{90})

Occurrence

Thorium occurs widely distributed in nature though in small proportions. Its important minerals are *thorite*, (SiO_2. ThO_2). nH_2O and *thorianite* which contains 55–80% ThO_2, 11–32% UO_2 and a little ceria earths. Thorium is found in Ceylon and Travancore *monazite* sands of India (about 9% of ThO_2). 80% of the world's thorium is located in India as monazite sand.

Extraction of Th from Monazite Sand

1. Preparation of thoria (ThO_2). Monazite sand is dissolved in conc. H_2SO_4 by heating at 200°C. The residue is leached with H_2O to have a solution containing sulphates of Th and some lanthanides (mainly La and Ce).

$$ThO_2 + 2H_2SO_4 \longrightarrow \underset{\text{(Solution)}}{ThSO_4} + 2H_2O$$

$$2(La, Ce)PO_4 + 3H_2SO_4 \longrightarrow \underset{\text{(Solution)}}{(La,Ce)_2(SO_4)_2} + 3H_3PO_4$$

Due to the formation of H_3PO_4 the solution containing the sulphates is sufficiently acidic. The solution is, therefore, neutralised by adding NaOH or MgO and pH adjusted so that $Th(HPO_4)_2$ gets precipitated, Leaving the phosphates of La and Ce, for the most part, in solution.

$$Th(SO)_4)_2 + 2H_3PO_4 \underset{H^+}{\overset{HO^-}{\rightleftarrows}} Th(HPO_4)_2 + 2H_2SO_4$$

Now the precipitate of $Th(HPO_4)_2$ is heated with Na_2CO_3 to form crude thoria (ThO_2) containing La and Ce as chief impurities.

$$Th(HPO_4)_2 + 3Na_2CO_3 \longrightarrow \underset{\text{(Crude)}}{ThO_2} + 2Na_3PO_4 + 3CO_2 + H_2O$$

The crude thoria is treated with oxalic acid and ammonium oxalate solution. Thorium oxalate so formed remains in solution, while the oxalate of La and Ce are left behind as residue. Solution containing $Th(C_2O_4)_2$ is dried and ignited when ThO_2 is formed. It is dissolved in HNO_2 and $Th(NO_3)_4$. $4H_2O$ formed is crystallised. The nitrate on heating gives pure ThO_2.

2. Preparation of thorium metal. The oxide ThO_2 is heated with carbon in a current of chlorine when $ThCl_4$ is precipitated which on being reduced with Ca metal gives Th.

$$ThO_2 + C + 2Cl_2 \longrightarrow ThCl_4 + CO_2$$
$$ThCl_4 + 2Ca \longrightarrow Th + 2CaCl_2$$

Extraction of Th by Electrolysis

The electrolysis of a mixture of thorium chloride and potassium chloride in a graphite crucible using graphite electrode furnishes thorium of about 88% purity.

Properties

Thorium is available as a dark grey or iron grey podwer; sp, gr. 10.11. The metal is stable in air at 120°, but it takes fire just below redness. Water does not react with the metal, unless the metal contains carbide. When thorium is heated in chlorine, thorium chloride is formed with incandescence. Bromine and iodine have also a similar action on it. Hydrofluoric acid has no action on it; hydrogen, however, evolves, when hydrochloric acid acts on it. Thorium sulphide is formed when thorium is heated with sulphur. Hydrogen sulphide also reacts with red-hot thorium to give thorium sulphide. Sulphuric acid reacts with thorium slowly, and sulphur dioxide, evolves. Thorium nitride is formed when the metal is heated with nitrogen. Solution of alkalies have no marked action on the metal.

Thoria Mantles and Uses of Thorium

Thoria has an immense use in the preparation of incandescent gas mantles. Mixtures of thoria with traces of ceria have been used in the form of pastilles for searchlights and headlights of cars. Magnesium flash light powders also often contain some thorium preparations. Thorium alloys have been used as reducing agents and thoria as a contact catalyst. In the nuclear chemistry, thorium containing substances have a very important future awl hence controls have been imposed on thoria industry which is everywhere the state monopoly.

Uranium (U_{92})

Occurrence

Uranium is not found free in nature. It occurs in the combined state in a few scarce minerals. Its most important minerals are : (*i*) *Pitchblende* or *uraninite* in

which uranium is present as U_3O_8 or $2UO_2.2UO_3$ or uranium uranate, $U(UO_4)_2$. It contains 75–90% of the oxide and is found in Australia. Bohemia, Hungary Norway, India, East Africa etc : (*ii*) *Carnotite* $K_2O.2UO_3.V_2O_5.3H_2O$ or $2K(UO_2)VO_4.3H_2O$ (potassium uranyl ortho vanadate) which contains both uranium and radium. It occurs in *Jaduquda mines* of Bihar (*iii*) *Antunite*, $K(UO_2)PO_4$ $8H_2O$ (*potassium uranyl orthophosphate*). It is found in Congo. In India at present the principal sources of uranium ore are the *Jaduguda mines* of Bihar. In 1964 rich deposits of high grade uranium ore have been found in Bhatin area of Bihar. Another important source of uranium in India is the *monazite sand* of Travancore.

Extraction of Uranium From Pitchblende

1. Acid digestion process. First of all pitchblende is concentraed by gravity process to remove sand, clay etc. and then concentrated ore is roasted in excess of air whereby S, As and Sb are removed as their volatile oxides. Silver, if present in the mineral, is removed, as insoluble AgCl by roasting the mineral at 800°C with NaCl. The roasted ore is digested with dil. H_2SO_4 in presence of MnO_2 (an oxidising agent) for about 24 hours when Ba, Pb, Ba, etc. are precipitated as sulphates and uranium goes into solution as *uranyl sulphate*, UO_2SO_4.

$$\underset{\text{(In mineral)}}{2U_3O_8} + 6H_2SO_4 + \tfrac{1}{2}O_2 \longrightarrow \underset{\substack{\text{Uranyl sulphate}\\ \text{(Soluble)}}}{3UO_2SO_4} + 3H_2O$$

UO_2SO_4 present in solution is converted into *sodium uranyl carbonate*, $N_4UO_2(CO_3)_3$ by the addition of Na_2CO_3.

$$UO_2SO_4 + 3Na_2CO_3 \longrightarrow \underset{\substack{\text{Sod. uranyl car-}\\ \text{bonate (solution)}}}{Na_4UO_2(CO_3)_3} + Na_2SO_4$$

The solution containing $Na_4UO_2(CO_3)_3$ is now neutralised with HCl in order to decompose it into *uranyl chloride*, UO_2Cl_2 and then saturated with H_2S gas so that Pb, Cu etc. are precipitated as their sulphides. The solution of UO_2Cl_2 is now treated with excess of NH_4OH whereby we get the precipitate of *ammonium diuranate*, $(NH_4)_2U_2O_7$ which, when strongly ignited in air, gives the oxide, U_3O_8.

$$Na_4UO_2(CO_3)_3 + 6HCl \longrightarrow \underset{\substack{\text{Uranyl chloride}\\ \text{(Solution)}}}{UO_2Cl_2} + 4NaCl + 3H_2O + 3CO_2$$

$$2UO_2Cl_2 + 6NH_4OH \text{ (excess)} \xrightarrow{\text{Ignite}} \underset{\substack{\text{Ammonium}\\ \text{diuranate}}}{(NH_4)_2U_2O_7} + 4NH_4Cl + 3H_2O$$

$$3(NH_4)_2U_2O_7 \longrightarrow 2U_3O_8 + 6NH_3 + 3H_2O + O_2$$

When U_3O_8 is reduced by carbon by heating in an electric furnace, uranium is obtained.

$$U_3O_8 + 8C \longrightarrow 3U + 8CO$$

98–99% of pure uranium can be obtained by reducing U_3O_8 by Mg, Ca or Al (*Allumino-thermic process*).

$$3U_3O_8 + 16Al \longrightarrow 9U + 8Al_2O_3$$

Burger reduced U_3O_8 by the vapours of calcium in vacuo.

2. Alkali digestion process. The roasted ore is digested with Na_2CO_3—$NaHCO_3$ mixture solution whereby U_3O_8 present in the mineral is converted into soluble $Na_4UO_2(CO_3)_3$. The solution containing $Na_4UO_2(CO_3)_3$ is treated with NaOH which precipitates uranium as *sodium diuranate*, $Na_2U_2O_7$.

$$\underset{\text{(In mineral)}}{U_3O_8} + 3Na_2CO_3 + 6NaHCO_3 + \tfrac{1}{2}O_2 \longrightarrow \underset{\text{(Soluble)}}{3Na_4UO_2(CO_3)_3} + 3H_2O$$

$$Na_4UO_2(CO_3)_3 + 6NaOH \longrightarrow \underset{\substack{\text{Sod. diuranate}\\ \text{(ppt.)}}}{Na_2U_2O_7} + 6Na_2CO_3 + 3H_2O$$

The precipitate of $Na_2U_2O_7$ is dissolved in dil. H_2SO_4 and the solution is treated with NH_4OH. The precipitate of $(NH_4)_2U_2O_7$ thus obtained on strong ignition in air gives U_3O_8.

$$\underset{\text{(ppt)}}{Na_2U_2O_7} + H_2SO_4 \longrightarrow Na_2SO_4 + \underset{\text{(Soluble)}}{H_2U_2O_7}$$

$$H_2U_2O_7 + 2NH_4OH \longrightarrow \underset{\substack{\text{Ammon. diuranate}\\ \text{(ppt)}}}{(NH_2)_2U_2O_7}\downarrow + 2H_2O$$

$$3(NH_4)_2U_2O_7 \xrightarrow{\text{Ignition}} 2U_3O_8 + 6NH_3 + 3H_2O + O_2$$

The oxide, U_3O_8, is reduced, as in acid digestion process, to uranium.

Extraction of Uranium From Carnotite

In addition to uranium, carnotite also contains Ba, V, Fe, Al, Ra etc. From this ore uranium is obtained as a by-product. The ore is treated with conc. HNO_3 at 100°C. The heating is done by the steam. Most of the ore dissolves in HNO_3 and the solution thus obtained is noutralised by NaOH and then treated with $BaCl_2$ and H_2SO_4 whereby Ba and Ra are precipitated as their sulphate, and U and V are converted into *soluble* UO_2SO_4 and $VOSO_4$ respectively. This filtrate which also contains Fe and Al is treated with excess of boiling solution of Na_2CO_3 which precipitates Fe and Al (*Reject*), and UO_2SO_4 and $VOSO_4$ are converted into *solub1e* $Na_4UO_2(CO_3)_3$ and Na_2VO_4 (*sod. vanadate*) respectively.

$$UO_2SO_4 + 3Na_2CO_3 \longrightarrow \underset{\text{(Soluble)}}{Na_4UO_2(CO_3)_3} + Na_2SO_4$$

$$2VOSO_4 + 5Na_2CO_3 + \tfrac{1}{2}O_2 \longrightarrow \underset{\text{(Soluble)}}{2Na_3VO_4} + 3Na_2SO_4 + 5CO_2$$

The solution containing $Na_4UO_2(CO_3)_3$ and Na_3VO_4 is neutralised by HNO_3 and treated with NaOH. This treatment precipitates uranium as $Na_2U_2O_7$.

$$Na_4UO_2(CO_3)_3 + 6HNO_3 \longrightarrow UO_2(NO_3)_2 + 4NaNO_3 + 3H_2O + 3CO_2$$

$$2UO_2(NO_3)_2 + 6NaOH \longrightarrow \underset{\text{ppt}}{Na_2U_2O_7} + 4NaNO_3 + 3H_2O$$

The precipitate of $Na_2U_2O_7$ is converted into $(NH_4)_2U_2O_7$ as in alkali digestion process.

$$Na_2U_2O_7 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2U_2O_7$$

$$H_2U_2O_7 + 2NH_4OH \longrightarrow \underset{\text{ppt.}}{(NH_4)_2U_2O_7 \downarrow} + 2H_2O$$

$(NH_2)_2U_2O_7$ on strong ignition in air gives U_3O_8 which can be reduced to uranium as already discussed.

Properties

The metal uranium resembles nickel in appearance. The pure sample is white, but on contamination with some nitride, it assumes yellow tint. It is malleable, takes polish, is softer than steel, but becomes hard and brittle when alloyed with carbon and chilled. It melts at 1850°. The powdered metal burns in air when heated to 160°, in chlorine at 150° and in fluorine at the room temperature. It also burns in iodine, sulphur vapour and nitrogen at higher temperature. It also decomposes water though slowly at the room temperature, yet rapidly on boiling. It reacts with ammonia at higher temperatures to give out nitrogen, dissolves in dilute mineral acids, giving out hydrogen, and evolves sulphur dioxide from concentrated sulphuric acid. The caustic alkalies have no action upon the metal. Uranium will displace mercury, silver, copper and tin from the solution of their salts. When a solution of uranium salt is exposed to light, it shows fluorescence. Uranium is a radioactive element and gives a series of disintegration products.

Nitrogen combines directly with uranium at 1000° forming *uranium nitride*, U_3N_4. Carbon also directly combines with uranium giving *uranium carbide*, UC_2.

Uses

In ceramics, uranium compounds are sometimes used to give coloured glasses, orange or yellow. Its salts have also been used as mordants for silk and wool. The metal and its carbide are one of the best catalysts in the Haber's synthesis of ammonia. Uranyl nitrate is used as a reagent in volumetric determination of phosphate and arsenates. Uranium steels are also of technical importance. The metal is used in nuclear reactors.

University Questions

1. How is titanium metal extracted in a pure form from ilimenite and rutile ores. *(Meerut 82, 88 Jodhpur 85; Allahabad 88; Bundelkhand 88)*
2. How does vanadium occur in nature? Discuss the extraction of vanadium from either vanadinite or carnotito. *(Raj. 87; Meerut 82; Indore 86)*
3. What are important ores of chromium? Describe the extraction of the metal from it chief ores. Give the chemical principles involved in the extraction process. *(Meerut 81, 82, 87; Garhwal 88; Allahabad 89; Gorakhpur 86; Sambalpur 86; Agra 85)*
4. Name the important ores of molybdenum. How is the metal extracted? What are its uses? *(Meerut M.Sc. 82, 85; Bharathiar 85)*

5. What are the important ores of tungsten? How is the metal obtained from its ores ? *(Madras 85, 86; Madurai 85)*

6. Outline the method for the extraction of Mn-metal from its ores. Give all the equations of reactions involved. *(Allahabad 87; Punjab 86; Meerut 86; Bundelkhand 88; Madras 85; Lucknow 85)*

7. Give the names of important ores of iron. *(Raj. 86)*

8. How is pig iron produced from iron ore? *(Agra 86; Raj. 86)*

9. How is pig iron converted into wrought iron and steel? *(Agra 86)*

10. What are alloy steels? Mention three elements that are used in preparing them? What special properties are produced in these metals ? *(Madras 86; Bharathiar 86)*

11. Write a note on alloy steels. Name their uses. *(Bharathiar 86; Punjab 84; Delhi 85; Madurai 85)*

12. Mention two important ores of cobalt. Explain with equations, how is the metal is extracted from its ores ? *(Madras 86; Punjab 85)*

13. What are the chief ores of nickel ? Describe the extraction of nickel (*i*) by Mond's process (*ii*) from Sudbery ores. What by-products are obtained in (*ii*) process. Give the utility of the metal in industry. *(Jiwaji 84; Allahabad 88; Meerut 82, 84; Garhwal 88; Gorakhpur 85)*

14. Discuss the method and give the chemical principles involved in the extraction of Pt from native ore. *(Allahabad 85, 88; Jodhpur 84; Agra 82, 84, 87, 88; Bharathiar 86)*

15. How is Pt obtained from Sudbury nickel ores? *(Meerut 83)*

16. Discuss briefly the extraction of Cu from its ore. Give all equations involved. *(Punjab 86; Madurai 86)*

17. Name the important ores of Silver. Describe the extraction of this metal by cyanide process. Give equations. *(Raj. 87)*

18. How is gold extracted from its ores? Discuss the chemical reactions involved in methods employed. *(Allahabad 89)*

19. What are the important ores of Zn? Describe the commercial method of the extraction of Zn. What are the common uses of Zn? *(Madras 85; Sambalpur 86; Agra 86; Poona 85)*

20. Discuss the methods of extraction of chromium from one of its important ores. *(Allahabad 99)*

21. (*i*) What happens when gold is heated with aqua regia.

(*ii*) Give important ores of Ni. Describe Mond's process of extracting Ni from sulphide ore.

(*iii*) Write notes on (*a*) Ni and Pt catalysts (*b*) Alloys of Cu and Zn. *(Kanpur 2000)*

22. Name the two ores of titanium. How is this metal extracted? *(Himachal Pradesh 99)*

23. Name two important ores of cobalt and discuss the chemistry of its extraction. *(Himachal Pradesh 2000)*

24. How is uranium extracted from one of its main ores ? Discuss the chemical principle of the extraction and give method of preparation and use of one of its compounds. *(Kumaon 2000)*

25. How is vanadium extracted from one of its important ores 7 Explain all the steps giving chemical equations. Give method of preparation of V_2O_5. *(Kumaon 2000)*

26. (*a*) Name two chief ores of Ni with their formulae.

(*b*) How would you extract Ni from its important ores? *(Gauhati (General) 2000)*

27. (*a*) What element is prepared from chromite ore? Discuss its different oxidation states. Mention its two important alloys and their uses.

(*b*) Name the members of titanium family. How is titanium prepared from rutile ? Give preparation of one of its important compounds. *(Lucknow 2000)*

28. (*a*) With particular reference to the electronic configuration of 4*f* block elements discuss the isolation of oxides of lanthanones from monazite sand.

(*b*) Discuss ion exchange method for the separation of lanthanones. *(Lucknow 2000)*

29. Name the important ores of Cr. How is this metal obtained from Chromite ore in pure form ? How is chromealum obtained from $K_2Cr_2O_7$? Explain the reactions giving equations. *(Avadh 2000)*

30. (*i*) Explain how the properties of iron are affected by the addition of carbon?

(*ii*) Give an account of 'heat treatment of steel'. *(Bharathiar 2000)*

31. (*i*) Discuss the extraction of chromium from its oxide ore.

(*ii*) Discuss briefly (*a*) Tempering of steel (*b*) Influence of chromium on the properties of steel. *(Bangalore 2001)*

32. What are the important ores of Th ? Write in brief the extraction of Th from monazite ore. Give its important uses. *(M.J.P. Rohilkhand M.Sc. 2008)*

33. How is uranium obtained from its ores ? State the important properties and uses of the metal. *(M.J.P. Rohilkhand 2009)*

34. What are important ores of nickel ? How is nickel extracted from pentandite. Describe its important properties. *(Meerut 2009)*

CHAPTER

47 Some Compounds of d- and f-Block Elements

Compounds of Titanium

Different Oxidation States of Titanium in Its Compounds

Titanium forms compounds in 0, +2, +3, +4 and –1 oxidation states. The electronic configuration of Ti^0 atom and of, Ti^{2+}, Ti^{3+}, Ti^{4+} and Ti^{1-} ions are as : $Ti^0 \rightarrow 2, 8, 3s^2p^6d^2, 4s^2$; $Ti^{2+} \rightarrow 2, 8, 3s^2p^6d^2, 4s^0$; $Ti^{3+} \rightarrow 2, 8, 3s^2p^6d^1, 4s^0$; $Ti^{4+} \rightarrow 2, 8, 3s^2p^6d^2, 4s^0$; $Ti^{1-} \rightarrow 2, 8, 3s^2p^6d^3, 4s^2$. Compounds having Ti metal in +4 oxidation state are the most stable and hence the compounds in lower oxidation states are readily oxidised to +4 state even by water or air.

Ti (+4) compounds are generally covalent and resemble, in certain respects, the corresponding compounds of group IVA elements. Ti (+3) and Ti (+2) compounds are mainly ionic. They act as active reducing agents.

$$2Ti^{3+} \xrightarrow{\text{Heat}} Ti^{4+} + Ti^{2+}$$

$$2Ti^{2+} \xrightarrow{\text{Water}} Ti^{4+} + Ti^0$$

Ti (0) and Ti (–1) compounds are rare. Examples of compounds having Ti metal in different oxidation state are : *Ti (0) compounds* : $[Ti(dipy)_3]^0$; *Ti (+2) compounds*; TiO, $TiCl_2$; Ti (+3) *compounds (called titanous compounds)* : $TiCl_3$, Ti_2O_3, $Ti(OH)_3$, $[Ti(H_2O)_6]^{3+}$, $[TiF_6]^{3-}$; *Ti (+4) compounds (called titanic compounds)* : TiO_2, $TiCl_4$, $TiBr_4$, TiI_4, $TiOCl_2$, $Ti(SO_4)_2$, $TiOSO_4$; *Ti (–1) compounds* : $[Ti(dipy)_3]^-$. Now let us discuss some important compounds of titanium.

1. Titanium Trichloride or Titanous Chloride, $TiCl_3$

It is the most important compound of Ti (+3). It is prepared by reducing $TiCl_4$ with H_2 in an electrically heated spiral in a water cooled tube or with Ag at 200°C.

$$2TiCl_4 + H_2 \longrightarrow 2TiCl_3 + 2HCl$$

$$TiCl_4 + Ag \longrightarrow TiCl_3 + AgCl$$

Anhydrous $TiCl_3$ is a violet powder. It disproportionates into $TiCl_4$ and $TiCl_2$.

$$2TiCl_3 \longrightarrow TiCl_3 + TiCl_2$$

It is a powerful reducing agent since it reduces chlorates and perchlorates to chlorides, Fe^{3+} to Fe^{2+}, Cu^{2+} to Cu, and persulphate to SO_4^{2-}. Due to this property $TiCl_3$ is used in volumetric analysis of the above mentioned compounds. An aqueous

solution of $TiCl_3$, when added to a dilute solution of a gold salt, produces an intense violet colour, due to the reduction of the gold salt followed by the absorption of colloidal gold on hydrous TiO_2. This reaction has been used as a very delicate test for gold.

2. Titanium Dioxide, TiO_2

Preparation. This compound is also called ***titanic dioxide*** or ***titania.*** This is prepared by adding an aqueous solution of NH_3 to $TiCl_4$ and then heating the precipitate of $Ti(OH)_4$ thus obtained.

$$TiCl_4 + 4NH_3 + 4H_2O \longrightarrow \underset{\text{ppt.}}{Ti(OH)_4} + 4NH_4Cl$$

$$Ti(OH)_4 \xrightarrow{\Delta} TiO_2 + 2H_2O$$

TiO_2 can also be obtained from rutile ore. This ore is first converted into $TICl_4$ by heating the mixture of rutile ore and carbon with Cl_2 and then $TiCl_4$ is oxidised to pure TiO_2 with O_2.

$$TiO_2 + C + 2Cl_2 \xrightarrow{\Delta} TiCl_4 + CO_2$$

$$TiCl_4 + O_2 \longrightarrow TiO_2 + 2Cl_2$$

TiO_2 can also be obtained from ilmenite ore, $FeTiO_3$ as discussed in the extraction of Ti.

Properties : TiO_2 occurs in nature in three crystalline forms which are *rutile, anatase* and *brookite.* Rutile is the commonest form and forms tetragonal transparent to opaque, red or yellowish crystals. This form is stable above 1040°. The anatase modification also crystallises in the tetragonal system but with the different axial ratio. This form is stable upto 860°. Brookite form crystallises in rhombic form and is stable between 860–1040°. The rutile form of TiO_2 is considered to be the most stable. The rutile or brookite forms are metastable below 860° and thus are converted into anatase by suitable heat treatment.

$$\textit{Anatase} \overset{860°C}{\rightleftarrows} \textit{Brookite} \overset{1040°C}{\rightleftarrows} \textit{Rutile}$$

Natural TiO_2 is impure due to the presence of iron oxide as an impurity contaminated with it. Pure TiO_2 is colourless (amorphous white powder) when cold, and yellowish when hot.

It melts at about 1800° and looses O_2 to form Ti_2O_3 [$4TiO_2 \xrightarrow{>1800°} 2Ti_2O_3 + O_2$]. It is insoluble in H_2O and dil. acids but dissolves in hot conc. H_2SO_4 and HF due to the formation of soluble Ti (+4) salts. It is amphoteric oxide but more acidic than basic. It dissolves in alkalies to form titanates (TiO_3^{2-}). [$TiO_2 + 2NaOH \rightarrow Na_2TiO_3 + H_2O$]. On heating with carbon in a current of Cl_2, it forms $TiCl_4$. With dry Cl_2, it gives $TiCl_4$ [$TiO_2 + 2Cl_2$ (dry) $\rightarrow TiCl_4 + O_2$]. It is reduced to Ti metal by heating it with carbon or Al metal.

$$TiO_2 + C \longrightarrow Ti + CO_2$$

$$3TiO_2 + 4Al \longrightarrow 3Ti + 2Al_2O_3$$

On passing the vapours of CCl_4 over TiO_2 at high temperature. $TiCl_4$ is formed.

$$TiO_2 + CCl_4 \text{ (vapours)} \longrightarrow TiCl_4 + CO_2$$

Uses. (*i*) Because of its high opacity, inertness towards H_2S, high covering power, light weight, non-poisonous nature, ease of wetting and disperssion in oil as well as resistance to high temperature it is used as a white pigment under the name *titan white*. Mixed with $BaSO_4$ it is sold under the trade name *titanox*. (*ii*) It can be also be used for interior protection purpose. When applied externally the film gets chalked out. (*iii*) It is also used (*a*) in making non-greasable paper (*b*) in the manufacture of arc lamp electrodes (*c*) in gas mantles, (*d*) for the preparation of glazes, (*e*) in making components for use in radio and television sets (*f*) as an additive in the manufacture of fibre glass (*g*) in the manufacture of artificial gems (*h*) in enamelling of porcelain goods (*i*) in the surface of white leather (*j*) in rubber industry to soften rubber (*k*) as a whitener in cosmetics (*e.g.* in face powder, cold creams etc.) (*l*) in preparing printing and decorating inks.

3. Titanium Tetrachloride, $TiCl_4$

Preparation : This compound is also called ***titanic chloride*** and is prepared (*i*) by heating the rutile ore with carbon in a current of Cl_2 (see the preparation of TiO_2) (*ii*) by the action of of dry Cl_2 on TiO_2 (see the properties of TiO_2) (*iii*) by passing vapours of CCl_4 at high temperature over TiO_2 (see the properties of TiO_2) (*iv*) from ilmenite ore (see the extraction of Ti metal).

Properties : It is a colourless, strongly fuming liquid. It has m.pt. = –30°C and b.pt. = 136.4°C. It is rapidly hydrolysed by excess of H_2O. [$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl$]. If water is not present in excess, hydrolysis is incomplete and *titanium oxy-chloride*, $TiOCl_2$ is formed [$TiCl_4 + H_2O \rightarrow TiOCl_2 + 2HCl$].

It is a strong *Lewis acid* (*i.e.* electron pair acceptor) and hence can accept electron pairs form donor molecules like NH_3 and PCl_5, forming the addition compounds like $TiCl_4.6NH_3$, $TiCl_4.8NH_3$ and $TiCl_4.PCl_5$ etc.

$TiCl_4$ can be reduced to free metal by heating it with Mg, Na, NaH etc. When $TiCl_4$ is treated with amalgamated Na or with H_2 in the silent electric discharge, it is reduced to $TiCl_2$. $TiCl_4$ can also be reduced to $TiCl_2$ by heating it with titanium shavings.

$$TiCl_4 + H_2 \longrightarrow TiCl_2 + 2HCl$$

$$TiCl_4 \xrightarrow[\text{Titanium shavings}]{900°C} 2TiCl_2$$

When $TiCl_4$ is heated with H_2 by an electrically heated spiral in a water-cooled tube, anhydrous $TiCl_3$ gets deposited on the cold walls of the tube. The reduction of $TiCl_4$ with Ag at 200°C also gives $TICl_3$.

$$2TiCl_4 + H_2 \longrightarrow 2TiCl_3 + 2HCl.$$

$$TiCl_4 + Ag \longrightarrow TiCl_3 + AgCl.$$

With NH_4Cl yellow crystals of *ammonium chlorotitanate*, $(NH_4)_2[TiCl_6].2H_2O$ are obtained.

$$TiCl_4 + 2NH_4Cl + 2H_2O \longrightarrow (NH_4)_2[TiCl_6].2H_2O$$

$TiCl_4$ dissolves in conc. HCl, forming chloro complexes of the formulae, $TiCl_4.HCl.H_2O$ or $H^+[TICl_5(H_2O)]$ and $TiCl_4.2HCl$ or $2H^+[TiCl_6]^{2-}$. On heating $TiCl_4$ with anhydrous HF, TiF_4 is obtained.

$$TiCl_4 + 4HF \longrightarrow TiF_4 + 4HCl$$

Uses. It is used : (*i*) to form irritating smoke-clouds and dense fogs in war time. (*ii*) for the production of titanium metal by reducing it with Mg (*Kroll process*). *Na*(*I.C.I. process*), NaH etc. (*iii*) in the manufacture rutile gems and organic titanium compounds.

