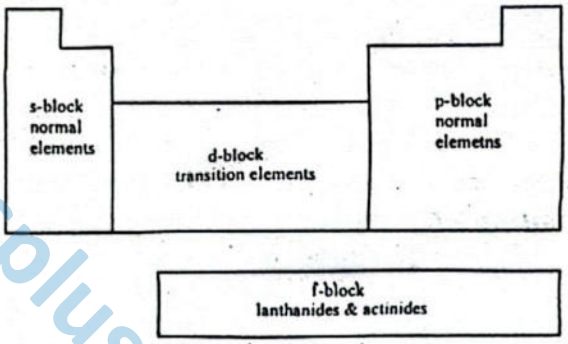
Chapter # 06
Transition Elements

6.1 INTRODUCTION

Elements, which have partially filled d or f-subshells in atomic state or in any of their commonly occurring oxidation states

d-block, **f**-block are called transition elements. It is because these are present in between **s** and **p**-block elements in periodic table and their properties are in transition between metallic character of **s**-block elements and non-metallic character of **p**-block elements.



ELECTRONIC CONFIGURATION

Electronic configuration of three series of **d**-block elements is shown below

Cr has $3d^5 4s^1$ configuration. Similarly Cu has $3d^{10}4s^1$ configuration. It is due to extra stability of half-filled and full-filled orbitals.

3d-block elements		4d-block elements		5d-block elements	
Elements	Electronic configuration	Elements	Electronic configuration	Elements	Electronic configuration
Sc (21)	[Ar] $3d^1 4s^2$	Y (39)	[Kr] $4d^1 5s^2$	La (57)	[Xe] $5d^1 6s^2$
Ti (22)	[Ar] $3d^2 4s^2$	Zr (40)	[Kr] $4d^2 5s^2$	Hf (72)	[Xe] $4f^{14}5d^2 6s^2$
V (23)	[Ar] $3d^3 4s^2$	Nb (41)	[Kr] $4d^4 5s^1$	Ta (73)	[Xe] $4f^{14}5d^3 6s^2$
Cr (24)	[Ar] $3d^5 4s^1$	Mo (42)	[Kr] $4d^5 5s^1$	W (74)	[Xe] $4f^{14}5d^4 6s^2$
Mn (25)	[Ar] $3d^5 4s^2$	Te (43)	[Kr] $4d^5 5s^2$	Re (75)	[Xe] $4f^{14}5d^5 6s^2$
Fe (26)	[Ar] $3d^{16} 4s^2$	Ru (44)	[Kr] $4d^7 5s^1$	Os (76)	[Xe] $4f^{14}5d^6 6s^2$
Co (27)	[Ar] $3d^7 4s^2$	Rh (45)	[Kr] $4d^8 5s^1$	Ir (77)	[Xe] $4f^{14}5d^7 6s^2$
Ni (28)	[Ar] $3d^8 4s^2$	Pd (46)	[Kr] $4d^{10}$	Pt (78)	[Xe] $4f^{14}5d^9 6s^1$
Cu (29)	[Ar] $3d^{10} 4s^1$	Ag (47)	[Kr] $4d^{10} 5s^1$	Au (79)	[Xe]$4f^{14}5d^{10}6s^1$
Zn (30)	[Ar] $3d^{10} 4s^2$	Cd (48)	[Kr] $4d^{10} 5s^2$	Hg (80)	[Xe]$4f^{14}5d^{10}6s^2$

		3d					4s
Sc	(Ar)	↑					↑↓
Ti	(Ar)	↑	↑				↑↓
V	(Ar)	↑	↑	↑			↑↓
Cr	(Ar)	↑	↑	↑	↑	↑	↑
Mn	(Ar)	↑	↑	↑	↑	↑	↑↓
Fe	(Ar)	↑↓	↑	↑	↑	↑	↑↓
Co	(Ar)	↑↓	↑↓	↑	↑	↑	↑↓
Ni	(Ar)	↑↓	↑↓	↑↓	↑	↑	↑↓
Cu	(Ar)	↑↓	↑↓	↑↓	↑↓	↑↓	↑
Zn	(Ar)	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

6.1.1 Typical and Non-Typical Elements

Elements which show typical properties of transition elements are called typical transition elements.

While

Elements which do not show typical properties of transition elements are called non-typical transition elements.

Explanation

- Group IIB include Zn, Cd and Hg. These elements do not have partially filled **d**-orbital in atomic state or in their ionic state. Moreover these elements do not show typical properties of transition elements except complex formation.
- Similarly group IIIB elements include Sc, Y and La. They are transition elements as they have one electron in **d**-subshell. These elements do not show typical properties of transition elements. These mostly exist as tripositive ions. In this state their **d**-orbital is empty.
- Hence elements of group IIIB and IIB are called non-typical transition elements. While other elements are called typical transition elements.
- Coinage metals include Cu, Ag and Au. These are typical transition elements. Because Cu^{2+} has $3d^9$ configuration, Ag^{2+} has $4d^9$ configuration and Au^{3+} has $5d^8$ configuration.

> **f**-block elements include Lanthanides and Actinides. These are called inner transition elements while **d**-block elements are called outer transition elements.

Period	Group IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB	VIIIB	VIIIB	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VII
1	H																	HE
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	S	Te	I	Xe
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Ti	Pb	Bi	Po	At	Rn
7	Fr	Ra	Ac	104	105	106	107											

Transition Elements (IIIB–IIB)

6.2 PROPERTIES OF TRANSITION ELEMENTS

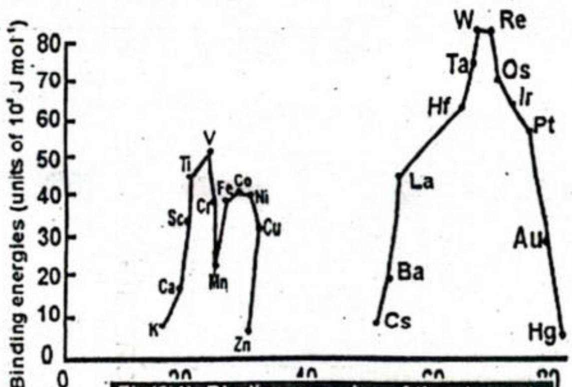
Due to similar electronic configuration, transition metals show many similarities.

- They are all metals. Some of them are very important in industry e.g. Ti, Fe, Cr, Ni, Cu, Mo, Zr, Nb, Ta, Th etc.
- They are hard with high melting points and boiling points.
- They are good conductors of heat and electricity.
- They form alloys with one another and with other elements.
- Generally, they show variable valencies.
- Their ions and compounds are coloured in solid as well as in solution form. Typical transition elements have at least one coloured oxidation state.

6.2.1 GENERAL CHARACTERISTICS

1. BINDING ENERGIES

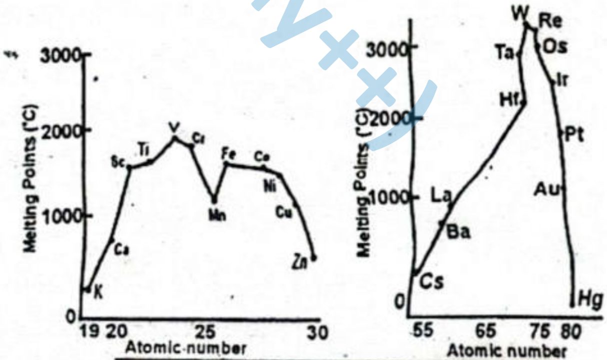
- Transition metals show good mechanical properties. These are hard, malleable and ductile.
- The hardness shows that these have strong metallic bonding. It is because **s**-electrons of outer shell as well as **d**-electrons of inner shell also take part in bonding.
- In transition series, binding forces increases from left to right upto middle and then decreases. It is because number of unpaired electrons increases upto VB and VIB group and then decreases upto group IIB where it becomes zero.
- Therefore, binding is stronger upto group VIB and weakens progressively upto group IIB as shown in fig. 6.1.
- In first transition series the general increase in binding energy ends at vanadium. This is due to changes in metallic structure, e.g. Mn.
- In third transition series, binding forces increases upto tungsten due to involvement of all 5d electrons.



