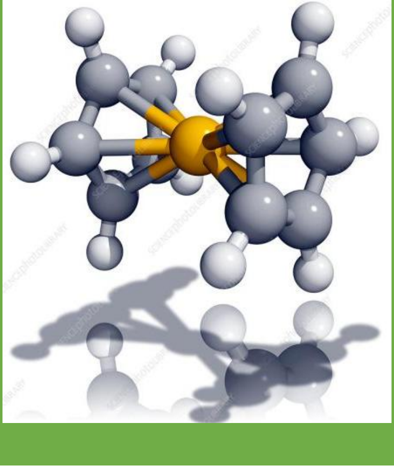
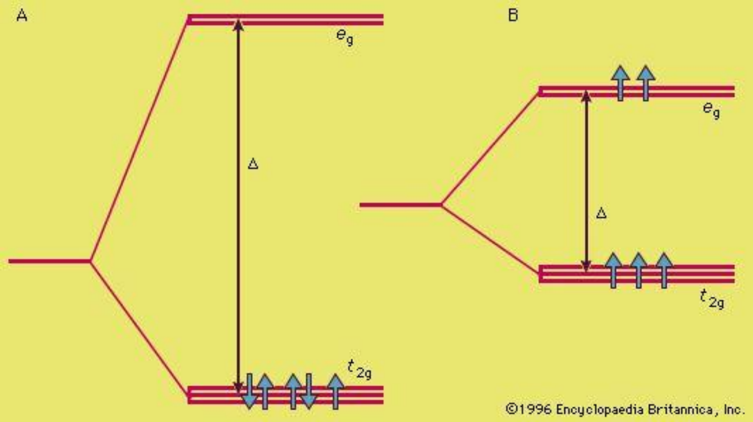
CHEMISTRY
M.Sc. Second Semester
INORGANIC CHEMISTRY
MSCCH-506





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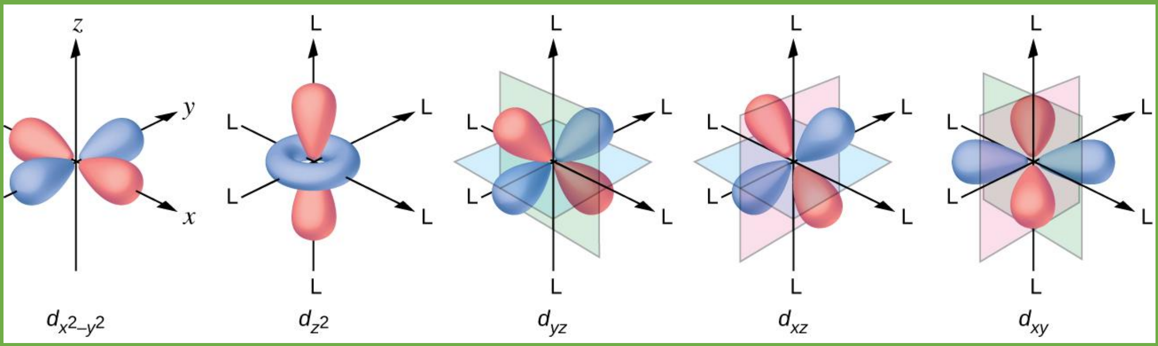

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DEPARTMENT OF CHEMISTRY
UTTARAKHAND OPEN UNIVERSITY HALDWANI

MSCCH-506

INORGANIC CHEMISTRY-II

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REACTION MECHANISM OF TRANSITION METAL COMPLEXES - I

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Unit-First

REACTION MECHANISM OF TRANSITION METAL COMPLEXES-I

1.1 INTRODUCTION :

Synthesis of coordination compounds has always been an important and major part of modern chemistry. This chapter mainly focus on the discussion of reaction and their mechanism occurs in coordination compounds, which are either substitution reactions or oxidation-reduction reactions. Substitution reactions are those in which only change in coordination of transition metal takes place; however, the oxidation state of metal ion remains unchanged. Oxidation-reduction reactions are those in which electrons are transferred between two metal atoms without change in coordination of both the metal atoms in coordination compounds. Reactions of coordination compounds have some similarities with reactions of other molecules those may be organic or inorganic. Therefore, to understand the various reactions of coordination compounds the familiar concepts of those similar reactions of other organic and inorganic molecules may be used. However, due to more complex geometries and more possibilities for rearrangement in coordination compounds the metal atoms exhibit more inconsistency in their reactions; therefore, some additional and different factors also influence the nature of reactions. The reactions of coordination complexes may be divided as; a) Substitution reactions at the metal center (it involve both S_N^1 and S_N^2 types of reaction mechanisms); b) oxidation-reduction reactions; and c) reactions of ligands that do not change the attachments to the central metal atom.