Uses of titanium compounds. (*i*) The uses of TiO_2 and $TiCl_4$ have already been described. (*ii*) Double salts of Ti like $TiOC_2O_4.K_2C_2O_4.H_2O$, $Na_2SO_4.Ti_2(SO_4)_3.5H_2O$ etc. are used as mordants in the dyeing of textile and leather. (*iii*) $TiCl_2$ is used as a reducing agent in the laboratory for the titration of Fe^{3+}. $TiCl_3$ and $Ti_2(SO_4)_3$ are used for removing certain dyes from the goods so that they may be redyed. They are also used for removing stains. (*iv*) TiC has been used as a catalyst during the preparation of nitrogen- hydrogen and nitrogen-oxygen compounds. TiC is also used for the preparation of hard metals or cutting alloys. (*v*) Titanium boride is one of the hardest substances known and hence is used as an abrasive.

Compounds of Vanadium

Different Oxidation States of Vanadium in Its Compounds

Vanadium forms compounds in 0, +1, +2, +3, +4, +5 and –1 oxidation states. The electronic configuration V^0 atom and of V^+, V^{2+}, V^{3+}, V^{4+}, V^{5+} and V^- ions are : $V^0 \rightarrow 2, 8, 3s^2p^6d^3, 4s^2$; $V^+ \rightarrow 2, 8. 3s^2p^6d^3, 4s^1$; $V^{2+} \rightarrow 2, 8, 3s^2p^6d^3, 4s^0$; $V^{3+} \rightarrow 2, 8, 3s^2p^6d^2, 4s^0$; $V^{4+} \rightarrow 2, 8, 3s^2p^6d^1, 4s^0$; $V^{5+} \rightarrow 2, 8, 3s^2p^6d^0, 4s^0$; $V^- \rightarrow 2, 8, 3s^2p^6d^4, 4s^2$. Examples of compounds having vanadium in different oxidation states are : *V*(0) *compounds* : $V(CO)_6$, $V(dipy)_3$; *V* (*+1*) *compounds* : $[V(dipy)_3]^+$; *V* (*+2*) *compounds* : VO, VS, VX_2 (X = Cl, Br, I), VSO_4, $[V(H_2O)_6]^{2+}$, $[V(CN)_6]^{4-}$; *V* (*+3*) *compounds* : V_2O_3, V_2S_3, $V(OH)_3$, VX_3 (X = F, Cl, Br, I), VOX (X = Cl, Br), $[VCl_4]^-$ $[VF_6)^{3-}$, $[V(H_2O)_6]^{3+}$; *V* (*+4*) *compounds* : VO_2, VX_4 (X = F, Cl), $VOSO_4$, VOX_2 (X = F, Cl, Br), $V(NO_3)_2$, $[VCl_6]^{2-}$; *V*(*+5*) *comounds* : V_2O_5, VOX_3 (X = F, Cl, Br), VF_5, $[VF_6]^-$, NH_4VO_3, $Na_3VO_4.12H_2O$; *V* (*–1*) *compounds* : $[V(CN)_5(NO^+)]^{5-}$, $[V(CO)_6]^-$. Compounds in lower oxidation states are very unstable and act as powerful reducing agents; sometimes so sufficiently powerful that they can liberate H_2 even from H_2O. The most stable oxidation states are + 4 and. +5. Vanadium forms compounds of three main types : (*i*) Interstitial compounds with C, N_2 or H_2 (*ii*) Giant molecular compounds with electronegative elements like O, S, F etc. Examples of such compounds are : VO, VS, V_2O_3. V_2S_3, VF_3 etc. (*iii*) Salts in which vanadium atom is the central atom in complex anions. Now let us discuss some important compounds of vanadium.

1. Vanadium Pentoxide, V_2O_5

Preparation. It can be prepared (*i*) by heating ammonium metavanadate, NH_4VO_3 or (*ii*) by the hydrolysis of vanadium (V) oxychloride, $VOCl_3$

$$2NH_4VO_3 \xrightarrow{\Delta} V_2O_5 + 2NH_3 + H_2O$$
$$2VOCl_3 + 3H_2O \longrightarrow V_2O_5 + 6HCl$$

Properties. It is a yellowish red powder and undergoes reversible dissociation in the temperature range 700–1125°C

$$2V_2O_5 \rightleftharpoons 2V_2O_4 + O_2$$

When V_2O_5 is reacted with Cl_2 at elevated temperature, $VOCl_3$ is obtained. When Cl_2 gas is passed over a mixture of V_2O_5 and carbon, $VOCl_2$ is formed.

$$2V_2O_5 + 6Cl_2 \longrightarrow 4VOCl_3 + 3O_2$$
$$V_2O_5 + 3C + 3Cl_2 \longrightarrow 2VOCl_3 + 3CO$$

When V_2O_5 is reduced with K, *hypovanadium oxide* (V_2O_2) is obtained.

$$V_2O_5 + 6K \longrightarrow V_2O_2 + 3K_2O$$

When V_2O_5 is reduced by H_2 or sulphur, *vanadium trioxide* (V_2O_3) is obtained.

$$V_2O_5 + 2H_2 \xrightarrow{\Delta} V_2O_3 + 2H_2O$$
$$V_2O_5 + S \longrightarrow V_2O_3 + SO_2$$

When V_2O_5 is reduced with SO_2, H_2S or HX, or by fusion with oxalic acid ($H_2C_2O_4$), *vanadinin tetoxide* (V_2O_4) is obtained.

$$V_2O_5 + SO_2 \xrightarrow{\Delta} V_2O_4 + SO_3$$
$$V_2O_5 + H_2S \longrightarrow V_2O_4 + H_2O + S$$
$$V_2O_5 + 2HX \longrightarrow V_2O_4 + H_2O + X_2$$

When V_2O_5 is heated with Ca metal, V_2O_5 gets reduced to *vanadium metal.*

$$V_2O_5 + 5Ca \longrightarrow 5CaO + 2V$$

Reduction of a solution of V_2O_5 in conc. H_2SO_4 by means of SO_2 gives a blue solution which, on evaporation, gives the bright blue crystals of *acid vanadyl sulphate*, $2VOSO_4.\ H_2SO_4.\ xH_2O$. When this acid *vanadyl sulphate* is heated with conc. H_2SO_4 at 260°, a grey-green crystalline powder of *anhydrous vanadyl sulphate*, $VOSO_4$ is obtained.

V_2O_5 dissolves in HCl to give salts like vanadyl (IV) oxychloride, $VOCl_2$ or VCl_5

$$V_2O_5 + 6HCl \longrightarrow 2VOCl_2 + 3H_2O + Cl_2$$
$$V_2O_5 + 10HCl \longrightarrow 2VCl_5 + 5H_2O$$

With HNO_3, V_2O_5 gives metavanadic acid, HVO_3

$$V_2O_5 + 2HNO_3 \longrightarrow 2HNO_3 + N_2O_5$$

V_2O_5 dissolves in the excess of acids to give the complex anions like $[H_2V_{10}O_{28}]^{4-}$, $[HVO_{10}O_{28}]^{6-}$ and $[V_{10}O_{28}]^{6-}$ within the pH range = 1.3 to 6.5. V_2O_5 dissolves in alkalies to form a series of vanadates like *orthovanadates* (*e.g.* Na_3VO_4), *metavanadates* (*e.g.* $NaVO_3$) and *pyrovanadates* (*e.g.* $Na_4V_2O_7$). These vanadates are analogous to phosphates. At high pH value, sodium ortho vanadate, Na_3VO_4 is obtained by the action of V_2O_5 on NaOH.

$$V_2O_5 + 6NaOH \longrightarrow 2Na_3VO_4 + 3H_2O$$

As the pH is lowered, protonation of VO_4^{3-} ion and subsequent polymerisation takes place, and different types of anions are obtained as shown below :

$$VO_4^{3-} \longrightarrow [VO_2(OH)_3]^{2-} \longrightarrow [(VO_2)_2(OH)_5]^{3-} \longrightarrow [(VO_2)_3(OH)_6]^{3-}$$

When heated with carbon at high temperature, vanadium carbide (VC) is obtained. When V_2O_5 is melted with Na_2CO_3, Na_3VO_4 is obtained.

$$2V_2O_5 + 4C \longrightarrow 4VC + 5O_2$$

$$V_2O_5 + 3Na_2CO_3 \longrightarrow 2Na_3VO_4 + 3CO_2 \uparrow$$

Uses : V_2O_5 is used : (*i*) as a catalyst in a number of reactions. Some such reactions are : (*a*) oxidation of SO_2 to SO_3 used in the manufacture of H_2SO_4 by contact process. (*b*) oxidation of anthracene to anthraquinone. (*c*) oxidation of phenanthrene to phenanthraquinone (*d*) oxidation of toluene to benzaldehyde to benzoic acid. (*e*) oxidation of ethyl alcohol to acetaldehyde. (*ii*) in the preparation of vanadium glass. This glass is prepared by adding 0.02% vanadium as V_2O_5 to ordinary glass. This glass cuts out completely the harmful actinic rays which injure the eye and brings about fadings of organic compounds. Such glass is used particularly in textile store windows. Such glasses protect the eyes against day-light glare. (*iii*) in the preparation of ferro-vanadium alloy which is used as a scavenger in the manufacture of special steels. (See *uses of vanadium*).

2. Sodium Orthovanadate, $Na_3VO_4.12H_2O$

Preparation : It is prepared : (*i*) by dissolving V_2O_5 in NaOH, followed by crystallisation or by treating sodium pyrovanadate, $Na_4V_2O_7$ with NaOH (*ii*) by melting V_2O_5 with Na_2CO_3

$$V_2O_5 + 6NaOH \longrightarrow 2Na_3VO_4 + 3H_2O$$

$$Na_4V_2O_7 + 2NaOH \longrightarrow 2Na_3VO_4 + H_2O$$

$$V_2O_5 + 3Na_2CO_3 \longrightarrow 2Na_3VO_4 + 3CO_2 \uparrow$$

Properties and uses : It is soluble in H_2O. It is isomorphous with sodium orthophosphate dodecahydrate, $Na_3PO_4.12H_2O$. This compound is used (*i*) as a catalyst in the dyeing of leather to black colour. (*ii*) in making good quality, fire-flowing blue-black ink and marking inks. (*iii*) in volumetric analysis for certain oxidation-reduction reactions. The estimations by means of this reagent include metals such as Fe, Mo, Sn and Cu, and organic compounds such as citric acid, lactic acid, tartaric acid, aldehydes, ketones and sugars.

3. Ammonium Metavanadate, NH_4VO_3

It is obtained : (*i*) by adding an ammonium salt like NH_4Cl to a solution of $NaVO_3$, (*ii*) by treating metavanadic acid, HVO_3 with NH_3.

$$NaVO_3 + NH_4Cl \longrightarrow NH_4VO_3 + NaCl$$

$$HVO_3 + NH_3 \longrightarrow NH_4VO_3$$

Compounds of Chromium

Different Oxidation States of Chromium in Its Compounds

Chromium forms compounds in 0, +2, +3 and + 6 oxidation states. The electronic configuration of Cr^0 atom and of Cr^{2+}, Cr^{3+} and Cr^{6+} ions are as; $Cr^0 \rightarrow$ 2, 8,

$3s^2p^6d^5$, $4s^1$; $Cr^2 \rightarrow 2, 8, 3s^2p^6d^4, 4s^0$; $Cr^{3+} \rightarrow 2, 8, 3s^2p^6d^3, 4s^0$; $Cr^{6+} \rightarrow 2, 8, 3s^2p^6d^0, 4s^0$. Compounds having Cr metal in +3 state are the most stable. Cr (+2) compounds are strong reducing agents while those of Cr (+6) are strong oxidising agents.

Examples of compounds of Cr in different oxidation states are : *Cr(0) compounds* : $Cr(CO)_6$; *Cr(+2) compounds* (called *chromous compounds*) : CrX_2 (X = Cl, Br, I), $(CH_3COO)_2Cr$, CrO, $Cr(OH)_2$; *Cr(+3) compounds* (called *chromic compounds*) CrX_3 (X = Cl, Br, I), $Cr_2(SO_4)_3.18H_2O$, $Cr_2(SO_4)_3.6H_2O$, $K_2SO_4.Cr_2(SO_4)_3.24H_2O$, Cr_2O_3, $Cr(OH)_3$; *Cr(+6) compounds* : CrO_3, K_2CrO_4, $K_2Cr_2O_7$, CrO_2Cl_3.

Acidic character of oxides. With the increase in the oxidation state of Cr, the acidic character of the oxides of this metal also increases. For example :

Oxides :	CrO	Cr_2O_3	CrO_3
Oxidation state of Cr :	+2	+3	+6
Nature :	Basic	Amphoteric	Acidic

CrO is basic, since it gives Cr (+2) salt with an acid.

$$\underset{\text{(Basic)}}{CrO} + H_2SO_4 \longrightarrow CrSO_4 + H_2O$$

Cr_2O_3 is amphoteric because it gives salts with both acids and alkalies.

$$\underset{\text{(Amphoteric)}}{Cr_2O_3} + 3H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 3H_2O$$

$$\underset{\text{(Amphoteric)}}{Cr_2O_3} + 2KOH \longrightarrow \underset{\text{Pot. chromite}}{2KCrO_2} + H_2O$$

CrO_3 is the anhydride of chromic acid (H_2CrO_4) and is distinctly acid. It gives chromates with alkalies.

$$\underset{\text{(Acidic)}}{CrO_3} + 2NaOH \longrightarrow Na_2CrO_4 + H_2O$$

Covalent character of compounds. With the increase in the oxidation state of Cr, the covalent character of the compounds of Cr also increases. Thus Cr(+2) compounds are ionic, Cr(+3) compounds ionise to some extent while those of Cr(+0) are covalent.

Now let us discuss some important compounds of chromium.

1. Chromous Chloride, $CrCl_2$

Preparation : *Anhydrous $CrCl_2$* is prepared : (*a*) by heating chromic chloride, $CrCl_3$ in a current of H_2 or (*b*) by heating Cr metal in a current of dry HCl gas

$$2CrCl_3 + H_2 \longrightarrow 2CrCl_2 + 2HCl$$

A solution of $CrCl_2$ is obtained by reducing $K_2Cr_2O_7$ solution with Zn and HCl in the absence of air. When $K_2Cr_2O_7$ is heated with conc. HCl, Cl_2 is given off and $CrCl_3$ is obtained.

$$K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2 \uparrow$$

Now when Zn metal is added to the above solution, nascent hydrogen is evolved which reduces $CrCl_3$ to blue chromous chloride, $CrCl_2$

$$CrCl_3 + H \text{ (From Zn/HCl)} \longrightarrow CrCl_2 + HCl$$

Properties. $CrCl_2$ forms white deliquescent silky needles which dissolve in H_2O to give a blue solution. It is a powerful reducing agent and is readily oxidised in air to $CrCl_3$. Its vapour density, even above 1500°C, indicates appreciable association [$Cr_2Cl_4 \rightleftharpoons 2CrCl_2$]. When treated with HF, it gives CrF_2.

2. Chromous Acetate, $(CH_3COO)_2Cr$

Preparation. This compound is prepared as red precipitate by adding a saturated solution of CH_3COONa to the blue solution of $CrCl_2$.

$$CrCl_2 + 2CH_3COONa \longrightarrow \underset{\text{Red ppt.}}{(CH_3COO)_2Cr \downarrow} + 2NaCl$$

$CrCl_2$ used in the above reaction is obtained by reducing $CrCl_3$ by nascent hydrogen obtained by the action of Zn on HCl. $CrCl_3$ is obtained by the action of HCl on $K_2Cr_2O_7$ in the absance of air.

$$K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2 \uparrow$$
$$CrCl_3 + H \text{ (From Zn/HCl)} \longrightarrow CrCl_2 + HCl$$

Properties and uses : $(CH_3COO)_2Cr$ forms red crystals which are fairly stable in acids and hence is used for the preparation of other Cr(+2) salts.

3. Chromic Oxide or Chromic Sesquioxide or Chrome Green, Cr_2O_3

Preparation : This oxide is used as a green pigment for oil paints and hence is also called *chrome green*. It is prepared by the reactions represented by the following chemical equations :

$$2Cr(OH_3) \xrightarrow{\Delta} Cr_2O_3 + 3H_2O$$
$$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} Cr_2O_3 + 4H_2O + N_2 \uparrow$$
$$K_2Cr_2O_7 + 2NH_4Cl \xrightarrow{\Delta} Cr_2O_3 + 2KCl + 4H_2O + N_2 \uparrow$$
$$Na_2Cr_2O_7 + S \xrightarrow[\text{Heat in an iron pot}]{} Cr_2O_3 + Na_2SO_4$$
$$4CrO_2Cl_2 \text{ (vapours)} \xrightarrow[\text{Pass vapour in red hot tube}]{} Cr_2O_3 + O_2 + 4Cl_2$$

Properties and uses : It is a green powder with very high melting point and is very refractory. It dissolves in fused borax or glass and gives a green colour and hence is used in tining glass and painting procelain. It is not decomposed by heat nor reduced by H. It is reduced to metal when heated with carbon (better with Al powder) at a high temperature. It is an amphoteric oxide because it forms salts with acids and chromites when fused with alkalies

$$Cr_2O_3 + 3H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 3H_2O$$
$$Cr_2O_3 + 2NaOH \longrightarrow 2NaCrO_2 + H_2O$$

When it is fused with an alkali in presence of air or an oxidising agent, a chromate is formed.

$$2Cr_2O_3 + 8NaOH + 3O_2 \longrightarrow 4Na_2CrO_4 + 4H_2O$$

If it is ignited too strongly, it becomes passive towards both acid and base. When fused with an oxide of MO type, it gives a crystalline compound of the

composition, $MO.Cr_2O_3$. It is used (*i*) as a green pigment for oil, paints under the name *chrome-green. Guignet's green*, $Cr_2O_3.2H_2O$ is also used as a pigmant and is formed by fusing $K_2Cr_2O_7$ with boric acid and treating the resulting product with water. (*ii*) in tining glass and painting porcelain.

4. Potassium Chromic Sulphate or Chrome Alum $K_2SO_4.\ Cr_2(SO_4)_3.\ 24H_2O$

Preparation : It crystallises out when $K_2Cr_2O_7$ is reduced by sulphur dioxide in presence of sulphuric acid.

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

On standing, beautiful dark purple octahedral crystals of chrome alum separate.

$$K_2SO_4 + Cr_2(SO_4)_3 + 24H_2O \longrightarrow \underbrace{K_2SO_4.Cr_2(SO_4)_3.24H_2O}_{\text{Chrome alum}}$$

Properties and uses : The crystals of chrome alum possess a deep violet colour and are isomorphous with other alums. It forms a violet solution in cold water but if heated to 70°C, the colour of the solution becomes green. It is used (*i*) as a mordant in dyeing and calico-printing. (*ii*) for tanning leather. (*iii*) in photography (during fixing) for hardening of the negatives.

5. Chromium Trioxide or Chromic Oxide, CrO_3

Preparation. This oxide is the anhydride of unknown chromic acid, H_2CrO_4 and hence is also called ***chromic acid anhydride***. It is obtained as deep red needle-like crystals when a well-cooled solution of $K_2Cr_2O_7$ is treated with conc. H_2SO_4.

$$K_2Cr_2O_7 + H_2SO_4\ (\text{cold}) \longrightarrow \underset{\substack{\text{Red}\\ \text{crystals}}}{2CrO_3} + K_2SO_4 + H_2O$$

The crystals of CrO_3 are filtered by means of a Buchner funnel containing asbestos, washed with pure HNO_3 and dried in a current of warm air to remove the adhering HNO_3.

Properties : This compound forms deep red needlelike crystals which are deliquescent. It is highly poisonous and damages to the kidneys. When heated to 198°C it melts and gives a dark liquid and then, on further heating, O_2 gas is evolved.

$$4CrO_3\ (\textit{solid}) \xrightarrow{198^\circ} 4CrO_3\ (\text{liquid}) \xrightarrow{>198^\circ} 2Cr_2O_3 + 3O_2$$

It is soluble in water, giving a red solution. This red solution is strongly acidic and contains several chromic acids. The simplest of these acids is *chromic acid.* H_2CrO_4

$$CrO_3 + H_2O \rightleftarrows H_2CrO_4$$

It is a powerful oxidising agent and its oxidising action is based on the following equation.]

$$2CrO_3 \longrightarrow Cr_2O_3 + O$$

When CrO_3 oxidises any substance, the oxide itself is reduced to Cr(+3) salt. Thus it oxidises SO_2, acidified H_2S, $FeSO_4$, $SnCl_2$ as shown by the following equations :

$$2CrO_3 + 3SO_2 \longrightarrow Cr_2(SO_4)_3$$
$$2CrO_3 + 3H_2S + 3H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 6H_2O + S$$
$$2CrO_3 + 6FeSO_4 + 6H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 6H_2O$$
$$2CrO_3 + 3SnCl_2 + 12HCl \longrightarrow 2CrCl_3 + 3SnCl_4 + 6H_2O$$

When CrO_3 is dissolved in calculated amount of NH_3, ammonium dichromate, $(NH_4)_2Cr_2O_7$ is formed.

$$2CrO_3 + 2NH_3 + H_2O \longrightarrow (NH_4)_2Cr_2O_7$$

Uses : CrO_3 in the form of $H_2CrO_4(K_2Cr_2O_7)$ and conc. H_2SO_4 is used as an oxidising agent in volumetric analysis and for cleaning glass apparatus. CrO_3 dissolved in glacial acetic acid is used as an oxidising agent and us a disinfectant to wash foul ulcers and ores.

6. Potassium Chromate, K_2CrO_4

Preparation : On commercial scale is prepared from chromite ore, $FeO.Cr_2O_3$. The ore is first concentrated by Wilfley table method (gravity separation method). The concentrated ore is mixed with excess of K_2CO_3 and roasted in a reverberatory furnace at a high temperature in the presence of free supply of air. By this operation the chromite ore, $FeO.Cr_2O_3$ is converted into soluble potassium chromate, K_2CrO_4

$$\underset{\text{Chromite ore}}{4[FeO.Cr_2O_3]} + 8K_2CO_2 + 7O_2 \text{ (From air)} \xrightarrow{\Delta} \underbrace{\underset{\text{Soluble}}{8K_2CrO_4} + \underset{\text{Insoluble}}{2Fe_2O_3}}_{\text{Roasted mass}} + 8CO_2 \uparrow$$

The roasted mass containing K_2CrO_4 and Fe_2O_3 is extracted with water when K_2CrO_4 goes into solution and Fe_2O_3 is left behind as a residue. In the process of roasting some quantity of CaO is also added so that the mixture of chromite ore and K_2CO_3 may become porous.

K_2CrO_4 can also be prepared from $K_2Cr_2O_7$. To the water solution of $K_2Cr_2O_7$ calculated amount of KOH or K_2CO_3 is added. On evaporating the resulting solution lemon-yellow crystals of anhydrous potassium chromate are obtained.

$$K_2Cr_2O_7 + 2KOH \longrightarrow 2K_2CrO_4 + H_2O$$
$$K_2Cr_2O_7 + K_2CO_3 \longrightarrow 2K_2CrO_4 + CO_2 \uparrow$$

Properties : It forms lemon-yellow crystals (m.p. = 968°C) which is isomorphous with K_2SO_4. It is highly soluble in water and its solution is yellow in colour and on the addition of acids, it becomes red due to the formation of dichromate.

$$2K_2CrO_4 + H_2SO_4 \longrightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O$$

Conversely, a red dichromate solution turns yellow on the addition of alkali on account of the chromate formation.

$$K_2Cr_2O_7 + 2KOH \longrightarrow 2K_2CrO_4 + H_2O$$

On being heated above 670°C it changes to a *red modification* which melts at 970°C. An acidified solution of K_2CrO_4 acts as an oxidising agent.

$$2K_2CrO_4 + 5H_2SO_4 \longrightarrow 2K_2SO_4 + Cr_2(SO_4)_3 + 5H_2O + 3O$$

Thus it liberates I_2 from KI, oxidises H_2S to S, SO_2 to H_2SO_4, HCl to Cl_2 etc.

When potassium chromate solution is added to silver nitrate solution, brick red precipitate of *silver chromate*, Ag_2CrO_4 is formed. Soluble barium and lead salts give with potassium chromate yellow precipitates of barium and lead chromates, $BaCrO_4$ and $PbCrO_4$.

Uses : It is used (*i*) as a reagent in the laboratory (*ii*) as an indicator in Mohr's volumetric method of silver estimation (*iii*) as an inhibitor for corrosion.

7. Lead Chromate or Chrome Yellow, $PbCrO_4$

Preparation : This compound occurs naturally as *crocosite*. $PbCrO_4$ is obtained as a yellow precipitate by mixing an aqueous solution of K_2CrO_4 with that of $PbCH_3COO)_2$.

$$(CH_3COO)_2Pb + K_2CrO_4 \longrightarrow \underset{\text{Yellow ppt.}}{PbCrO_4} + 2CH_3COOK$$

Properties : It is a yellow solid and is least soluble of all the lead salts. It is precipitated in presence of ammonium acetate. It is insoluble in dilute but dissolves in concentrated HNO_3. It is also soluble in concentrated NaOH forming sodium plumbite and chromate.

$$PbCrO_4 + 4NaOH \longrightarrow \underset{\text{Sod. plumbite}}{Na_2PbO_2} + Na_2CrO_4 + 2H_2O$$

When $PbCrO_4$ is boiled with cold dilute solution of NaOH, *basic lead chromate*, $Pb(OH)_2.PbCrO_4$ (*chrome red*) is formed as red precipitate.

$$2PbCrO_4 + 2NaOH \text{ (\textit{cold and dilute solution})} \longrightarrow \underset{\substack{\text{Basic lead chromate} \\ \text{(red ppt.)}}}{Pb(OH)_2.PbCrO_4} + Na_2CrO_4$$

Uses : Lead chromate is used as a yellow pigment under the name of *chrome yellow, cologne yellow* or *lemon chrome.*

8. Basic Lead Chromate or Chrome Red, $PbCrO_4$ $Pb(OH)_2$.

As already stated, this compound is prepared by boiling $PbCrO_4$ with cold dilute solution of NaOH.

$$2PbCrO_4 + 2NaOH \text{ (\textit{cold and dilute solution})} \longrightarrow \underset{\substack{\text{Basic lead chromate} \\ \text{(red ppt.)}}}{Pb(OH)_2.PbCrO_4} + Na_2CrO_4$$

It is used as a red pigment under the name of *chrome red.*

9. Potassium Dichromate, $K_2Cr_2O_7$

Manufacture : $K_2Cr_2O_7$ is manufactured from chromite ore, $FeO.Cr_2O_3$ by a method which consists of four steps *viz.* (*i*) *Concentration of the chromite ore.* (*ii*) *Conversion of the concentrated chromite ore into* Na_2CrO_4 *(Roasting of the concentrated ore).* (*iii*) *Conversion of* Na_2CrO_4 into $Na_2Cr_2O_7$. For these three steps see "*Extraction of chromium metal from chromite ore*". (*iv*) *Conversion of* $Na_2Cr_2O_7$ *to* $K_2Cr_2O_7$. Hot solution of $Na_2Cr_2O_7$ obtained as above in step (*iii*) is

treated with the calculated quantity of KCl whereby less soluble $K_2Cr_2O_7$ separates out from the solution on crystallisation.

$$Na_2Cr_2O_7 + 2KCl \longrightarrow \underset{\text{More soluble}}{2NaCl} + \underset{\text{Less soluble}}{K_2Cr_2O_7}.$$

Properties : $K_2Cr_2O_7$ forms orange-red prismatic crystals which melt at 396°C. It is moderately soluble in cold water and freely so in hot water. When heated to a white heat, it decomposes to give potassium chromate, K_2CrO_4 and O_2 gas is evolved.

$$4K_2Cr_2O_7 \xrightarrow{\Delta} 4K_2CrO_4 + 2Cr_2O_3 + O_2\uparrow$$

When an alkali is added to an orange-red solution of $K_2Cr_2O_7$, a yellow solution results. The yellow colour of the solution is due to the formation of K_2CrO_4.

$$\underset{\text{Orange-red}}{K_2Cr_2O_7} + 2KOH \longrightarrow \underset{\text{Yellow}}{2K_2CrO_4} + H_2O$$

$$\underset{\text{Orange-red}}{K_2Cr_2O_7} + 2NaOH \longrightarrow \underset{\text{Yellow}}{K_2CrO_4} + H_2O + Na_2CrO_4$$

On acidifying, the yellow colour of K_2CrO_4 again changes to orange-red due to the reformation of $K_2Cr_2O_7$.

$$\underset{\text{Yellow}}{2K_2CrO_4} + H_2SO_4 \longrightarrow \underset{\text{Orange-red}}{K_2Cr_2O_7} + K_2SO_4 + H_2O$$

This interconversion is explained on the basis of the fact that in $K_2Cr_2O_7$ solution, orange-red $Cr_2O_7^{2-}$ ions are in equilibirium with yellow $Cr_2O_4^{2-}$ ions.

$$\underset{\text{Orange-red}}{Cr_2O_7^{2-}} + H_2O \rightleftarrows \underset{\text{Yellow}}{2CrO_4^{2-}} + 2H^+$$

On adding an alkali, the concentration of H^+ ions decreases and hence the above reaction proceeds in the forward direction producing yellow solution containing CrO_4^{2-} ions. On the other hand when an acid is added, the concentration of H^+ ions increases and hence the above reaction proceeds in the backward direction producing the orange solution containing $Cr_2O_7^{2-}$ ions. The above description makes it evident that since both $Cr_2O_7^{2-}$ and CrO_4^{2-} ions are present in a dichromate solution, $K_2Cr_2O_7$ will precipitate a salt of lower solubility product with Pb^{2+} or Ba^{2+} ions. Thus when $K_2Cr_2O_7$ is treated with $Pb(NO_3)_2$, $PbCrO_4$ and not $PbCr_2O_7$ is precipitated. This is because of the fact that $PbCrO_4$ has less solubility product than $PbCr_2O_7$.

$$K_2Cr_2O_7 + 2Pb(NO_3)_2 + H_2O \longrightarrow \underset{\text{ppt.}}{2PbCrO_4} + 2KNO_3 + 2HNO_3$$

With cold H_2SO_4, red crystals of chromium trioxide, CrO_3 are formed. When $K_2Cr_2O_7$ is heated with H_2SO_4, O_2 gas is evolved.

$$K_2Cr_2O_7 + H_2SO_4 \text{ (cold)} \longrightarrow \underset{\text{Red crystals}}{2CrO_3} + K_2SO_4 + H_2O$$

$$2K_2Cr_2O_7 + 8H_2SO_4 \xrightarrow{\Delta} 2K_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2$$

When solid $K_2Cr_2O_7$ is heated with conc. H_2SO_4 and a soluble chloride like NaCl, deep red vapours of chromyl chloride, CrO_2Cl_2 are produced.

$$K_2Cr_2O_7 + 4NaCl + 3H_2SO_4 \text{ (concentrated)} \xrightarrow{\Delta} \underset{\text{Red vapours}}{2CrO_2Cl_2} + K_2SO_4 + 2Na_2SO_4 + 3H_2O$$

$K_2Cr_2O_7$ is a powerful oxidising agent. In presence of dil. H_2SO_4, one molecule of this compound gives three atoms of oxygen as shown below :

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

Thus in presence of dil H_2SO_4, it liberates I_2 from KI solution, oxidises Fe(+2) salts to Fe(+3) salts, oxidises H_2S to S, oxidises SO_2 to H_2SO_4.

$$K_2Cr_2O_7 + 7H_2SO_4 + 6KI \longrightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2$$

or $$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 7H_2O + 3I_2$$

$$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3Fe_2(SO_4)_3$$

or $$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$$

$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$$

or $$Cr_2O_7^{2-} + 8H^+ + 2H_2S \longrightarrow 2Cr^{3+} + 7H_2O + 3S$$

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

or $$Cr_2O_7^{2-} + 2H^+ + 3SO_2 \longrightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O$$

When $K_2Cr_2O_7$ is heated with conc. HCl, Cl_2 is given off and chromic chloride ($CrCl_3$) is obtained.

$$K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2 \uparrow$$

Now when Zn metal is added to the above solution, nascent hydrogen is evolved which reduces $CrCl_3$ to blue chromous chloride, $CrCl_2$.

$$CrCl_3 + H \text{ (From Zn/HCl)} \longrightarrow CrCl_2 + HCl$$

Now when a saturated solution of CH_3COONa is added to the blue solution of $CrCl_2$ obtained as above, a red precipitate of chromous acetate, $(CH_3COO)_2Cr$ is obtained.

$$CrCl_2 + 2CH_3COONa \longrightarrow \underset{\text{Red ppt.}}{(CH_3COO)_2Cr \downarrow} + 2NaCl$$

Uses. Potassium dichromate finds extensive use in dyeing, calico-printing and chrome-tanning. It is used as an oxidising agent and in the preparation of various chromium compounds like Cr_2O_3, CrO_3, $K_2SO_4.Cr_2(SO_4)_3.24H_2O$, CrO_2Cl_2, K_2CrO_4, $CrCl_3$, $Cr(CH_3COO)_2$ etc. It is also used in photography. A mixture of $K_2Cr_2O_7$ and conc. H_2SO_4, usually known as *chromic acid mixture*, has strong oxidising properties and is used as a cleaning agent for glassware etc. It is also used in leather industry (*chrome tanning*).

