# Transition Metals

1) Characteristics of transition metals.
2) Oxidation states of transition metals.
3) Complex ions and metal Complexes.
4) Shape of Complex ions.
5) d-orbitals in complex ions for octahedral complexes.
6) Reasons for colour of transition metal compounds.
7) Catalytic property of transtition metals.

## # Transition metal.

→ Those d-block elements which have partially or incompletely filled d-orbitals in their atomic or ionic state are called transition metals.

OR

Those elements that lies between s-block and p-block elements and show transitional behavior.

There are four transition series in modern periodic table.

a) First transition series or 3d series. → Not typical or not transitional metal
   Scandium (z=21) to zinc (z=30)
b) Second transition series or 4d series.
   Yttrium (z=39) to Cadmium (z=48)
c) Third transition series or 5d series.
   Lanthanum (z=57) and Hafnium (z=72) to Mercury (z=80)
d) Fourth transition series or 6d series.
   Actinium (z=89) and Rutherfordium (z=104) to Copernicium (z=112)

Q. Why zinc, Cadmium and mercury are not transition metal.
Q→ Because due to completly filled of electron. So, it is d-block element and not transition metal.

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

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# General characteristics of transition metals.

- The general electronic configuration of transition metal is $(n-1)d^{1-10}ns^{1-2}$ where d subshell is partially filled
- They have high melting and boiling point due to participation of more number of unpaired electrons during chemical bonding.
  - More is the number of unpaired electrons higher is the melting and boiling point.
- They have high enthalpy of atomization due to strong metallic bonding.
- They show variable oxidation states and valencies due to comparable energy of (n-1)d and ns orbital.
- Due to their similar atomic size they can form alloys with each other or with other elements.
- They show catalytic property due to partially filled d-orbital.
- Transition metal compounds are coloured. The colour arises due to transition of electrons from lower energy d-orbitals to higher energy d-orbital which is known as d-d transition.
- They have tendency to form complex ions/compounds due to partially filled d-orbital.

Examples:-

$[Cu(NH_3)_4]SO_4$ → Tetramine Copper sulphate

$[Ag(NH_3)_2]Cl$ → Diammine Silver Chloride

$[Cr(H_2O)_6]^{+++}$ → Hexa aqua Chromine

- Transition metals and their compounds show paramagnetic property due to presence of unpaired electrons in d-orbitals.

Mathematically,

Magnetic moment ($\mu$) = $\sqrt{n(n+2)}$ BM, where n = number of unpaired electrons.

Q. Calculate the magnetic moment of Fe.

$Fe(26) = [Ar]4s^2 3d^6$

| ↑↓ | ↑ | ↑ | ↑ | ↑ |
|---|---|---|---|---|

$n = 4$

$\mu = \sqrt{4(4+2)} = \sqrt{24} = 4.89$ BM

The elements with $d^0$ or $d^{10}$ electronic configuration are diamagnetic in nature.

| II B/12 |
|---|
| $30^{Zn}$ |
| $48^{Cd}$ |
| $80^{Hg}$ |

# Non typical transition metals.

Those d-block elements which have completely filled d-orbitals and do not show the characteristic properties of true transition metals are called non-typical transition metals. Zn, Cd & Hg are non-typical transition metals

# Characteristics of non-typical transition metals

a) The general electronic configuration is $(n-1)d^{10}ns^2$.
b) They have low melting and boiling point due to the absence of unpaired electrons.
c) They do not show variable valency and oxidation state.
d) They do not form coloured compounds (i.e. their compounds are colourless.)

Examples :- $ZnSO_4$, $ZnCO_3$, $ZnO$

e) They are diamagnetic in nature. (completely filled d-orbitals)

# Oxidation state of transition metals

Transition metals show variable oxidation states except first and last member of each, all other transition metals exhibit variable oxidation state.

The main reason for this is due to the fact that there is only a small difference in energy of electrons of $(n-1)d$ and ns-orbitals. This results involvement of electrons of both orbitals in bonding. The oxidation states of transition metals depends of number of d-orbitals.

The variable oxidation states of 3d series are:-

| Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|---|---|---|---|---|---|---|---|---|---|
| +3 | +2 | +2 | +2 | +2 | +2 | +2 | +2 | +1 | +2 |
| | +3 | +3 | +3 | +3 | +3 | +3 | +3 | +2 | |
| | +4 | +4 | +4 | +4 | +4 | +4 | +4 | | |
| | | +5 | +5 | +5 | +5 | | | | |
| | | | +6 | +6 | +6 | | | | |
| | | | | +7 | | | | | |

Highest oxidation state of 3d series is +7 i.e. Mn

# The highest oxidation state shown by transition metal is +8.

Ruthenium (Ru) = 4d series

Osmium ($O_s$) = 5d series

# Complex ion and Metal complex

Complex ion is defined as an electrically charged species formed by combination of central metal cation (T. M.) and ligands. The charge on complex ion may be +ve or -ve.

Example:- $[Cu(NH_3)_4]^{++}$, $[Ag(NH_3)_2]^{+}$, $[Cr(H_2O)_6]^{+++}$, $[Ni(H_2O)_6]^{++}$, $[Fe(CN)_6]^{4-}$, $[Ag(CN)_2]^{-}$, $[CuCl_4]^{--}$.