Although, it is still a matter of continuous study to predict products and to select appropriate reaction conditions to achieve the desired product. However, the current knowledge and huge number of known reactions is now sufficient (but not complete) to provide considerable information.

1.2 OBJECTIVES :

At the end of this unit learner would be able to know

- Importance of synthesis of coordination compounds

- Various types of reactions involve in coordination compounds
- Geometrical consideration of intermediate formed in the reactions of coordination compounds
- About the reactivity and inertness of the complexes
- Various kinds of hydrolysis reaction of coordination compounds and their mechanism
- How to derive the rate law expression of these reactions (i.e. kinetic study)
- Which are the factors that can influence the rates of hydrolysis reactions of coordination compounds
- What are the anation reactions

1.2 ENERGY CONSIDERATION OF A REACTION :

The energy consideration for a reaction is an important parameter for its successful completion. In general, all chemical reaction occurs with migration from one energy minimum (the reactants) through a high energy transition state (TS) to another energy minimum (the product). Let us consider a reaction (as given) in which reactant A and B-C react together to give A-B and C as product.

$$A + B\text{-}C \longrightarrow A\text{-}B + C$$

The energy profile diagrams for the possible changes of energy of above transformation are presented in figure 1.1 and figure 1.2. From the given figure the formation of product takes place via the formation of a transition state which involves the formation of an activated complex [A···B···C].

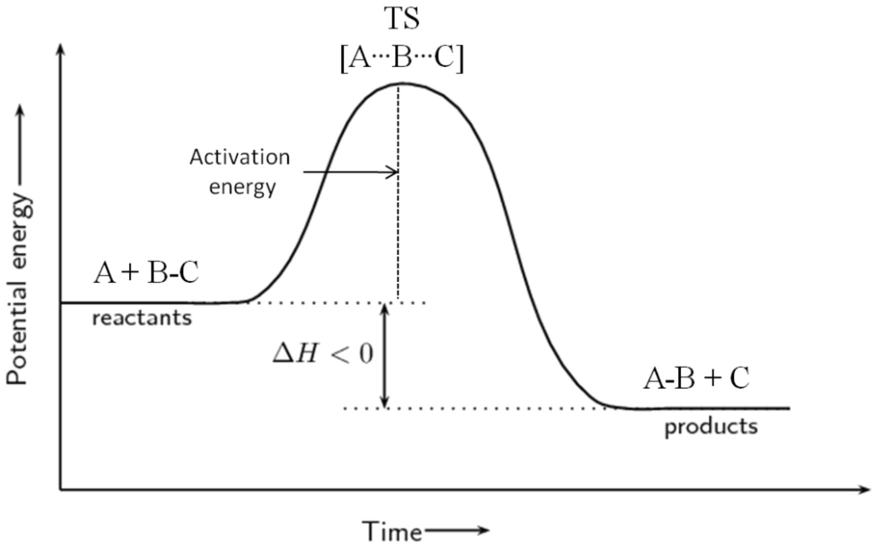


Figure 1.1: Energy profile diagram for exothermic reaction

The activated complex is the highest energy complex molecule with partial bonds forms along the reaction pathway; it cannot be isolated since it is a hypothetical state of formation of complex molecule. The energy required for the formation of such activated complex is the known as activation energy and it would be the difference between the energy of reactants and the energy of the activated complex. Depending on the energy of reaction (*i.e.* energy difference between reactants and products), reactions can be classified in to two category; 1) exothermic reaction and 2) endothermic reaction. An exothermic reaction is that in which energy of reaction (*i.e.* energy difference between reactants and products) ΔH is negative (-ve); however, an endothermic reaction is that in which energy of reaction (*i.e.* energy difference between reactants and products) ΔH is positive (+ve). For every exothermic reaction, the reactant has higher energy than that of product. Thus for an exothermic reaction energy is released during the formation of product. Similarly, for every endothermic reaction, the reactant has higher energy than that of product, and thus the energy is required to perform the reaction. The energy profile curve for exothermic reaction and endothermic reaction are shown in figure 1.1 and figure 1.2.