Fig(6.1) Binding energies of the elements of the first and third transition series.

2. MELTING AND BOILING POINTS

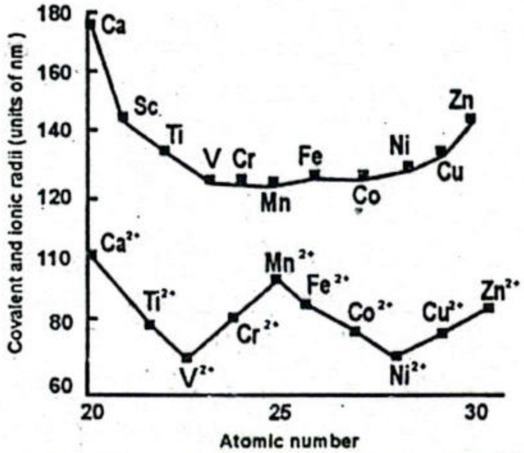
- These have very high melting points and boiling points due to strong binding forces.
- Melting points increases upto middle and then decreases to a minimum at the end of series.
- It is due to increase in binding forces upto middle and then decrease upto end.



Fig(6.2) Melting points of the elements of the first and the third transition series.

3. COVALENT RADII AND IONIC RADII

- At the start of series, covalent radii rapidly decrease and then become almost constant.
- At the end of series covalent radii shows a slight increase.
- This increase is because, at the end of series, inner **d**-orbital is contracted due to greater number of electrons and it has a greater shielding effect. Thus outer electrons are moved away from nucleus. Hence covalent radii increase.
- Periodicity of ionic radii is not much regular.

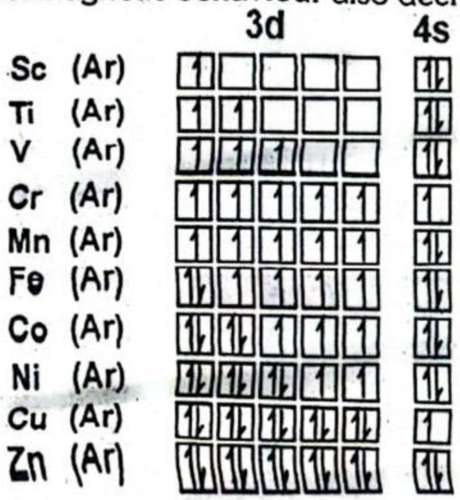


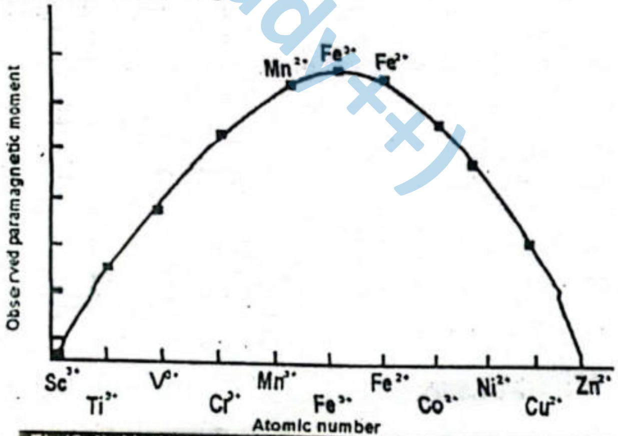
Fig(6.3) Convalent radii (o-) and ionic radii (for for M^{2+})(-o)of first transition series elements.

4. PARAMAGNETISM

Substances, which are weakly attracted by strong magnetic field, are called paramagnetic substances. While
Substances, which are weakly repelled by strong magnetic field, are called diamagnetic substances.

- Paramagnetic behaviour is caused by unpaired electrons. It is because, moving electrons have magnetic moments.
- When electrons are paired, their magnetic moments cancel the effect of each other thus the substance become diamagnetic. However, if the electron is unpaired, it shows its magnetic moments. Thus the substance becomes paramagnetic.
- Magnetic moment of a substance increases with increase in number of unpaired electrons.
- Thus maximum paramagnetic moment is shown by Fe^{3+} and Mn^{2+} while it decreases on both sides of these ions. It is because these ions have maximum unpaired electrons i.e. 5 each.
- On both sides of these ions number of unpaired electrons decreases to zero thus paramagnetic behaviour also decreases as shown in fig.





Fig(6.4) Variation in the paramagnetic effect shown by the selected ions across thre first transition series.

5. OXIDATION STATE

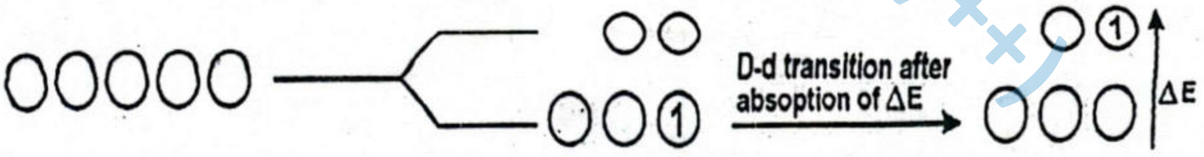
- Transition elements show <u>variable oxidation state</u>. It is because **d**-electrons of inner d-orbital are also involved in bonding in addition to outer **s**-electrons.
- Due to presence of <u>larger number of unpaired electrons</u> these can show <u>variable valency</u>.
- All elements of <u>3d series</u> show an oxidation state of <u>+2</u> in addition to <u>higher oxidation states</u>.

		Oxidation states						
Sc	[Ar] $3d^1 4s^2$		2	3				
Ti	[Ar] $3d^2 4s^2$		2	3	4			
V	[Ar] $3d^3 4s^2$		2	3	4	5		
Cr	[Ar] $3d^5 4s^1$		2	3	4	5	6	
Mn	[Ar] $3d^5 4s^2$	1	2	3	4	5	6	7
Fe	[Ar] $3d^6 4s^2$	1	2	3	4	5	6	
Co	[Ar] $3d^7 4s^2$		2	3	4	5		
Ni	[Ar] $3d^8 4s^2$		2	3	4			
Cu	[Ar] $3d^{10} 4s^1$	1	2	3				
Zn	[Ar] $3d^{10} 4s^2$		2					

- <u>+2 oxidation state is produced due to involvement of **s**-electrons in bonding</u>.
- <u>For higher oxidation states, **d**-electrons also become involve in bonding</u>.
- First five elements show highest oxidation state when all their **s** and **d**-electrons are involved in bonding. After Mn number of oxidation state decreases because **d**-orbital fill up with electrons and few unpaired electrons are available for bonding.

6. COLOR

- Transition elements and their compounds show colors. <u>The colors of these substances are due to **d**-orbitals</u>.
- During bond formation, **d**-orbitals of transition elements are <u>split up into two sets of energy levels</u>. One set of energy level has higher energy than other.
- When light falls, an electron in lower set of energy level may absorb energy and it goes to higher energy set of **d**-orbitals. <u>This is called **d-d** transition</u>. The energy difference between two sets of **d**-orbitals varies from ion to ion. Thus each ion <u>absorb a particular set of wavelengths</u> while transmit the remaining set of wavelengths. Thus it gives different colour to each ion.



Fig(6.5) Absorption of yellow light by $[Ti(H_2O)_6]^{3+}$

- e.g. In $[Ti(H_2O)_6]^{3+}$, <u>yellow light is absorbed</u> while <u>blue and red lights are transmitted</u>. Thus the solution of $[Ti(H_2O)_6]^{3+}$ shows <u>violet colour</u>.

7. Interstitial Compounds

- Transition metals have close packed structure in which interstices are present.
- Small non-metallic atoms like H, B, C and N can enter into these interstices and adsorbed on the surface of metal atoms to form interstitial compounds.
- These compounds are non-stoichiometric in nature and do not obey the laws of chemical combination.
- Sometimes they are also called interstitial alloys.