# Note:-

The total charge of complex ions is algebrain sum of charge of central atom and charge of ligands.

Example:-

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

  Charge of Fe = +2

  Charge of CN = -1

  Charge of 6CN = -6

  Total charge of complex ion = +2 + (-6)

  = -4

* $[Cr(H_2O)_6]^{+++}$

  Charge of Cr = +3

  Charge of $H_2O$ = 0

  Total charge of complex ion = +3+0

  = 3

# Note:-

1) Positively charged complex ion are called cation is complexes.

2) Negatively charged complex ion are called anion is complexes.

For example

1) $[Cu(NH_3)_4]^{++}$
2) $[Ni(H_2O)_6]^{++}$

# Reasons for formation of complex ions

a) They have vacant d-orbital which have appropriate energy to accept lone pair of electrons from ligands (L → M).
b) They have small atomic size and high charge density due to which they can attract lone pair of electrons from ligands.

MCQs.

Transition Metal can form complex ions due to
a) presence of vacant d-orbital
b) Small atomic size
c) High charge density
d) All of above

# Metal Complex / Complex Compound

An addition compound that contain atleast one complex ion (either cation or anion complex) and cannot be disassociated into its constituents ions is called complex compound

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

$$[Cu(NH_3)_4]SO_4 \longrightarrow [Cu(NH_3)_4]^{++} + SO_4^{2-}$$

During formation of complex compound, there exist coordinate covalent bond between ligand and central metal cation. Thus, complex compound are called Co-ordination compounds.

* Terms used in complex compound.

1.) Centre of co-ordination :- It is the central metal cation in which ligands are attached by forming co-ordinate covalent bond.

For example :-

$[Cr(NH_3)_6]Cl_3$

$Cr^{+++}$ → centre of co-ordination

$NH_3$ → ligand.

2.) Ligand :- Molecular or ionic species that are capable of donating lone pair of electrons to central metal cation are called Ligands. They are electron rich species and they may be +ve, -ve & neutral.

Eg :-

$Cl^-$, $F^-$, $CN^-$, $C_2O_4^{--}$, $OH^-$, $NH_3$, $H_2O$, EDTA, NO, CO

Ethylene diammine (en), $NO_2^+$

MCQs

* Ligands are Lewis base : capable to donate lone pair of electrons. ~~Central metal cations are Lewis acid.~~

* Central metal cations are Lewis acid : Capable to accept lone pair of electrons.

On the basis of point of attachment (no. of coordinate covalent bond formed), ligands are of following types.

a) Monodentate ligand / Unidentate ligand

→ The ligand which have only one point of attachment or which can form only one coordinate covalent bond with central metal cation.

Examples:- $F^-$, $Cl^-$, $OH^-$, $CN^-$, $NH_3$, $H_2O$, etc

b) Bidentate ligand

→ The ligand which have two point of attachment or which can form two co-ordinate bond with central metal cation.

Examples:- $CO_3^{--}$, $SO_4^{--}$, $C_2O_4^{--}$ (Oxalato), $H_2\ddot{N}-CH_2-CH_2-\ddot{N}H_2$ (ethylene diamine) (en)

c) Polydentate ligand

→ The ligands which can donate more than two lone pair of electrons is called polydentate ligand.

MCQ Eg:- EDTA → Hexadentate ligand.

3.) Co-ordination Number :- The number of ligands attached to central metal cation is coordination number of complex compound.

Examples:-

$[Cu(NH_3)_4]SO_4$ — Coordination Number = 4

$[Cr(H_2O)_6]^{+++}$ — Coordination number = 6

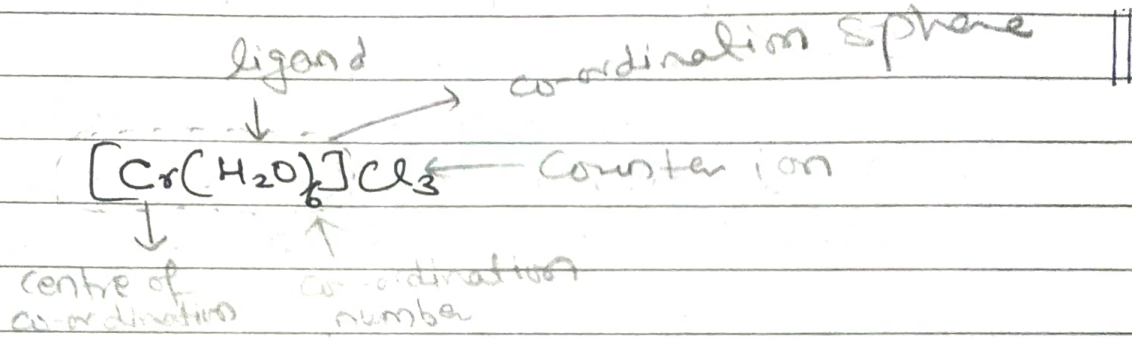
$K_4[Fe(CN)_6]$ — Co-ordination Number = 6

$[Ag(NH_3)_2]Cl$ — Co-ordination Number = 2

4.) **Co-ordination sphere :-** The central metal cation and ligands enclosed inside a square bracket is co-ordination sphere. It behaves as ~~co-ordination~~ single entity.