10. Chromyl Chloride, CrO_2Cl_2

Preparation : When solid $K_2Cr_2O_7$ is heated with conc. H_2SO_4 and a soluble salt (*e.g.* NaCl), deep red vapours of CrO_2Cl_2 are obtained.

$$K_2Cr_2O_7 + 4NaCl + 3H_2SO_4 \text{ (concentrated)} \xrightarrow{\Delta} \underset{\substack{\text{Chromyl chloride (red vapours)}}}{2CrO_2Cl_2} + K_2SO_4 + 2Na_2SO_4 + 3H_2O$$

Properties : It is a dark red liquid (b.pt. = 116.7°C and m.pt. = 16.5°C). It is miscible with organic solvents like CCl_4 and CS_2. It is photosensitive but otherwise it is stable. It is hydrolysed by H_2O, giving a yellow solution of H_2CrO_4.

$$CrO_2Cl_2 + 2H_2O \longrightarrow \underset{\substack{\text{Yellow solution}}}{H_2CrO_4} + 2HCl$$

The solution of CrO_2Cl_3 gives a yellow precipitate of $PbCrO_4$ with $(CH_3COO)_2Pb$.

$$CrO_2Cl_2 + 2H_2O + (CH_3COO)_2Pb \longrightarrow \underset{\substack{\text{Yellow ppt.}}}{PbCrO_4} + 2HCl + 2CH_3COOH$$

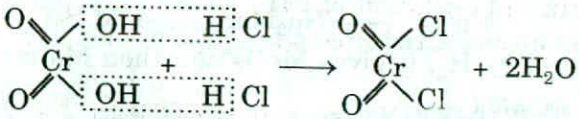
It is a powerful oxidising agent. A solution of CrO_2Cl_2 in CS_2 oxidises toluene to benzaldehyde (*Etard's reaction*). When CrO_2Cl_2 is added to a saturated solution of KCl, red crystals of *potassium chloro-chromate*, $KCrO_3Cl$ (*Petigot's salt*) are formed. With NaOH, it gives Na_2CrO_4.

$$CrO_2Cl_2 + KCl + H_2O \longrightarrow KCrO_3Cl + 2HCl$$

$$CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O$$

Uses : It is used : (*i*) as an intermediate product in the identification of Cl^- ions. (*ii*) as an excellent oxidising agent in organic chemistry,. *e.g.* its solution in CS_2 is used to oxidise toluene to benzaldehyde.

CrO_2Cl_2 is an acid chloride of chromic acid, $CrO_2(OH)_2$ in which OH groups have been replaced by Cl-atoms.



Compounds of Molybdenum

Different Oxidation States of Molybdenum in its Compounds

Molybdenum forms compounds in –2, 0, +2, +3, +4, +5 and +6 oxidation states. The electronic configuration of Mo^0 atom and of Mo^{2+}, Mo^{3+}, Mo^{4+}, Mo^{5+} and Mo^{6+} ions are : $Mo^0 \rightarrow 2, 8, 18, 4s^2p^6d^5, 5s^1$; $Mo^{2+} \rightarrow 2, 8, 18, 4s^2p^6d^4, 5s^0$; $Mo^{3+} \rightarrow 2, 8, 18, 4s^2p^6d^3, 5s^0$; $Mo^{4+} \rightarrow 2, 8, 18, 4s^2p^6d^2, 5s^0$; $Mo^{5+} \rightarrow 2, 8, 18, 4s^2p^6d^1, 5s^0$; $Mo^{6+} \rightarrow 2, 8, 18, 4s^2p^6d^0, 5s^0$. Compounds having Mo metal in +6 oxidation state are the most stable. Examples of compounds of Mo in different oxidation states are : *Mo (0) compounds* : $Mo(CO)_6$, $[Mo(py)_3(CO)_3]$; *Mo(+ 2) compounds* : $[Mo(diars)_2\ X_2]$, $[Mo(CN)_6]^{4-}$, *Mo(+3) compounds* : Mo_2O_3, Mo_2S_3, $[Mo(H_2O)_3\ Cl_3]^0$, $[MoCl_6]^{3-}$; *Mo(+4) compounds* : MoO_2, $MoCl_4$, $[Mo(NCS)_6]^{2-}$, MoS_2

; *Mo(+5) compounds* : Mo_2S_5, MoF_5. $MoOCl_3$, $MoCl_5(g)$, $(Mo(CN)_8]^{3-}$; *Mo(+6) compounds* : MoO_3, MoS_3, MoF_6, MoO_2F_2, $(MoO_4]^{2-}$, $[MoF_8]^{2-}$. Now let us discuss some important compounds of molybdenum.

1. Molybdenum Trioxide, MoO_3

Preparation : It is prepared : (*i*) by heating Mo metal or MoS_2 in air or O_2. (*ii*) by heating MoO_2 with HNO_3, (*iii*) by heating normal ammonium molybdate, $(NH_4)_2MoO_4$ alone or by beating ammonium paramolybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$ alone or with HNO_3.

$$2Mo + 3O_2 \longrightarrow 2MoO_3 \; ; \; 2MoS_2 + 7O_2 \longrightarrow 2MoO_3 + 4SO_2$$

$$MoO_2 + 2HNO_3 \longrightarrow MoO_3 + H_2O + 2NO_2$$

$$(NH_4)_2MoO_4 \xrightarrow{\Delta} 2NH_3 + H_2O + MoO_3$$

$$(NH_4)_6Mo_7O_{24}.4H_2O \xrightarrow{\Delta} 7H_2O + 6NH_3 + 7MoO_3$$

$$(NH_4)_6Mo_7O_{24}.4H_2O + 6HNO_3 \xrightarrow{\Delta} 7H_2O + 6NH_4NO_3 + 7MoO_3$$

Properties : At room temperature MoO_3 is colourless but on heating it becomes yellow. Although MoO_3 is regarded as the anhydride of molybdic acid, H_2MoO_4, it does not form this acid directly. It is more soluble in cold water than in hot water. MoO_3 dissolves in alkalies to form *normal molybdates* of $M_2[MoO_4]$ type.

$$MoO_3 + 2MOH \longrightarrow M_2[MoO_4]$$

A solution of MoO_3 in HNO_3, when evaporated, gives a white crystalline powder of molybdic acid, H_2MoO_4. When heated with dry HCl at about 150-200°C, it gives a pale yellow water-soluble sublimate of the composition, $MoO_3.2HCl$ or $MoO(OH)_2Cl$. When MoO_3 is dissolved in an alkali sulphide and then the solution so obtained is acidified, MoS_3 is formed.

$$MoO_3 \xrightarrow{+Na_2S} Na_2MoS_4 \xrightarrow{+H^+} M_2S_3$$

On being reduced by H_2, it gives MoO_2 and then Mo metal.

$$MoO_3 + H_2 \xrightarrow{300\text{–}470°C} MoO_2 + H_2O; \; MoO_2 + 2H_2 \xrightarrow{600°C} Mo + 2H_2O$$

With hot conc. NH_4OH, normal ammonium molybdate, $(NH_4)_2MoO_4$ is formed.

$$MoO_3 + 2NH_4OH \longrightarrow (NH_4)_2MoO_4 + H_2O$$

Now when the solution containing $(NH_4)_2MoO_4$ is evaporated, crystals of *ammonium paramolybate*, $(NH_4)_6[Mo_7O_{24}]$ or $6NH_3.7MoO_3.3H_2O$ are obtained.

$$7MoO_3 + 6NH_4OH \longrightarrow (NH_4)_6[Mo_7O_{24}] + 3H_2O$$

2. Molybdic Acid, $H_2MoO_4.H_2O$

It is obtained by treating ammonium molydate with HNO_3 and allowing the solution to crystallise in *cold*. It is a yellow crystalline powder slightly soluble in water, giving an acidic solution. This acid is much weaker than H_2CrO_4. It dissolves in alkalies, forming molybdates.

3. Ammonium Molybdate, $(NH_4)_2MoO_4$

Preparation : This compound is obtained by the treatment of MoO_3 with NH_4OH and evaporating the solution to crystallisation.

Properties : It is a white crystalline powder, soluble in water and insoluble in alcohol. $(NH_4)_2MoO_4$ easily loses NH_3 while $(NH_4)_6[Mo_7O_{24}]$ is quite stable in air. The solution of ammonium molybdate in dil. HNO_3 slowly deposits yellow α-molybdic acid, H_2MoO_4. H_2O which, on warming at 70°C with H_2O forms white β-molybdic acid, H_2MoO_4. The two acids have different X-ray spectra and vapour pressure. When a solution of ammonium molybdate and HCl is dialysed, colloidal molybdic acid is obtained. On heating the salt alone or with HNO_3, MoO_3, is obtained (see the preparation of MoO_3). When a phosphate or an arsenate is heated with conc. HNO_3 and $(NH_4)_2MoO_4$ solution, yellow precipitate of ammonium phosphomolybdate, $(NH_4)_3PO_4.12MoO_3$ or ammonium arsenomolybdate, $(NH_4)_3AsO_4.\ 12MoO_3$ is obtained.

$$Ca_3(PO_4)_2 + 6HNO_3 \longrightarrow 3Ca(NO_3)_2 + 2H_3PO_4$$

$$12(NH_4)_2MoO_4 + 21HNO_3 + H_3PO_4 \longrightarrow (NH_4)_3PO_4.12MoO_3 + 12H_2O + 21NH_4NO_3$$

Ammonium phospho-molybdate (yellow ppt.)

$$12(NH_4)_2MoO_4 + 21HNO_3 + H_3AsO_4 \longrightarrow (NH_4)_3AsO_4.12MoO_3 + 12H_2O + 21NH_4NO_3$$

Ammonium arseno-molybdate (yellow ppt.)

Uses (*i*) On the basis of the above reactions, $(NH_4)_2MoO_4$ is used in the laboratory for the detection and estimation PO_4^{3-} and AsO_4^{3-} ions. When As_2S_3 or As_2S_5 is boiled with conc. HNO_3, arsenic acid, H_3AsO_4 is produced which gives a yellow precipitate of ammonium arsenomolybdate, $(NH_4)_3AsO_4.12MoO_3$ with $(NH_4)_2MoO_4$.

$$As_2S_3 + 10HNO_3 \longrightarrow 2H_3AsO_4 + 10NO_2 + 2H_2O + 3S$$

$$As_2S_5 + 10HNO_3 \longrightarrow 2H_3AsO_4 + 10NO_2 + 2H_2O + 5S$$

$$H_3AsO_4 + 12(NH_4)_2\ MoO_4 + 21HNO_3 \longrightarrow (NH_4)_3AsO_4.12MoO_3 + 21NH_4NO_3 + 12H_2O$$

yellow ppt.

(*ii*) $(NH_4)_3\ MoO_4$ is also used as a catalyst for dehydrogenation in petroleum and coal technology.

4. Molybdenum Blue

Preparation : It is obtained : (*i*) by treating molybdic acid or an acidic solution of a molybdate with a reducing agent like SO_2, H_2S, HI, hydrazine, glucose, zinc or molybdenum metal or (*ii*) by reducing MoO_3 in 25–75% H_2SO_4 with Cu^+ ions or, Sn^{2+} ions in presence of sunlight.

Properties : Molybdenum blue is a deep blue colloidal solution. The actual colour of the solution depends on the concentration of molybdenum, pH of the medium, nature of the reducing agent and temperature of the reaction. The

solution resembles indigo blue in appearance. It is very soluble in water and also in some of the organic solvents. The exact structure of molybdenum blue is not known. It is supposed to be a mixture of hydrated oxides of molybdenum with hydroxyl groups. The mean oxidation state (O.5) of Mo atom is between 5 and 6. Some molybdenum blues are crystalline while others are amorphous. Examples are : (*i*) *Crystalline molybdenum blues* : $MoO_{2.0}(OH)$ (Mean O.S. of Mo = 5); $MoO_{2.6}.\ nH_2O$ (O.S. = 5.20); $MoO_{2.5}\ (OH)_{0.5}$ (O.S = 5.50); $MoO_{2.38}.H_2O$(O.S = 5.76) (*ii*) *Amorphous molybdenum blues* : $MoO_{2.75}.\ nH_2O$ (O.S. = 5.50), $MoO_{2.88}.nH_2O$(O.S. = 5.76). On heating molybdenum blue above 350°C. only H_2O molecules are lost while the OH groups remain attached. This may suggest that OH groups are involved in bridging of different groups.

Uses : Formation of molybdenum blue is utilised in the detection and calorimetric determination of Mo. Phosphorus is indirectly estimated by this method. Because of the colloidal nature of molybdenum blue, it is easily absorbed on vegetable and animal fibres and hence is used for dyeing those fibres.

Compounds of Tungsten

Different Oxidation States of Tungsten in Its Compounds

Tungsten forms compounds in 0 *e.g.* [$(W(CO)_6$, $[W(CO)_5X]^-$ etc.], + 2 (*e.g.* WX_2, [W(diars) $(CO)_4I]^+$ etc.), +3 (*e.g.* $[W(diars)(CO)_3\ Br_2]^+$), +4 (*e.g.* WO_2, WCl_4, $[W(OH_2Cl_5]^{2-}$). +5 (*e.g.* WF_6^-) and +6 (*e.g.* WO_3, WX_6, WO_2Cl_2, WO_4^{2-} etc.) oxidation states. Compounds containing tungsten in + 6 oxidation state are the most stable. Important compounds are discussed below :

1. Tungsten Trioxide or Tungstic Oxide, WO_3

Preparation : It is obtained by the following methods :

$$H_2WO_4 \xrightarrow{\text{Dehydration}} WO_3 + H_2O$$

$$2W + 3O_2 \xrightarrow{\Delta\ (500°C)} 2WO_3$$

$$2WS_2 + 7O_2\ (\text{from air}) \xrightarrow{\text{Roasting}} 2WO_3 + 4SO_2$$

$$\underset{\text{Amm. tungstate}}{(NH_4)_2\ WO_4} \xrightarrow{\Delta} WO_3 + 2NH_3 + H_2O$$

$$Na_2WO_4 + 2HNO_3 \longrightarrow WO_3 + 2NaNO_3 + H_2O$$

WO_3 can also be obtained from wolframite ore, (Fe, Mn)WO_4 as discussed earlier.

Properties : It is a soft lemon-yellow coloured powder, but turns orange on heating. It melts at 1470° to a green liquid. It is insoluble in water and acids (excepting HCl).

$$WO_3 + 4HF \longrightarrow \underset{\substack{\text{Hydrofluo-}\\\text{tungstic acid}}}{H_2WO_2F_4} + H_2O$$

It dissolves in alkalies to form tungstate.

$$WO_3 + 2NaOH \longrightarrow Na_2WO_4 + H_2O$$

When heated with H_2 it is reduced to W metal *via* W_2O_5 and WO_2.

$$\underset{\text{Yellow}}{WO_3} \xrightarrow{H_2} \underset{\text{Blue}}{W_2O_5} \xrightarrow{H_2} \underset{\text{Brown}}{WO_2} \xrightarrow{H_2} W$$

When heated with C, Mg etc., W metal is obtained directly. When heated with Cl_2 it gives volatile oxychloride, WO_2Cl_2 while with H_2S it gives WS_3

$$WO_3 + 3C \longrightarrow 3CO + W \; ; \; WO_3 + 3Mg \longrightarrow 3\,MgO + W$$

$$2WO_3 + 2Cl_2 \longrightarrow 2WO_2Cl_2 + O_2 \; ; \; WO_3 + 3H_2S \longrightarrow WS_3 + 3H_2O$$

Uses : It is used (*i*) as a mordant in dyeing and ceramic industry (*ii*) as a pigment in oil and water colours.

2. Tungstic Acid, H_2WO_4

Preparation : A precipitate of this acid may be obtained by treating a solution of any soluble tungstate with acid. The precipitate of the acid may be white ($H_2WO_4.H_2O$) or yellow (H_2WO_4) according as the precipitation has been made from cold solution or hot solution.

$$(NH_4)_2WO_4 + H_2SO_4 \longrightarrow \underset{\substack{\text{Yellow}\\ \text{ppt.}}}{H_2WO_4} + (NH_4)_2SO_4$$

Properties and uses : The hydrated acid ($H_2WO_4.H_2O$) is somewhat soluble in water but the anhydrous acid (H_2WO_4) is neither soluble in H_2O nor in any acid, excepting HF. With HF hydrofluotungstic acid, $H_2WO_2F_4$ is formed. With alkalies, H_2WO_4 forms tungstates. On heating WO_3 is obtained.

$$H_2WO_4 + 4HF \longrightarrow H_2WO_2F_4 + 2H_2O$$

$$H_2WO_4 + Na_2OH \longrightarrow Na_2WO_4 + 2H_2O$$

$$H_2WO_4 \xrightarrow{\Delta} WO_3 + H_2$$

The composition of various tungstic acids is as : *meta tungstic acid*—$WO_3.H_2O$ or H_2WO_4 *para tungstic acid*—$WO_3.2H_2O$ or $H_2WO_4.2H_2O$ or H_2WO_5; *ortho tungstic acid*—$WO_3.3H_2O$ or $H_2WO_4.2H_2O$ or H_6WO_6. Tungstic acid is used in ceramic industry and in making pigments.

3. Tungsten Bronzes, M_xWO_3

Preparation. These are the *non-stoichiometirc compounds* having a general formula, M_xWO_3(M = Li, Na, K etc. and $x < 1$). These are also called *metal-tungstate bronzes.* They are obtained by reducing alkali metal or alkaline earth metal tungstates by H_2, metallic Na, metallic W or electrically. These are insoluble in water, chemically inert, have metallic lustre and are conductors of electricity.

Properties and uses : These are highly coloured. Their colour depends on the value of x as shown below :

x =	*0.93*	*0.64*	*0.46*	*0.32*
Colour =	*Gole yellow*	*Orange*	*Red-violet*	*Blue-violet*

These are resistant to the action of acids excepting HF. In the presence of an alkali, these are oxidised by O_2. In this oxidation reaction W^{5+} in M_xWO_3 is oxidised to W^{5+} state. Tungsten bronzes are used as pigments.

4. Tungsten Halides

The known halides given by tungsten are : (*i*) *Fluorides* : WF_6. (*ii*) *Chlorides* : WCl_6, WCl_5, WCl_4, WCl_2. (*iii*) *Bromides* : WBr_6 (very unstable), WBr_5, WBr_2. (*iv*) *Iodides* : WI_4, WI_2. Of these WF_6 and WCl_6 are the most important.

WF_6 can be prepared by any of the following methods :

$$W + 3F_2 \longrightarrow WF_6$$

$$WCl_6 + 6HF \text{ (anhydrous)} \longrightarrow WF_6 + 6HCl$$

$$WCl_6 + 2AsF_3 \longrightarrow WF_6 + 2AsCl_3$$

$$WCl_6 + 3SbF_5 \longrightarrow WF_6 + 2SbF_3Cl_2$$

It is colourless or slightly yellow coloured gas. It is hydrolysed by H_2O, forming WO_3.

$$WF_6 + 3H_2O \longrightarrow WO_3 + 6HF$$

It is extremely volatile diamagnetic compound. It attacks all metals except Pt and Au. in presence of traces of moisture, it attacks glass because of the production of HF (due to hydrolysis). It behaves a Lewis acid and forms addition compounds with NH_3, pyridine (py) and methylamine ($CH_3.NH_2$) (*e.g.* $WF_6.4NH_3$, $WF_6.3py$, $WF_6.3CH_3NH_2$). With NaF it gives crystalline solid $WF_6.2NaF$ in which W is 8-coordinated. With $SbCl_6$ it gives WCl_6.

Tungesten hexachloride WCl_6 can be prepared by the following reactions :

$$W + 3Cl_2 \xrightarrow{300^\circ} WCl_6$$

$$WS_2 + 4Cl_2 \xrightarrow{\Delta} WCl_6 + S_2Cl_2$$

$$2WO_3 + 6Cl_2 \xrightarrow[\text{In } CCl_4 \text{ in a sealed tube at } 280^\circ]{} 2WCl_6 + 3O_2$$

Pure WCl_6 is steel blue coloured compound, slowly attacked by cold water, but rapidly by hot H_2O.

$$WCl_6 + 4H_2O \longrightarrow H_2WO_4 + 6HCl$$

Other reactions of WCl_6 are given below :

$$WCl_6 + 5HBr \longrightarrow WBr_5 + HCl + \tfrac{1}{2}Cl_2$$

$$WCl_6 + 2NH_3 \longrightarrow WN_2 + 6HCl$$

$$WCl_6 \xrightarrow{H_2} WCl_5 \longrightarrow WCl_4 \longrightarrow WCl_2$$

Compounds of Manganese

Different Oxidation States of Manganese in Its Compounds

Manganese forms compounds in –1, 0, +1, +2, +3, +4, +5, +6 and +7 oxidation states. The electronic configuration of Mn^0 atom and of Mn^+, Mn^{2+}, Mn^{3+}, Mn^{4+},

Mn^{5+}, Mn^{6+} and Mn^{7+} ions are : $Mn^0 \rightarrow 2, 8, 3s^2p^6d^5, 4s^2$; $Mn^+ \rightarrow 2, 8, 3s^2p^6d^5, 4s^1$; $Mn^{2+} \rightarrow 2, 8, 3s^2p^6d^5, 4s^0$; $Mn^{3+} \rightarrow 2, 8, 3s^2p^6d^4, 4s^0$; $Mn^{4+} \rightarrow 2, 8, 3s^2p^6d^3, 4s^0$; $Mn^{5+} \rightarrow 2, 8, 3s^2p^6d^2, 4s^0$; $Mn^{6+} \rightarrow 2, 8, 3s^2p^6d^1, 4s^0$; $Mn^{7+} \rightarrow 2, 8, 3s^2p^6d^0, 4s^0$. Compounds having Mn atom in +2 oxidation state are the most stable. Examples of compounds of Mn in different oxidation states are : *Mn(–1) compounds* : $[Mn(CO)_5]^-$; *Mn(o) compounds* : $Mn_2(CO)_{10}$; *Mn*(+1) *compounds* : $[Mn(CN)_6]^{5-}$, $[Mn(CO)_5]^+$; *Mn*(+2) *compounds* (called *manganous compounds*) : MnO, $MnCl_2$, $MnCO_3$, $MnSO_4$, $Mn(NO_3)_2$, $MnCl_4^{2-}$, $[Mn(H_2O)_4]SO_4.4H_2O$; *Mn*(+3) *compounds* (called *manganic compounds*) : Mn_2O_3, MnF_3, $Mn_2(SO_4)_3$ $[Mn(CN)_6]^{3-}$; *Mn*(+4) *compounds* : MnO_2, $Mn(SO_4)_2$, $[MnCl_6]^{2-}$; *Mn*(+5) *compounds* : $Na_3MnO_4.10H_2O$; *Mn*(+6) *compounds* : K_2MnO_4 ; *Mn*(+7) *compounds* : $KMnO_4$, Mn_2O_7. Out of the above compounds the oxides of Mn (*viz.* MnO, Mn_2O_3, Mn_3O_4. MnO_2 and Mn_2O_7) and potassium permanganate ($KMnO_4$) are the most important. These are discussed below.

1. Manganeous Oxide MnO

Preparation : This oxide is prepared by the following reactions :

$$MnO_2 + H_2 \xrightarrow{\Delta} MnO + H_2O; \quad Mn(COO)_2 \xrightarrow{\Delta} MnO + CO + O_2$$

Properties and uses : This is a grayish-green powder and insoluble in water. It is strongly basic and forms manganous salts [*i.e.* Mn(II) salts] with acids. It is quickly oxidised by air in the cold to Mn_2O_3. It has a NaCl lattice. It is used as an intermediate for the preparation of Mn(II) salts, as a nutrient in agriculture, and in welding.

2. Manganic Oxide, Mn_2O_3

Preparation : This compound is also called ***manganese sesquioxide.*** It can be obtained by the following reactions :

$$4MnO + O_2 \xrightarrow{\Delta} 2Mn_2O_3 \; ; \quad 4MnO_2 \xrightarrow{\Delta} 2Mn_2O_3 + O_2$$

The *hydrous oxide*, $Mn_2O_3.H_2O$ is obtained as :

$$2Mn(OH)_2 + \tfrac{1}{2}O_2 \longrightarrow Mn_2O_3.H_2O$$

Properties : It is a black amorphous powder. Above 1000°C it decomposes into Mn_3O_4, liberating O_2. This oxide is weakly basic and dissolves in hot dil. acids to form Mn(II) salts and MnO_2.

$$6Mn_2O_3 \xrightarrow{> 1000°C} 4Mn_3O_4 + O_2$$

$$Mn_2O_3 + H_2SO_4 \longrightarrow MnSO_4 + MnO_2 + H_2O$$

$$Mn_2O_3 + 2HNO_3 \longrightarrow Mn(NO_3)_2 + MnO_2 + H_2O$$

Mn_2O_3 dissolves in conc. HCl, forming $MnCl_2$ with the evolution of Cl_2.

$$Mn_2O_3 + 6HCl \longrightarrow 2MnCl_2 + Cl_2 + 3H_2O$$

Structure : Mn_2O_3 has O = Mn—O—Mn = O structure which is supported by magnetic susceptibility. In this oxide Mn is in +3 oxidation state.