8. Alloy Formation

- Transition metals of a particular series have almost similar sizes. Thus these can replace each other in crystal lattice to form substitutional alloys.
- e.g. Alloy steel is an alloy of iron with Cr, Mn and Ni. This alloys steel has many useful properties.
- Other examples are brass, bronze, coinage alloys etc.

6.3 COMPLEX COMPOUNDS

Compounds containing complex ions or complex molecules and can exist independently are called complex compounds or co-ordination compounds

Example and Explanation

When an aqueous solution of $Fe(CN)_2$ is mixed with an aqueous solution of KCN then a new compound is obtained. This new compound ionizes in water as K^+ ion and $[Fe(CN)_6]^{4-}$ ion, (ferrocyanide ion). Its formula is $K_4[Fe(CN)_6]$

$$Fe(CN)_2 + 4KCN \longrightarrow K_4[Fe(CN)_6] \longrightarrow 4K^+ + [Fe(CN)_6]^{4-}$$

$[Fe(CN)_6]^{4-}$ is called complex ion. Thus $K_4[Fe(CN)_6]$ is called complex compound.

Generally, a complex compound may contain

- A simple cation and a complex anion e.g. $K_4[Fe(CN)_6]$
- A complex cation and a simple anion e.g. $[Cr(NH_3)_6]Cl_3$

6.3.1 COMPONENTS OF COMPLEX COMPOUNDS

CENTRAL METAL ION

A metal atom or ion (usually a transition element) surrounded by a number of ligands is called a central metal atom or ion,

Example

In $K_4[Fe(CN)_6]$ and $[Cr(NH_3)_6]Cl_3$. Fe and Cr are the central metal ions.

LIGAND

The atom or ions or neutral molecules which surround the central metal atom or ion by donating electron pairs are called ligands.

Examples

In $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$, CN^- is the ligand.
In $[Cr(NH_3)_6]Cl_3$ and $[Ag(NH_3)_2]Cl$, NH_3 is the ligand

TYPES OF LIGANDS

Unidentate ligands

The ligands having only one donor atom are called unidentate ligand

Examples

NH_3 , Cl^- , CN^- , I^- etc.

Polydentate ligands

Ligands having two or more donor atoms are called polydentate ligands

These ligands are further classified into bidentate, tridentate ligands etc, depending on the number of donor atoms.

Examples

Ethylenediammine (bidentate) , EDTA (hexadentate) etc.

$$H_2N—CH_2\text{-}CH_2\text{-}NH_2$$
ethylenediammine

Oxalate ion $\begin{array}{l} COO^- \\ | \\ COO^- \end{array}$ is a bidentate ligand and its coordination with the metal ion occurs through its negatively charged oxygen atoms.

COORDINATION NUMBER

The number of lone pair of electrons provided by the ligands to the central metal atom or ion is called the coordination number of the central metal atom or ion.

Examples

In $K_4[Fe(CN)_6]$, co-ordination number of Fe is 6.
In $[Cu(NH_3)_4]SO_4$, co-ordination number of Cu is 4

Coordination Sphere

The central metal atom or ion alongwith ligands is called the coordination sphere. It is placed in square brackets. It may be anionic, cationic or neutral

Examples

In $K_4[Fe(CN)_6]$,	$[Fe(CN)_6]^{4-}$	is the anionic co-ordination sphere.
In $[Cu(NH_3)_4]SO_4$,	$[Cu(NH_3)]^{2+}$	is the cationic co-ordination sphere.
In $[Ni(CO)_4]$,	$[Ni(CO)_4]^6$	is the neutral co-ordination sphere.

Charge on the Coordination Sphere

It is the algebraic sum of the charges present on the central metal ion and the total charge on the ligands.

Example

$[Fe(CN)_6]^{4-}$

Charge on iron	= + 2
Total chare on six CN^- ions	= – 6
Charge on the coordination sphere	= –6+2 = – 4

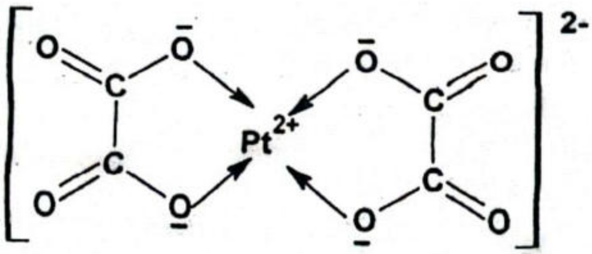
6.3.2 Chelates

When all the donor atoms of a polydentate ligand are coordinated with the same metal ion, a complex compound is formed which contains one or more rings in its structure. It is called a Chelate.

Metal chelates are more stable metal complexes.

Example

When two oxalato ligands $C_2O_4^{2-}$ (bidentate ligand) are coordinated with Pt^{2+} ion, dioxalato platinate (II) ion is obtained. Each oxalate ligand forms a five membered ring with the cation



Dioxalatoplatinate(II) ion

6.3.3 NOMENCLATURE

Complex compounds are named according to the rules given by Inorganic nomenclature committee of IUPAC.

Following are the rules

ORDER OF NAMING IONS

- Cations are named before anions.

Examples

$FeCl_2$: Iron (II) chloride

$[Cu(NH_3)_4]SO_4$: Tetraammine copper (II) sulphate

- Non-ionic or Neutral molecules are given one word name.

Examples

$[Co(NH_3)_3Cl_3]$: Triamminedichlorocobalt (III)

$[Pt(NH_3)_2Cl_2]$: Diamminedichloroplatinum (II)

NAMING OF LIGANDS

(i) Neutral ligands

Neutral ligands have no special ending. These are named as neutral molecule except NH_3 (ammine), H_2O (aquo), NO (nitrosyl), CO (carbonyl)

(ii) Ionic ligands

- Negative ligands has ending **–o.**

  Examples

  Cl^- (chloro), CN^- (cyano), I^- (iodo), NO_2^- (nitro) etc.

- Positive ligands has ending **–ium.**

  Examples

  $NH_2-NH_3^+$ (hydrazinium), NO_2^+ (nitronium), NO^+ (nitrosonium) etc.

(iii) Prefixes di, tri, tetra etc are used to indicate the number of ligands of one type

NAMING OF CENTRAL METAL ION

(i) If co-ordination sphere is positive or neutral, metal name is written as such.

(ii) If co-ordination sphere is negative, then suffix –ate is added to the metal name.

(iii) Oxidation state of central metal atom is indicated by Roman numeral in parenthesis at the end of metal name.

NAMING OF CO-ORDINATION SPHERE

(i) Ligands are named first.

(ii) Ligands are named in alphabetical order, regardless of the charge and number of each

(iii) Central metal atom is named last, followed by oxidation state with in parenthesis.

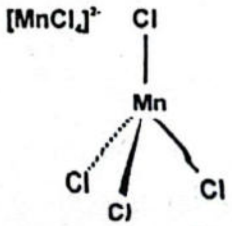
In writing the formula of a complex ion, the symbol of the central metal atom is placed first. It is followed by the names of the ionic ligands in alphabetical order, then neutral ligands in alphabetic order. The formula of the whole complex ion is enclosed in square brackets.

Examples:

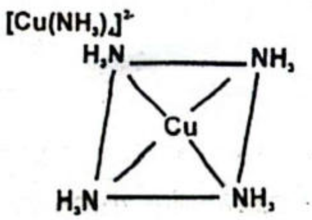
$K_4[Fe(CN)_6]$	Potassium hexacaynoferrate(II)
$[PtCl(NO_2)(NH_3)_4]SO_4$	Tetraamminechloronitroplatinum(IV) sulphate
$[Co(NH_3)_3(NO_2)_3]$	Triamminetrinitrocobalt(III)
$Na_2[Fe(CN)_5NO]$	Sodium pentacyanonitrosylferrate(III)
$[Ni(CO)_4]$	Tetracarbonylnickle(0)
$K_3[Fe(CN)_6]$	Potassium hexacyanoferrate(III)
$K_2[Cu(CN)_4]$	Potassium tetracyanocuprate(II)
$[Ag(NH_3)_2]Cl$	Diamminesilver(I) chloride
$[Co(NH_3)_6]Cl_3$	Hexaamminecobalt(III) chloride
$[CrCl_2(H_2O)_4]Cl$	Tetraaquadichlorochromium(III) chloride
$(NH_4)_2[PtCl_6]$	Ammonium hexachloroplatinate(IV)
$[Co(H_2O)_6]^{2+}$	Hexaaquacobalt(II) ion
$[Ni(CN)_4]^{2-}$	Tetracyanonicklate(II) ion

6.3.4 GEOMETRY OF COMPLEXES

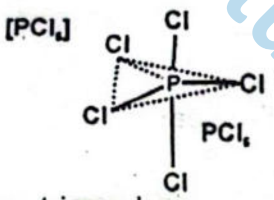
The geometry of complexes depends upon the type of hybridization taking place in the valence shell of the central metal atom. Following is the brief summary of geometry of complex compounds.