**Example:-** $[Cu(NH_3)_4]^{++}$

#




## MCQs

1.) Which is not a ligand for a transitional metal complex?
a) CO b.) $CO_2$ c) NO d.) $NH_3$

2.) Which of the following is not a metal complex?
a) $k_3[Fe(CN)_6]$ b.) $k_4[Fe(CN)_6]$
c.) $[Cu(NH_3)_4]SO_4$ d.) $FeSO_4(NH_4)_2SO_4$ 6H2O Mohr's salt

3.) During formation of complex, ligands and transition metal forms
a) ionic bond b.) Covalent bond
c) Hydrogen bond d.) Coordinate covalent bond

4.) EDTA is a multidentate ligand. Its denticity or multiplicity is
a) 2 b.) 4 c) 5 d.) 6

# Shape of complex ions: Werner's coordination theory

Werner's proposed a theory to explain the formation, shape and important properties of complex compounds.

postulates

a) In complex compounds, central metal cation exhibits two types of valency.
   i) Primary valency  ii) Secondary valency.

b) Primary valency refers to the oxidation state of central atom which is satisfied by negative ions while the secondary valency refers to coordination number which is satisfied by ligands.

c) Primary valency is non-directional while secondary valency is directional and directed towards the fixed position in the space around the central atom.

Thus, the geometry (shape) of complex ion is determined by secondary valency or coordination number.

* Shapes of complex ion

a) Linear complex ion ($ML_2$)

→ The complex ion will have linear geometry when two ligands are attached to central atom or coordination number is 2. The bond angle between metal and ligands is 180°. Such complexes are formed by sp hybridization

Example

$[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$, $[Cu(NH_3)_2]^+$

$[H_3N: \rightarrow Ag \leftarrow :NH_3]^+$

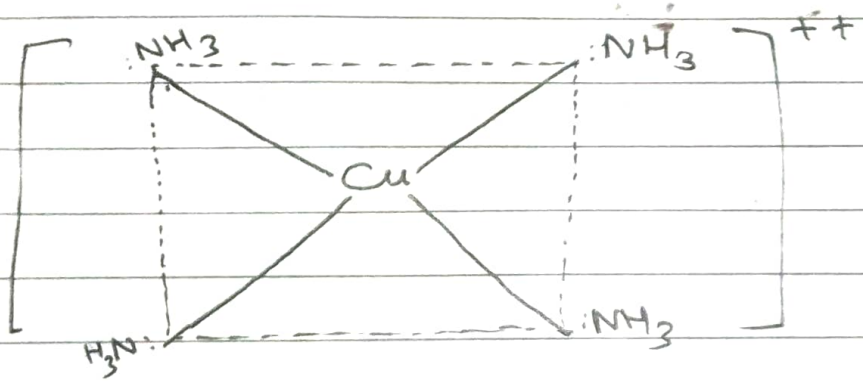
b) Square planar complex ion ($ML_4$)

→ The complex ion will have square planar geometry when four ligands are attached to central atom or coordination number is 4. The bond angle between metal and ligands is 90°. Such complexes are formed by $dsp^2$ hybridization. The central metal has $d^8$ electronic configuration.

Example :-

$[Cu(NH_3)_4]^{++}$, $[Ni(CN)_4]^{2-}$, $[Pt(NH_3)_4]^{2+}$

1)




① $[Cu(NH_3)_4]^{++}$

$Cu(G.S.) = [Ar]$ 3d: ↑↓ ↑↓ ↑↓ ↑ ↑ ; 4s: ↑

$Cu^{++} = [Ar]$ 3d: ↑↓ ↑↓ ↑↓ ↑ ↑ ; 4s: ☐

$[Cu(NH_3)_4]^{++} = [Ar]$ 3d: ↑↓ ↑↓ ↑↓ ↑↓ xx ; 4s: xx ; 4p: xx xx 1

$NH_3$ $NH_3$ $NH_3$ $NH_3$

$dsp^2$

Tetraammine ion copper is paramagnetic.

② $[Ni(CN)_4]^{2-}$

$Ni(G.S.) = [Ar]$ 3d: ↑↓ ↑↓ ↑↓ ↑ ↑ ; 4s: ↑↓

$Ni^{++} = [Ar]$ 3d: ↑↓ ↑↓ ↑↓ ↑↓ 1 ; 4s: ☐ ; 4p

$[Ni(CN)_4]^{2-} = [Ar]$ 3d: ↑↓ ↑↓ ↑↓ ↑↓ xx ; 4s: xx ; 4p: xx xx ☐

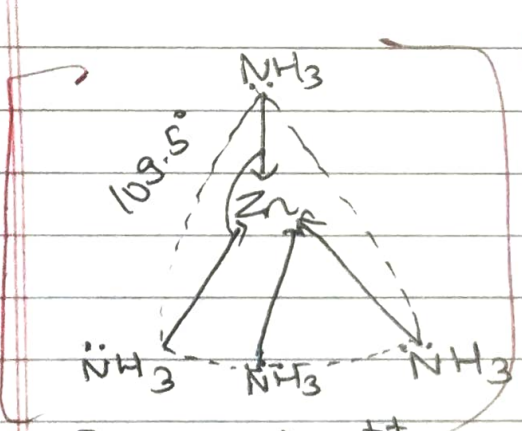
$d^8$ $CN^-$ $CN^-$ $CN^-$ $CN^-$

c) Tetrahedral Complex ion

→ The complex ion will have tetrahedral geometry when 4 four ligands are attached to central metal atom or co-ordination number is 4. The bond angle between metal and ligands is 109.5°. Such complexes are formed by $sp^3$ hybridization. The central metal has $d^0$ or $d^{10}$ electronic configuration.