3. Manganese Tetroxide. Mn_3O_4

Preparation : It is also called ***mangano-manganic oxide*** or ***red oxide of manganese.*** It may be prepared by heating any oxide of Mn.

$$6MnO + O_2 \xrightarrow{\Delta} 2Mn_3O_4$$

$$3MnO_2 \xrightarrow[\text{absence of air}]{\text{Heat in the}} Mn_3O_4 + O_2$$

$$6Mn_2O_3 \xrightarrow[\text{(in air)}]{> 95°C} 4Mn_3O_4 + O_2$$

Properties : It is a brownish-red powder. It slowly dissolves in conc. cold H_2SO_4, forming a red solution containing $MnSO_4$ and $Mn_2(SO_4)_3$. With dil. HNO_3 it gives $Mn(NO_3)_2$ and MnO_2 while with HCl, $MnCl_2$ is formed and Cl_2 is evolved.

$$Mn_3O_4 + 4H_2SO_4 \longrightarrow MnSO_4 + Mn_3(SO_4)_3 + 4H_2O$$

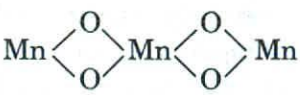
$$Mn_3O_4 + 4HNO_3 \longrightarrow 2Mn(NO_3)_2 + MnO_2 + 2H_2O$$

$$Mn_3O_4 + 8HCl \longrightarrow 3MnCl_2 + Cl_2 + 4H_2O$$

Structure : Mn_3O_4 has the structure shown in the margin.

4. Magnanese Dioxide, MnO_2

Preparation. The pure MnO_2 is prepared by heating $Mn(NO_3)_2$ while the hydrated form, $MnO_2.H_2O$ (called maganous acid, H_2MnO_3) is prepared by the alkaline oxidation of Mn(II) salt by sodium hypochlorite or bleaching powder.



Structure of Mn_3O_4

$$Mn(NO_3)_2 \xrightarrow{\Delta} MnO_2 + 2NO_2$$

$$Mn^{2+} + 2OH^- + ClO^- \longrightarrow MnO_2.H_2O + Cl^-$$

Properties : It is a black powder, insoluble in water and a good conductor of electricity. When heated above 530°C in air, it loses O_2 to form Mn_3O_4. It acts as a basic oxide towards cold acids like HCl, forming salts containing Mn in +4 oxidation state. With conc. H_2SO_4, $MnSO_4$ is formed and O_2 is evolved. HNO_3 has no action on MnO_2

$$3MnO_2 \xrightarrow{>530°C} Mn_3O_4 + O_2$$

$$MnO_2 + 4HCl \text{ (cold and concentrated)} \longrightarrow MnCl_4 + 2H_2O$$

$$2MnO_2 + 2H_2SO_4 \text{ (concentrated)} \longrightarrow 2MnSO_4 + 2H_2O + O_2$$

In the presence of excess of H^+ ions, MnO_2 acts as a strong oxidising agent. In showing this behaviour Mn^{4+} changes to Mn^{2+} ion.

$$\underset{(Mn = +4)}{MnO_2} + 4H^+ + 4e^- \longrightarrow \underset{(Mn = +2)}{Mn^{2+}} + 2H_2O$$

Thus in presence of hot dil. H_2SO_4, MnO_2 oxidises oxalic acid to CO_2, Fe(II) salt to Fe (III) salt and chloride to Cl_2

$$C_2O_4^{2-} + MnO_2 + 4H^+ \longrightarrow Mn^{2+} + 2H_2O + 2CO_2$$
$$2Fe^{2+} + MnO_2 + 4H^+ \longrightarrow 2Fe^{3+} + Mn^{2+} + 2H_2O$$
$$MnO_2 + 4H^+ + 2Cl^- \longrightarrow Mn^{2+} + 2H_2O + 2Cl_2$$

In presence of air or oxidising agents (*e.g.* KNO_3, $KClO_3$) MnO_2 reacts with fused KOH to give potassium manganate, K_2MnO_4.

$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$

Structure : Since in MnO_2, Mn is in +4 state, the structure of MnO_2 is O = Mn = O which has also been supported by magnetic susceptibility.

Uses : MnO_2 is used : (*i*) as a depolariser in Lechanehe cell and dry cells. In these cells MnO_2 oxidises H_2 liberated at the cathode and thus counteracts polarisation. (*ii*) as a decolouriser in glass. (*iii*) in forming, with ferric oxide, a dark brown glaze which is used in pottery. (*iv*) as a catalyst in the preparation of O_2 from $KClO_3$. (*v*) as a dies in paints and varnishes. (*vi*) in the preparation of Cl_2 in the laboratory. (*vii*) in dyestuff industry and in varnish manufacture. (*viii*) in the manufacture of metallic manganese, manganates, permanganates and a number of its salts.

5. Manganese Heptoxide, Mn_2O_7

Preparation : It is also called ***permanganic anhydride***, since in water it gives a solution of *permanganic acid*, $HMnO_4$. When a solution containing concentrated sulphuric acid and potassium permanganate is cooled, and water is carefully added, a dark reddish brown liquid separates out, which is probably Mn_2O_7. It is very unstable.

$$2KMnO_4 + 2H_2SO_4 \longrightarrow (MnO_3)_2SO_4 + K_2SO_4 + 2H_2O$$
$$(MnO_3)_2SO_4 + H_2O \longrightarrow Mn_2O_7 + H_2SO_4$$

Properties : It is a dark-brown only liquid (density = 2.4) which solidifies on cooling to 5.9°C. It gives violet vapours at 40–50°C, but explodes violently on warming or in presence of organic matter giving MnO_2 and O_2.

$$2Mn_2O_7 \longrightarrow 4MnO_2 + 3O_2$$

It is acidic in character, since it dissolves in H_2O to give a violet solution of *permanganic add*, $HMnO_4$. It is, therefore, known as *permanganic anhydride*.

$$Mn_2O_7 + H_2O \longrightarrow 2HMnO_4$$
$$(cf. Cl_2O_7 + H_2O \longrightarrow 3HClO_4)$$

It is a powerful oxidising agent and organic matter like dry wood, paper etc. catches fire when dropped into it.

6. Potassium Permanganate, $KMnO_4$

This compound is the salt of permanganic acid, $HMnO_4$ which is an unstable acid and exists only in solution.

Preparation : It may be prepared by acidifying the solution of potassium manganate, K_2MnO_4 by H_2SO_4.

$$3K_2MnO_4 + 2H_2SO_4 \longrightarrow 2K_2SO_4 + 2KMnO_4 + MnO_2 \downarrow + 2H_2O$$

or
$$3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 \downarrow + 2H_2O$$

Manufacture. *On a large scale* it is prepared from the mineral pyrolusite, MnO_2. The finely powdered pyrolusite mineral is fused with KOH in presence of

air or an oxidising agent like KNO_3. $KClO_3$ etc. This treatment gives us fused green coloured potassium manganate, K_2MnO_4.

$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$

or

$$2MnO_2 + 4OH^- + O_2 \longrightarrow 2MnO_4^{2-} + 2H_2O$$

$$MnO_2 + 2KOH + KNO_3 \longrightarrow K_2MnO_4 + KNO_2 + H_2O$$

or

$$MnO_2 + 2OH^- + NO_3^- \longrightarrow MnO_4^{2-} + NO_2^- + H_2O$$

$$3MnO_2 + 6KOH + KClO_3 \longrightarrow 3K_2MnO_4 + KCl + 3H_2O$$

or

$$3MnO_2 + 6OH^- + ClO_3^- \longrightarrow 3MnO_4^{2-} + Cl^- + 3H_2O$$

The fused K_2MnO_4 obtained as above is extracted with water and the solution, after filtration, is converted into potassium permanganate ($KMnO_4$) by any of the following methods :

(*a*) Stadeler's process. In this method Cl_2 is passed through the green solution of K_2MnO_4 until it becomes purple due to the formation of K_2MnO_4. Here Cl_2 oxidises K_2MnO_4 into $KMnO_4$.

$$2K_2MnO_4 + Cl_2 \longrightarrow 2KCl + 2KMnO_4$$

or

$$\underset{\text{Green}}{2MnO_4^{2-}} + Cl_2 \longrightarrow 2Cl^- + \underset{\text{Purple}}{2MnO_4^-}$$

(*b*) By the action of CO_2 or O_3. In this process CO_2 or O_3 is passed though the green solution of K_2MnO_4 until it becomes purple.

$$3K_2MnO_4 + 2H_2O + 4CO_2 \longrightarrow 2KMnO_4 + MnO_2 + 4KHCO_3$$

or

$$\underset{\text{Green}}{3MnO_4^{2-}} + 2H_2O + 4CO_2 \longrightarrow \underset{\text{Purple}}{2MnO_4^-} + MnO_2 + 4HCO_3^-$$

$$2K_2MnO_4 + H_2O + O_3 \longrightarrow 2KMnO_4 + 2KOH + O_2$$

or

$$\underset{\text{Green}}{2MnO_4^{2-}} + H_2O + O_3 \longrightarrow \underset{\text{Purple}}{2MnO_4^-} + 2OH^- + O_2$$

(*c*) Electrolytic oxidation process. Now-a-days the conversion of K_2MnO_4 into $KMnO_4$ is done by the electrolytic oxidation process in which K_2MnO_4 solution is placed in a cell in which a rotating iron wire-net cylinder acts as the anode and an inlet pipe made of iron acts as the cathode. Anode and cathode are properly insulated from each other. Anode is made to revolve, during electrolysis, mechanically by a revolving pulley. K_2MnO_4 solution is sent inside the cell through the inlet pipe and electric current is passed.

Reactions : On passing electric current H_2O ionises to give hydrogen (*at cathode*) and oxygen (*at anode*).

$$H_2O \longrightarrow 2H^+ \text{ (}At\ cathode\text{)} + O^{2-} \text{ (}At\ anode\text{)}$$

Oxygen liberated at anode oxidises manganate (MnO_4^{2-}) into permanganate (MnO_4^-) while hydrogen gets collected at the cathode.

$$2 \times [MnO_4^{2-} \longrightarrow MnO_4^- + e^-] \qquad (At\ anode)\ ...(i)$$

$$2H^+ + 2e^- \longrightarrow H_2 \qquad (At\ cathode)\ ...(ii)$$

On adding (*i*) and (*ii*), we get :

$$2MnO_4^{2-} + 2H^+ \longrightarrow 2MnO_4^- \text{ (}At\ anode\text{)} + H_2 \text{ (}At\ cathode\text{)}$$

or $\underset{\text{Green solution}}{2K_2MnO_4} + 2H_2O \longrightarrow \underset{\text{Purple solution}}{2KMnO_4} + H_2 + 2KOH$

The purple solution of $KMnO_4$ obtained as above is filtered through asbestos, concentrated and allowed to crystallise when $KMnO_4$ deposits as deep purple-red rhombic prisms.

Properties : Potassium permanganate forms dark purple lustrous crystals giving deep pink colour in solution. It is isomorphous with potassium perchlorate. Its solubility in water at 20° is only about 7% whilst it dissolves more at higher temperatures (25% at 63°C). It gives off O_2 at 200°C.

$$2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$$

At red heat K_2MnO_4 formed as above is decomposed into permanganite, K_2MnO_3 and O_2.

$$2K_2MnO_4 \longrightarrow 2K_2MnO_3 + O_2$$

When an alkaline solution of $KMnO_4$ is heated, O_2 is evolved.

$$4KMnO_4 + 4KOH \longrightarrow 4K_2MnO_4 + 2H_2O + O_2$$

$$\text{or } 4MnO_4^- + 4OH^- \longrightarrow 4MnO_4^- + 2H_2O + O_2$$

With *well cooled* conc. H_2SO_4, it gives Mn_2O_7 which decomposes on warming.

$$2KMnO_4 + 2H_2SO_4 \longrightarrow Mn_2O_7 + 2KHSO_4 + H_2O$$

$$2Mn_2O_7 \longrightarrow 4MnO_2 + 3O_2$$

With *warmed* conc. H_2SO_4 oxygen gas is evolved.

$$4KMnO_4 + 6H_2SO_4 \longrightarrow 2K_2SO_4 + 4MnSO_4 + 6H_2O + 5O_2$$

When heated in a current of H_2, solid $KMnO_4$ gives KOH, MnO and steam.

$$2KMnO_4 + 5H_2 \longrightarrow 2KOH + 2MnO + 4H_2O$$

A mixture of $KMnO_4$ with sulphur and charcoal burns when heated, and explodes like a gun powder when rubbed. A well powdered mixture of $KMnO_4$ and oxalic acid catches five spontaneously in a few seconds. When a drop of glycerine is poured over powdered $KMnO_4$, the same thing happens. $KMnO_4$ is a powerful oxidising agent. Its oxidising property depends on whether the oxidation takes place in alkaline, neutral or acid solution.

(a) In alkaline solution, MnO_4^- ion (Mn = +7) is first reduced to MnO_4^{2-} ion (Mn = +6) and then to insoluble MnO_2 (Mn = +4). The solution first changes from purple (due to MnO_4^-) to green (due to MnO_4^{2-}) and finally it becomes colourless (MnO_2).

$$\underset{\substack{\text{Purple}\\(Mn = +7)}}{2KMnO_4} + 2KOH \longrightarrow \underset{\substack{\text{Green}\\(Mn = +6)}}{2K_2MnO_4} + H_2O + O \quad ...(i)$$

$$\underset{\substack{\text{Green}\\(Mn = +6)}}{2K_2MnO_4} + 2H_2O \longrightarrow \underset{\substack{\text{Colourless}\\(Mn = +4)}}{2MnO_2} + 4KOH + 2O \quad ...(ii)$$

On adding : $\underset{\substack{\text{Purple}\\(Mn = +7)}}{2KMnO_4} + H_2O \xrightarrow{\text{Alkali}} \underset{\substack{\text{Colourless}\\(Mn = +4)}}{2MnO_2} + 2KOH + 3O \quad ...(iii)$

This is the complete equation which represents the oxidising action of $KMnO_4$ in alkaline medium.

From equation (*iii*) it is evident that two molecules of $KMnO_4$ in alkaline solution give three oxygen atoms (*i.e. six equivalents*) and, therefore, *the equivalent weight of $KMnO_4$ as an oxidising agent in alkaline solution is one-third of its molecular weight.*

Equations (*i*), (*ii*) and (*iii*) can also be written in the ionic forms as follows :

$$\underset{\text{Purple (Mn = +7)}}{2MnO_4^-} + 2OH^- \longrightarrow \underset{\text{Green (Mn = +6)}}{2MnO_4^{2-}} + H_2O + O$$

$$\underset{\text{Green (Mn = +6)}}{2MnO_4^{2-}} + 2H_2O \longrightarrow \underset{\text{Colourless (Mn = +4)}}{2MnO_2} + 4OH^- + 2O$$

On adding :

$$\underset{\text{Purple (Mn = +7)}}{2MnO_4^-} + H_2O \xrightarrow{\text{Alkali}} \underset{\text{Colourless (Mn = +4)}}{2MnO_2} + 2OH^- + 3O$$

or

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$$

Thus in alkaline medium, $KMnO_4$ oxidises iodides (I^-) to iodates (IO^-_3), NH_3 to N_2 and nitrotoluene to nitrobenzoic acid.

$$2MnO^-_4 + H_2O + I^- \xrightarrow{\text{Alkali}} 2MnO_2 + 3OH^- + IO_3^-$$

$$2MnO^-_4 + C_6H_4\begin{matrix}NO_2\\CH_3\end{matrix} \longrightarrow 2MnO_2 + 2OH^- + C_6H_4\begin{matrix}NO_2\\COOH\end{matrix}$$

$$2MnO_4^- + 2NH_3 \longrightarrow MnO_2 + 2OH^- + N_2 + 2H_2O$$

(*b*) In neutral solution, $KMnO_4$ is directly reduced to MnO_2.

$$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3O$$

or

$$2MnO_4^- + H_2O \longrightarrow 2OH^- + 2MnO_2 + 3O$$

or

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + OH^-$$

This equation is the same as for alkaline medium. Evidently, *in neutral medium as well, the equivalent weight of $KMnO_4$ is one-third of its molecular weight.* It is obvious from the equation representing the oxidising action of $KMnO_4$ in neutral medium that an alkali is generated in the reaction. This alkali makes the medium alkaline even if we start with the neutral solution. It is for this reason that the equations representing the oxidising property of $KMnO_4$ in alkaline and neutral media are the same. Thus in neutral medium, $KMnO_4$ oxidises Mn^{2+} salt to MnO_2, $Na_2S_2O_3$ to Na_2SO_4, H_2S to S.

$$2MnO_4^- + 2Mn^{2+} + 2H_2O \longrightarrow 5MnO_2 + 4H^+$$

$$8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$$

$$2MnO_4^- + 4H_2S \longrightarrow 2MnS + S + SO_4^{2-} + 4H_2O$$

(c) In acidic medium (dil. H_2SO_4), MnO_4^- ion is reduced to Mn^{2+} ion and five O-atoms are rendered available from two MnO_4^- ions.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$

or

$$\underset{\substack{\text{Purple}\\(Mn = +7)}}{2MnO_4^-} + 6H^+ \longrightarrow \underset{\substack{\text{Colourless}\\(Mn = +2)}}{2Mn^{2+}} + 3H_2O + 5O$$

The reduction of MnO_4^- ion into Mn^{2+} ion as shown above can also be represented by the following ionic equation :

$$\underset{\substack{\text{Purple}\\(Mn = +7)}}{MnO_4^-} + 8H^+ + 5e^- \longrightarrow \underset{\substack{\text{Colourless}\\(Mn = +2)}}{Mn^{2+}} + 4H_2O$$

It is obvious that *in acid solution the equivalent weight of $KMnO_4$ is one-fifth of its molecular weight.*

In acidic medium $KMnO_4$ oxidises Fe(II) salts to Fe(III) salts, oxalic acid to CO_2, H_2S to S, SO_2 to H_2SO_4, sulphites to sulphates, KI to I_2, H_2O_2 to O_2 halogen acids to halogens.

$$MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

$$2MnO_4^- + 16H^+ + 3S^{2-} \longrightarrow 2Mn^{2+} + 5S + 8H_2O$$

$$2MnO_4^- + 2H_2O + 5SO_2 \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+$$

$$2MnO_4^- + 6H^+ + 5SO_3^{2-} \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$$

$$2MnO_4^- + 16H^+ + 10I^- \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O$$

$$2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 5O_2 + 8H_2O$$

$$2MnO_4^- + 16H^+ + 10X^- \longrightarrow 2Mn^{2+} + 5X_2 + 8H_2O$$

Uses : $KMnO_4$ is used (*i*) as an oxidising agent in the laboratory as well as in industry; (*ii*) in volumetric estimations of ferrous salts, oxalic acid, H_2O_2 etc.; (*iii*) as a disinfectant and a germicide on account of its oxidising property; (*iv*) in qualitative analysis for detecting halides and oxalates. (*v*) in the manufature of saccharin, benzoic acid, acetaldelyde etc.; (*vi*) for bleaching waxes; (*vii*) for the detection of double bond in organic compounds. For this purpose alkaline $KMnO_4$ solution under the name *Bayer's reagent* is used. (*viii*) as a source of reactive form of MnO_2 which is used in place of pyrolusite in the manufacture of dry cells.

Compounds of Iron

Different Oxidation States of Iron in Its Compounds

The most important compounds of iron are those in which Fe is in +2 and +3 oxidation state. Compounds containing Fe in +2 (divalent) and +3 (trivalent) oxidation state are called *ferrous* and *ferric* compounds respectively. Compounds containing Fe in –2, 0, +1, +4 and +6 oxidation state are also known, although their number is very little. Examples are : *compound containing Fe (–2)* : $[Fe(CO)_4]^{2-}$; *compounds containing Fe(0)* : $Fe(CO)_5$. $Fe_2(CO)_9$, $Fe_3(CO)_{12}$; *compounds containing Fe (+1)* : $[Fe^+(NO^+)]^{2+}SO_4^{2-}$; *compounds containing Fe(+4)* :

$[Fe\ (diars)_2\ Cl_2]^{2+}$; *compound containing Fe (+5)* : $[FeO_4]^{3-}$; *compound containing Fe (+6)* : $[FeO_4]^{2-}$. Let us discuss some important compounds of iron.

1. Ferrous Sulphate or Green Vitriol, $FeSO_4.7H_2O$

Preparation : This is the most important ferrous salt. It is also called ***green vitriol.*** We also call it as ***copperas*** because it is a by-product of the hydrometallurgy of copper. In the laboratory it is prepared :

(i) By dissolving iron in dil. H_2SO_4, filtering, evaporating and crystallising

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$$

(iii) From Kipp's waste. Kipp's waste (or residue) contains $FeSO_4$ also with free H_2SO_4. The waste is heated with a small quantity of scrap iron which reacts with excess of H_2SO_4 to give $FeSO_4$ and nascent hydrogen. This nascent hydrogen reduces any ferric iron, if present, to ferrous state. On allowing the hot solution to stand, crystals of $FeSO_4.7H_2O$ separate out.

Manufacture. On a large scale it is obtained by the slow oxidation of iron pyrites in the, presence of air and moisture. The pyrites are exposed to air in big heaps and the following reaction takes place :

$$2FeS_2 + 2H_2O + 7O_2 \longrightarrow 2FeSO_4 + 2H_2SO_4$$

The free H_2SO_4 is removed by the addition of scrap iron which also reduces any ferric sulphate formed. . On erystallisation we get green coloured crystals containing seven molecules of water of crystallisation. These crystals are monoclinic and are isomorphous with $MgSO_4.7H_2O$. Ferrous sulphate containing 6, 5. 3, 2, 1 molecules and no water of crystallisation is also known.

Properties *(i)* Ferrous sulphate forms pale green monoclinic crystals of heptahydrate, $FeSO_4.7H_2O$ which is isomorphous with the corresponding heptahydrates of cobalt; nickel, chromium, manganese, magnesium, zinc etc. *i.e.* with $MSO_4.7H_2O$ where M = Co, Ni, Cr, Mn, Mg, Zn etc. Crystalline hydrates having 6, 5, 4, 3 and 2 water mole. cules are also known. $FeSO_4.5H_2O$ is isomorphous with blue vitriol, $CuSO_4.5H_2O$. Anhydrous salt (*i.e.* $FeSO_4$) is white.

(ii) Action of heat. When heated to redness, $FeSO_4$ and $FeSO_4.\ 7H_2O$ both decompose giving a residue of Fe_2O_3 which is used as a pigment under the name of *rogue* or *venetian red.*

$$2FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_2 + SO_3$$

$$2[FeSO_4.7H_2O] \xrightarrow{\Delta} Fe_2O_3 + H_2SO_4 + SO_2 + 13H_2O$$

(iii) Reducing properties. it is an active reducing agent, *e.g.*

(a) It decolorises acidified $KMnO_4$ solution

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

(b) It turns acidified $K_2Cr_2O_7$ green

$$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$$

(c) It reduces NO_2 to NO which then gives nitrosoferrous sulphate, $Fe(NO)SO_4$

$$2FeSO_4 + H_2SO_4 + NO_2 \longrightarrow Fe_2(SO_4)_3 + H_2O + NO$$

$$FeSO_4 + NO \rightleftarrows \underset{\text{Nitrosoferrous sulphate}}{Fe(NO)SO_4}$$

(*d*) *It reduces silver and gold salts to metal.*

$$Ag^+ + Fe^{2+} \longrightarrow Ag \downarrow + Fe^{3+}$$

$$Au^{3+} + 3Fe^{2+} \longrightarrow Au \downarrow + 3Fe^{3+}$$

(*e*) *It reduces* $HgCl_2$ *to* Hg_2Cl_2

$$2HgCl_2 + 2Fe^{2+} \longrightarrow Hg_2Cl_2 + 2Fe^{3+} + 2Cl^-$$

(*iv*) *Formation of addition compound with NO.* A cold solution of ferrous sulphate absorbs NO forming dark brown nitroso ferrous sulphate, $Fe(NO)SO_4$ which is destroyed by the action of heat.

$$FeSO_4 + NO \rightleftarrows \underset{\text{Nitroso ferrous sulphate}}{Fe(NO)SO_4}$$

(*v*) *Action of air.* When exposed to air, the green crystals of $FeSO_4$ effloresce and turn brown due to the formation of basic ferric sulphate, $Fe(OH)SO_4$. Its formation is due to the surface oxidation of $FeSO_4$ to $Fe(OH)SO_4$.

$$\underset{\text{Green}}{4FeSO_4} + 2H_2O + O_2 \longrightarrow \underset{\text{Brown}}{4Fe(OH)SO_4}$$

(*vi*) *Formation of double salts.* With sulphates of alkali metals it readily forms double salts with the composition, $R_2SO_4.FeSO_4.6H_2O$ where, R = an alkali metal or NH_4^+ radical. Out of these double salts, *ferrous ammonium sulphate* (called *Mohr's salt*), $(NH_4)_2SO_4.FeSO_4.6H_2O$ is of great use and has been discussed below.

(*vii*) *Acid character.* It is readily soluble in H_2O, the solution is acidic in nature duo to its hydrolysis

$$FeSO_4 + 2HOH \rightleftarrows Fe(OH)_2 + H_2SO_4$$

The solution readily passes into ferris state by atmospheric oxidation.

$$4FeSO_4 + 2H_2SO_4 + O_2 \longrightarrow 2Fe_2(SO_4)_3 + 2H_2O$$

(*viii*) *Action of KCN.* When excess of KCN is added to ferrous sulphate solution, potassium ferrocyanide, $K_4[Fe(CN)_6]$ is formed.

$$FeSO_4 + 2KCN \longrightarrow \underset{\text{Brown ppt.}}{Fe(CN)_2} + K_2SO_4$$

$$Fe(CN)_2 + 4KCN \longrightarrow K_4[Fe(CN)_6]$$

$$\overline{FeSO_4 + 6KCN \longrightarrow K_4[Fe_2(CN)_6] + K_2SO_4}$$

Uses. It is used (*i*) in the manufacture of writing ink, ferrous ammonium sulphate (*Mohr's salt*), iron alum, ferric oxide (*rouge*) etc. (*ii*) as a mordant in dyeing. (*iii*) as a weed-killer in agriculture. (*iv*) as a reducing agent. (*v*) as a reagent in the laboratory. (*vi*) for clarifying water.

2. Ferrous Ammonium Sulphate (Mohr's Salt), $(NH_4)_2SO_4.FeSO_4.6H_2O$

This compound is also called *Mohr's salt* and is a double salt. Ferrous ammonium sulphate is obtained by mixing ferrous sulphate and ammonium sulphate in molecular proportions and crystallising the double salt from the saturated solution of the mixture. A few drops of H_2SO_4 and a little iron wire is added before concentration to prevent oxidation of ferrous sulphate to ferric sulphate. It forms pale green crystals which do not easily effloresce. Its solution

is also not as readily oxidised as that of ferrous sulphate. It is, therefore. employed in volumetric analysis in place of ferrous sulphate in preference to ferrous sulphate.

3. Potassium Ferrocyanide, $K_4[Fe(CN)_6]$

Preparation : Its IUPAC name is potassium hexacyanoferrate (II). On a small scale, it is prepared by mixing a solution of ferrous sulphate with that of potassium cyanide until a small amount of the precipitated ferrous cyanide remains undissolved. The solution on evaporation followed by cooling yields crystals of potassium ferrocyanide

$$FeSO_4 + 2KCN \longrightarrow Fe(CN)_2 + K_2SO_4$$
$$Fe(CN)_2 + 4KCN \longrightarrow K_4[Fe(CN)_6]$$

Manufacture (*a*). On a large scale, it is prepared from coal gas which contains 0.2 percent of hydrogen cyanide as an impurity. The coal gas when allowed to pass through a washer containing ferrous sulphate and potassium hydroxide yields potassium ferrocyanide. The following reactions take place :

$$HCN + KOH \longrightarrow KCN + H_2O$$
$$6KCN + FeSO_4 \longrightarrow K_4Fe(CN)_6 + K_2SO_4$$

(*b*) On a large scale, it is also obtained from coal gas by another method. This gas, when allowed to pass through hydrated iron oxide [a mixture of $Fe(OH)_2$ and $Fe(OH)_3$], gets purified by absorbing hydrogen cyanide on hydrated iron oxide and forms ferric ferro cyanide, also known as *Prussian's blue*, $Fe_7C_{18}N_{18}$. The following reactions take place :

$$Fe(OH)_2 + 2HCN \longrightarrow Fe(CN)_2 + 2H_2O$$
$$Fe(OH)_3 + 3HCN \longrightarrow Fe(CN)_3 + 3H_2O$$
$$3Fe(CN)_2 + 4Fe(CN)_3 \longrightarrow \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3} \text{ or } Fe_7C_{18}N_{18}$$

Prussian blue, formed is treated with $Ca(OH)_2$ when calcium ferrocyanide is formed.

$$Fe_7C_{18}N_{18} + 6Ca(OH)_2 \longrightarrow \underset{\text{soluble}}{3Ca_2[Fe(CN)_6]} + \underset{\text{ppt.}}{4Fe(OH)_3}$$

Calcium ferrocyanide is extracted with water and then treated with potassium carbonate solution when potassium ferrocyanide is obtained.

$$\underset{\text{cal. ferro cyanide}}{Ca_2[Fe(CN)_6]} + K_2CO_3 \longrightarrow 2CaCO_3 + K_4[Fe(CN)_6]$$

Calcium carbonate is removed by filtration and the filtrate when evaporated yields the crystals of potassium ferrocyanide.