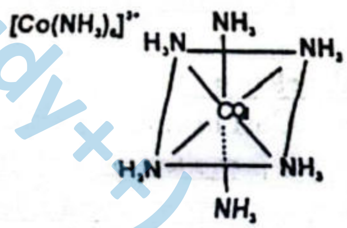
tetrahedral (sp^3)



Square planar (dsp^2)



trigonal bipyramidal (dsp^3)



octahedral (sp^3d^2)

6.4 IRON

History

Iron has been known since prehistoric days. It was used in Egypt in 1500B.C. Chinese also used iron as early as 2500B.C. In subcontinent iron was produced around 600B.C.

Ores of Iron

Following are the important ores of iron

Magnetite: Fe_3O_4

Haematite: Fe_2O_3

Limonite: $Fe_2O_3.3H_2O$ etc.

6.4.1 COMMERCIAL FORMS OF IRON

Following three forms of iron are available commercially. They differ in carbon contents.

- Pig iron or cast iron — 2.5 to 4.5% carbon
- Wrought iron — 0.12 to 0.25% carbon
- Steel — 0.25 to 2.5% carbon

6.4.2 WROUGHT IRON

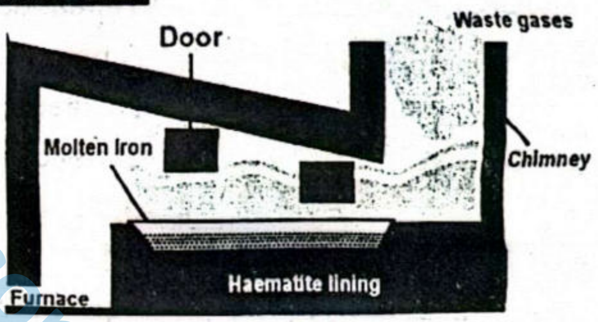
It is the purest form of commercial iron. It contains lowest percentage of carbon. It has upto 0.3% of impurities like S, P, Si and Mn, etc.

S = 0.2 to 0.15%, Mn = upto 0.25%, P = 0.04 to 0.2%

6.4.3 MANUFACTURE OF WROUGHT IRON FROM CAST IRON

Construction

- It is manufactured from cast iron by puddling.
- In pudding cast iron is heated in a special type of reverberatory furnace called puddling furnace.
- Low roof of this furnance deflects hot gases and flames downwards and melts cast iron.
- The hearth of furnace is lined with haematite (Fe_2O_3).



Fig(6.6) Puddling furnace for the manufacture of wrought iron.

Working

- Cast iron is placed on the hearth.
- It is melted by hot gases.
- It is stirred or puddled with long iron rods called rabbles through the doors to bring it in thorough contact with the lining of the hearth, i.e. Fe_2O_3.
- The haematite (Fe_2O_3) lining supplies oxygen.
- Oxygen oxidizes carbon, sulphur, silicon, manganese and phosphorus present in the cast iron to their oxides.

Oxides of carbon and sulphur are volatile and escape out at high temperature.

$$3C + Fe_2O_3 \longrightarrow 2Fe + 3CO$$

$$3S + 2Fe_2O_3 \longrightarrow 4Fe + 3SO_2$$

While oxides of manganese, silicon and phosphorous form slags.

$$3Si + 2Fe_2O_3 \longrightarrow 4Fe + 3SiO_2$$
$$2Mn + O_2 \longrightarrow 2MnO$$
$$MnO + SiO_2 \longrightarrow MnSiO_3 \text{ (slag)}$$
$$4P + 5O_2 \longrightarrow 2P_2O_5$$
$$Fe_2O_3 + P_2O_5 \longrightarrow 2FePO_4 \text{ (slag)}$$

- With the removal of impurities, melting point of metal rises and it becomes a semi-solid mass.
- It is then taken out in the form of balls or blooms on the ends of rabbles.
- It is hammered while hot to squeeze out as much of slag as possible.
- The product so obtained is called wrought iron.

6.4.4 STEEL:

It is an alloy of iron containing 0.25 to 2.5% of carbon and traces of S, P, Si and Mn. Carbon content of steel are intermediate between cast iron and wrought iron.

CLASSIFICATION OF STEEL:

Mild steel (0.1-0.2% C)

- It is fairly soft, malleable and ductile.
- It can be forged (shaped by hammering and pressing while hot).
- It is used in making tubes, nuts, bolts, bars and boiler plates.

Medium carbon steel (0.2-0.7% C)

- It is harder than mild steel. It is malleable and ductile.
- It is used in making rails, axles, castings.

High carbon steel (0.7-1.5% C)

- It is hard. It can be forged when % of C is less than 1.0%.
- Steel containing more than 1.0% carbon can not be forged.
- It is used to make hammers, taps, dies, cutting tools, machine tools, hard steel parts of machinery and all sorts of engines.

6.4.5 MANUFACTURING OF STEEL

- It can be manufactured from cast iron by removing some carbon alongwith sulphur, phosphorus and silicon.
- It can be manufacture by adding required amount of carbon to wrought iron. Some special constituents are also added e.g. tungsten, chromium, vanadium, molybdenum, manganese, nickel and cobalt. These give desired properties to the steel.

At present most of the steel is manufactured from cast iron.

PROCESSES

Following processes are used to produce steel

- Open hearth process (using cast iron, wrought iron or steel scarp)
- Bessemer process (using cast iron only)

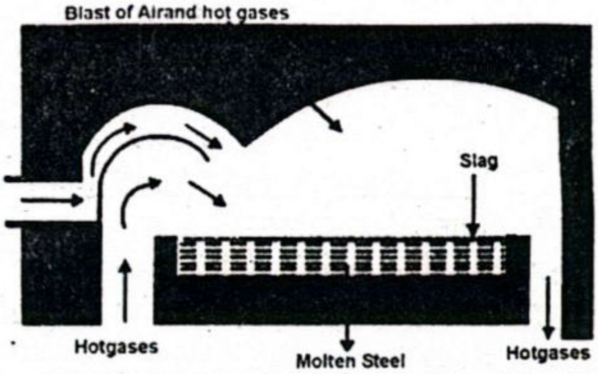
Some other processes are also used to prepare special type of steel from pure wrought iron.

6.4.6 OPEN HEARTH PROCESS

It is the most modern method of manufacturing steel.

Construction

- It is carried out in an open hearth furnace.
- This furnace has low roof to deflect hot gases and flames downward to melt the charge.
- Open hearth furnace works on the regenerative principle of heat economy.



Fig(6.7) Open Hearth furnace for the manufacture of stell from cast iron.

- **Open hearth process is of two types.**
  - ✓ When impurities are Mn, Si, etc. then furnace with acidic lining like SiO_2 is used.
  - ✓ When impurities are P and S, etc. then furnace with basic lining like dolomite (CaO, MgO) is used.