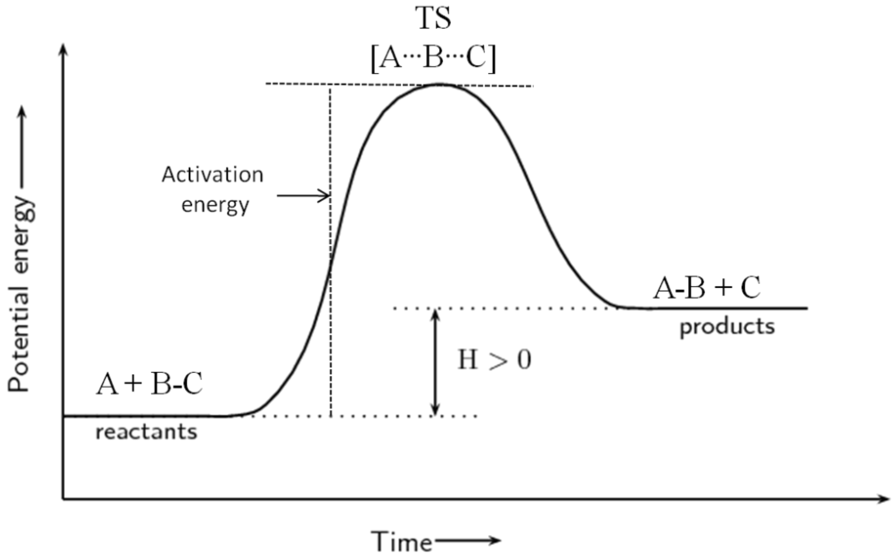


Figure 1.2: Energy profile diagram for endothermic reaction

1.3 REACTIONS OF TRANSITION METAL COMPLEXES :

As discussed earlier that, the reactions of transition metal complexes may be divided as;

1) Substitution reactions at the metal center (it involve both S_N^1 and S_N^2 types of reaction mechanisms);
2) Oxidation-reduction reactions; and
3) Reactions of ligands that do not change the attachments to the central metal atom.

The different types of reactions are individually discussed herewith in detail.

1.3.1 Substitution reactions in octahedral complexes:

Substitution reactions are those in which the replacement of one ligand by another incoming ligand takes place. Since ligands are nucleophilic in nature hence these replacement/substitution reactions are known as nucleophilic substitution reactions (S_N). However, there are some reactions known in which the central metal ion is replaced by another metal ion, these reactions are known as electrophilic substitution reactions (S_E).

Consider a general substitution reaction in which one of the ligand (X) is replaced by another ligand (Y).

$$[MX_6] + Y \rightarrow [MX_5Y] + X$$

Although there are several mechanisms by which nucleophilic substitution reactions (S_N) may occur, however, most of these reactions follow the two types of mechanism frequently. These are:

a) Nucleophilic substitution reactions of first order kinetics (S_N^1)
b) Nucleophilic substitution reactions of second order kinetics (S_N^2)

a). Nucleophilic substitution reactions of first order kinetics (S_N^1): According to this mechanism the reacting complex first undergoes dissociation of one of the metal-ligand bond at which ligand substitution has to take place. This dissociation of metal-ligand bond leads the formation of a penta-coordinated intermediate. The penta coordinated intermediate then readily bonded with the new ligand Y to result the substituted product. The overall mechanism may be shown as:

$$[MX_6] \rightarrow [MX_5] + X \text{ .... } slow\ step$$

$$[MX_5] + Y \rightarrow [MX_5Y] \text{.................. } fast\ step$$

In above mechanism in first step the metal ligand bond of complex $[MX_6]$ get dissociates to give a penta coordinated intermediate $[MX_5]$, this step is a slow step. In second step the penta coordinated intermediate reacts with new ligand to give the substituted product. The second step is a fast step. According the chemical kinetics the slowest step of the multistep reaction is the rate determining step; therefore, in above reaction the rate of reaction depends only on the concentration of $[MX_6]$. The rate law for such reaction may be represented as:

$$\textbf{Rate} = k\,[\mathrm{MX_6}]$$

Since the rate of above reaction depends only on the concentration of one molecule hence this reaction is also known as **Unimolecular Nucleophilic Substitution Reaction i.e. $S_N{}^1$ mechanism.** As the reaction involves the dissociation of metal ligand bond (which is the key step of this mechanism) hence this reaction is also known as **dissociative nucleophilic substitution reaction (D).**