Example:-

$[Zn(NH_3)_4]^{++}$, $[NiCl_4]^{2-}$, $[Ni(CO)_4]$




$Zn(30) = [Ar]\ 4s^2\ 3d^{10}$

$Zn^{++} = [Ar]\ 4s^0\ 3d^{10}$

① $[Zn(NH_3)_4]^{++}$

| | 3d | 4s |
|---|---|---|
| $Zn(G.S.)$ = [Ar] | ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ | ↑↓ |
| $Zn^{++}$ = [Ar] | ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ | |
| $[Zn(NH_3)_4]^{++}$ = [Ar] | ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ | ✕✕ ($NH_3$) ✕✕ ✕✕ ✕✕ ($NH_3$ $NH_3$ $NH_3$) |

② $[NiCl_4]^{2-}$

| | 3d | 4s |
|---|---|---|
| $Ni(G.S.)$ = [Ar] | ↑↓ ↑↓ ↑↓ ↑ ↑ | ↑↓ |
| $Ni^{++}$ = [Ar] | | |

d) Octahedral complex ion ($ML_6$)

→ The complex ion will have octahedral geometry when six ligands are attached to central metal cation or coordination number is 6. The bond angle between metal and ligands is

The octahedral complex may be

a) Inner-orbital octahedral complex ($d^2sp^3$)

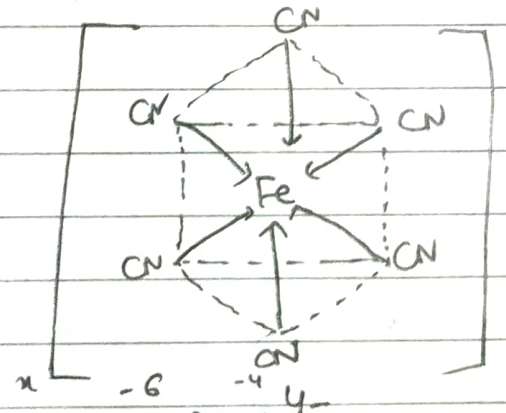
b) Oute-orbital octahedral complex. ($sp^3d^2$)

a) Inner-orbital octahedral complex:

→ Such complexes are formed when $(n-1)d$ orbital participate in hybridization. They have $d^2sp^3$ hybridization

Eg:-

$[Fe(CN)_6]^{4-}$, $[Co(CN)_6]^{3-}$, $[Cr(NH_3)_6]^{3+}$




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

$Fe(GS) = [Ar]$ ↑↓ ↑↓ ↑↓ ↑ ↑ ↑↓

$Fe^{++} = [Ar]$ ↑↓ ↑ ↑ ↑ ↑

$[Fe(CN)_6]^{4-} = [Ar]$ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ | ↑↓ | ↑↓ ↑↓ ↑↓

4s 4p

$CN^-$ $CN^-$ | $CN^-$ | $CN^-$ $CN^-$ $CN^-$

→ $CN^-$ being strong ligand, it can pair up unpaired electrons.

→ This complex ion is diamagnetic in nature.

→ Such complexes are called low spin complexes.

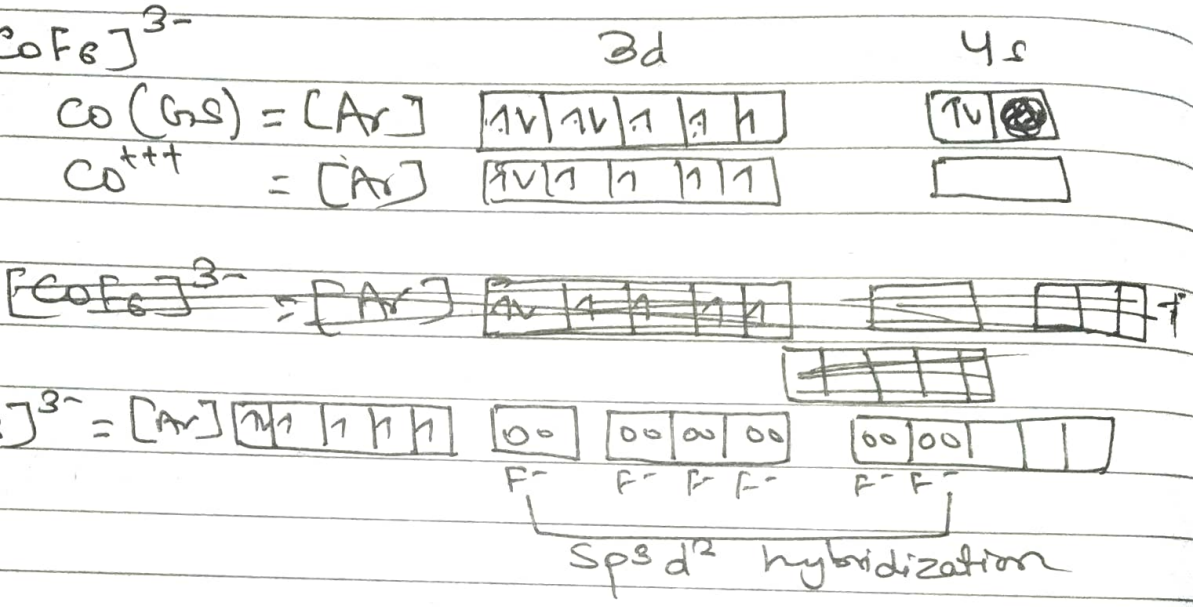
b) Outer-orbital octahedral complex ion:-