Working

- A mixture of cast iron, scrap steel and quick lime is charged into the furnace. At about 1600°C Si, Mn, C, S, and P are burnt out and removed according to the following reactions.

$$C + \frac{1}{2} O_2 \longrightarrow CO$$
$$Si + O_2 \longrightarrow SiO_2$$
$$Mn + \frac{1}{2} O_2 \longrightarrow MnO$$

- CO escapes in flue gases. Silica (SiO_2) combines with CaO, MnO and FeO to from silicates (slag) which float on the surface of the molten metal.

$$SiO_2 + CaO \longrightarrow CaSiO_3 \quad \textit{(slag)}$$
$$SiO_2 + MnO \longrightarrow MnSiO_3 \quad \textit{(slag)}$$
$$SiO_2 + FeO \longrightarrow FeSiO_3 \quad \textit{(slag)}$$

- Phosphorus and sulphur react with Fe_2O_3 to form P_2O_5 and SO_2.

$$2Fe_2O_3 + 3S \longrightarrow 4Fe + 3SO_2$$
$$5Fe_2O_3 + 6P \longrightarrow 10Fe + 3P_2O_5$$

- These oxides react with calcium oxide to form slag.

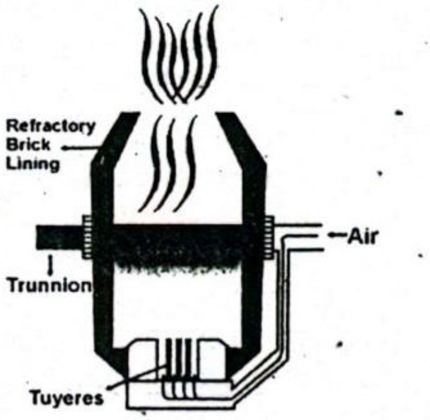
$$P_2O_5 + 3CaO \longrightarrow Ca_3(PO_4)_2 \quad \textit{(slag, fertilizer)}$$
$$SO_2 + CaO \longrightarrow CaSO_3 \quad \textit{(slag)}$$

- Percentage of carbon in steel is checked at regular intervals.
- When this is reduced to about 0.1%, then calculated amount of ferromanganese (Fe, Mn, C) is added.
- Manganese desulphurises the steel. Carbon raises the carbon contents to the required values. After giving time for mixing, a little more ferromanganese is added.
- Then charge is allowed to run into moulds where it solidifies to ingots.
- The whole process takes about 10 hours.
- Slag contains calcium phosphate. It is ground to powder and sold as a fertilizer.

6.4.7 BESSEMER'S PROCESS

Construction

- The furnace called Bessemer's converter.
- It is a pear shaped vessel made of steel plates.
- At the bottom the converter there are number of holes through which hot air can be introduced.
- The converter is held on a central axis. It can be tilted for feeding and pouring out the finshed materials.



Fig(6.8) Bessemer's converter for the manufacture of steel from cast iron.

Working

- Molten pig or cast iron (25 to 30 tons) from the blast furnace is fed into the converter.
- Hot air blast in passed through the perforated base.

  This oxidizes carbon, silicon and manganese.

$$C + \frac{1}{2} O_2 \longrightarrow CO$$
$$Si + O_2 \longrightarrow SiO_2$$
$$Mn + \frac{1}{2} O_2 \longrightarrow MnO$$

- These oxides form a slag of $MnSiO_3$. Heat evolved during oxidation keep the iron in molten state.

$$MnO + SiO_2 \longrightarrow MnSiO_3$$

- CO produced burns at the mouth of the converter with a blue flame. Iron is partly oxidized to ferric oxide (Fe_2O_3) which also extracts carbon from cast iron to form CO.

$$4Fe + 3O_2 \longrightarrow 2Fe_2O_3$$
$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$

- Within 10 to 15 minutes the flame due to CO finishes showing that carbon is completely oxidized.
- At this stage ferromanganese is added to correct the proportion of carbon to obtain the desired qualities.
- A *blast of air* is blown for few moments for thorough mixing.
- Addition of Mn gives increased hardness and tensile strength.
- To remove entrapped bubbles of gases (below holes) such as O_2, N_2, CO_2 a little Al or *ferrosilicon* is added. Al removes nitrogen as nitride and oxygen as oxide.

$$2Al + N_2 \longrightarrow 2AlN$$

- At the end of the operation, the molten steel is poured out into moulds for casting.

6.5 CORROSION

The process of chemical decay of metals due to the action of surrounding medium is called corrosion.

Explanation

When metals come in contact with atmospheric gases, the surface of metals is coated with oxides, sulphides, carbonates etc. sometimes these compounds form a compact layer on the surface. Thus metal is protected from further attack.

However, if water is present then layers of oxides, sulphides and carbonates are dissolved in water. Thus corrosion penetrates into the metal. Further water promotes electrochemical process which is the main cause of rapid corrosion.

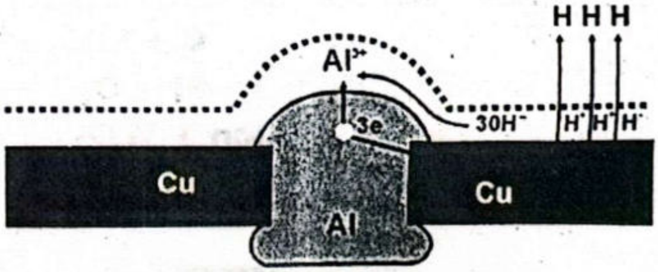
THEORIES OF CORROSION

Two important theories of corrosion are

- Acid theory
- Electrochemical theory

6.5.1 ELECTROCHEMICAL THEORY

100% pure metal does not corrode.
Impurities present in metal promote corrosion.
Consider an example



Fig(6.9) Diagram of the corrosion of aluminium in contact with copper.

- Let Al is present in contact with Cu.
- Moisture and CO_2 are present on the surface of metal.
- Water ionizes to H^+ and OH^- ions.
- CO_2 is dissolved in water to produce H_2CO_3 which ionizes into H^+ and HCO_3^- ions.

$$H_2O \rightleftharpoons H^+ + OH^-$$
$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$
$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

In other words, metals are actually immersed in a solution of H^+, OH^- and HCO_3^- ions.
Thus a Galvanic cell is set up.
In this cell, Al releases electrons and changes into Al^{3+} ion. It acts as negative electrode while Cu acts as positive electrode. It is because Al is more reactive than Cu and is present above Cu in electrochemical series.

Al^{3+} ions combine with OH^- ions to form $Al(OH)_3$ ions. Thus Al starts dissolving.

$$Al \longrightarrow Al^{3+} + 3e^-$$
$$3H^+ + 3e^- \longrightarrow 3/2\ H_2$$

Thus Al corrodes rapidly when in contact with Cu.

Generally

When an active metal (higher in electrochemical series) is in contact with less active metal (lower in electrochemical series). The active metal corrodes rapidly while other remains intact.

6.5.2 PREVENTION OF CORROSION

Prevention of corrosion is very important. In case of iron, its corrosion is about ***¼ th*** of its annual production. Thus corrosion must be prevented.

Following methods are generally used

Coating of Metals

It is the simplest method. In this metal surface is coated with oil, paint, varnish or enamel.

Alloying

Corrosion can be prevented by alloying of metal with other metals.

e.g corrosion of Fe is prevented by alloying it with Ni, Cr etc.

Metallic Coating

A protective layer of another metal on the surface of metal can also prevent corrosion.

6.5.3 TIN PLATING OR COATING IRON WITH TIN (CATHODE COATING)

In this process, a clean sheet of iron is dipped in molten tin. It is then passed through hot pairs of rollers. Thus surface of iron is coated with a thin layer of tin. *Tin itself is very* stable. Thus it prevents the rusting of metal.

It is used in the manufacture of tin canes, oil containers and other similar articles.

If the protective layer is damaged then iron comes in direct contact with moisture. A galvanic cell is set up in which tin acts as cathode while iron acts as anode. Electrons flow from iron to tin. Iron is oxidized to Fe^{3+} Which from $Fe(OH)_3$ on combining with OH^- ions. On the surface of tin H^+ ions are discharged to H_2 gas. Thus iron dissolves more rapidly.

Hence, it can be concluded that tin plated iron is rusted more rapidly than non-plated iron, if tin coating is damaged.

6.5.4 GALVANIZING OR ZINC COATING (ANODE COATING)

It is done by dipping clear iron sheets in a $ZnCl_2$ bath and heating. Iron sheets are removed and rolled into Zn bath and air cooled.