Properties. (*i*) Potassium ferrocyanide forms lemon yellow crystals which are associated with 3 molecules of water of crystilization. Thus, the molecular formula is $K_4[Fe(CN)_6].3H_2O$.

(*ii*) *Action of heat.* When heated to 42°C, trihydrate loses its three molecules of water of crystallization. On further heating, it decomposes to yield iron carbide, potassium cyanide and nitrogen.

$$K_4[Fe(CN)_6] \longrightarrow 4KCN + FeC_2 + N_2$$

(*iii*) *Action of H_2SO_4.* When it is boiled with dil. sulphuric acid, hydrogen cyanide is evolved.

$$K_4[Fe(CN)_6] + 3H_2SO_4 \longrightarrow FeSO_4 + 3K_2SO_4 + 6HCN$$

When treated with conc. H_2SO_4, it yields carbon monoxide.

$$K_4[Fe(CN)_6] + 6H_2SO_4 + 6H_2O \longrightarrow 2K_2SO_4 + 3(NH_4)_2SO_4 + 6CO + FeSO_4$$

(*iv*) *Reducing property.* It is a reducing agent and is oxidized by Cl_2, O_3, H_2O_2 or acidified $KMnO_4$ to potassium ferricyanide.

$$2K_4[Fe(CN)_6] + Cl_2 \longrightarrow 2KCl + 2K_3[Fe(CN)_6]$$

$$2K_4[Fe(CN)_6] + O_3 + H_2O \longrightarrow 2KOH + 2K_3[Fe(CN)_6] + O_2$$

(*v*) *Action of metallic salts.* (*a*) With zinc salts, it yields a white ppt. of zinc ferrocyanide.

$$K_4[Fe(CN)_6] + 2ZnSO_4 \longrightarrow \underset{\text{Zinc ferrocyanide}}{Zn_2[Fe(CN)_6]} + 2K_2SO_4$$

(*b*) With copper salts, it yields a red brown ppt. of cupric ferrocyanide.

$$2CuSO_4 + K_4[Fe(CN)_6] \longrightarrow Cu_2[Fe(CN)_6] + 2K_2SO_4$$

(*c*) With ferric salts, it produces Prussian blue.

$$Fe^{3+} + K_4Fe(CN)_6 \longrightarrow \underset{\text{Soluble Prussian blue}}{KFe[Fe^{2+}(CN)_6]} + 3K^+$$

Uses : (*i*) It is used as a reagent in the laboratory for testing Fe^{3+}, Cu^{2+} and Zn^{2+} ions. (*ii*) It is used for making blue prints. (*iii*) It is need for making Prussian blue pigment. (*iv*) It is used for the preparation of pure CO and for the manufacture f $K_3[Fe(CN)_6]$.

4. Ferric Chloride, $FeCl_3$

Preparation : *Anhydrous ferric chloride* is prepared by passing dry Cl_2 over heated iron filing when the salt sublimes at 315°C in a receiver as iron-black crystals with a green iridescence.

$$2Fe + 3Cl_2 \longrightarrow 2FeCl_3$$

In solution it is obtained by dissolving Fe_2O_3 or $Fe(OH)_3$ in HCl or by saturating a solution of $FeCl_2$ with Cl_2.

$$Fe_2O_3 + 6HCl \longrightarrow 2FeCl_3 + 3H_2O$$

$$Fe(OH)_3 + 3HCl \longrightarrow FeCl_3 + 3H_2O$$

$$2FeCl_2 + Cl_2 \longrightarrow 2FeCl_3$$

The solution on evaporation and cooling deposits yellow crystals of the hydrate, $FeCl_3.6H_2O$ or $Fe_2Cl_6.12H_2O$. Other hydrates that separate from the aqueous solution contain Fe_2Cl_6 with 7, 5 and 4 molecules of water.

Properties. (*i*) $FeCl_3$ is not an ionic compound but is a covalent compound as is indicated by its volatility and solubility in non-polar solvents like ether and alcohol. However, it dissolves in H_2O to give Fe^{3+} and Cl^- ions.

(*ii*) Anhydrous $FeCl_3$ forms iron black crystals with a green iridescence. These crystals sublime at 283°C and its vapour density at 450°C corresponds to the formula Fe_2Cl_6. At high temperatures dissociation of Fe_2Cl_6 occurs into $FeCl_3$

molecules so that its vapour density progressively decreases on heating and corresponds to the formula $FeCl_3$ at 750°C. At higher temperatures the vapour density further decreases, probably due to the dissociation of $FeCl_3$ into $FeCl_2$ and Cl_2.

$$Fe_2Cl_6 \overset{750°}{\rightleftarrows} 2FeCl_3 \overset{\text{Above } 750°C}{\rightleftarrows} 2FeCl_2 + Cl_2 \uparrow$$

(*iii*) *Formation of double salts.* It forms a number of garnet- red double salts with other chlorides, *e.g.* $FeCl_3.2KCl.H_2O$; $FeCl_3.2NH_4Cl.H_2O$; $FeCl_3.MgCl_2.H_2O$ etc.

(*iv*) *Oxidising properties.* It is an oxidising agent and oxidises various substances. In these reactions it itself is reduced to $FeCl_2$. Thus it oxidises $SnCl_2$ to $SnCl_4$, SO_2 to H_2SO_4, H_2S to S, nascent hydrogen to HCl and liberates I_2 from KI solution.

$$2FeCl_3 + SnCl_2 \longrightarrow SnCl_4 + 2FeCl_2$$
$$SO_2 + 2FeCl_3 + 2H_2O \longrightarrow H_2SO_4 + 2HCl + 2FeCl_2$$
$$H_2S + 2FeCl_3 \longrightarrow S + 2HCl + 2FeCl_2$$
$$FeCl_3 + H \longrightarrow FeCl_2 + HCl$$
$$2FeCl_3 + 2KI \longrightarrow 2KCl + I_2 + 2FeCl_2$$

(*v*) *Action of $Na_2S_2O_3$.* $FeCl_3$ reacts with sodium thiosulphate, $Na_2S_2O_3$ to form sodium tetrathionate, $Na_2S_4O_6$

$$2FeCl_3 + 2Na_2S_2O_3 \longrightarrow 2NaCl + Na_2S_4O_6 + 2FeCl_2$$

(*vi*) It is hygroscopic and dissolves readily in H_2O, the solution is strongly acidic due to hydrolysis

$$FeCl_3 + 3HOH \rightleftharpoons Fe(OH)_3 + HCl$$

(*vii*) *Action of NH_3 and NOCl.* It absorbs NH_3 and nitrosyl chloride, NOCl to form $FeCl_3.6NH_3$ and $FeCl_3.NOCl$ respectively.

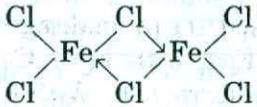
(*viii*) *Formation of various hydrates.* $FeCl_3$ solution deposits crystal of various hydrates at various temperatures $Fe_2Cl_6.12H_2O$ (37°); $Fe_2Cl_6.7H_2O$ (32.5°); $Fe_2Cl_6.5H_2O$ (56°); $Fe_2Cl_6.2H_2O$ (73.50°)

(*ix*) *Action of heat.* On heating $FeCl_3.6H_2O$ is changed into Fe_2O_3, and H_2O and HCl are liberted.

$$2[FeCl_3.6H_2O] \overset{\Delta}{\longrightarrow} Fe_2O_3 + 9H_2O + 6HCl$$

This reaction clearly shows that anhydrous $FeCl_3$ cannot be prepared by simply heating the hydrated ferric chloride, $FeCl_3.6H_2O$.

Structure. Ferric chloride is a covalent compound and a *dimerised molecule*, Fe_2Cl_6 which has the structure shown below.



Structure of Fe_2Cl_6

Uses. (*i*) Ferric chloride solution coagulotes blood and hence is used as a styptic, *i.e.*, in stopping bleeding. (*ii*) It is also used as an oxidising agent in organic dye stuff industry. (*iii*) It is also used as a mordant in dyeing.

5. Potassium Ferricyanide, $K_3[Fe(CN)]_6$

Preparation : Its IUPAC name is potassium hexacyanoferrate (III). It is prepared by the oxidation of potassium ferrocyanide solution by chlorine, hydrogen peroxide or nitric acid. The ferricyanide is separated by repeated fractional crystallization.

$$2K_4[Fe(CN)_6] + Cl_2 \longrightarrow 2K_3[Fe(CN)_6] + 2KCl$$
$$2K_4[Fe(CN)_6] + H_2O_2 \longrightarrow 2K_3[Fe(CN)_6] + 2KOH$$

It is also prepared by the electrolytic oxidation of slightly alkaline solution of potassium ferrocyanide.

$$2[Fe(CN)_6]^{4-} + 2H_2O \longrightarrow 2[Fe(CN)_6]^{3-} + H_2 + 2OH^-$$

Properties : It forms dark red crystals. It is comparatively less stable than potassium ferrocyanide. As it undergoes easy reduction to potassium ferrocyanide in alkaline medium. it acts as a useful oxidizing agent in alkaline medium.

$$2K_3Fe(CN)_6 + 2KOH \longrightarrow 2K_4Fe(CN)_6 + H_2O + O$$

Thus, it oxidizes hydrogen sulphide to sulphur, litharge into lead dioxide, chromic oxide into potassium chromate and sulphur dioxide into sulphuric acid.

$$2K_3[Fe(CN)_6] + 2KOH + H_2S \longrightarrow 2K_4[Fe(CN)_6] + 2H_2O + S$$
$$2K_3[Fe(CN)_6] + 2KOH + PbO \longrightarrow 2K_4[Fe(CN)_6] + H_2O + PbO_2$$
$$6K_3[Fe(CN)_6] + 10KOH + Cr_2O_3 \longrightarrow 6K_4[Fe(CN)_6] + 5H_2O + 2K_2CrO_4$$
$$2K_3[Fe(CN)_6] + 2KOH + SO_2 \longrightarrow 2K_4[Fe(CN)_6] + H_2SO_4$$

The alkaline solution, of potassium ferricyanide is readily reduced to potassium ferrocyanide by H_2O_2, sodium amalgam or hydrazine.

$$2K_3[Fe(CN)_6] + H_2O_2 + 2KOH \longrightarrow 2K_4[Fe(CN)_6] + 2H_2O + O_2$$
$$4K_3[Fe(CN)_6] + 4KOH + N_2H_4 \longrightarrow 4K_4[Fe(CN)_6] + 4H_2O + N_2$$

When potassium ferricyanide is treated with ferrous sulphate solution, ferrous ion is first oxidized to ferric ion while ferricyanide ion is reduced to ferrocyanide ion. Then, the ferric ions react with ferrocynanide ions to form patassium ferric ferrocyanide (Turnbull's blue).

$$\underset{\substack{\text{Ferricyanide}\\\text{ion}}}{Fe^{2+} + [Fe(CN)_6]^{3-}} \longrightarrow \underset{\substack{\text{Ferrocyanide}\\\text{ion}}}{Fe^{3+} + [Fe(CN)_6]^{4-}}$$

$$K^+ + Fe^{3+} + [Fe(CN)_6]^{4-} \longrightarrow \underset{\substack{\text{Potassium ferric ferrocyanide}\\\text{(Turnbull's blue)}}}{K^+Fe^{3+}\,[Fe^{2+}(CN)_6]^-}$$

Uses : $K_3[Fe(CN)_6]$ is used (*i*) in making blue prints. (*ii*) as an external indicator in the titration of Fe^{2+} with $K_2Cr_2O_7$. (*iii*) in qualitative analysis to distinguish ferrous salt from a ferric salt. With ferrous salts, it yields a deep blue ppt. of Turnbull's blue while with ferric salts it yields deep brown ppt.

Compounds of Cobalt

Like iron the important oxidation states exhibited by cobalt in its compounds are +2 and +3. The compounds in +2 and +3 oxidation states are called *cobaltous* and *cobaltic compounds* respectively. Important compounds of Co are discussed below :

1. Cobalt Nitrate, $Co(NO_3)_2.6H_2O$

It is obtained by dissolving the metal, its oxide or carbonate in nitric acid. The anhydrous salt is made by the action of nitrogen pentoxide on the hydrated salt. The hexahydrate forms pink slightly deliquescent crystals, highly soluble in water. On heating it decomposes to give Co_3O_4. It is used as a reagent in blow-pipe analysis 'and in the preparation of cobalt pigments and ceremics.

2. Complex Compounds

Cobalt forms complexes in –1,0 +1, +2, +3 and +4 oxidation states. Complexes in +3 state are important. All known Co(+3) complexes are *octahedral* except the one *viz.* heteropoly tungetate which is *tetrahedral.* Octahedral complexes like $[CoF_3]^{3-}$ which contain weak F^- ligands are *high-spin complexes (outer-orbital–sp^3d^2* hybridisation) and, therefore, show *paramagnetic character corresponding to the presence of four unpaired electrons.* Other octahedral complexes are *low-spin (inner-orbital–d^2sp^3* hybridisation) and, hence, are *diamagnetic due to the presence of all paired electrons.* Important complex compounds of Co(+3) are discussed below. It may be noted that the coordination number of Co(+3) in these complexes is six.

(*i*) Sodium cobaltinitrite or sodium hexanitro cobaltate (III), $Na_3[Co(NO_2)_6]$. It is prepared by mixing well cooled solutions of $Co(NO_3)_2$ and $NaNO_2$ and acidifying the mixture with glacial CH_3COOH. In this reaction HNO_2 produced by the interaction between $NaNO_2$ and CH_3COOH oxidises $Co(NO_2)_2$ to $Co(NO_2)_3$ which combines with $NaNO_2$ to give $Na_3[Co(NO_2)_6]$. Thus this reaction takes place through the following steps :

$$[NaNO_2 + CH_3COOH \longrightarrow HNO_2 + CH_3COONa] \times 2$$
$$2NaNO_2 + Co(NO_3)_2 \longrightarrow Co(NO_2)_2 + 2NaNO_3$$
$$Co(NO_2)_2 + 2HNO_2 \longrightarrow Co(NO_2)_3 + H_2O + NO$$
$$Co(NO_2)_3 + 3NaNO_2 \longrightarrow Na_3[Co(NO_2)_6]$$

$$Co(NO_3)_2 + 7NaNO_2 + 2CH_3COOH \longrightarrow Na_3[Co(NO_2)_6] + 2CH_3COONa + 2NaNO_3 + H_2O + NO$$

or
$$Co^{2+} + 7NO_2^- + 2H^+ \longrightarrow [Co(NO_2)_6]^{3-} + H_2O + NO$$

On treating the solution with alcohol, sodium cobaltinitrite is separated out as a yellow crystalline powder. The complex is fairly soluble in water. With aqueous solution containing soluble ammonium or potassium salts a yellow precipitate of slightly soluble complex is formed.

$$[Co(NO_2)_6]^{3-} + 3K^+ \longrightarrow \underset{\text{yellow precipitate}}{K_3[Co(NO_2)_6]}$$

This reaction is used for the detection and estimation of K^+ and NH_4^+ ions.

***(ii)* Potassium cobaltinitrite or potassium hexanitro cobaltate (III) or Fisher's salt, $K_3[Co(NO_2)_6]$.** It is prepared when KNO_2 is added to $Co(NO_3)_2$ solution acidified with CH_3COOH.

$$Co(NO_3)_2 + 7KNO_2 + 2CH_3COOH \longrightarrow K_3[Co(NO_2)_6] + 2CH_3COOK + 2KNO_3 + H_2O + NO$$

It is insoluble in water. It is a bright yellow powder which may be washed with potassium acetate solution and alcohol. $[Co(NO_2)_6]^{3-}$ ion is decomposed by alkalies to form hydroxides while strong acids decompose it into oxides of nitrogen. It is used (*i*) as a yellow pigment (*Indian yellow or cobalt yellow*) (*ii*) in painting porcelain blue.

***(iii)* Hexammine cobaltic chloride, $[Co(NH_3)_6]Cl_3$.** When a vigorous stream of air is drawn for several hours through a solution of a cobalt (II) chloride, $CoCl_2$, containing ammonia, ammonium chloride and some activated charcoal, good yield of hexamine cobalt (III) chloride is obtained.

$$4CoCl_2 + 4NH_4Cl + 20NH_3 + O_2 \longrightarrow 4[Co(NH_3)_6]Cl_3 + 2H_2O$$

In the absence of charcoal, replacement usually occurs to give, for example, $[Co(NH_3)_5Cl]^{2+}$ and $[Co(NH_3)_4(CO_3)]^+$. This forms orange-yellow crystals. Conductance measurement indicates the presence of four ions in its solution, *i.e.*, one cobalt and three chloride ions (ammonia molecules are netural). This is in accordance with the dissociation :

$$[Co(NH_3)_6]Cl_3 \rightleftarrows [Co(NH_3)_6]^{3+} + 3Cl^-$$

Compounds of Nickel

Different Oxidation States of Nickel in Its Compounds

Nickel forms compounds in 0, +2, +3 and +4 oxidation states. Examples are *Ni(0) compounds* : $Ni(CO)_4$, $Ni(PF_3)_4$, $[Ni(CN)_4]^{4-}$; *Ni(+2) compounds* (called *nicklous compounds*) : NiO, $NiSO_4$, $[Ni(CN)_4]^{2-}$, $[Ni(dmg)_2]^0$; *Ni(+3) compounds* : Ni_2O_3, $[NiBr_3(PEt_3)_2]^0$; *Ni(+4) compounds* : NiO_2. $K_2[NiF_6]$. Compounds of Ni in +2 oxidation state are the most stable. Some compounds of Ni are discussed below :

1. Nickel Sulphate, $NiSO_4.7H_2O$

This compound forms heptahydrate rhombic crystals, isomorphous with cobalt and ferrous sulphates. Nickel sulphate is prepared by dissolving its hydroxide or carbonate in dilute sulphuric acid or by heating nickel nitrate, $Ni(NO_3)_2.6H_2O$ with concentrated sulphuric acid. If a saturated solution of nickel sulphate is heated to 54°, monoclinic crystals of $NiSO_4.6H_2O$ are obtained. The crystals are green. When heated above 280°C, yellow anhydrous $NiSO_4$ is formed. If anhydrous nickel sulphate is dissolved in a concentrated solution of ammonia, an unstable dark blue salt, tetrammine nickel sulphate, $Ni(NH_3)_4SO_4.2H_2O$ is formed similar to cuprammonium salts. Besides this complex salt, nickel sulphate also forms a double salt with ammonium sulphate, known as nickel ammonium sulphate $NiSO_4.(NH_4)_2SO_4.6H_2O$, which is extensively used in nickel plating.

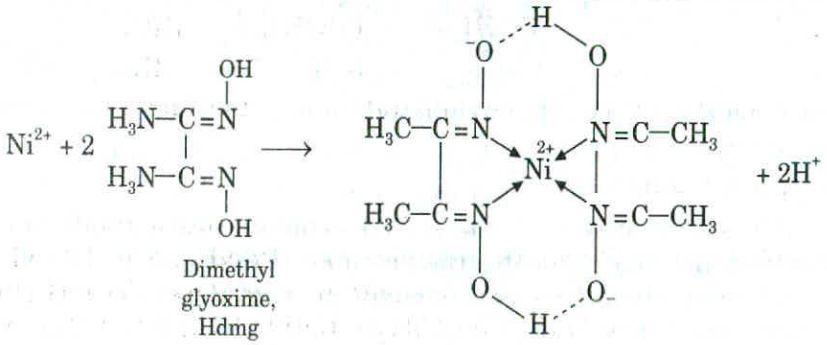
2. Nickel Ammonium Sulphate, $NiSO_4.(NH_4)_2SO_4.6H_2O$

This compound is obtained by mixing, the solution of $NiSO_4.7H_2O$ with that of $(NH_4)_2SO_4$ and then evaporating the solution to crystallisation. The compound forms bluish green crystals. This compound is used for nickel electroplating.

3. Bis-(dimethyl glyoximato) Nickel (II), $Ni(dmg)_2$

It is an important complex compound of Ni(+2). In this complex dmg^- ion acts as a bidentate ligand. dmg^- is the abbreviation used for dimethylglyoxime ion which is obtained by removing one H-atom from the oxime group (> N—OH) present in dimethylglyoxime (abbreviated as Hdmg).

When dimethylglyoxime is added to an alkaline solution of a Ni^{2+} salt, red precipitate of *bis*-(dimethyl glyoximato) nickel (II), $Ni(dmg)_2$ is obtained.



It is a chelate complex. It is electrically neutral and covalent in character. Its covalent character accounts for its low solubility in water. It may be seen from the structure that the co-ordination of dmg^- ion (ligand) to Ni^{2+} ion occurs through both its N-atoms making two 5-membered rings. Further two 6-membered rings are also formed by H-bonding between NOH and ON. H-bonding stabilises the structure of the complex. The complex is diamagnetic and has square planar shape. It is an inner-orbital complex. The formation of $Ni(dmg)_2$ is used in detecting as well as estimating nickel.

Compounds of Platinum

Different Oxidation States of Platinum

Platinum chiefly forms two series of compounds—*platinous* and *platinic* corresponding to +2 and +4 oxidation states of platinum respectively. The compounds in +1 (*e.g.* PtCl), +3 ($PtCl_3$), +5(PtF_5) and +6(PtO_3) oxidation states are also known but these are rare. Here we shall discuss only platinic compounds which are more important than the platinous compounds.

1. Platinic Chloride, $PtCl_4$. It is formed when chloroplatinic acid, H_2PtCl_6 is heated at 370°C in chlorine.

$$H_2PtC_6 \longrightarrow PtCl_4 + 2HCl$$

It forms reddish-brown slightly hygroscopic crystalline mass. It dissolves in water giving yellowish-red solution which is strongly acidic and seems to contain a complex acid, $H_2[PtCl_4(OH)_2]$ or $PtCl_4.2H_2O$, because it forms silver salt, $Ag_2[PtCl_4(OH)_2]$ and on electrolysis the platinum is discharged at the anode as a part of the anion.

$$H_2[PtCl_4(OH)_2] \rightleftarrows 2H^+ + [PtCl_4(OH)_2]^{2-}$$

$PtCl_4$ liberates I_2 from KI and gives H_2PtCl_6 with HCl.

$$PtCl_4 + 4KI \longrightarrow PtI_2 + I_2 + 4KCl$$

$$PtCl_4 + 2HCl \longrightarrow H_2PtCl_6$$

With KOH, $Pt(OH)_4$ is precipitated and with KCN it gives potassium platinocyanide, $K_2[Pt(CN)_4]$.

$$PtCl_4 + 4KOH \longrightarrow Pt(OH)_4 \downarrow + 4KCl$$

$$PtCl_4 + 6KCN \longrightarrow K_2[Pt(CN)_4] + 4KCl + (CN)_2 \downarrow$$

Platinic chloride is used for the preparation of potassium chioroplinate which is used in photography.

2. Complex Compounds

Pt forms complex compounds in +2 and +4 oxidation states. Important examples of such complex are (*i*) *Platinous ammines* like $[Pt(NH_3)_4]Cl_2$. $[Pt(NH_3)_3Cl]$ Cl, $[Pt(NH_3)_2Cl_2]^0$, $K[Pt(NH_3)Cl_3]$ (*ii*) *Tetrachloro complexes* like $H_2[PtCl_4]$ (*iii*) *Tetracyano complexes* like $K_2[Pt(CN)_4].3H_2O$, $Ba[Pt(CN)_4].4H_2O$. The majority of Pt(+2) complexes are four coordinate. They are diamagnetic with dsp^2 hybridisation and have square planar geometry. These are quite inert. Important examples of complex compounds formed by Pt(+4) are : (*i*) *Platinic ammines* like $[Pt(NH_3)_6]Cl_4$, $[Pt(NH_3)_5Cl]Cl_3$, $[Pt(NH_3)4Cl_2]Cl_2$, $[Pt(NH_3)_3Cl_3]Cl$, $[Pt(NH_3)_2Cl_4]^0$, $K[Pt(NH_3)Cl_5]$ (*ii*) *Hexachloro complexes* like H_2 $[PtCl_6]$, $(NH_4)_2[PtCl_6]$. Complexes of Pt(+4) are remarkably stable and kinetically inert. All these are *octahedral* resulting from d^2sp^3 hybridisation (*inner orbital*). Since Pt(+4) is a d^6 system, all the electrons are paired and hence the complexes are *diamagnetic*. Now let us discuss some of the above complex compounds in detail :

(*i*) Chloroplatinous acid, $H_2[PtCl_4]$. In this complex compound Pt is in +2 oxidation state. Here the coordination number of Pt is 4. It is obtained by dissolving PCl_2 in HCl or by the reduction of H_2PtCl_6 with SO_2.

$$PtCl_2 + 2HCl \longrightarrow H_2PtCl_4$$

$$H_2PtCl_6 + 2H_2O + SO_2 \longrightarrow H_2PtCl_4 + H_2SO_4 + 2HCl$$

The acid does not crystallise but forms a dark-brown amorphous solid on evaporation. Its salts are called *chloroplatinites*. Potassium chloro platinite, K_2PtCl_4 may be better prepared by reducing chloroplatinate, K_2PtCl_6 by cuprous chloride.

$$K_2PtCl_6 + Cu_2Cl_2 \longrightarrow 2CuCl_2 + K_2PtCl_4$$

The salt forms dark red crystals and is used in platinum printing in photography. The corresponding ammonium, silver or lead salts are also known.

(*ii*) Potassium platinocyanide, $K_2[Pt(CN)_4].3H_2O$. It is obtained as yellow needles by mixing solutions of $PtCl_2$ and KCN in proper proportions and evaporating the solution to crystallisation.

$$PtCl_2 + 4KCN \longrightarrow K_2[Pt(CN)_4] + 2KCl$$

***(iii)* Barium platinocyanide, $Ba[Pt(CN)_4].4H_2O$.** It is prepared by warming $H_2[PtCl_6]$ solution with baryta water, $Ba(OH)_2$ and HCN and passing in SO_2 until the solution becomes colourless.

$$H_2[PtCl_6] + 5Ba(OH)_2 + 4HCN + SO_2 \longrightarrow Ba[Pt(CN)_4] + BaSO_4 + 3BaCl_2 + 8H_2O$$

$BaSO_4$ is filtered off and the filtrate is crystallised to get $Ba[Pt(CN)_4].4H_2O$. It is a lemon-yellow powder which is soluble in water. It is used for fluorescent screens in X-ray work.

***(iv)* Chloroplatinic acid, $H_2[PtCl_6]$. Preparation :** It is an important complex compound in which platinum metal is in +4 oxidation state and the co-ordination number of Pt is 6. It is best prepared by the action of aqua-regia on platinum.

$$\underbrace{2HNO_3 + 6HCl}_{\text{Aqua-regia}} + Pt \longrightarrow H_2PtCl_6 + 4H_2O + 4NOCl$$

The solution is evaporated to remove excess of acid and on cooling reddish brown needles of $H_2PtCl_6.6H_2O$ are left behind.

Properties. (*a*) It forms reddish-brown deliquescent crystals which dissolve in water to give a bright yellow coloured solution. It is a strong dibasic acid and ionises as :

$$H_2PtCl_6 \rightleftarrows 2H^+ + [PtCl_6]^{2-}$$

(*b*) *Action of heat.* When heated to 370°C in Cl_2 or at 165° in H_2, $PtCl_4$ is formed. At 390°C in Cl_2, $PtCl_3$ is formed while at 580°C in Cl_2 it gives $PtCl_2$.

$$H_2PtCl_6 \xrightarrow[\text{at 370°C}]{\text{Heat in } Cl_2} PtCl_4 + 2HCl$$

(*c*) *Electrolysis.* When its solution is electrolysed, metallic platinum is deposited on the cathode as a result of the reducing action of the liberated hydrogen.

(*d*) *Reduction.* When reduced with Zn or formic acid (HCOOH) finely divided powder of *platinum black* is obtained, and when reduced with SO_2, chloroplatinous acid, H_2PtCl_4 is formed.

$$H_2PtCl_6 + 2HCOOH \longrightarrow \underset{\text{black}}{\overset{\text{platinum}}{Pt}} + 6HCl + 2CO_2$$

$$H_2PtCl_6 + SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2HCl + H_2PtCl_4$$

(*e*) *Formation of chloroplatinates.* It forms stable salts which are called *chloroplatinates*. Important examples are $Li_2PtCl_6.6H_2O$, $Na_2PtCl_6.6H_2O$, K_2PtCl_2, $(NH_4)_2PtCl_2$, Ag_2PtCl_6 etc. Out of these chloroplatinates ammonium chloroplatinate, $(NH_4)_2PtCl_2$ is the most important and is discussed on the next page.