→ Such complexes are formed when nd orbital participate in hybridization. They have $sp^3d^2$ hybridization.

Example:-

$[FeF_6]^{3-}$, $[CoF_6]^{3-}$, $[Fe(H_2O)_6]^{2+}$

$[CoF_6]^{3-}$




→ $F^-$ being weak ligand, it cannot pair up unpaired electrons.

→ This complex is highly paramagnetic in nature.

→ Such complexes are called high spin complexes

# ~~Crystal field~~

# d-orbitals in complex ion (simple explanation by crystal field theory) for octahedral complexes.

# Crystal field theory (CFT)

This theory was proposed by Hans Bethe and modified by Van Vleck. It assumes that the

attraction between central metal cation and ligand is electrostatic ie. purely ionic in nature. This theory is more successful in interpreting many important properties like colour and magnetic behaviour of complexes.

## Assumptions of CFT

a) This theory considers complex as a combination of central metal cation surrounded by suitable ligands. Ligands are treated as point charges or point dipoles.

b) The bonding between central metal cation and ligand arises due to electrostatic attraction.

c) The attraction between central metal ion and ligand is purely ionic type.

d) The interaction between the electrons of ligands and electrons of metal is entirely repulsive in nature. It is these repulsive force that is responsible for splitting of d-orbitals.

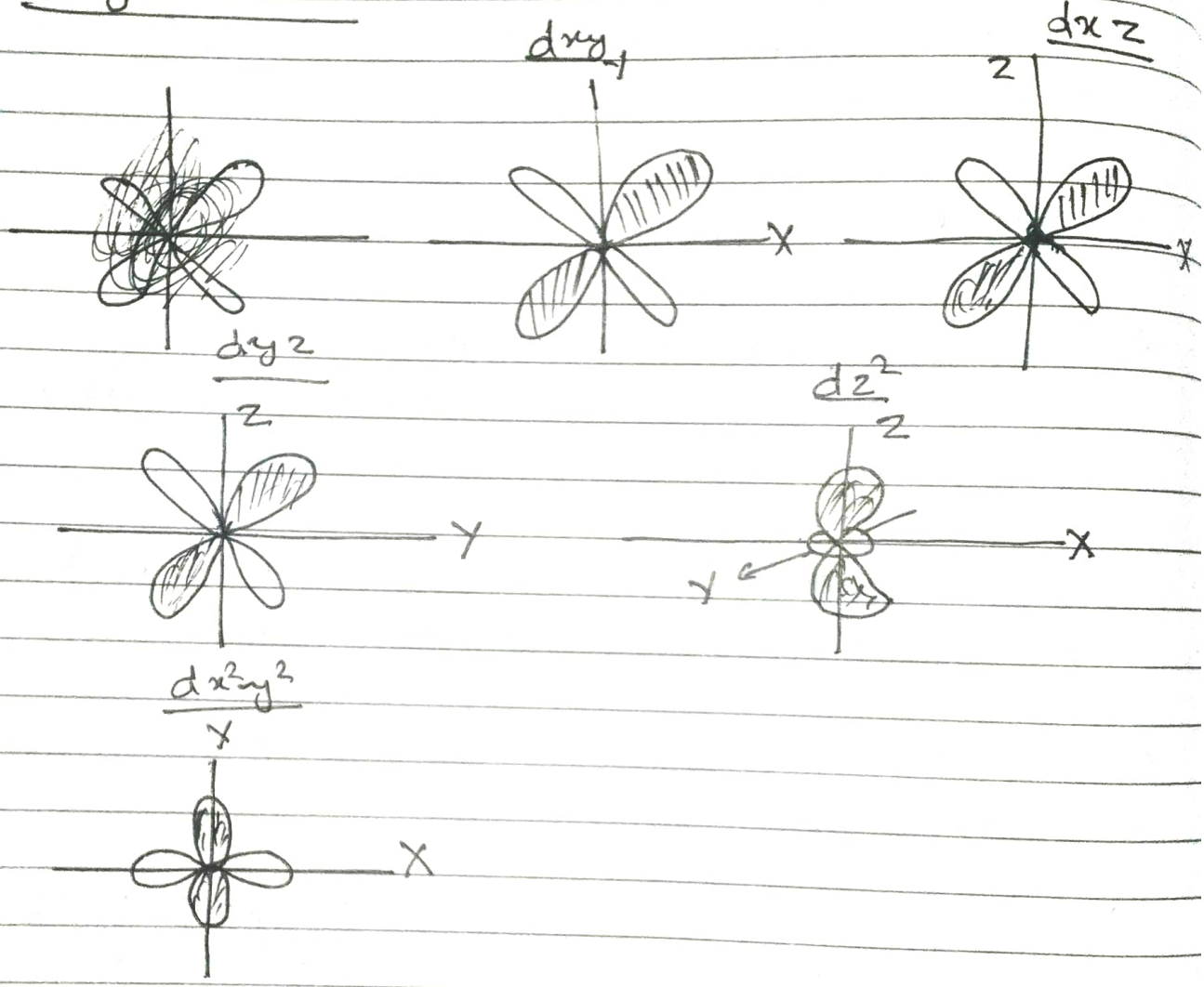
e) The d-orbitals which are degenerate have their degeneracy destroyed by the approach of ligands during the complex formation.