If protective coating of Zn is destroyed then a galvanic cell is set up. In this cell Zn acts as anode and iron as cathode. Electrons flow from Zn to iron. Thus Zn decays while Fe remains intact. This is called sacrificial corrosion.

$$Fe^{2+} + Zn \longrightarrow Zn^{2+} + Fe$$

This type of galvanizing is used in water pipes.

6.6 CHROMATES AND DICHROMATES

CHROMATES

Chromates are the salts of chromic acid, H_2CrO_4. This acid exists only in aqueous solution. During isolation from solution they decompose immediately into chromic anhydride (Cr_2O_3) and water. However, their salts are quite stable.

6.6.1 POTASSIUM CHROMATE (K_2CrO_4)

Preparation

- Chromates of alkali metals are soluble in water. These are obtained by oxidizing trivalent chromium compounds in the presence of an alkali.

$$2KCrO_2 + 3Br_2 + 8KOH \longrightarrow 2K_2CrO_4 + 6KBr + 4H_2O$$

- Fusing Cr_2O_3 with an alkali in the presence of an oxidant, e.g. potassium chlorate, can also produce chromates.

$$Cr_2O_3 + 4KOH + KClO_3 \longrightarrow 2K_2CrO_4 + KCl + 2H_2O$$

- Chromates are usually prepared from natural chromite ($FeO.Cr_2O_3$). It is strongly heated with potassium carbonate in the presence of the oxygen. The resulting fused mass contains potassium chromate, which can be extracted with water.

$$4FeCr_2O_3 + 8K_2CO_3 + 9O_2 \longrightarrow 8K_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

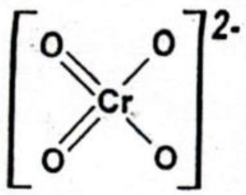
6.6.2 PROPERTIES

- Almost all the chromates are yellow in colour.
- Some of them are used as pigments. e.g. insoluble lead chromate, $PbCrO_4$, is used for the preparation of yellow oil colour called yellow crown.
- K_2CrO_4 and $K_2Cr_2O_7$ show similar properties because in an aqueous solution $Cr_2O_7^{2-}$ and CrO_4^{2-} ions exist in equilibrium.

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

- If an alkali is added to this solution, hydroxyl ions will remove hydrogen ion in solution. Thus equilibrium will shift to left and dichromate ions will be converted into chromate ions. Similarly addition of acid will shift equilibrium to right and dichromate ions will be formed.

Structure of Chromate Ion



DICHROMATES AND DICHROMIC ACID

Dichromates are the salts of dichromic acid, $H_2Cr_2O_7$. This acid exists only in aq. solution. During isolation from solution it decomposes immediately into chromic anhydride (Cr_2O_3) and water. However, its salts are quite stable.

6.6.3 POTASSIUM DICHROMATE ($K_2Cr_2O_7$)

PREPARATION

(1) From Potassium Chromate

$K_2Cr_2O_7$ can be prepared from K_2CrO_4. In an aq. solution $Cr_2O_7^{2-}$ and CrO_4^{2-} ions exist in equilibrium.

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

In an acidic medium the equilibrium will shift in the forward direction. Thus chromate ions are changed into dichromate ions.

(2) From Sodium Chromate

Sometimes sodium dichromate is converted into potassium dichromate by reacting it with KCl.

$$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$$

6.6.4 PROPERTIES

PHYSICAL PROPERTIES:

- It is an orange red crystalline solid.
- Its melting point is 396°C
- It is fairly soluble in water.

OXIDIZING PROPERTIES

Dichromates are powerful oxidizing agents. Oxidation is carried out in an acid solution. In this process hexavalent chromium ion is reduced to trivalent chromium ion.

1. Reaction With H_2S

It oxidizes H_2S to free S in the presence of sulphuric acid.

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$
$$3H_2S + 3[O] \longrightarrow 3H_2O + 3S$$
$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$$

2. Reaction With Ferrous Sulphate

It oxidizes ferrous sulphate to ferric sulphate in the presence of sulphuric acid.

$$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$$

3. Reaction With Potassium Iodide

It oxidizes KI to iodine in the presence of H_2SO_4.

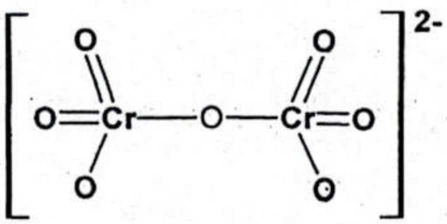
$$K_2Cr_2O_7 + 4H_2SO_4 + 6KI \longrightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2$$

4. **Chromyl Chloride Test**

When solid potassium dichromate is heated with solid metal chloride in the presence of concentrated sulphuric acid chromyl chloride is produced. This test is used for the detection of metal chlorides.

$$K_2Cr_2O_7 + 6H_2SO_4 + 4NaCl \longrightarrow 2KHSO_4 + NaHSO_4 + 2CrO_2Cl_2 + 3H_2O$$

Structure of Dichromate Ion



USES:

1. It is used in dyeing.
2. It is used in leather industries for chrome tanning.
3. It is used as an oxidizing agent.

6.7 POTASSIUM PERMANGANATE ($KMnO_4$)

It is salt of permanganic acid, $HMnO_4$. It is an unstable acid and exists only in solution.

PREPARATION

Laboratory Preparation

It is prepared by acidifying the solution of potassium manganate, $KMnO_4$ by H_2SO_4.

$$3K_2MnO_4 + 2H_2SO_4 \longrightarrow 2K_2SO_4 + 2KMnO_4 + MnO_2 + 2H_2O$$

Industrial Preparation

It is prepared from mineral pyrolusite, MnO_2. Finely powdered mineral is fused with KOH in the presence of air or an oxidizing agent like KNO_2 or $KClO_3$, etc. This gives green coloured potassium manganate, K_2MnO_4, in fused state.

$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$
$$MnO_2 + 2KOH + KNO_3 \longrightarrow K_2MnO_4 + KNO_2 + H_2O$$
$$3MnO_2 + 6KOH + KClO_3 \longrightarrow 3K_2MnO_4 + KCl + 3H_2O$$

The fused K_2MnO_4 obtained is extracted with water. The solution, after filtration, is converted into potassium permanganate ($KMnO_4$) by any of the following methods.

- **Stadeler's process:**
  In this method Cl_2 is passed through green solution of K_2MnO_4 until it becomes purple due to the formation of $KMnO_4$. Hence Cl_2 oxidizes K_2MnO_4 into $KMnO_4$.

$$2K_2MnO_4 + Cl_2 \longrightarrow 2KCl + 2KMnO_4$$

- **By Passing CO_2**
  In this process CO_2 is passed though the green solution of K_2MnO_4 until it becomes purple.

$$3K_2MnO_4 + 2H_2O + 4CO_2 \longrightarrow 2KMnO_4 + MnO_2 + 4KHCO_3$$

- **Electrolytic oxidation process:**
  In this process an aqueous solution of K_2MnO_4 is electrolyzed. Water is decomposed to give hydrogen gas at cathode and oxygen gas at anode. Oxygen liberated at anode oxidizes manganate ion $(MnO_4)^{2-}$ into permanganate ion $(MnO_4)^-$, while hydrogen is liberated at cathode.

$$3K_2MnO_4 + H_2O + [O] \longrightarrow 2KMnO_4 + 2KOH$$

  Purple solution of $KMnO_4$ obtained is filtered through asbestos. It is then concentrated and allowed to crystallize. Crystals of $KMnO_4$ deposits as deep purple-red rhombic prisms.

6.7.1 PROPERTIES

PHYSICAL PROPERTIES

- It forms dark purple lustrous crystals which gives deep pink colour in solution.
- Its solubility in water at 20^0C is only about 7%. It dissolves more at higher temperature (25% at 63^0C).

OXIDIZING PROPERTIES

Potassium permanganate is a powerful oxidizing agent. Oxidation is usually carried out in an acid solution.