(*f*) *Action of bases.* With a number of bases (*e.g.* $C_6H_5NH_2$), chloroplatinic acid forms stable crystalline compound and hence it is used in their estimations.

$$2C_6H_5NH_2 + H_2PtCl_6 \longrightarrow [C_6H_5NH_2]_2H_2PtCl_6$$

(*g*) *Action of H_2S.* When H_2S is passed into a hot solution of H_2PtCl_6, platinic sulphide (PtS_2) is obtained as a black precipitate.

$$H_2PtCl_6 + 2H_2S \longrightarrow PtS_2 + 6HCl$$

(*h*) *Action of KI.* When hot solution of H_2PtCl_6 is treated with KI, platinic iodide (PtI_4) is formed.

$$H_2PtCl_6 + 4KI \longrightarrow PtI_4 + 4KCl + 2HCl$$

(*i*) *Conversion of $H_2[PtCl_6]$ into PtO_2.* When the solution of $H_2[PtCl_6]$ is treated with a caustic alkali, alkali metal chloroplatinate, $M_2[PtCl_6]$ is formed. The action of CH_3COOH on this alkali metal chloroplatinate gives $H_2[Pt(OH)_6]$ which on heating gives PtO_2.

$$H_2[Pt(OH)_6] \xrightarrow{\Delta} 4H_2O + PtO_2$$

(*j*) *Action of baryta water, HCN and SO_2.* When H_2PtCl_6 is warmed with baryta water, $Ba(OH)_2$ and HCN and SO_2 is passed in until the solution becomes colourless, barium platinocyanide, $Ba[Pt(CN)_4]$ is formed.

$$H_2PtCl_6 + 5Ba(OH)_2 + 4HCN + SO_2 \longrightarrow \underset{\text{solution}}{Ba[Pt(CN)_4]} + \underset{\text{ppt.}}{BaSO_4} + 3BaCl_2 + 8H_2O$$

$BaSO_4$ is filtered off and the filtrate is crystallised to get the crystals of $Ba[Pt(CN)_4]$.

Uses. H_2PtCl_6 is used : (*i*) for the determination of molecular weight of bases (*ii*) for preparing spongy Pt and many platinum compounds like $PtCl_4$ etc. (*iii*) for the gravimetric estimation of organic bases (*iv*) as a tanning agent in photography.

(*v*) Ammonium chloroplatinate, $(NH_4)_2[PtCl_6]$. Preparation : It is an important salt of chloroplatinic acid, H_2PtCl_6. It is also called *ammonium platinicchloride.* It is prepared by adding NH_4Cl to a solution of H_2PtCl_6 or by treating H_2PtCl_6 with NH_3.

$$H_2[Pt\ Cl_6] + 2NH_4Cl \longrightarrow (NH_4)_2[PtCl_6] + 2HCl$$
$$H_2[Pt\ Cl_6] + 2NH_3 \longrightarrow (NH_4)_2[PtCl_6]$$

Properties. (*a*) it is a yellow substance which is sparingly soluble in H_2O.

(*b*) *Action of heat.* On heating *spongy platinum* is obtained.

$$(NH_4)_2Pt\ Cl_6 \longrightarrow \underset{\substack{\text{Spongy}\\ \text{platinum}}}{Pt} + 2NH_3 + 2HCl + 2Cl_2 \uparrow$$

(*c*) *Action of liq. NH_3.* When $(NH_4)_2[PtCl_6]$ is treated with liq. NH_3, hexammino platinic chloride, $[Pt(NH_3)_6Cl_4$ is obtained

$$(NH_4)_2[PtCl_6] + 6NH_3 \longrightarrow [Pt(NH_3)_6]Cl_4 + 2NH_4Cl.$$

(*d*) *Action of hydrazine hydrochloride, $N_2H_4.2HCl$.* When hydrazine hydrochloride is added to an ammoniacal solution of $(NH_4)_2[PtCl_6]$, ammonium chloroplatinate is reduced to metallic platinum some of which gets deposited on the inside of the tube as a *platinum mirror.*

$$(NH_4)_2[Pt\ Cl_6] + N_2H_4.2HCl + 6NH_3 \longrightarrow Pt + N_2 + 8NH_4Cl$$

Uses. The formation of $(NH_4)_2[PtCl_6]$, followed by its decomposition, forms the basis of the *refining of platinum metal.*

Compounds of Copper

Copper forms two types of compounds : (*i*) *Copper (+1) or cuprous compounds* in which copper is *monovalent*, and (*ii*) *Copper (+2) or cupric compounds* in which copper is *divalent.* When cupric or cuprous is not stated in the case of a salt of copper, cupric is implied *e.g.* copper sulphate implies cupric sulphate. Most of the *cuprous compounds are usually colourless and diamagnatic* as 3*d* orbital is completely filled ($Cu^+ \rightarrow 3d^{10}$). Cu_2O, Cu_2S etc. which are red and black are exceptions. These are generally insoluble in water. The soluble compounds of Cu(+1) are *unstable in aqueous solution, since they disproportionate* to Cu^{2+} and Cu.

$$2Cu^+ \longrightarrow Cu + Cu^{2+}$$

Most of the *anhydraus cupric compounds are colourless* while the *hydrated cupric compounds are blue* due to the formation of blue hydrated ion, $[Cu(H_2O)_4]^{2+}$ or $[Cu(H_2O)_6]^{2+}$. Important compounds of Cu are Cu_2O, CuCl, etc. which are discussed below :

1. Cuprous Oxide, Cu_2O

Preparation : It is also called ***red oxide of copper.*** It is obtained by heating copper in air or by very strongly heating cupric oxide alone or with copper. It is also precipitated in red or orange form when alkaline cupric sulphate solution (or Fehling'a solution) is reduced by substances like glucose or aldehydes.

$$CuSO_4 + 2NaOH \longrightarrow Na_2SO_4 + Cu(OH)_2 \longrightarrow CuO + H_2O$$

$$\underset{\text{Cupric oxide}}{2CuO} + \underset{\text{Glucose}}{C_5H_{11}O_5.CHO} \longrightarrow \underset{\text{Cuprous oxide}}{Cu_2O} + \underset{\text{Gluconic acid}}{C_5H_{11}O_6.COOH}$$

$$2Cu(OH)_2 + \underset{\text{Acetaldehyde}}{CH_3CHO} \longrightarrow Cu_2O + \underset{\text{Acetic acid}}{CH_3COOH} + 2H_2O$$

Properties. (*i*) It is a dull red powder. It is practically insoluble in water.

(*ii*) *Action of acids.* Cuprous oxide reacts with dilute acids, forming cupric salts

$$Cu_2O + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$

$$Cu_2O + 4HCl \longrightarrow 2H[CuCl_2] + H_2O$$

(*iii*) *Action of ammonia.* It dissolves in ammonia and gives complex compounds called amines.

$$Cu_2O + 4NH_3 + 4H_2O \longrightarrow 2[Cu(NH_3)_2]OH$$

(*iv*) *Action of alkali cyanide.* It dissolves in alkali cyanide (*e.g.* KCN) solution forming a colourless complex, $K_2[Cu(CN)_3]$

$$Cu_2O + 6KCN + H_2O \longrightarrow 2K_2[Cu(CN)_3] + 3KOH$$

Uses. It is used (*i*) for making ruby glass and enamel. (*ii*) as pigment. (*iii*) in the manufacture of antirust paints. (*iv*) as a pesticide.

2. Cuprous Chloride, CuCl or Cu_2Cl_2

Preparation : It is obtained by the following reactions :

$$CuCl_2 + Cu \xrightarrow[\text{of conc. HCl}]{\text{Heat in presence}} 2CuCl.$$

$$2CuCl_2 + 2H \xrightarrow{\text{Reduction}} 2CuCl + 2HCl$$

$$2CuCl_2 + SO_2 + 2H_2O \xrightarrow{\text{Reduction}} 2CuCl + H_2SO_4 + 2HCl$$

$$2CuCl_2 \xrightarrow{450^\circ} 2CuCl + Cl_2$$

Properties. (*i*) Cuprous chloride is a colourless crystalline substance, insoluble in water but soluble in HCl and NH_4OH. When exposed to air, it is slowly oxidised to green basic cupric chloride, $3CuO.\ CuCl_2.3H_2O$.

(*ii*) *Action of oxidising agents.* With oxidising agents, it is converted into cupric chloride.

$$2CuCl + 2HCl + O \longrightarrow 2CuCl_2 + H_2O$$

(*iii*) An acidified solution of cuprous chloride absorbs oxygen and carbon monoxide while an ammoniacal solution absorbs acetylene.

$$4CuCl + 4HCl + O_2 \longrightarrow 4CuCl_2 + 2H_2O$$

This reaction is utilised in the manufacture of chlorine by *Deacon's process.*

$$\underset{}{CuCl} + 2CO \longrightarrow \underset{\text{Addition compound}}{CuCl.2CO}$$

This addition compound decomposes on heating, regenerating carbon monoxide. This reaction is, therefore, *employed in gas analysis* for separation of carbon monoxide.

$$\underset{}{2CuCl} + \underset{\text{Acetylene}}{C_2H_2} \longrightarrow \underset{\text{Copper acetylide}}{C_2Cu_2} + 2HCl$$

Acetylene can be regenerated by treating the acetylide with strong HCl. The reaction is, therefore, *used in the purification and separation of acetylene.*

(*iv*) *Action of alkalies.* Cuprous chloride solution gives with alkalies a yellow ppt. of cuprous oxide which gradually changes to red colour.

$$2CuCl + 2NaOH \longrightarrow \underset{\text{Yellow ppt. changing to red}}{Cu_2O} + 2NaCl + H_2O$$

(*v*) *Action of H_2S.* With H_2S, a black precipitate of cuprous sulphide Cu_2S is produced.

$$CuCl + H_2O \longrightarrow \underset{\text{black ppt.}}{Cu_2S} + 2HCl$$

Uses. Ammoniacal solution of cuprous chloride is used in gas analysis for absorbing acetylene while HCl solution of it is used for absorbing CO and oxygen.

3. Basic Cupric Acetate or Verdigris, $Cu(CH_3COO)_2.Cu(OH)_2$

Preparation : It is prepared by exposing thin sheets of copper to the action of vinegar, CH_3COOH and air.

$$2Cu + 2CH_3COOH + O_2 \longrightarrow (CH_3COOH)_2Cu.Cu(OH)_2$$

Properties : It is greenish blue powder. It is sparingly soluble in cold water but dissolves in dilute acids and ammonia.

Uses. (*i*) Because of its fairly good covering power, it is used as green pigment, (*ii*) used in dyeing and calico-printing, (*iii*) used in making insecticide and fungicides, (*iv*) when verdigris is mixed with As_2O_3, cupric aceto arsenite, (called *paris green*) $Cu_3(AsO_3)_2$. $Cu(CH_3COO)_2$ which is poisonous is obtained.

4. Cupric Sulphate or Blue Vitriol, $CuSO_4.5H_2O$

Preparation : This compound is generally called ***copper sulphate*** and is *Nila Thotha.* In the laboratory, it is prepared by the action of cupric oxide, carbonate or hydroxide on dilute sulphuric acid followed by evaporation and crystallisation.

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$
$$CuCO_3 + H_2SO_4 \longrightarrow CuSO_4 + H_2O + CO_2$$
$$Cu(OH)_2 + H_2SO_4 \longrightarrow CuSO_4 + 2H_2O$$

Manufacture. (*i*) On a large scale copper sulphate is obtained by boiling copper turnings with concentrated sulphuric acid. Blue solution of copper sulphate is formed.

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$$

(*ii*) It is also obtained by treating copper scrappings in hot dilute sulphuric acid in presence of air.

$$2Cu + H_2SO_4 + O_2 \longrightarrow 2CuSO_4 + 2H_2O.$$

Copper scrap or copper turnings are packed in a lead lined vertical tower. Dilute sulphuric acid is sprayed at the top and percolates through copper chips. A current of air and steam is blown from below. Copper dissolves in dilute sulphuric acid in the presence of air to give a solution of copper sulphate which is collected at the base. This solution of copper sulphate contains a lot of dilute acid and is recirculated in the tank by means of a pump to get a concentrated solution which is led into crystallisation tanks. On cooling, crystals of *pentahydrate copper sulphate.* $CuSO_4.5H_2O$ are deposited.

(*iii*) In another process, the mineral copper pyrites, ($Cu_2S.Fe_2S_3$) is roasted in air. Iron oxide and copper sulphate are formed. The roasted mass is treated with water. Copper sulphate dissolves and is separated by filtration. On crystallisation crystals of $CuSO_4.5H_2O$ are formed.

Anhydrous copper sulphate, which is a white powder, is obtained by heating pure $CuSO_4.5H_2O$ in the powdered form in a U-tube at 230°C in a current of dry air until the weight corresponds with $CuSO_4$.

Properties. (*i*) Copper sulphate forms deep blue crystals of the composition $CuSO_4.5H_2O$. Copper sulphate is fairly soluble in water.

(*ii*) *Action of heat.* On heating copper sulphate loses its water of crystallisation. On heating to 100°C it gives $CuSO_4.H_2O$ and when heated to 230°C it becomes white anhydrous $CuSO_4$.

The white anhydrous copper sulphate decomposes at about 720°C to give cupric oxide and sulphur trioxide.

$$\underset{\text{Blue}}{CuSO_4.5H_2O} \xrightarrow{100°C} \underset{\text{Pale blue}}{CuSO_4.H_2O} \xrightarrow{230°C} \underset{\substack{\text{Colourless}\\(\text{amorphous})}}{CuSO_4} \xrightarrow{720°C} CuO + SO_3$$

(*iii*) Copper sulphate gives all the general reactions of sulphates.

(*iv*) *Action of potassium iodide.* Copper sulphate gives white cuprous iodide with potassium iodide.

$$2CuSO_4 + 4KI \longrightarrow 2K_2SO_4 + 2CuI + I_2$$

(*v*) *Action of alkalies.* Alkalies produce a pale blue precipitate of copper hydroxide.

$$CuSO_4 + 2NaOH \longrightarrow \underset{\text{Pale blue ppt.}}{Cu(OH)_2} + Na_2SO_4$$

(*vi*) *Action of NH_4OH.* With ammonium hydroxide, precipitate of $Cu(OH)_2$ is first produced but it dissolves in excess of it forming a bright blue solution, the colour being due to the formation of *cuprammonium ion*, $[Cu(NH_3)_4]^{2+}$

$$\underset{\text{Small amount}}{CuSO_4 + 2NH_4OH} \longrightarrow \underset{\text{ppt.}}{Cu(OH)_2} + (NH_4)_2SO_4$$

$$\underset{\text{Large amount}}{CuSO_4 + 4NH_4OH} \longrightarrow \underset{\substack{\text{Cuprammonium}\\\text{sulphate}\\(\text{Deep blue soln.})}}{Cu(NH_3)_4SO_4} + 4H_2O$$

(*vii*) *Action of potassium ferrocyanide.* Reddish brown precipitate of cupric ferrocyanide is formed.

$$2CuSO_4 + K_4[Fe(CN)_6] \longrightarrow 2K_2SO_4 + Cu_2[Fe(CN)_6]$$

(*viii*) *Action of potassium sulphocyanide.* Oupric sulphocyanide is formed.

$$CuSO_4 + 2KCNS \longrightarrow K_2SO_4 + \underset{\text{Cupric sulphocyanide}}{Cu(CNS)_2}$$

(*ix*) *Action of KCN.* With KCN it gives a yellow ppt. of cupric cyanide which decomposes to give cuprous cyanide and cyanogen. Cuprous cyanide dissolves in excess of KCN to give potassium cuprocyanide.

$$CuSO_4 + 2KCN \longrightarrow Cu(CN)_2 + K_2SO_4$$

$$\underset{\substack{\text{Cupric}\\\text{cyanide}}}{2Cu(CN)_2} \longrightarrow \underset{\substack{\text{Cuprous}\\\text{cyanide}}}{Cu_2(CN)_2} + \underset{\text{Cyanogen}}{(CN)_2}$$

$$Cu_2(CN)_2 + 6KCN \longrightarrow \underset{\text{Potassium cuprocyanide}}{2K_3Cu(CN)_4}$$

(*x*) *Addition of electropositive metals.* Electropositive metals like zinc or iron precipitates copper from a solution of copper sulphate.

$$CuSO_4 + Fe \longrightarrow FeSO_4 + Cu$$

(*xi*) *Action of H_2S.* With H_2S it gives a black ppt. of copper sulphide.

$$CuSO_4 + H_2S \longrightarrow \underset{\text{Black ppt.}}{CuS} + H_2SO_4$$

Uses. It is used : (*i*) in electroplating, in electrotyping and in the purification of copper. (*ii*) in agriculture as a germ killer and fungicide. *Bordeaux mixture* is copper sulphate mixed with lime and is extensively used for dusting vines and potatoes. (*iii*) in calico-printing, dyeing and the preparation of other compounds of copper. (*iv*) in analysis (as anhydrous salt). (*v*) in medicine as an antiseptic.

5. Cupric Cyanide, $Cu(CN)_2$

Preparation : This compound as such has not been isolated so for. It is formed as a yellow precipitate when a small quantity of KCN is added to a cold solution of $CuSO_4$

$$CuSO_4 + 2KCN \longrightarrow \underset{\text{Yellow ppt.}}{Cu(CN)_2} + K_2SO_4$$

Properties. (*i*) It is extremely unstable and rapidly decomposes even at ordinary temperature to give cuprous cyanide, CuCN and free cyanogen, $(CN)_2$

$$2Cu(CN)_2 \longrightarrow 2CuCN + (CN)_2$$

(*ii*) It dissolves in the excess of KCN, forming potassium cupri cyanide, $K_2[Cu(CN)_4]$.

$$Cu(CN)_2 + 2KCN \text{ (excess)} \longrightarrow K_2[Cu(CO)_4]$$

(*iii*) It forms coordination compound, $[Cu(py)_2](CN)_2$, with pyridine,

6. Complex Compounds of Cuprous Ion

(*i*) Complexes with hydrochloric acid. Cuprous oxide Cu_2O or cuprous chloride, Cu_2Cl_2, when dissolved in hydrochloric acid gives *hydrocuprochloric acid*, $HCuCl_2$, in which copper goes to the anion $[CuCl_2]^-$:

$$Cu_2O + 2HCl \rightleftharpoons Cu_2Cl_2 + H_2O$$

$$Cu_2Cl_2 + 2HCl \rightleftharpoons 2HCuCl_2 \rightarrow 2H^+ + 2[CuCl_2]^-$$

(*ii*) Complexes with ammonium hydroxide. When cuprous oxide is treated with ammonium hydroxide, a complex is formed in which copper goes to the cation, $[Cu(NH_3)_2]^+$

$$Cu_2O + H_2O \rightleftharpoons 2CuOH$$

$$CuOH \rightleftharpoons Cu^+ + OH^-$$

$$Cu^+ + 2NH_3 + OH^- \rightleftharpoons [Cu(NH_3)_2]OH$$

A similar complex is obtained when cuprous chloride dissolves in ammonia. The complex is *cuproamine chloride* which is a salt of the cupromine base

$$Cu^+ + Cl^- + 2NH_3 \rightleftharpoons [Cu(NH_3)_2]Cl \rightleftharpoons [Cu(NH_3)_2]^+ + Cl^-$$

(*iii*) Complexes with alkali cyanides. When potassium cyanide, cuprous oxide as well as its salt gives *potassium cuprocyanide*, $K_3Cu(CN)_4$ or $K_2Cu(CN)_4$:

$$Cu_2O + 6KCN + H_2O \rightleftharpoons 2K_2Cu(CN)_3 + 2KOH$$

When potassium cyanide is added to copper(*ic*) sulphate, cupric cyanide, $Cu(CN)_2$, first precipitated, at once decomposes to cuprous cyanide and cyanogen :

$$CuSO_4 + 2KCN \longrightarrow Cu(CN)_2 + K_2SO_4$$
$$2Cu(CN)_2 \longrightarrow Cu_2(CN)_2 + (CN)_2$$

Cuprous cyanide dissolves in an excess of KCN to give cuprocyanide :

$$Cu_2(CN)_2 + 6KCN \rightleftharpoons 2K_3Cu(CN)_4$$
$$K_3Cu(CN)_4 \rightleftharpoons 3K^+ + [Cu(CN)_4]^{3-}$$

The second dissociation constant of $[Cu(CN)_4]^{3-} \rightleftharpoons Cu^+ + 4CN^-$ is very small; the complex is thus so stable that it gives no precipitate with H_2S (copper and cadmium separation).

***(iv)* Complexes with hypo solution.** When cupric sulphate solution is mixed with hypo solution, the blue colour of the former is discharged forming sodium cuprous thiosulphate (cupric sulphate is reduced to cuprous) :

$$CuSO_4 + Na_2S_2O_3 \longrightarrow Na_2SO_4 + CuS_2O_3$$
$$2CuS_2O_3 + Na_2S_2O_3 \longrightarrow 2NaCuS_2O_3 + Na_2S_4O_6$$

On boiling or on acidification, cuprous sulphide is precipitated :

$$2NaCuS_2O_3 + H_2O \longrightarrow Cu_2S + Na_2S_2O_3 + H_2SO_4$$

7. Complex Compounds of Cupric Ion

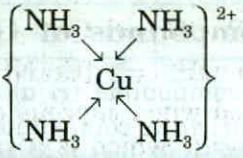
Cupric hydroxide, when dissolved in aqueous ammonia, gives a blue soluble complex of cupriamine hydroxide, $[Cu(NH_3)_4]$ (OH).

$$Cu(OH)_2 + 4NH_3 \longrightarrow Cu(NH_3)_4(OH)_2 \rightleftharpoons [Cu(NH_3)_4]^{2+} + 2(OH)^-$$

If ammonium hydroxide be added in excess to a solution of copper sulphate, the precipitate hydroxide again dissolves yielding an intense blue solution. If a layer of alcohol is carefully poured over this solution, and evaporation prevented by corking, deep blue rhombic crystals of *cupriamine sulphate* are obtained :

$$CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-}$$
$$Cu^{2+} + 4NH_3 \rightleftharpoons Cu(NH_3)_4^{2+}$$
$$Cu(NH_3)_2^{2+} + SO_4^{2-} + 4H_2O \longrightarrow Cu(NH_3)_4SO_4.4H_2O$$

If a hot solution of cupric chloride saturated with ammonia gas be cooled, *cupriamine chloride*, $Cu(NH_3)_4Cl_2$ crystallises. The structure of *cupriamine ion* is



Compounds of Silver

In its familiar compounds, Ag is in +1 oxidation state (*monovalent*) while in a few compounds it is in +2 state (*divalent*). Important compounds of Ag are discussed below :

1. Silver Nitrate or Lunar Caustic, $AgNO_3$

Preparation. It is usually prepared by dissolving Ag in hot dil. HNO_3 in a porcelain or stainless steel vessel

$$3Ag + 4HNO_3 \longrightarrow 3AgNO_3 + 2H_2O + NO$$

Properties. It forms colourless transparent rhombic crystals of density 4.35 and m.pt. = 212°C. In the fused state it can be cast into sticks called *lunar caustic* due to its strong caustic action. It is highly soluble in water and its solubility increases with the rise of temperature. Its aqueous solution slowly darkens when exposed to light. It is also soluble in alcohol, pyridine etc. On heating above its melting point, it decomposes into $AgNO_2$ and O_2. When heated to red, it decomposes to metallic Ag.

$$2AgNO_3 \longrightarrow 2AgNO_2 + O_2;\ 2AgNO_3 \longrightarrow 2Ag + 2NO_2 + O_2$$

It is decomposed by organic matter such as skin, paper, cloth or cork especially under the action of light to finely divided metallic silver (black). With NH_4OH solution a brown precipitate of Ag_2O is obtained which dissolves in the excess of NH_4OH forming a complex, $[Ag(NH_3)_3]NO_3$.

$$2AgNO_3 + 2NH_4OH \longrightarrow \underset{\text{Brown ppt.}}{Ag_2O} + 2NH_4NO_3 + H_2O$$

$$Ag_2O + 2NH_4OH + 2NH_4NO_3 \longrightarrow 2[Ag(NH_3)_2]NO_3 + 3H_2O$$

Solid $AgNO_3$ absorbs NH_3 gas to give the addition compound, $AgNO_3.3NH_3$.

Uses. It is used as a laboratory reagent and in volumetric analysis for the estimation of chlorides. Silver halides prepared from it are used in photography. It is also used as an indelible ink for marking purposes, in silvering mirrors, as a caustic in surgery under the name of *lunar caustic*, as a starting material for the preparation of other silver componnds and as a reagent for arsine in the Gutzeit test.

2. Silver Nitride or Fulminating Silver, Ag_3N

It is obtained by the action of ammonia on freshly precipitated silver oxide. It is an explosive black powder. Above 140°C, it explodes spontaneously. It is decomposed by HNO_3 to Ag and NH_4NO_3. Similarly it reacts with H_2SO_4 and HCl. When added to KCN solution, it decomposes with the evolution of NH_3.

$$Ag_3N + 6KCN + 3H_2O \longrightarrow 3K[Ag(CN)_2] + 3KOH + NH_3$$

Compounds of Gold

Gold forms two series of compounds (*i*) *aurous* compounds in which gold shows + 1 oxidation state, and (*ii*) *auric* compounds wherein gold is in +3 oxidation state. Compounds in +3 oxidation state are more common. The following compounds of gold are important.

1. Aurous chloride, AuCl

Preparation. It is prepared by heating auric chloride ($AuCl_3$) to 175°C.

$$AuCl_3 \xrightarrow{175°C} AuCl + Cl_2$$

Properties. It is a light-yellow powder which is insoluble in water. When heated above 175°C, it gets decomposed into metallic gold and free Cl_2.

$$2AuCl \xrightarrow{> 175°C} 2Au + Cl_2$$

When treated with H_2O at ordinary temperature, it is decomposed into metallic Au and $AuCl_3$.

$$3AuCl \longrightarrow AuCl_3 + 2Au$$

AuCl combines with alkali metal chlorides (*e.g.* KCl) to form chloroaurates (I), $M[AuCl_2]$. When treated with Cl_2, $AuCl_3$ is formed.

$$AuCl + KCl \longrightarrow K[AuCl_2] \text{ [}\textit{Pot. dichloroaurate (I)}\text{]}$$
$$AuCl + Cl_2 \longrightarrow AuCl_3$$

2. Auric Chloride, $AuCl_3$

Preparation : When the yellow crystals of hydrated chloroauric acid, $HAuCl_4.4H_2O$ are heated at 200°C, deep red crystals of *anhydrous auric chloride*, $AuCl_3$ are obtained.

$$HAuCl_4.4H_2O \xrightarrow{200°C} AuCl_3 + HCl + 4H_2O$$

The preparation of *anhydrous auric chloride* can also be done as follows : Gold is first reacted with chlorine to give auric chloride which is dissolved in a little water. This is gently heated, in order to convert any contaminated aurous chloride into metallic gold which is thrown down as a precipitate and is filtered out, and then the solution evaporated and heated to 150°C. This gives anhydrous auric chloride. It is soluble in ether.

Properties : Anhydrous $AuCl_3$ is a deep red crystalline substance which is freely soluble in water. When crystallised from water solution, orange crystals of dihydrate, $AuCl_3.2H_2O$ are obtained. Auric chloride is non-polar (covalent) and does not ionise in aqueous solutions. The non-polar character is further shown by its low melting point (290°), volatility and its solubility in organic solvents as alcohol and ether. It is susceptible to photo-reduction and is reduced to metallic gold by H_2O_2 in presence of an alkali metal or by SO_2. Gold is easily displaced from $AuCl_3$ solution by the metals like Fe, Zn, Mg, Al, Ag, Pb etc. When KOH or NaOH is added to a solution of $AuCl_3$, $Au(OH)_3$ is precipitated which dissolves in the excess of the alkali forming potassium or sodium aurate (III), $M[AuO_2]$ (M = K or Na).

$$AuCl_3 + 3NaOH \longrightarrow \underset{\text{ppt.}}{Au(OH)_3} + 3NaCl$$

$$Au(OH)_3 + NaOH \longrightarrow \underset{\text{Sod. aurate (III)}}{Na[AuO_2]} + 2H_2O$$

When $AuCl_3$ is digested with NH_3, fulminating gold. $HN = Au—NH_2$ is obtained.

$$AuCl_3 + 2NH_3 \longrightarrow \underset{\text{Fulminating gold}}{HN = Au—NH_2} + 3HCl$$

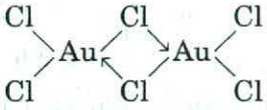
Auric chloride with hydrochloric acid gives auri-chloric acid or chloroauric acid. Similarly with calculated amounts of potassium chloride, it gives potassium aurichloride, also known as potassium chloroaurate; and similarly the sodium salt with common salt :

$$AuCl_3 + HCl \longrightarrow \underset{\text{Chloroauric acid}}{H[AuCl_4]}$$

$$AuCl_3 + NaCl \longrightarrow \underset{\text{Sod. chloroaurate}}{Na[AuCl_4]}$$

On heating $AuCl_3$ decomposes to form AuCl. [$AuCl_3 \xrightarrow{\Delta} AuCl + Cl_2$]. Gold chloride solution is not very stable. It decomposes readily in neutral solution to form aurous chloride and hydrogen peroxide. [$AuCl_3 + 2H_2O \rightarrow AuCl + 2HCl + H_2O_2$]. It decomposes on exposure to sunlight or in presence of reducing substances to metallic gold.

The vapour density of auric chloride shows that it is a dimeric molecule, Au_2Cl_6



Uses : Hydrochloroauric acid, $H[AuCl_4].4H_2O$ under the name of gold chloride is used in photography as a toning agent.