b). Nucleophilic substitution reactions of second order kinetics ($S_N{}^2$): According to this mechanism the incoming ligand first adds to the reacting complex and formed a hepta-coordinated intermediate. The hepta-coordinated intermediate then readily decomposes to result the substituted product. The overall mechanism may be shown as:

$$[MX_6] \;+\; Y \;\rightarrow\; [MX_6Y] \;\ldots\ldots\ldots\ldots\; slow\ step$$

$$[MX_6Y] \;\rightarrow\; [MX_5Y] \;+\; X \;\ldots\ldots\ldots\ldots\ldots\ldots fast\ step$$

In above mechanism in first step the reacting complex [MX_6] get associated with incoming ligand to give a hepta coordinated intermediate [MX_6Y], this step is a slow step. In second step the hepta coordinated intermediate loses a ligand to give the substituted product. The second step is a fast step. According the chemical kinetics the slowest step of the multistep reaction is the rate determining step; therefore, in above reaction the rate of reaction depends on the concentration of [MX_6] and Y. The rate law for such reaction may be represented as:

$$\textbf{Rate} = k\,[\mathrm{MX_6}][\mathrm{Y}]$$

Since the rate of above reaction depends only on the concentration of two molecule hence this reaction is also known as **Bimolecular Nucleophilic Substitution Reaction i.e. $S_N{}^2$ mechanism.** As the reaction involves the association of reacting complex with incoming ligand, hence this reaction is also known as **associative nucleophilic substitution reaction (A).**

Apart from these two mechanism substitution reaction also occurs through interchanging of ligands. An **interchange substitution reaction** (**I**) is a direct replacement of the ligand of reacting complex with the incoming ligand and it does not proceeds via formation of an intermediate. The reaction proceeds through the formation of a single transition state leading to the conversion of reactants to products.

$$[MX_6] \;+\; Y \;\rightarrow\; [MX_5Y] \;+\; X$$

If the above reaction is irreversible the interchange substitution reaction mechanism was found to follow second order kinetics. The rate of this reaction depends upon the concentration of reacting complex and the incoming ligand.

$$\textbf{Rate} = k\,[\mathrm{MX_6}][\mathrm{Y}]$$

However, if the interchange substitution reaction is reversible, then according to the steady state approximation approach the rate of this reaction was found to have pseudo first order reaction kinetics. This will be discussed separately in the kinetics of substitution reactions section.

1.3.2 Types of intermediates formed during unimolecular and biomolecular nucleophilic substitution reaction:

Let us first consider the ***unimolecular nucleophilic substitution reaction (S_N^1) or dissociative substitution reaction (D)*** in which a complex [MX_6] is a reacting complex and Y is the incoming nucleophile. Since, the first step of this reaction is a dissociation of metal-ligand bond which results the formation of an intermediate. In dissociative S_N^1 reaction, penta-coordinated intermediate is formed which may have two types of geometries *i.e.* a) square pyramidal (SP), and b) trigonal bipyramidal (TBP).

The intermediate [MX_5] with square pyramidal geometry is formed by the dissociation of metal-ligand (M-X) bond causing the least disturbance in original octahedral geometry. The intermediate [MX_5] is then attacked by incoming ligand Y to give [MX_5Y] as product. However, the intermediate [MX_5] with trigonal bipyramidal geometry is formed by the dissociation of metal-ligand (M-X) bond and the remaining five M-X bonds of intermediate [MX_5] immediately adjust the bond angles to produce an intermediate with trigonal bipyramidal geometry which is then attacked by incoming ligand Y to give the product. Since, the trigonal bipyramidal (TBP) intermediate involves the shifting of at least two metal-ligand bonds; however, no such shifting is required during the formation of a square pyramidal (SP) intermediate. It has been observed that under normal conditions the square pyramidal geometry is relatively more stable than the trigonal bipyramidal geometry, therefore, the unimolecular nucleophilic substitution reaction (S_N^1) or dissociative substitution reaction (D) proceeds through a square pyramidal (SP) intermediate under normal conditions.