1. Reaction With H_2S

It oxidizes H_2S to S.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$
$$5H_2S + 5[O] \longrightarrow 5H_2O + 5S$$
$$2KMnO_4 + 3H_2SO_4 + 5H_2S \longrightarrow K_2SO_4 + 2MnSO_4 + 5S + 8H_2O$$

2. **Reaction With $FeSO_4$**

It oxidizes $FeSO_4$ to $Fe_2(SO_4)_3$.

$$2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

3. **Reaction With Oxalic Acid**

It oxidizes oxalic acid to CO_2 and H_2O.

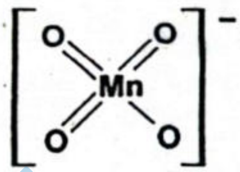
$$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

4. **Reaction With KOH**

When alkaline solution of $KMnO_4$ is heated, O_2 gas is evolved

$$2KMnO_4 + 4KOH \longrightarrow 4K_2MnO_4 + 2H_2O + O_2$$

Structure of Permanganate ion



Uses:

- It is used as an oxidizing agent.
- It is used as a disinfectant and a germicide.
- It is used in the manufacture of many organic compounds.

Q.1 Fill in the blanks.

(i) The property of paramagnetism is due to the presence of _____ electrons.
(ii) MnO_4^{1-} ion has_____ colour and $Cr_2O_7^{2-}$ has _______ colour.
(iii) When potassium chromate is treated with an acid _______ is produced.
(iv) The d-block elements are located between _____ and _____ block elements.
(v) Oxidation number of Fe in $K_4[Fe(CN)_6]$ is ______ with in $K_3[Fe(CN)_6]$ is _______.
(vi) The presence of _______ in a metal promotes corrosion.
(vii) If Cu is in contact with Aliminium _______ get corroded.
(viii) Complexes having sp^3d^2 hybridization has_______ shape.
(ix) In naming the complexes, all the ligands are named in __________.
(x) In an aqueous solution, CrO_4^{2-} and $Cr_2O_7^{2-}$ exist in the form of _______.

Answers:
(i) unpaired (ii) purple, orange red (iii) $K_2Cr_2O_7$ (iv) s, p
(v) +2, +3 (vi) impurities (vii) Al (viii) octahedral
(ix) alphabetical order (x) equilibrium

Q.2 Indicate True of False

(i) A substance, which is attrated into a magnetic field, is said to be diamagnetic.
(ii) Compounds of the transition elements are mostly coloured.
(iii) Fe^{3+} ions are blue when hydrated.
(iv) An extreme case of paramagnetism is called diamagnetism.
(v) Tin plating is used to protect iron sheets from corrosion.
(vi) In Galvanizing, Zinc prevents corrosion of iron.
(vii) Tin plated iron gets rusted more rapidly when the protective coating is damaged than unplated iron.
(viii) The name of anionic ligands in a complex end in suffix 'O'.
(ix) Pig iron contains greater percentage of carbon than steel.
(x) Complex compounds having dsp^2 hybridization have tetrahedral geometry.

Answers:
(i) False (ii) True (iii) False (iv) False (v) True
(vi) True (vii) True (viii) True (ix) True (x) False

Q.3 Multiple choice questions. Encircle the correct answer

(i) Which of the following is a non-typical transition element?
(a) Cr (b) Mn (c) Zn (d) Fe

(ii) Which of the following is a typical transition metal
(a) Sc (b) Y (c) Ra (d) Co

(iii) f-Block elements are also called
(a) non-typical transition elements (b)outer transition elements
(c) normal transition elements (d) Inner transition elements

(iv) The strength of binding energy of transition elements depends upon
(a) number of electrons pair (b)number of unpaired electrons
(c) number of neutrous (d)number of protons

(v) Group VIB of transition elements contains
(a)Zn, Cd, Hg (b)Fe, Ru, Os (c)Cr, Mo,W (d)Mn, Te, Re

(vi) Which is the formula of tetrammine chloro-nitro-platinum (IV) sulphate
(a) $[Pt(NH_3)_4(NO_2)]SO_4$ (b) $[Pt NO_2Cl(NH_3)]SO_4$
(c) $[PtCl(NO_2)(NH_3)_4]SO_4$. (d) $[Pt(NH_3)_4(NO_2)Cl]SO_4$

(vii) The percentage of carbon in different types of iron products is in the order of
(a)cast iron > wrought iron > steel (b) wrought iron > steel > cast iron
(c)cast iron > steel > wrought iron (d)cast iron = steel > wrought iron

(viii) The colulur of transition metal complexes is due to
(a)d-d transition of electrons (b) loss of s-electrons
(c)paramagnetic nature of transition elements (d) ionization

(ix) Coordination number of Pt in $[Pt\,Cl(NO_2)(NH_3)_4]^{2-}$ is
(a) 2– (b) 4 (c) 1 (d) 6

(x) The total number of transition elements is
(a) 10 (b) 14 (c) 40 (d) 58

ANSWERS TO MULTPLE CHOICE QUESTIONS

(i) Ans: (c)	(ii) Ans: (d)
Zn is a non-typical transition element because its d- orbital is completely filled. Its some properties are different from transition elements. Choice (c) is correct.	Co is a typical transition element because it shows all the properties of typical transition elements. Choice (d) is correct.
(iii) Ans: (d)	**iv) Ans: (b)**
f-block elements are also called inner transition elements. Choice (d) is correct.	The strength of binding energy of transition elements depends upon number of unpaired electrons Choice (b) is correct.
(v) Ans: (c)	**(vi) Ans: (c)**
Transition elements present in group VI-B are Cr, Mo, and W. Choice (c) is correct.	The formula of tetra-ammine chloro-nitro platinum (iv) sulphate is $[PtCl(NO_2)(NH_3)_4]SO_4$. Choice (c) is correct.

(vii) Ans: (c)	(viii) Ans: (a)
The percentage of carbon in different types of iron products is in the following order Cast iron > steel >wrought iron Choice (c) is correct.	During the formation of transition metal complexes the d- orbital split into two energy levels. One level has lower energy than original d-orbital and other has little higher energy. So when these electrons jump from lower to higher energy level and then returns to the lower energy level they emit the light. That is why the complexes of transition elements are coloured. Basically it is d-d transition of electrons. Choice (a) is correct.
(ix) Ans: (d)	**(x) Ans: (d)**
Co-ordination number of platinum in $[Pt\ Cl\ (NO_2)\ (NH_3)_4]^{2-}$ is 6 because six ligands are attached to the platinum. Choice (d) is correct.	The total number of transition elements is 58.So option (d) is correct.

Q 4. **How does the electronic configuration of valence shell affect the following properties of the transition elements?**

(a) Binding energy **(b) Paramagnetism**
(c) Melting points **(d) Oxidation states**

See Section 6.2.1

Q 5. **Explain the following terms giving examples,**

(a) Ligands **(b) Coordination sphere**
(c) Substitutional alloy **(d) Central metal atom**

See Section 6.3.1

Q 6. **Describe the rules for naming the coordination complexes and give examples.**

See Section 6.3.3

Q 7. **What is the difference between wrought iron and steel. Explain the Bessemer's process for the manufacture of steel.**

See Section 6.4.1 & 6.4.7

Q 8. **Explain the following giving reasons.**

(a) Why does damaged tin plated iron get rusted quickly?

In tin plated iron a protective layer of tin is deposited on iron. If protective coating of tin is damaged, then iron comes in contact with moisture of the air. A galvanic cell is established in which tin acts as cathode and iron acts as anode.

The electrons flow from iron toward tin. Where they discharge H^+ ions of moisture and leaving behind OH^- ions in solution.

H_2O	→	$H^+ + OH^-$
Fe	→	$Fe^{3+} + 3e^-$
$2H^+ + 2e^-$	→	H_2
$Fe^{3+} + 3OH^-$	→	$Fe(OH)_3$

Hydroxide ions react with ferric ions to form ferric hydroxide, which rapidly dissolves in the water. Therefore, tin plated iron gets rust rapidly when protective coating is damaged at any place.

(b Under what conditions does aluminium corrode?

Aluminium corrodes only, when it is in contact with those metals, which have greater reduction potential than aluminium in the presence of moisture. In the presence of moisture if aluminium is in contact with copper, silver or gold then Al is corroded. Thus two conditions are necessary for aluminium corrosion.