3. Fulminating Gold, HN = Au—NH_2

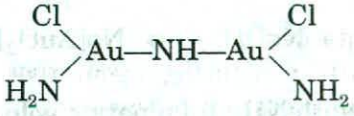
It is obtained by treating auric chloride solution with ammonia :

$$AuCl_3 + 2NH_3 \longrightarrow HN = Au—NH_2 + HCl$$

It is also obtained by treating auric hydroxide with ammonia.

$$Au(OH)_3 + 2NH_3 \longrightarrow HN = Au—NH_2 + 3H_2O$$

Properties : It is an olive green powder of variable composition. The dry mass explodes violently on heating or percussion, forming Au, N_2, NH_3 and steam. It dissolves in HCl to form tetrachloro auric acid, $H[AuCl_4]$ and NH_4Cl. It readily dissolves in alkali cyanide solutions. It is converted to non-explosive compounds by the action of H_2S and by careful heating with S. It is reduced to Au with explosion by $SnCl_2$. Raschig (1980) formulated it as $HN = Au—NH_2.\frac{3}{2}H_2O$. According to Weitz (1915) the fulminating gold produced by the action of NH_3 on $AuCl_3$ solution contains some chlorine and, therefore, he suggested the following structure to this compound.



4. Complex Compounds

Gold forms stable complexes in +1 and +3 oxidation states. 2-coordinate complex compounds given by Au(+1) are *linear* involving *sp*-hybridisation whereas 4-

coordinate complexes are probably *tetrahedral* resulting from sp^3 hybridisation. Both the types of complexes are *diamagnetic*. The 4-coordinate complexes given by Au(+3) are *diamagnetic* and *square planar* with dsp^2 hybridisation while the 5-coordination complexes are *trigonal bipyramidal* and 6-coordinate complexes are *octahedral*. The following are important complexes formed by gold.

(*i*) Potassium aurocyanide, $K[Au(CN)_2]$. Preperation. It is obtained by the following methods :

(*a*) Gold is dissolved in aqua regia and precipitated with ammonia forming fulminating gold. It is washed and dissolved in potassium cyanide and crystallised.

(*b*) Fine gold is treated with potassium cyanide solution in contact with atmospheric oxygen :

$$4Au + 8KCN + O_2 + 2H_2O \longrightarrow 4KAu(CN)_2 + 4KOH$$

Properties. It is a colourless substance and soluble in water. When heated with HCl at 50°C, yellow crystals of AuCN are produced.

$$KAu(CN)_2 + HCl \longrightarrow KCl + HCN + AuCN$$

When Zn is added, gold is precipitated.

$$KAu(CN)_2 + Zn \longrightarrow K_2[Zn(CN)_2] + \underset{\text{ppt.}}{2Au}$$

Uses : It is used in gold plating.

(*ii*) Sodium aura (*i*) thiosulphate, $Na_3[Au(S_2O_3)_2]$. Preparation. Just as hypo forms a complex with silver chloride, a similar complex is obtained by adding auric chloride to hypo solution.

$$4Na_2S_2O_3 + AuCl_3 \longrightarrow Na_3[Au(S_2O_3)_2] + Na_2S_4O_6 + 3NaCl$$

Hypo is side by side oxidised to sodium tetrathionate as in iodine reaction.

Properties and uses. It crystallises in colourless needles, fairly soluble in water. It is not reduced by $FeSO_4$, oxalic acid or $SnCl_2$. It is used in medicine as *sanochrysin* (Greek *chrusos*).

(*iii*) Tetrachloroauric acid or gold chloride, $H[AuCl_4]$. Preparation. When metallic gold is dissolved in aqua regia, a bright yellow solution of $HAuCl_4$ is obtained

$$2Au + 3HNO_3 + 11HCl \longrightarrow \underset{\text{Solution}}{2HAuCl_4} + 6H_2O + 3NOCl$$

On evaporating the solution, yellow deliquescent crystals of tetrahydrate chloroauric acid, $HAuCl_4.4H_2O$ deposit. This as called *gold chloride* of commerce. It can also be prepared by the action of HCl on $AuCl_3$,

$$HCl + AuCl_3 \longrightarrow HAuCl_4$$

Properties. (*a*) It soluble in water and in donor organic solvents. It is converted into $AuCl_3$ when heated at 200°C in a current of Cl_2.

(*b*) *Reduction.* It is easily reduced to metallic gold by reducing agents like $FeSO_4$, $SnCl_2$ and even by H_2.

$$HAuCl_4 + 3FeSO_4 \longrightarrow Fe_2(SO_4)_3 + FeCl_3 + HCl + Au$$

$$2HAuCl_4 + 3SnCl_2 \longrightarrow 3SnCl_4 + 3HCl + 2Au$$

$$2HAuCl_4 + 3H_2 \longrightarrow 8HCl + 2Au$$

(*c*) *Action of KI.* Reaction with KI precipitates AuI.

$$HAuCl_4 + 3KI \longrightarrow \underset{\text{ppt.}}{AuI} + 3KCl + HCl + I_2$$

(*d*) *Reaction with alkalies.* Alkalies precipitate $Au(OH)_3$ which dissolves in excess of the alkali solution to form soluble complex, $Na[Au(OH)_4]$

$$HAuCl_4 + 4NaOH \longrightarrow \underset{\text{ppt}}{Au(OH)_3} + 4NaCl + H_2O$$

$$Au(OH)_3 + NaOH \longrightarrow \underset{\text{Soluble complex}}{Na[Au(OH)_4]}$$

(*e*) *Reaction with KCN.* First AuCN is obtained as precipitate which in excess of KCN dissolves due to the formation of soluble complex, $K[Au(CN)_2]$

$$HAuCl_4 + 3KCN \longrightarrow \underset{\text{ppt}}{AuCN} + 3KCl + HCl + (CN)_2$$

$$AuCN + KCN \longrightarrow \underset{\text{Soluble complex}}{K[Au(CN)_2]}$$

(*f*) *Reaction with H_2S.* With H_2S the acid yields a precipitate which is probably a mixture of Au_2S and Au_2S_3.

(*g*) *Formation of chloroaurates.* The salts of the acid are called *chloroarates.* When a solution of the acid reacts with an alkali chloride, alkali chloreurate, $M[AuCl_4].nH_2O$ is obtained in solution which on evaporation gives the crystals of the salt.

Uses. The acid and its sodium and potassium salt are used in photography for toning and printing.

Structure : $[AuCl_4]^-$ ion is diamagnetic and has square planar geometry arising from dsp^2 hybridisation of Au atom.

***(iv)* Potassium auricyanide, $K[Au(CN)_4]$.** A hot concentrated solution of auric chloride when mixed with potassium cyanide gives auricyanide which crystallises out.

$$AuCl_3 + 4KCN \longrightarrow KAu(CN)_4 + 3KCl$$

The salt gives a precipitate of $AgAu(CN)_4$ with silver nitrate which on treatment with hydrochloric acid gives silver chloride and auricyanic acid, $HAu(CN)_4$. $KAu(CN)_4$ is used in gold plating.

Compounds of Zinc and Cadmium

Zinc and cadmium both are always in +2 (bivalent) oxidation state in their compounds. Some of their important compounds are discussed below.

1. Zinc Oxide or Philosopher's Wool, ZnO

Preparation : It occurs in nature as the mineral *zincite* or *red zinc ore.* It is obtained by the calcination of zinc carbonate, nitrate or hydroxide,

$$ZnCO_3 \longrightarrow ZnO + CO_2$$

$$2Zn(NO_3)_2 \longrightarrow 2ZnO + 4NO_2 + O_2$$

$$Zn(OH)_2 \longrightarrow ZnO + H_2O$$

Zinc oxide prepared by burning zinc vapour in air is collected as white wooly flocks and hence is also known as *philosopher's wool.*

Properties : It is a white amorphous powder which becomes sulphur-yellow on heating but becomes white on cooling. It is insoluble in water. It is an amphoteric oxide since it dissolves readily in acids forming the zinc salt and in alkalies forming zincates.

$$ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$$
$$ZnO + NaOH \longrightarrow \underset{\text{Sod. zincate}}{Na_2ZnO_2} + H_2O$$

When heated in dry hydrogen above 450° or with carbon, it is reduced to metallic zinc. When it is heated with a solution of $Ca(NO_3)_2$, a green mass is formed which is due to the formation of *cobalt zincate*, $CoZnO_2$ (double oxide, ZnO.CoO) which is known as *Rinmann's green.*

$$ZnO + H_2 \longrightarrow H_2O + Zn$$
$$ZnO + C \longrightarrow Zn + CO\uparrow$$
$$2Co(NO_3)_2 \longrightarrow 2CoO + 4NO_2 + O_2$$
$$ZnO + CoO \longrightarrow ZnO.CoO \text{ or } CoZnO_2$$

Uses : Zinc oxide is used (*i*) as a white paint under the name of *zinc white* or *chinese white* although it does not possess as good a covering powder as white lead. It is, however, sometimes preferred because it is not blackened by H_2S. (*ii*) as a catalyst when mixed with Cr_2O_3 in the manufacture of methyl alcohol from water gas and H_2. (*iii*) as a filler for soft rubber (*iv*) as an alsorbent in surgical dressing. (*v*) for the preparation of cement and hard resins. (*vi*) for the preparation of other zinc compounds. (*vii*) The green mass obtained by heating ZnO with $Co(NO_3)_2$ is used as a pigment under the name of *Rinmann's green.*

2. Zinc Chloride, $ZnCl_2.2H_2O$

Preparation. It is prepared by dissolving zinc oxide, carbonate or hydroxide in dilute hydrochloric acid

$$ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$$

The solution so obtained on concentration and cooling gives the crystals of $ZnCl_2.2H_2O$. *Anhydrous zinc chloride* cannot be prepared merely by heating the crystals of $ZnCl_2.2H_2O$ because a basic chloride Zn(OH)Cl is formed during decomposition which on further heating gives ZnO.

$$ZnCl_2.2H_2O \longrightarrow Zn(OH)Cl + HCl + H_2O$$
$$Zn(OH)Cl \longrightarrow ZnO + HCl$$

Hence anhydrous zinc chloride is obtained either by heating zinc in a current of chlorine gas or by distilling a mixture of zinc powder and mercuric chloride.

$$Zn + Cl_2 \xrightarrow{\Delta} ZnCl_2$$
$$Zn + HgCl_2 \longrightarrow ZnCl_2 + Hg\uparrow$$

Properties. It is a white crystalline solid, deliquescent and soluble in water. On beating it forms the oxychloride and finally the oxide. Its concentrated solution sets to a hard mass when mixed with zinc oxide and the product is used as a dental filling.

Uses. (*i*) Zinc chloride finds us as a dehydrating agent and a catalyst. (*ii*) Timber is impregnated with a solution of zinc chloride to stop dry rot. (*iii*) It is

employed in making parchment paper, vulcanised fibre, cold water glues and adhesives. (*iv*) It is also used in the manufacture of dry cells.

3. Zinc Sulphate or White Vitriol $ZnSO_4.7H_2O$

Preparation : It is found in nature as an anhydrous salt *viz. zincosite* and as hydrated salt *viz., zinc vitriol.* It is obtained by dissolving metallic zinc, its oxide, or carbonate in dil. H_2SO_4. On concentrating the solution to crystallisation below 39°, colourless efflorescent crystals of *heptahydrate*, $ZnSO_4.\ 7H_2O$ deposit

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

Above 39°C, *hexahydrate*, $ZnSO_4.6H_2O$ and above 70°C *monohydrate*, $ZnSO_4.H_2O$ is deposited. *On a large scale* it may be obtained by dissolving zinc scrap in dil. H_2SO_4 or by roasting *zinc blende* (ZnS) and extracting the mass with water.

$$ZnS + 2O_2 \xrightarrow{\Delta} ZnSO_4$$

Properties : It is a colourless, crystalline solid and effloreacent substance. It is freely soluble in water.

On heating water of crystallisation is lost according to the following scheme.

$$ZnSO_4.7H_2O \xrightarrow[-H_2O]{70°C} ZnSO_4.6H_2O \xrightarrow[-5H_2O]{100°C} ZnSO_4.H_2O \xrightarrow{200°C\ (-H_2O)} ZnSO_4 \xrightarrow{800°C} ZnO + SO_3 \longrightarrow SO_2 + O_2$$

$ZnSO_4.7H_2O$ is isomorphous with $MgSO_4.7H_2O$, $FeSO_4.7H_2O$, $NiSO_4.7H_2O$, $CoSO_4.7H_2O$, $CrSO_4.7H_2O$ and $MnSO_4.7H_2O$. With alkali metal sulphates and $(NH_4)_2SO_4$ it forms double salts of the type, $M_2SO_4.ZnSO_4.6H_2O$.

Uses : Zinc sulphate is used (*i*) as an eye wash (*ii*) as a mordant in dyeing and calico printing (*iii*) for making lithopone–a white paint obtained by mixing barium sulphide with a solution of zinc sulphate (*iv*) in zinc plating baths and in the electrolytic refining of zinc.

4. Zinc Sulphide, ZnS

Preparation : It occurs in nature as *zinc blende* and is the principal source of zinc metal. It is prepared by passing hydrogen sulphide through an alkaline solution of zinc salt in the presence of ammonium chloride. It can also be obtained as a white precipitate when H_2S is passed through a solution of a zincate.

$$ZnCl_2 + H_2S \longrightarrow ZnS + 2HCl$$

$$Na_2ZnO_2 + H_2S \longrightarrow \underset{\text{white ppt.}}{ZnS} + 2NaOH$$

Properties : Zinc sulphide occurs in two forms *viz.* α-ZnS and β-ZnS. It is a white amorphous substance, insoluble in water and alkali. It readily dissolves in

all dilute mineral acids but not in acetic acid, liberating sulphuretted hydrogen. Pure ZnS does not show any phosphorescenece property but in presence of traces of sulphides of Cu, Ag, Mn, Bi, etc. it becomes strongly phosphorescent. The phosphorescent suiphide is called *Sidot's blende.*

Uses : A mixture of ZnS and $BaSO_4$ is called ***lithopone*** which is used as a white pigment in paint. It is also used as a pigment in paint, rubber and paper. The phosphorescent ZnS which is called *Sidot's blends* is used in making fluorescent screens for X-ray and radioactivity works. The phosphorescent ZnS is prepared by passing H_2S through a solution obtained by dissolving 5 mgs. of zinc ammonium sulphate, 0.1 gm. of $MnCl_2$ and 1 gm. of NaCl in 100 ml. of H_2O. The white ppt. so obtained is filtered off without washing and then heated to whiteness in a covered crucible in an atmosphere of H_2S. The phosphorescent ZnS is also used for preparing luminous paints of watches. Luminous paint of watches is a mixture of phosphorescent ZnS and trace of radium salt.

5. Lithopone, ($ZnS + BaSO_4$)

It is a mixture of ZnS and $BaSO_4$ and is obtained by the simultaneous precipitation of zinc sulphide and barium sulphate by mixing solutions of barium sulphide and zinc sulphate.

$$BaS + ZnSO_4 \longrightarrow \underbrace{BaSO_4 + ZnS}_{\text{Lithopone}}$$

The precipitate is thoroughly washed and dried. It is then heated to red heat in specially constructed retorts. The hot mass is quenched in cold water and then ground wet. This process of quenching increases the whiteness of the pigment and its covering power. The whole mass is then dried and finally ground to a fine powder. It is a valuable white pigment and is used in wall paints and cheaper grades of enamel paints. It does not get blackened when expossed to H_2S but slowly drakens on exposure to light due to the liberation of metallic zinc from ZnS. In dark the metal is again changed into white ZnO by the atmospheric oxidation and therefore the paint regains its original whiteness. It is much cheaper than white lead $2PbCO_3.Pb(OH)_2$ and is non-poisonous. It has good covering power but is inferior to white lead and zinc oxide. In bright light it darknes to some extent due to the separation of zinc and is, therefore, preferred for interior decoration. It is also finding use in the rubber industry in the manufacture of white goods, also in the manufacture of lacquers, oil cloth and linolenm.

6. Zinc Carbonate, $ZnCO_3$

It ocours in nature as *calamine.* It is obtained as a precipitate when sodium bicarbonate is added to zinc sulphate solution.

$$ZnSO_4 + 2NaHCO_3 \longrightarrow ZnCO_3 + Na_2SO_4 + H_2O + CO_2 \uparrow$$

Sodium carbonate is not used because it precipitates basic zinc carbonate, $2ZnCO_3.3Zn(OH)_2.H_2O$. It is a white powder, insoluble in water which decomposes on heating into ZnO and CO_2 at 300°C

$$ZnCO_3 \xrightarrow{300^\circ} ZnO + CO_2$$

It is used (*i*) in making ointment for curing skin diseases (*ii*) in the preparation of cosmetics (*iii*) as a fire proofing agent (*iv*) as a reinforcing pigment in rubber.

7. Cadmium Sulphide, CdS

It occurs as *greenokite* in nature. It is prepared by passing H_2S gas into a cadmium salt solution in neutral, alkaline or feebly acidic media. It is usually yellow in colour but the colour varies from lemon yellow to orange depending upon the conditions of precipitation. It is used : (*i*) as a yellow pigment under the name of *cadmium yellow* in making oil and water colours (*ii*) in the manufacture of *cadmipone* which is a mixture of CdS and $BaSO_4$ and is used as a red pigment (*iii*) in luminoscent pigments usually with ZnS to produce yellow and fluorescence and phosphorescence.

Compounds of Mercury

Mercury forms compounds in + 1 and + 2 oxidation states. Compounds in these states are called **mercurous** and **mercuric compounds** respectively. Of these, the mercuric salts are more stable and important. A mercuric salt can easily be converted to mercurous either by the action of some reducing agent and in some cases by the action of mercury. The action of an acid on excess of mercury generlly produces mercurous salts.

Experimental Evidences to Show That Mercurous Ion is Hg_2^{2+}

There has been some doubt regarding the structure of mercurous ion in mercurou salts. Experiments of H.B. Baker on the vapour density of very dry mercurous chloride, of Beckman on the freezing point of a solution of mercuous chloride in fused mercuric chloride and of Ogg on the E.M.F. of suitable concentration cells have indicated beyond doubt that the mercurous compounds contain the group—Hg—Hg—. *i.e.* the two atoms in mercurous ion are joined by a covalent linkage and one valency of each atom is free from combination Thus the metal is actually diatomic in the mercurous ion which can be written as Hg_2^{++} and exists in equilibrium :

$$Hg^{2+} + Hg^0 \longrightarrow Hg_2^{2+} \text{ or } (—Hg—Hg)^{2+}$$

Following are some additional evidences which support Hg_2^{2+} structure for the mercurous ion.

***(i)* Raman spectra.** Raman spectra of the nitrates of all the metals are the same due to covalent bonding in NO_3^- ion but that of an aqueous solution of mercurous nitrate contains *an extra strong line* which is due to $(Hg—Hg)^{2+}$ or Hg_2^+ ion.

***(ii)* X-ray study.** The X-ray study of crystalline mercurous chloride shows that the molecule has a linear structure, Cl—Hg—Hg—Cl in which the mercury atoms are always associated in pairs. This proves the presence of Hg—Hg bond in mercurous compounds.

***(iii)* Electrical conductivity.** The value of electrical conductivity of an aqueous solution of mercurous nitrate has been found similar to that of $Pb(NO_3)_2$ and not to that of $AgNO_3$. Hence on the analogy of Pb^{2+}, the mercurous ion should be Hg_2^{2+} and consequently mercurous nitrate should be $Hg_2(NO_3)_2$ and not $Hg(NO_3)$.

Now let us discuss some important compounds of mercury :

1. Mercurous Chloride or Calomel, Hg_2Cl_2

Preparation : This is the most important mercurous compound. This compound occurs in nature as the mineral *horn quick silver.* It is prepared : (*i*) by heating an intimate mixture of $HgCl_2$ and metallic Hg in appropriate proportions in an iron pot. (*ii*) by adding a soluble chloride (*e.g.* NaCl) or dil. HCl to the solution of $Hg_2(NO_3)$. (*iii*) by reducing $HgCl_2$ solution with SO_2.

$$HgCl_2 + Hg \longrightarrow Hg_2Cl_2$$
$$Hg_2(NO_3)_2 + 2NaCl \longrightarrow Hg_2Cl_2 + 2NaNO_3$$
$$Hg_2(NO_3)_2 + 2HCl \longrightarrow Hg_2Cl_2 + 2HNO_3$$
$$2HgCl_2 + 2H_2O + SO_2 \longrightarrow Hg_2Cl_2 + 2HCl + H_2SO_4$$

Properties : It is a white amorphous substance of density 7.16 It is very sparingly soluble in H_2O but dissolves in aqua regia, Cl_2 water, hot conc. HNO_3 etc. With HNO_3 it gives $HgCl_2$.

$$3Hg_2Cl_2 + 8HNO_3 \longrightarrow 3HgCl_2 + 3Hg(NO_3)_2 + 2NO + 4H_2O$$

When gently heated or rubbed, it becomes yellow, and darkens when exposed to light. This is due to the partial decomposition of Hg_2Cl_2 into $HgCl_2$ and Hg. When treated with NH_3, it turns black due to the formation of finely divided metallic Hg and mercuric amino chloride, $Hg(NH_2)Cl$. On this basis Hg_2Cl_2 is also called *calomel* from the Greek word *Kalomelas* meaning beautiful black.

$$Hg_2Cl_2 + 2NH_3 \longrightarrow Hg + Hg(NH_2)Cl + NH_4Cl.$$

Uses : Hg_2Cl_2 is used : (*i*) as a purgative in medicine. (*ii*) in making calomel electrodes which are used in potentiometric titrations.

2. Mercurous Nitrate, $Hg_2(NO_3)_2.\ 2H_2O$

It is prepared by the action of cold dil. HNO_3 (density = 1.14) on an excess of metallic mercury which readily crystallises from the solution on standing.

$$6Hg + 8HNO_3 \longrightarrow 3Hg_2(NO_3)_2 + 4H_2O + 2NO$$

Properties : It is a colourless crystalline substance, soluble in water containing a little HNO_3 (to prevent hydrolysis). With excess of H_2O basic nitrate, $Hg_2(OH)NO_3$ is precipitated.

$$Hg_2(NO_3)_2 + H_2O \rightleftarrows Hg_2(OH)NO_3 + HNO_3$$

Dry $Hg_2(NO_3)_2$ decomposes on heating into HgO and NO_2. With HCl or soluble chlorides (*e.g.* NaCl) the solution of $Hg_2(NO_3)_2$ gives a white precipitate of Hg_2Cl_2

$$Hg_2(NO_3)_2 + 2HCl \longrightarrow Hg_2Cl_2 + 2HNO_3$$
$$Hg_2(NO_3)_2 + 2NaCl \longrightarrow Hg_2Cl_2 + 2NaNO_3$$

The solution of $Hg_2(NO_3)_2$ has strong reducing properties.

3. Mercuric Chloride or Corrosive Sublimate, $HgCl_2$

Preparation : This compound is known as *corrosive sublimate*, since it possesses corrosive properties and is prepared in the dry process by *sublimation.* It can be prepared by the action of Cl_2 on metallic Hg. *Commercially* it is prepared by heating a dry mixture $HgSO_4$, NaCl and little MnO_2.

$$HgSO_4 + 2NaCl \longrightarrow HgCl_2 + Na_2SO_4$$

$HgCl_2$ separates on sublimation on the cooler part of the flask. The cake of the sublimate is removed and $HgCl_2$ is purified by recrystallisation from hot water. The addition of MnO_2 prevents the formation of Hg_2Cl_2 from $Hg_2(SO_4)_2$ which is usually present in $HgSO_4$.

Properties : $HgCl_2$ forms colourless needles with m.pt. = 227°C and b.pt. = 302°C. It is sparingly soluble in cold H_2O but readily in hot water. It is a covalent. compound and dissolves in alcohol, ether and benzene. With metal chlorides crystalline compounds are formed, *e.g.* $KHgCl_3$, Na_2HgCl_4 etc. With alkalies HgO is precipitated.

$$HgCl_2 + 2NaOH \longrightarrow HgO + 2NaCl + H_2O$$

With PCl_5 a volatile crystalline compound, $2HgCl_2.2PCl_5$ is formed. When $HgCl_2$ is treated with $SnCl_2$, it is first reduced to Hg_2Cl_2 and then to metallic Hg.

$$2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 + SnCl_4$$

$$Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg + SnCl_4$$

When treated with KI solution, a yellow precipitate of HgI_2 is obtained. This precipitate dissolves in the excess of KI to form colourless *potassium tetra-iodo mercurate*, $K_2[HgI_4]$.

$$HgCl_2 + 2KI \longrightarrow \underset{\text{Yellow ppt.}}{HgI_2} + 2KCl$$

$$HgI_2 + 2KI \longrightarrow \underset{\text{Colourless}}{K_2[HgI_4]}$$

When treated with NH_3, a bulky white precipitate of mercuric amino chloride, $[Hg(NH_2)]Cl$ is obtained. This white precipitate is infusible and is known as infusible white precipitate.

$$HgCl_2 + 2NH_3 \longrightarrow [Hg(NH_2)]Cl + NH_4Cl$$

If $HgCl_2$ is treated with gaseous NH_3, a white precipitate of *diammine mercuric chloride,* $[Hg(NH_3)_2]Cl_2$ which is called fusible white precipitate is obtained. When SO_2 is passed through Hg_2Cl_2 solution, a white precipitate of Hg_2Cl_2 is obtained.

$$2HgCl_2 + SO_2 + 2H_2O \longrightarrow Hg_2Cl_2 + 2HCl + H_2SO_4$$

When a solution of $HgCl_2$ is boiled with mercuric oxide (HgO), mercuric oxy-chlorides like $2HgCl_2.HgO$ (red), $HgCl_2.2HgO$ (black), $HgCl_2.3HgO$ (yellow), $HgCl_2.4HgO$ (black) are obtained. When a bright copper foil is immersed in $HgCl_2$ solution, a grey film of Hg gets deposited on Cu foil.

$$HgCl_2 + Cu \longrightarrow CuCl_2 + Hg$$

Uses : $HgCl_2$ is used (*i*) as its 0.1% solution for sterilising the hands and instruments in surgery. (*ii*) for preserving wood, skins and furs against insect pests. (*iii*) in the preparation of dry cells. (*iv*) as a reagent in laboratory. (*v*) in preventing growth of fungi and bacteria in water, *e.g.* in thermostats. (*vi*) as an intensifier for negatives.

4. Mercuric Iodide, HgI_2

Preparation : It is obtained as a precipitate when solution of KI is added to that of $HgCl_2$.

$$HgCl_2 + 2KI \longrightarrow HgI_2 + 2KCl.$$

Properties : HgI_2 exists in two forms red and yellow. The red form is tetragonal and stable below 126°C while the yellow form is rhombic and is stable above 126°C. When the red form is heated to 126°C, it is changed to yellow form. HgI_2 is sparingly soluble in water but more soluble in alcohol. It dissolves in the excess of KI forming a colourless complex *viz.* potassium tetra-iodo mercurate, $K_2[HgI_4]$.

$$HgI_2 + 2KI \longrightarrow K_2[HgI_4]$$

Uses. HgI_2 is used as an ointment in the treatment of skin diseases.

5. Mercuric Sulphide or Vermilion, HgS

Preparation. This compound exists in two forms *red* and *black*. Both these forms occur native. The red form occurs as the mineral *cinnabar* which is the chief source of Hg. Red form is used as a pigment under the name of *vermilion*. Black variety is found native in small amounts with cinnabar as *metacinnabariate*. The black variety is obtained by passing H_2S gas through a solution of $HgCl_2$ acidified with HCl.

$$HgCl_2 + H_2S \longrightarrow \underset{\text{ppt.}}{HgS} + 2HCl$$

In the beginning the precipitate of HgS is white which changes to yellow, brown and finally black. On sublimation this black precipitate changes to red and is called vermilion. Vermilion (red variety) can also be prepared (*a*) by subliming metallic Hg with S (*b*) by heating Hg with potassium pentasulphide (K_2S_5) solution.

$$Hg + K_2S_5 \longrightarrow HgS + K_2S_4$$

Properties. (*i*) It is insoluble in H_2O, dil. and hot HNO_3 and boiling conc. HCl but dissolves in aqua regia forming $HgCl_2$.

$$3HgS + 2HNO_3 + 6HCl \longrightarrow 3HgCl_2 + 4H_2O + 2NO + 3S$$

(*ii*) *Action of heat.* On heating in air it gets decomposed into metallic Hg and SO_2.

$$HgS + O_2 \longrightarrow Hg + SO_2$$

(*iii*) *Action of boiling conc. H_2SO_4.* $HgSO_4$ is obtained.

$$HgS + 2H_2SO_4 \longrightarrow HgSO_4 + 2H_2O + SO_2 + S$$

(*iv*) *Reduction.* It is reduced to metallic Hg when heated with iron filings, Na_2CO_3 etc.

$$HgS + Fe \longrightarrow Hg + FeS$$

$$2HgS + 2Na_2CO_3 \longrightarrow 2Hg + 2Na_2S + 2CO_2 + O_2$$

Uses. Red variety of HgS is used (*i*) as a pigment under the name of *vermilion* (*ii*) in Ayurvedic medicines like *Makardhwaja* and *Rasa-Sindur*.