Q. Degenerate d-orbitals :- The five d-orbitals with equal energy is called degenerate d-orbitals.

eg orbitals → $dx^2-y^2$, $dz^2$

Five d-orbitals ($dxy$, $dyz$, $dxz$, $dx^2-y^2$, $dz^2$)

$t_{2g}$ orbital




# Crystal field theory for octahedral complexes

1. In octahedral complex, the metal is at the centre of octahedron and ligands are at six corners.

2. The lobes of eg orbitals ($dx^2-y^2$, $dz^2$) point along the axes while the lobes of $t_{2g}$ orbitals ($dxy$, $dyz$, $dxz$) lie between the axes.

3. The lobes of eg orbital that lie along the axes are closer to the direction of ligands while the lobes of $t_{2g}$ orbitals are somewhat far from the direction of ligands and experience lesser repulsion.

4. The lobes of eg orbitals are strongly repelled than $t_{2g}$ orbitals.

5. Thus, the approach of 6 ligands increases the energy of eg orbitals and the energy of $t_{2g}$ orbitals is lowered.

6. In presence of six ligands, the degenerate d-orbitals split into two sets with different energy as shown in diagram.

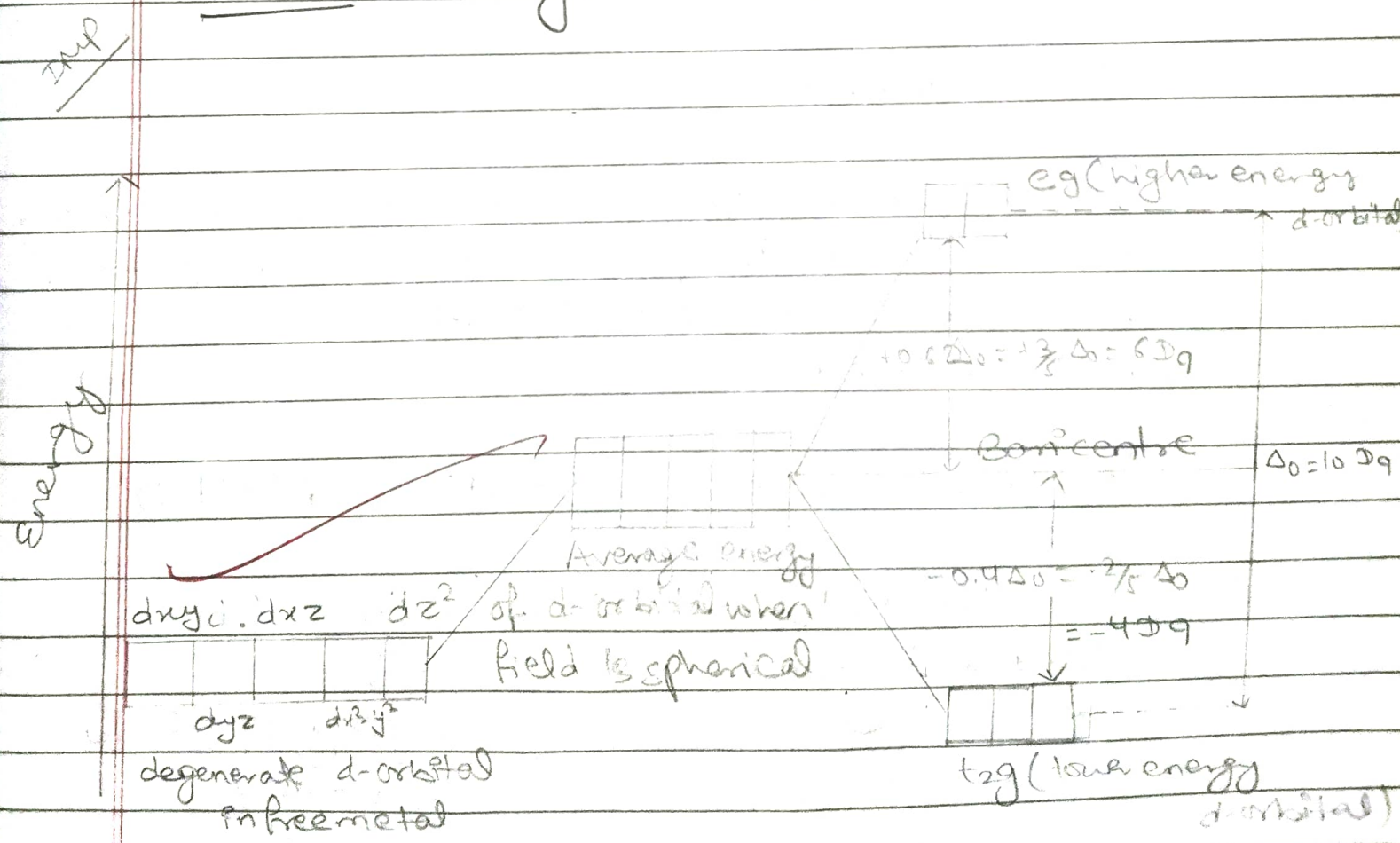



Fig. Crystal field splitting in Octahedral complex

$eg \rightarrow dx^2-y^2, dz^2$

$t_2g = dxy, dxz, dyz$

The increase in energy of 4 eg electron is equal to decrease in energy of 6 $t_2g$ electrons.

* Crystal field splitting :- The splitting of five degenerate d-orbitals into two sets ie. eg and $t_2g$ with different energy is called crystal field splitting.

* Crystal field splitting energy : The energy difference between two sets of d-orbital is called crystal field splitting energy (CFSE)