1. Moisture
2. Contact with metals having greater reduction potential than aluminium such as copper, gold and silver etc.

(c) How does the process of galvanizing protect iron from rusting?

The corrosion of iron can be prevented by galvanizing with zinc.

It is done by dipping clear iron sheets in a $ZnCl_2$ bath and heating. Iron sheets are removed and rolled into Zn bath and air cooled.

If protective coating of Zn is destroyed then a galvanic cell is set up. In this cell Zn acts as anode and iron as cathode. Electrons flow from Zn to iron. Thus, Zn decays while Fe remains intact. This is called sacrificial corrosion.

$$Fe^{2+} + Zn \longrightarrow Zn^{2+} + Fe$$

In this way, galvanizing protects iron form rusting. This type of galvanizing is used in water pipes.

Q 9. How chromate ions are converted into dichromate ions?

See Section 6.6.2

Q 10. Describe the preparation of $KMnO_4$ and K_2CrO_4.

See Section 6.7 & 6.6.3

Q 11. Give systematic names to following complexes,

(a) $[Fe(CO)_5]$
Pentacarbonyliron(0)

(b) $[Co(NH_3)_6]Cl_3$
Hexaminecobalt(III) chloride

(c) $[Fe(H_2O)_6]^{2+}$
Hexaquairon(II) ion

(d) $Na_3[CoF_6]$
Sodium hexafluorocobaltate(III)

(e) $K_2[Cu(CN)_4]$
Potassium tetracyanocupperate (II)

(f) $K_2[PtC1_6]$
Potassium hexachloroplatinate((IV)

(g) $[Pt(OH)_2(NH_3)_4]SO_4$
Tetraminedihyroxoplatinium(II) sulphate

(h) $[Cr(OH)_3(H_2O)_3]$
Triaquatrihydroxochromium(III)

TEST YOUR SKILLS — Marks: 85

OBJECTIVE

Time: 20 Minutes **Marks: 17**

Note: Over writing, cutting, erasing, using lead pencil will result in loss of marks.

Q1. Each question has four possible answers. Choose the correct answer and encircle it.

(i) Which is the general electronic configuration of d-block elements?
(a) $(n-1)d^{1-5}$ (b) $(n-1)d^{1-10}\ ns^2$ (c) $(n-1)d^{1-10}\ ns^1$ (d) All of the above

(ii) The oxidation state of Mn in $KMnO_4$ is
(a) +4 (b) +2 (c) +7 (d) -7

(iii) Which of the following does not show variable valency?
(a) Cr (b) Zn (c) Mn (d) Fe

(iv) Which of the following is paramagnetic?
(a) Mn^{2+} (b) Fe^{3+} (c) Fe^{2+} (d) All of above

(v) The hybridization of Cu in $[Cu(NH_3)_4]^{2-}$ is
(a) sp^2 (b) dsp^2 (c) d^2sp^2 (d) d^2sp^3

(vi) Group VIB of transition elements contain
(a) Zn,Cd,Hg (b) Fe,Ru,Os (c) Cr,Mo,W (d) Mn,Te,Re

(vii) The transition elements and their compounds are coloured due to splitting in
(a) d-orbital (b) f-orbital (c) s-orbital (d) All of the above

(viii) The first transition series ends on the element
(a) Scandium (b) Cadmium (c) Zinc (d) Mercury

(ix) The oxidation state of Fe in $K_4[Fe(CN)_6]$ is
(a) +3 (b) +2 (c) +1 (d) +4

(x) The shape of $[Co(NH_3)_6]^{3+}$ is
(a) Tetrahedral (b) Octahedral (c) Square planer (d) Pyramidal

(xi) Pig or cast iron contains carbon
(a) 0.12 to0.25% (b) 0.25 to 2.5% (c) 2.5 to 4.5% (d) 4.5 to 6.2%

(xii) Steel is manufactured by
(a) Open Hearth process (b) Bessemer process (c) Both of above (d) None of above

(xiii) Chromyl chloride test is performed to confirm
(a) Br^- ion (b) $SO_4^{\ 2-}$ ion (c) Cl^- ion (d) All of the above

(xiv) All chromates are mostly
(a) White (b) Yellow (c) Red (d) Green

(xv) Corrosion is prevented by
(a) Coating metal with paint or varnish (b) Alloying the metals
(c) Coating metal with another metal (d) All of the above

(xvi) Acidified $KMnO_4$ acts as
(a) reducing agent (b) Oxidizing agent (c) Dehydrating agent (d) all of these

(xvii) The process of zinc coating on iron is called
(a) Zn platting (b) galvanizing (c) Tin plating (d) All of the above

SUBJECTIVE

Time: 2:10 Hours **Marks: 68**

Note: Attempt any TWENTY TWO(22) questions from section-I and any THREE questions from section-II.

Section – I

Q2. Attempt any TWENTY TWO (22) questions. **(22x 2)=44**

(i) What are transition elements?
(ii) Why d-block and f-block elements are called transition elements?
(iii) Why is there a deviation in the electronic configuration of Cu and Cr?
(iv) What are typical and non-typical transition element?
(v) Explain m.p and b.p's increases upto the middle of transition series and then decreases.
(vi) In transition elements atomic size decreases at beginning then become constant and then

increase. Why?

(vii) Atomic size of transition elements do not very regularly.
(viii) What is paramagnetism?
(ix) What is the trend of Paramagnetism in transition metal series?
(x) How paramagnetic behaviour decreases on both side of transition metal series?
(xi) How colours are developed in complexes of transition metal series?
(xii) What are d-d transitions?
(xiii) Define Interstitial compounds.
(xiv) What are substitutional alloys?
(xv) Why transition metals form subsitutional alloys?
(xvi) What are coordination compounds?
(xvii) Define ligands.
(xviii) What are polydentate ligands. Give example?
(xix) What is coordination sphere?
(xx) What is coordination number?
(xxi) Define chelates. Give an example.
(xxii) What is puddling furnance?
(xxiii) What is the role of haematite. Lining during puddling of cast iron?
(xxiv) How entrapped air is removed from molten iron?
(xxv) Why aqueous solution of K_2CrO_4 and $K_2Cr_2O_7$ show similar chemical properties?
(xxvi) How chromate ions are converted into dichromate ions?
(xxvii) Define corrosion.
(xxviii) What is tin plating (cathode coating)?
(xxix) What is galvanising or Zn coating?
(xxx) What is chromyl chloride test?
(xxxi) Under what conditions Aluminium metal corrode.
(xxxii) How does $K_2Cr_2O_7$ act as an oxidising agent?
(xxxiii) What is sacrificial corrosion?

Section – II (Attempt any three questions) (8x 3)=24

Q. 3. (a)Discuss the following properties of transition elements. **(05)**

(i) Paramagnetism (ii) Oxidation state

(b)Draw structures of chromate, dichromate and permanganate? **(03)**

Q. 4. (a) Discuss briefly the complex compounds along with chelates? **(05)**

(b) How does $K_2Cr_2O_7$ reacts with the following? **(03)**

(i) H_2S (ii) $FeSO_4$ (iii) NaCl

Q. 5. (a)What is geometry of the following complexes? **(04)**

(i) $[MnCl_4]^{2-}$ (ii) $[PCl_5]$ (iii) $[Cu(NH_3)_4]^{2-}$ (iv) $[Co(NH_3)_6]^{3+}$

(b)Describe the process of manufacturing of wrought iron from cast iron? **(04)**

Q. 6. How steel is manufactured by open hearth and Bessemer process? **(08)**

Q. 7. (a)How electrochemical theory explain corrosion? **(03)**

(b)Give systematic names to the following compounds. **(05)**

(i) $K_4[Fe(CN)_6]$ (ii) $[Pt\ Cl_2\ (NH_3)_4]SO_4$ (iii) $[Cr\ (OH)_3\ (H_2O)_3]$

(iv) $[Co(NH_3)_6]Cl_3$ (v) $[Fe(H_2O)_6]^{2+}$