6. Mercury Fulminate, $2Hg(CNO)_2.H_2O$

It is obtained by adding alcohol to a solution of mercury in an excess of nitric acid. This substance is a violent explosive and is employed in detonators.

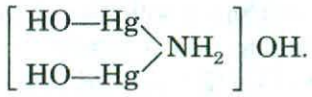
7. Mercuric Thiocyanate, $Hg(CNS)_2$

It is obtained as a white precipitate by mixing mercuric chloride solution with ammonium thiocyanate. On igniting it yields voluminous snake like tubes of ash due to the formation of oxides. It is used in making Pharaoh's serpent.

8. Millon's Base, $[Hg_2N]OH.2H_2O$ *or* $(OH)_2Hg_2NH_2(OH)$

It is obtained as a yellow compound by warming HgO with aqueous ammonia. It is a basic compound. With acids it gives a series of salts of the composition,

$[Hg_2N]X$ (X = Cl, Br, NO_3). Dehydration of this compound gives $[Hg_2N]OH.H_2O$ and explosive $[Hg_2N]OH$. The structure shown below has been suggested for Millon's base.



Structure of Millon's base, $(OH)_2\ Hg_2\ NH_2(OH)$

9. Nesseler's Reagent, $K_2[HgI_4]$

When excess of KI is added to $HgCl_2$ solution, a solution of potassium tetra-iodo mercurate, $K_2[HgI_4]$ is obtained. This solution of $K_2[HgI_4]$, when made strongly alkaline with KOH or NaOH, is known as *Nesseler's reagent.* Nesseler's reagent gives a brown precipitate of *iodide of Millon's base*, $NH_2Hg_2I_3$ with excess of NH_3.

$$\underset{\text{Nesseler's reagent}}{2K_2[HgI_4]} + 2NH_3 \longrightarrow \underset{\substack{\text{Iodide of Millon's base} \\ \text{(brown ppt.)}}}{NH_2Hg_2I_3} + 4KI + NH_4I$$

The formation of iodide of Millon's base has been utilised for the detection and determination of NH_3 by using Nesseler's reagent.

10. Iodide of Millon's Base, $NH_3Hg_2I_3$ *or* $I_2Hg_2NH_2I$

It is obtained when Nesseler's reagent reacts with excess of NH_3.

$$\underset{\text{Nesseler's reagent}}{2K_2[HgI_4]} + 2NH_3 \longrightarrow \underset{\text{Iodide of Millon's base}}{NH_2Hg_2I_3} + 4KI + NH_4I$$

The formation of iodide of Millon's base represented by the above chemical equation actually takes place through the following steps :

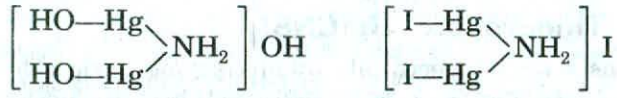
$$[K_2[HgI_4] \longrightarrow 2KI + HgI_2] \times 2$$

$$HgI_2 + 2NH_3 \longrightarrow \underset{\text{Mercuric amino iodide}}{Hg(NH_2)I} + NH_4I$$

$$Hg(NH_2)I + HgI_2 \longrightarrow \underset{\substack{\text{Iodide of} \\ \text{Millon's base}}}{NH_2Hg_2I_3}$$

On adding : $2K_2[HgI_4] + 2NH_3 \longrightarrow NH_2Hg_2I_3 + 4KI + NH_4I$

Corresponding to the structure of Millon's base, the structure of its iodide can be written as follows :



Structure of Millon's base, $(OH)_2\ Hg_2.NH_2(OH)$ — Structure of iodide of Millon's base

Compounds of Cerium

In aqueous solution, cerium exists in +3 and +4 oxidation states. Its salts in +3 and +4 salts are called *cerous* and *ceric* salts respectively. Ceric sulphate, $Ce(SO_4)_2$ and ceric ammonium sulphate, $Ce(SO_4)_2.2(NH_4)_2SO_4.2H_2O$ are its very important compounds and are discussed below :

1. Ceric Sulphate, $Ce(SO_4)_2$

The anhydrous salt is prepared by heating CeO_2 with cone. H_2SO_4 and forms an orange-yellow crystalline powder, insoluble in conc. H_2SO_4. It dissolves in H_2O, giving a brown-yellow solution from which the salt separates below 3°C as the dodecahydrate, between 3° and 42.5° as the octahydrate and above the latter temperature as the tetrahydrate. On diluting an aqueous solution of the salt, hydrolysis occurs and ultimately sparingly soluble basic salts get precipitated. Hence for use in volumetric analysis, the salt is dissolved in dil H_2SO_4(0.5 N or stronger), $Ce(SO_4)_2$ is widely used in volumetric analysis as an oxidising agent. The salt is used for the titration of Fe^{2+}, $C_2O_4^{2+}$, NO_2^-, Cu^+, Mo^{5+}, Te^{4+} and U^{4+} ions. It is also used as an oxidiser in preparative organic chemistry.

2. Ceric Ammonium Sulphate, $Ce(SO_4)_2.2(NH_4)_2SO_4.2H_2O$

This compound is also called *ammonium tetrasulphatocerate (IV)* and hence is represented as $(NH_4)_4[Ce(SO_4)_4].2H_2O$. It is prepared by adding $(NH_4)_2SO_4$ to $Ce(SO_4)_2$ solution containing excess of dil. H_2SO_4 to prevent the hydrolysis, followed by crystallisation This double salt is more soluble than $Ce(SO_4)_2$ and is, therefore, prepared for use as a volumetric reagent. Ionic equations showing the quantitative estimations of $C_2O_4^{2-}$, NO_2^-, I^-, H_2O_2, etc. made with this salt are given below :

$$C_2O_4^{2-} + 2Ce^{4+} \longrightarrow 2Ce^{3+} + 2CO_2$$

$$NO_2^- + 2Ce^{4+} + H_2O \longrightarrow 2Ce^{3+} + 2H^+ + NO_3^-$$

$$2I^- + 2Ce^{4+} \longrightarrow 2Ce^{3+} + I_2$$

$$H_2O_2 + 2Ce^{4+} \longrightarrow 2Ce^{3+} + 2H^+ + O_2$$

Compounts of Throium

Thorium is *tetravalent* in its compounds. Following are its important compounds.

1. Thorium Dioxide or Thoria, ThO_2

Preparation : It can be obtained by the following reactions :

$$Th + O_2 \xrightarrow{\Delta} ThO_2 \; ; \; Th(OH)_4 \xrightarrow{\Delta} ThO_2 + 2H_2$$

$$Th(NO_3)_2 \xrightarrow{\Delta} ThO_2 + 4NO_2 + O_2$$

It can also be obtained from monazite sand.

Properties and uses : It is white hygroscopie powder. Crystallised or strongly ignited thoria is almost insoluble in acids but on evaporation with conc. H_2SO_4 it is dissolved in it to form $Th(SO_4)_2$.

$$ThO_2 + 2H_2SO_4 \longrightarrow Th(SO_4)_2 + 2H_2O$$

When heated with carbon and boron, it forms carbide and boride of thorium respectively. Due to it resistance to heat and involatility it is used in the preparation of gas mantles. It is also used as a refractory material as well as a catalyst in

many organic reactions. It is employed in welding operations and also in medicines. Since ThO_2 increases the life of the tungsten filament, it is used as an additive to tungsten used for metal filament lamps. Since ThO_2 has high absorptive power for X-rays, it is used in X-ray diagnostic work as a contrast medium in the examination of the digestive organs. It is also used in ceramic industry. Mixtures of ThO_2 and ceria have been used for search lights, head lights of motor cars etc.

2. Thorium Nitrate, $Th(NO_3)_2$

Preparation : It is prepared by dissolving $Th(OH)_4$ in HNO_3.

$$Th(OH)_4 + 4HNO_3 \longrightarrow Th(NO_3)_2 + 4H_2O$$

Properties and uses : It is a white deliquescent salt which is soluble in water. On heating it gives ThO_2 in a very fine state of subdivision. Due to this property thorium nitrate is used in mantle industry. Thorium nitrate mixed with Mg powder is used for flash powders.

Compounds of Uranium

Uranium forms compounds in +2, +3, +4, +5 and +6 oxidation states. Following are the important compounds.

1. Uranium Dioxide, UO_2 (U = +4)

It is obtained by reducing higher oxides such as UO_3 or U_3O_8 with H_2, C or CO at elevated temperature [$UO_3 + CO \xrightarrow{500^\circ} UO_2 + CO_2 \uparrow$]. It is a brown, strongly basic oxide, insoluble in water and alkalies. When heated in air it burns to give U_3O_8. It dissolves slowly in most of the acids, but HNO_3 oxidises it to $UO_2(NO_3)_2$. It reduces $AgNO_3$ to metallic silver.

$$2AgNO_3 + UO_2 \longrightarrow UO_2(NO_3)_2 + 2Ag$$

2. Triuranium Octoxide or Urano-uranic Oxide, U_3O_8

This oxide is regarded as a double oxide of $U^{6+}O_3$ with either $U^{4+}O_2$ (*i.e.* $U_3O_8 = 2U^{6+}O_3.U^{4+}O_2$) or $U_2^{5+}O_5$ (*i.e.* $U_3O_8 = U^{6+}O_3.U_2^{5+}O_5$). This oxide occurs in pitchblende and is the most stable oxide. It is obtained by heating other oxides in O_2 or by heating uranyl acetate. It is green-coloured oxide. When it is reduced with H_2 or CO, UO_2 is obtained. It is not acted upon by HCl or H_2SO_4 but H_2F, gives UF_4 whereas HNO_3 gives $UO_2(NO_3)_2$. This oxide is used to some extent for colouring ceramic enamels.

3. Uranium Trioxide, UO_3 (U = +6)

It is obtained by heating $UO_2(NO_3)_2$ in O_2. It is yellow when pure but impure sample is orange-red. When strongly heated, it loses O_2 and passes to U_3O_8. It is amphoteric, forms uranates with alkalies and uranyl salts with acids.

$$UO_3 + 2NaOH \longrightarrow \underset{\text{Sodium uranate}}{Na_2UO_4} + H_2O$$

$$UO_3 + 2HNO_3 \longrightarrow \underset{\text{Uranyl nitrate}}{UO_2(NO_3)_2} + H_2O$$

4. Uranium Hexafluoride, UF_6

It is obtained by the direct combination of elements in presence of a little of Cl_2 or by the action of F_2 on UF_4. It is a colourless crystalline volatile substance and melts at 64.1°C. It attacks many metals and a large number of organic compounds. It is readily hydrolysed by water to uranyl fluoride, UO_2F_2 and is reduced to UF_4.

$$UF_6 + 2H_2O \longrightarrow UO_2F_2 + 4HF \; ; \; UF_6 \xrightarrow{\text{Reduction}} UF_4 + F_2$$

It is used in separating the uranium isotopes and thus in producing pure U^{235} nuclear fuel. It is a powerful fluorinating agent.

5. Uranyl Salts

These are the only common uranium salts which are derived from the *bivalent basic uranyl radical,* UO_2^{2+}. In these salts uranium is in +6 oxidation state. These salts are formed by the action of acids on uranium oxides especially UO_3. These are generally yellow crystalline substances, soluble in water. A uranyl salt with potassium ferrocyanide solution gives a red precipitate of *uranyl ferrocyanide.* Following are the important uranyl salts :

(*i*) Uranyl nitrate, $UO_2(NO_3)_2$, $6H_2O$. It is also known as uranium nitrate and is prepared by any of the following methods :

$$UO_3 + 2HNO_3 \longrightarrow UO_2(NO_3)_2 + H_2O$$

$$\underset{\text{Uranyl chloride}}{UO_2Cl_2} + 2AgNO_3 \longrightarrow UO_2(NO_3)_2 + 2AgCl$$

This substance crystallises as a lemon yellow hexahydrate, $UO_2(NO_3)_2.6H_2O$. It is soluble in water, alcohol and ether. In contact with H_2SO_4 it is first converted into $UO_2(NO_3)_2.3H_2O$ and then into $UO_2(NO_3)_2.2H_2O$. When $UO_2(NO_3)_2.3H_2O$ is heated at about 130° in a current of CO_2 having HNO_3 to check hydrolysis, $UO_2(NO_3)_2$ is obtained.

(*ii*) Uranyl acetate. $UO_2(CH_3COO)_2.2H_2O$. It is obtained by dissolving $UO_2(OH)_2$ or UO_3 in CH_3COOH.

$$UO_2(OH)_2 + 2CH_3COOH \longrightarrow UO_2(CH_3COO)_2 + 2H_2O$$

$$UO_3 + 2CH_3COOH \longrightarrow UO_2(CH_3COO)_2 + H_2O$$

When dihydrate is heated to 110°C it is converted into anhydrous salt. It gets decomposed at 275°C to UO_3. It is sparingly soluble in H_2O. This compound is of technical importance. It is used for making *Zn* or *Mg uranyl acetate* which is used as a qualitative reagent for the detection of sodium.

6. Uranates

These are the salts given by uranic acid, H_2UO_4. These are of two types namely *monouranates* (*e.g.* $NaUO_4$) and *diuranates* (*e.g.* $Na_2U_2O_7.6H_2O$, $(NH_4)2U_2O_7$). These are prepared as follows :

$$UO_3 + 2NaOH \longrightarrow Na_2UO_4 + H_2O$$

$$2UO_3 + 2NaOH \longrightarrow Na_2U_2O_7 + H_2O$$

$$UO_3 + Li_2CO_3 \longrightarrow Li_2UO_4 + CO_2 \uparrow$$

$$2UO_3 + Li_2CO_3 \longrightarrow Li_2U_2O_7 + CO_2 \uparrow$$

Uranates are insoluble in water and are orange or yellow in colour. Following are the important uranates :

(*i*) Sodium diuranate, $Na_2U_2O_7.6H_2O$. It is also called *sodium uranate* and is obtained as a yellow precipitate by adding NaOH to a uranyl salt solution. When hexahydrate salt is heated, anhydrous salt is obtained. Anhydrous salt is used in commerce as a colouring matter for glass and porcelain glazes under the name *uranium yellow.*

***(ii)* Ammonium diuranate, $(NH_4)_2U_2O_7$.** It is obtained as a yellow precipitate by adding NH_3 to a uranyl salt solution. The formation of this substance provides a convenient method for the gravimetric estimation of uranium.

University Questions

1. Give the preparation, properties and uses of the following : (*i*) titanox (*ii*) titanium dioxide (*iii*) titanous chloride. *(Meerut M.Sc. 84; Lucknow 82; Madras 86; Meerut 82)*
2. Discuss the preparation, properties and uses of : (*i*) Oxosalts of vanadium (*ii*) Vanadyl chloride (*iii*) Vanadium trichloride (*iv*) Vanadyl sulphate (*v*) V_2O_5 (*vi*) Ammonium vanadato. *(Lucknow 80; Madras 86; Madurai 85; Jiwaji 84; Meerut 82, 89; Bharathiar 86; Poona 86)*
3. Give the reasons for the following :
   (*i*) V_2O_5 is an important compound of vanadium. *(Raj. 79)*
   (*ii*) In V_2O_5 vanadium is in +5 oxidation state and hence should be colourless, but it is actually orange in colour. *(Delhi Hons. 86)*
4. Give the preparation, properties, uses and electronic structure of $K_2Cr_2O_7$. *(Allahabad 89; Meerut 82; Lucknow 80; Gorakhpur 81; M.D. Rohtak 84; Bharathiar 86; Jodhpur 84; Utkal 85)*
5. How can you get chronic anhydride, chromyl chloride and chrome alum from $K_2Cr_2O_7$? *(Gorakhpur 86; Meerut 89; Delhi 87; Madras 86; Jodhpur 84)*
6. A solution salt (X) when heated with conc. H_2SO_4 and solid $K_2Cr_2O_7$ gave a volatile compound of chromium (Y). This compound Y when passed through e solution NaOH and lead acetate containing CH_3COOH gave a yellow coloured precipitate (Z). Name X, Y and Z. Give chemical equations for the above stated reactions. *(Delhi 89)*
7. What happens when :
   (*i*) SO_2 reacts with acidified $K_2Cr_2O_7$ (give ionic equation). *(Jodhpur 86; Raj. 86; Andhra 86; Kerala 87; Agra 85)*
   (*ii*) $K_2Cr_2O_7$ is treated with KI in presence of acid. *(Agra 84, 85; Delhi 89)*
   (*iii*) $K_2Cr_2O_7$ acts on HCl. *(Punjab 85; GND 84)*
   (*iv*) A chloride and $K_2Cr_2O_7$ mixture is heated with conc. H_2SO_4. *(Meerut 88; Indore 86; Agra 85, 89)*
   (*v*) Chloroform is oxidised with acidified $K_2Cr_2O_7$. *(Meerut 89)*
   (*vi*) $K_2Cr_2O_7$ is treated with Fe^{2+} ions in an acidic medium. *(Delhi 88; Utkal 86)*
   (*vii*) An alkali is added to a solution of $K_2Cr_2O_7$. *(Delhi Hons. 86)*
8. Complete and balance the following equations :
   (*a*) $Cr_2O_7^{2-} + H^+ + I^- \rightarrow$ ..... *(Utkal 85, 86)*
   (*b*) $Cr_2O_7^{2-} + H^+ + Br^- \rightarrow$ ..... *(Delhi 87)*
   (*c*) $Cr_2O_7^{2-} + Fe^{2+} + H^+ \rightarrow$ ..... *(Punjab 86)*
   (*d*) $Cr_2O_7^{2-} + C_2O_4^{2-}$ (in acidic medium) $\rightarrow$ *(Raj. 81, 83)*
   (*e*) $K_2Cr_2O_7 + KI + HCl \rightarrow$ .....
   (*f*) $FeCl_2 + K_2Cr_2O_7 + HCl \rightarrow$ ..... *(Raj. 85)*
9. Give chemical equations to explain what happens when :
   (*i*) a solution of K_2CrO_4 containing H_2O_2 is acidified with H_2SO_4 in presence of ether or pyridine. *(Delhi 87; Delhi Hons. 87)*
   (*ii*) H_2O_2 is added to an aqueous solution of $K_2Cr_2O_7$ and the solution is acidified with H_2SO_4. *(Sambalpur 86)*

10. Starting from chrome iron ore, how would you obtain a pure specimen of $K_2Cr_2O_7$, $(NH_4)_2Cr_2O_7$, K_2CrO_4, Cr_2O_3, CrO_2Cl_2 and metallic chromium. *(Gorakhpur 84; Meerut 89)*

11. Describe the proprties and uses of ammonium molybdenate. *(Gorakhpur 81; Utkal 86)*

12. Describe the preparation, properties and uses of : (*i*) sodium silicotungstate (*ii*) tungsten hexachloride (*iii*) tungstic acid (*iv*) sodium tungstate. *(Madurai 86; Meerut M.Sc. 84; Madras 86)*

13. Write a note on "Heteropoly acids of tungsten". *(Meerut 82)*

14. What happens when :

(*i*) $KMnO_4$ reacts with H_2S in neutral medium. *(Meerut 87)*

(*ii*) $KMnO_4$ interacts with MnO_2 in the presence of KOH. (I.I.T. 87)

(*iii*) $KMnO_4$ reacts with HCl. *(Punjab 85; GND 84)*

(*iv*) Acidified $KMnO_4$ reacts with SO_2. *(Jodhpur 86; Raj. 86; Adndhra 86; Kerala 87)*

(*v*) $KMnO_4$ reacts with KI in alkaline medium. *(Meerut 88)*

(*vi*) Acidified $KMnO_4$ reacts with hydrazoic acid. *(Raj. 86)*

(*vii*) $KMnO_4$ is added to $MnSO_4$ solution in neutral medium. *(Utkal 85)*

15. Complete and balance the following equations :

(*i*) $MnO_4^- + H^+ + Cl^- \rightarrow$ ..... *(Utkal 85, 86)*

(*ii*) $MnO_4^- + H^+ + Fe^{2+} \rightarrow$ ..... *(Utkal 85, 86; Calicu 79)*

(*iii*) $MnO_4^- + H^+ + H_2O_2 \rightarrow$ ..... *(Raj. 85)*

(*iv*) $C_2H_4 + KMnO_4 + H_2SO_4 \rightarrow$ ..... *(Punjabi 85, 86)*

(*v*) $HCHO + KMnO_4 + HCl \rightarrow$ ..... *(Punjabi 85, 86)*

(*vi*) $MnO_4^- + SO_3^{2-} + H^+ \rightarrow$ ..... *(Raj. 81, 83)*

(*vii*) $MnO_4^- + H_2S + H^+ \rightarrow$ ..... *(Raj. 84)*

(*viii*) $KMnO_4 + KBr + H_2SO_4 \rightarrow$ ..... *(Calcutta 77)*

(*ix*) (*a*) $MnO_4^- + SO_2 + H_2O \rightarrow$ .....

(*b*) $MnO_4^- + Mn^{2+} + H_2O \rightarrow$ .....

(*c*) $MnO_4^- + NO_2^- + H_2O \rightarrow$ ..... *(Punjab 88; Meerut 86; Delhi 86, 87)*

16. Give the reasons for the following :

(*i*) $KMnO_4$ solutions is kept in dark bottles and freshly prepared where possible. *(Calicut 86)*

(*ii*) HCl cannot be used to acidify a permanganate solution in volumetric estimation of Fe^{2+} or $C_2O_4^{2-}$. *(Madras 86)*

(*iii*) $KMnO_4$ disproportionates in the presence of acids according to the equation : $4H^+ + 3[Mn^{+6}O_4]^{2-} \rightarrow 2[Mn^{+5}O_4]^- + Mn^{+4}O_2 + 2H_2O$. *(Poona 86)*

19. What happens when :

(*i*) Co (II) salt solution is treated with KNO_2 and dil. CH_3COOH. *(Delhi 89)*

(*iii*) CH_3COOH is added to a mixture of $NaHO_2$ and $Co(NO_3)_2$ solutions. *(Delhi 88)*

18. How is dimethylglyoxime complex of nickel prepared? What are its uses ? *(Madras 86; Madurai 85)*

19. What happens when :

(*i*) Chloroplatinic acid reacts with SO_2. *(Meerut 88)*

(*ii*) NH_4Cl is added to chloroplatinic acid. *(Agra 85)*

20. Starting from Pt, how will you get the following :

(*i*) Chlorides of Pt in different oxidation states. *(Madras 84; Madurai 86)*

(*ii*) Ammonium chloroplatinate. (*Indore 86; Punjab 82*)

21. What happens when :

(*i*) $CuSO_4$ solution reacts with excess of NH_4OH. (*MLNR 79; I.I.T. 73; Poona 86*)

(*ii*) $CuSO_4$ solution reacts with excess of KI solution. (*Bhararthiar 86; Meerut 89 S*)

(*iii*) $CuSO_4$ reacts with excess of KCN solution. (*Bharathiar 86*)

(*iv*) To $CuSO_4$ solution is added KI and then $Na_2S_2O_3$ solution. (*R.E.E. 83*)

(*v*) $CuSO_4$ solution is treated with hypo solution. (*Agra 85*)

(*vi*) $CuSO_4$ solution is treated with NH_4CNS. (*Madras 85*)

(*vii*) $CuSO_4$ solution in treated with $K_4[Fe(CN)_6]$ solution. (*Bharathiar 86*)

(*viii*) $CuSO_4$ solution reacts with H_2SO_4 and NH_4CNS solution. (*Bharathiar 86*)

(*ix*) Balance the following equations :

(*a*) $CuSO_4 + NH_4CNS \rightarrow$ ..... (*Madras 85*)

(*b*) $CuSO_4 + KI \rightarrow$ ..... (*Utkal 85, 86*)

22. Give the preparation, properties and uses of : (*i*) Basic copper acetate (*ii*) Malachit green; (*iii*) Cuprous oxide (*iv*) Cuprous chloride (*v*) CuCN. (*Raj. 85; Delhi 87, 87 S*

23. What happens when :

(*i*) PH_3 is passed into a solution of $AgNO_3$ (*MLNR 76*)

(*ii*) $AgNO_3$ is heated (*R.E.E. 83, 86*)

(*iii*) Solution of $AgNO_3$ is added to the solution of sodium thiosulphate. (*R.E.E. 82*)

(*iv*) $AgNO_3$ reacts with ammonia. (*Indore 85*)

(*v*) $AgNO_3$ reacts with HCl. (*Punjab 85, GND 84*)

(*vi*) The solution of NH_3 is treated with AgCl solution. (*I.I.T. 74*)

(*vii*) AgCl reacts with $Na_2S_2O_3$ solution. (*R.E.E. 73*)

24. Give the reasons for the following :

(*i*) On adding NaCl to $AgNO_3$ solution, a white precipitate of $AgNO_3$ is obtained but CCl_4 does not produce any precipitate.

(*ii*) AgCl precipitate dissolves in NH_4OH. (*Agra 85*)

OR

AgCl precipitate is soluble in ammonia. (*Delhi 85*)

(*iii*) AgCl is soluble in saturated KI, but AgI is soluble in saturated KCl. (*Delhi Hons. 87*)

25. Give the preparation, properties and uses of :

(*i*) chloroauric acid. (*Bharathiar 86*)

(*ii*) gold chloride. (*Bhagalpur 72; Madras 74; Gorakhpur 71*)

(*iii*) gold fulminate. (*Vikram 86*)

26. Write the preparation, properties and uses of :

(*i*) Lithopone (*Bharathiar 86; Jodhpur 85*)

(*ii*) $ZnSO_4$ (*Madurai 85; Andhra 85*)

(*iii*) $ZnCl_2$ (*Jammu 85*)

(*iv*) $CdSO_4$ (*Delhi 83*)

27. Give the reasons for the following :

(*i*) ZnO is yellow in colour when hot but is white when cold. (*Delhi Hons. 87; Punjab 85*)

(*ii*) It is usually not possible to prepare ZnO corresponding exactly to steichicometric formula, ZnO. (*Madras 85*)

(*iii*) Anhydrous $ZnCl_2$ cannot be prepared merely by heating the crystals of hydrated $ZnCl_2.2H_2O$.

28. What happens when :

(*i*) Hg_2Cl_2 is heated with NH_4OH. (*Meerut 89 S; MLNR 76*)

(*ii*) Hg_2Cl_2 reacts with aqua regia. (*MLNR 76*)

(*iii*) SO_2 is passed through corrosive sublimate. (*R.E.E. 73*)

(*iv*) NH_3 is added to $HgCl_2$. (*R.E.E. 73, 77*)

(*v*) $HgCl_2$ is heated with Hg in an iron vessel. (*R.E.E. 75*)

(*vi*) $HgCl_2$ is treated with NaOH solution. (*Delhi 83*)

29. Give the preparation, properties and uses of : (*i*) ceric ammonium sulphate (*ii*) ceric sulphate.

30. Give the preparation, properties and uses of : (*i*) Thoria (*ii*) Thorium nitrate. (*Meerut M.Sc. 84*)

Compounds of uranium

31. Discuss the preparation properties and uses of : (*i*) uranyl nitrate (*ii*) ammonium diuranate (*iii*) uranium hexafluorid (*iv*) uranyl acetate. (*Meerut 83; Lucknow 85; Madras 86; Madurai 86*)

32. (*a*) How is sodium nitroprusside prepared? How does it react with (*i*) Alkali metal sulphide (*ii*) $AgNO_3$ solution (*iii*) Alkalies

(*b*) Give the chemistry of chromyl chloride test.

(*c*) How does potasssium ferricyamide react with : (*i*) Ferrous sulphate (*ii*) Alkaline solution of lead oxide (*iii*) Ferric chloride. (*Himachal Pradesh 99*)

33. Give a brief account of preparation and properties of $K_2Cr_2O_7$. (*Gorakhpur 99*)

(*a*) Describe the preparation of chromyl chloride and discuss its structure. How does it react with water, NaOH and toluene?

(*b*) Draw the structure of TiO_2.

(*c*) Discuss the extraction of thorium from monazite sand.

(*d*) How is chromium acetate monohydrate prepared? (*Himachal Pradesh 2000*)

34. (*i*) Write down the methods of preparation and uses of : (*a*) $K_2Cr_2O_7$ (*b*) Sodium nitroprusside (*c*) Milon's base

(*ii*) What happens when :

(*a*) Cobalt nitrate reacts with $NaNO_3$ acidified with CH_3COOH.

(*b*) Cl_2 gas is passed through potassium ferrocyanide solution.

(*c*) A mixture of $Na_2Cr_2O_7$ and NH_4Cl a strongly heated. (*Kanpur 2000*)

35. Give preparation, important reactions, uses and structure of the following : (*i*) $TiCl_4$ (*ii*) $KMnO_4$. (*Lucknow 2000*)

36. Describe the method of preparation, properties and uses of : (*i*) Chlorauric acid (*ii*) $KMnO_4$. (*Avadh 2000*)

37. Calculate equivalent weight of $K_2Cr_2O_7$ in acidic medium, giving required reactions. (Meerut 2009)

38. Discuss the prepration, properties and uses of any two of the following : (i) $KMnO_4$ (ii) Sodium cobaltnitrite (ii) Potassium ferro cyanide. (*Meerut 2009*)