The magnitude of crystal field splitting depends on the field provided by ligands.

## Spectrochemical series

The arrangement of common ligands in ascending order on the basis of crystal field splitting is called spectrochemical series.

weak Field ligand

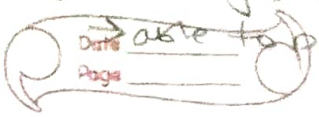
$I^- < Br^- < S^{--} < Cl^- < NO_3^- < F^- < OH^- < C_2O_4^{--} < H_2O$

$EDTA < NH_3 < en < NO_2^- < CN^- < CO$

Strong field ligand ↑ Strongest field ligand.

For high spin complex: $\Delta_0$ → weak field ligand → unable to pair up → Paramagnetic

$\Delta_0$ → strong field ligand → able to pair up




# High spin complex and low spin complex

High spin complex :- When $\Delta_0 < P$ (P = mean pairing energy) the electrons tend to remain unpaired and the electrons first occupy lower energy d-orbital ($t_{2g}$) and then occupy higher energy d-orbital ($e_g$).

For example,

$$d^4 = t_{2g}^3 e_g^1$$
$$d^6 = t_{2g}^4 e_g^2$$

Low spin complex :- When $\Delta_0 > P$, the electrons tend to pair up and the electrons first occupy lower energy d-orbital completely and then occupy higher energy d-orbital.

Examples

$$d^4 = t_{2g}^4 e_g^0$$

$$d^6 = t_{2g}^6 e_g^0$$

# Reason for color of transition metal compounds

Transition metal compounds are coloured due to following reasons:-

(a) Incompletely filled d-orbital (d-d transition)
(b) Charge transfer
(c) Polarization.

## @ Incompletely filled d-orbital

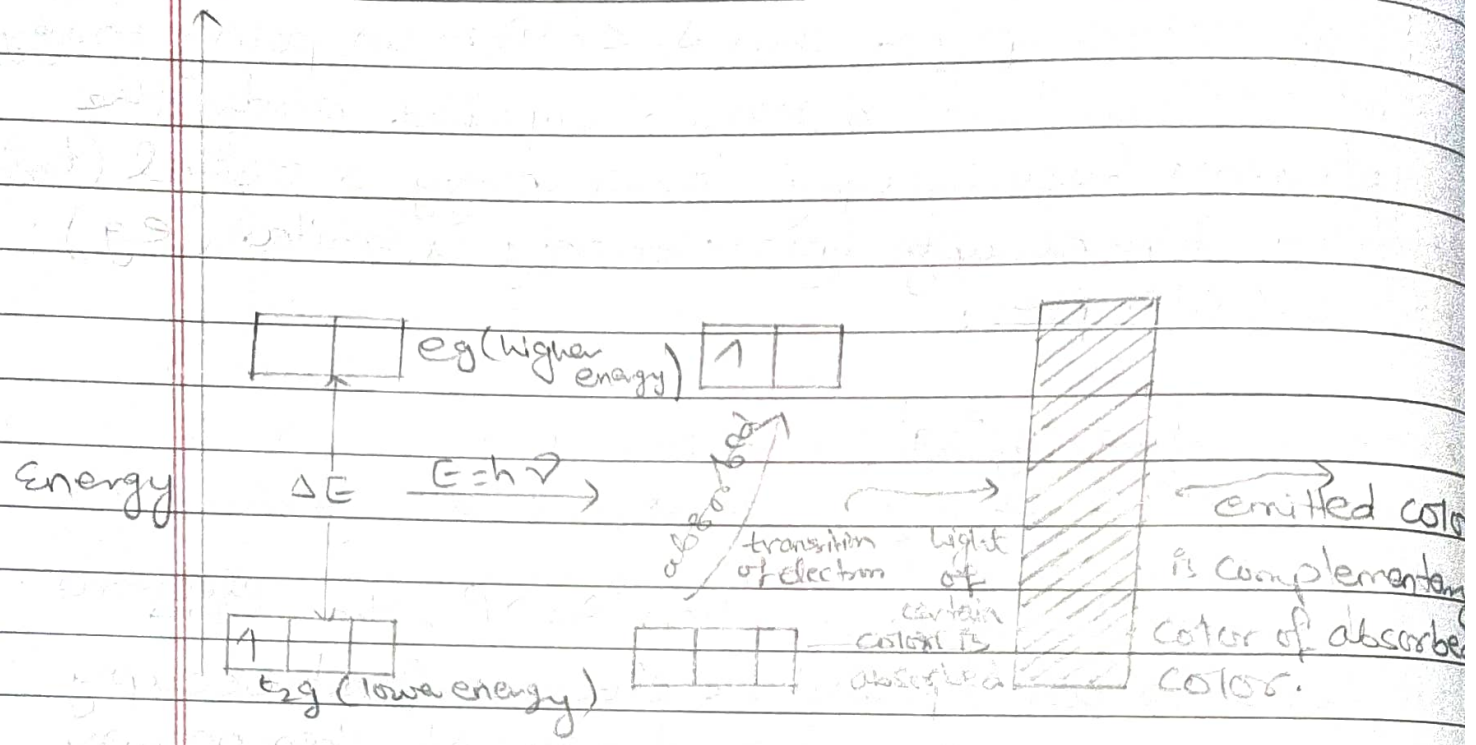
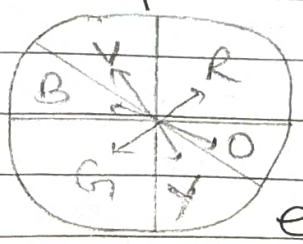



Fig. d-d transition.

Transition metals have partially filled d-orbitals of their penultimate shell due to which there possibility of transition of electrons from lower energy d-orbital ($t_{2g}$) to higher energy d-orbital ie. d-d transition ($t_{2g} \leftrightarrow eg$) is possible. The energy difference between these two d-orbitals is such that the wavelength of radiation emitted during this transition lies within the visible range of the spectrum. Hence most of the transition metal compounds are coloured.




complementary colour of each other.

$[Fe(H_2O)_6]^{++}$ ⟶ Green

$[Mn(H_2O)_6]^{++}$ ⟶ Pink

$[Cu(H_2O)_6]^{++}$ ⟶ Blue

⑥ Charge transfer

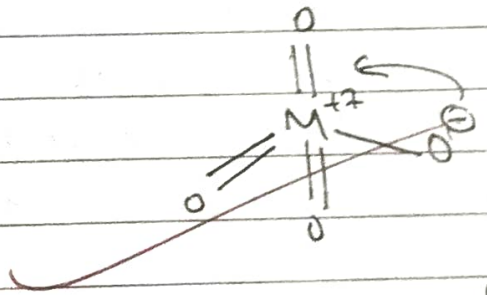
Sometime, the colour of transition metal compounds is due to the result of charge transfer in which absorption of light allows the electron to move from one ion to another ion resulting in the temporary change in the valence state of both ions. For example.

$$Fe^{++} + Ti^{++++} \longrightarrow Fe^{+++} + Ti^{+++}$$

The pink colour of $KMnO_4$ is not dele to d-d transition, it is due to transfer of charge from oxygen(O) to Manganese(Mn), reducing the oxidation state of Mn from (+7) to (+6)

Eg:-

$$KMnO_4 \longrightarrow K^+ + MnO_4^-$$




Q. Is the pink colour of $KMnO_4$ explained by d-d transition?

⇒ No, the pink colour of $KMnO_4$ is not explained by d-d transition. It is because ~~the pt~~ in $KMnO_4$, Mn is in +7 state i.e. there is no deelectron means no posibility of d-d transition. Thus, the colour is due to transfer of charge from O to Mn reducing the

oxidation state of Mn from +7 to +6.

# Catalytic property of transition metal

Catalytic property of transition metal can be explained on the basis of following theory.

a) Adsorption theory :-

The solid surface of transition metals provide sites for adsorption of reactant molecules. The occlusion property of transition metal weaken the bond of reactant and increases the rate of chemical reaction (ie. acts as catalyst)

b) Intermediate product formation theory :-

Transition metals have incompletely filled d-orbital and can show variable oxidation states due to which these elements can form unstable intermediate product with reactants providing alternative path with lower activation energy. Hence, the rate of reaction increases. The unstable intermediate product readily decomposes to give final product and catalyst.

Reactants (x+y) + Transition metal Catalyst (C) ⟶ Unstable intermediate product (x·y·c)

Unstable intermediat product (x·y·c) ⟶ Final product (z) + Transition metal (C).

# Some examples were transition metals act as catalyst

| | Transition metal | Application |
|---|---|---|
| 1. | Ni/Pd | Hydrogenation process (conversion of vegetable oil to vanaspati ghee |
| 2. | Finely divide Fe | Haber's process (Manufacture of ammonia) |
| 3. | Pt/Rh | Ostwald process (Manufacture of $HNO_3$) |
| 4. | $MnO_2$ | Thermal decomposition of $KClO_3$ |
| 5. | $V_2O_5$ | Contact process (Conversion of $SO_2$ to $SO_3$) |
| 6. | $TiCl_4$ | Zieglar Natta catalyst (Polymerization of alkenes) (Ethene to polyethene) |

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