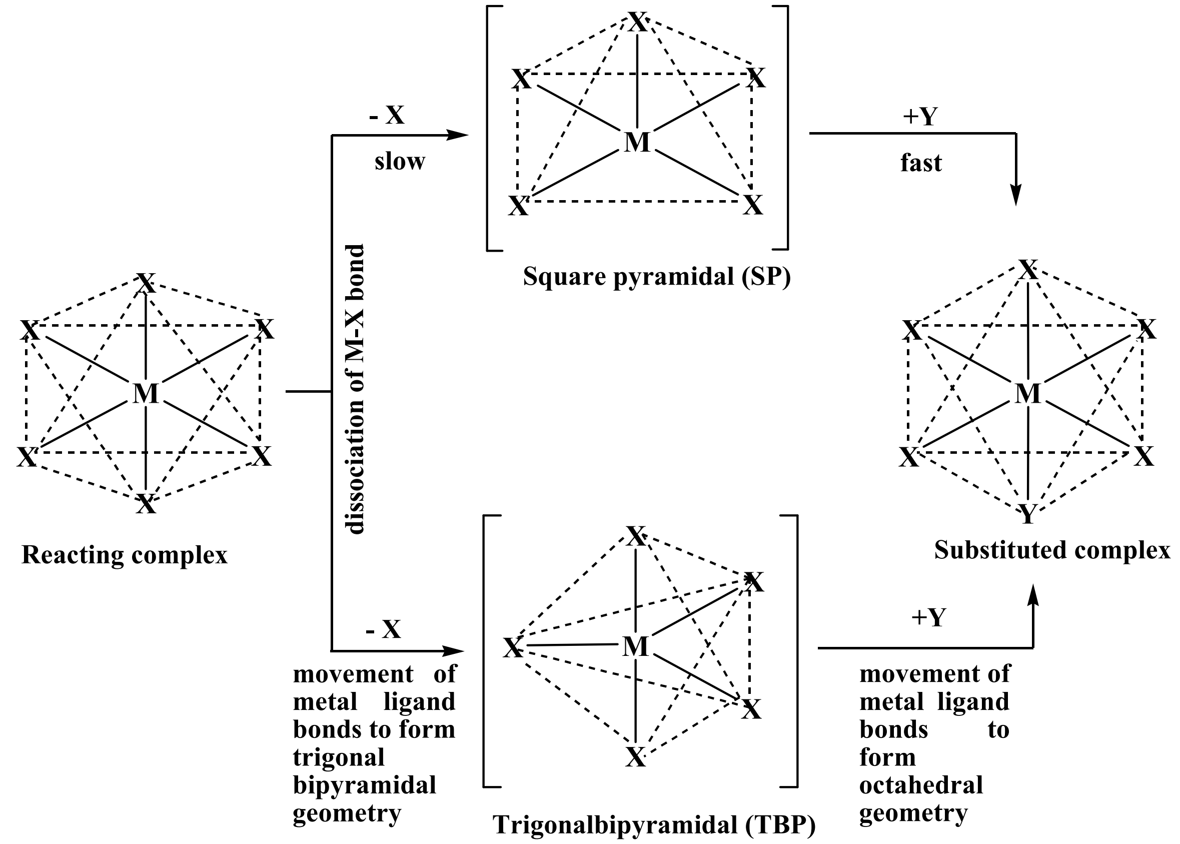


Figure 1.3 Mechanism of Substitution reaction in octahedral complexes

Secondly, if the above transformation occurs through ***bimolecular nucleophilic substitution reaction (S_N^2) or Associative substitution reaction (A)***, where the association of reacting complex with incoming ligand takes place in first step which leads the formation of seven coordinated intermediate. The seven coordinated intermediate may also have two possible geometries depending upon the nature of association of reacting complex with incoming ligand viz. a) pentagonal bipyramidal (PBP), and b) octahedral wedge (OW). The pentagonal bipyramidal intermediate is formed when incoming ligand Y approaches the metal ion through one of the edges of the octahedron. The formation of pentagonal bipyramidal (PBP) intermediate requires the shifting of at least four metal-ligand bonds to accommodate the incoming ligand. This shifting of metal-ligand bonds reduces the bond angle and it brings the bonded pair of electrons of ligand-metal-ligand bond angle closer to each other hence the ligand-ligand repulsion and the bond pair – bond pair repulsion increases the energy of the system. That makes the pentagonal bipyramidal intermediate less stable. However, the formation of octahedral wedge (OW) intermediate involves when incoming ligand Y approaches from the middle of one of the triangular faces of octahedron. As the incoming ligand Y approaches towards central metal M the outgoing ligand X starts moving towards the middle of another triangular face, this results the formation of octahedral wedge intermediate.

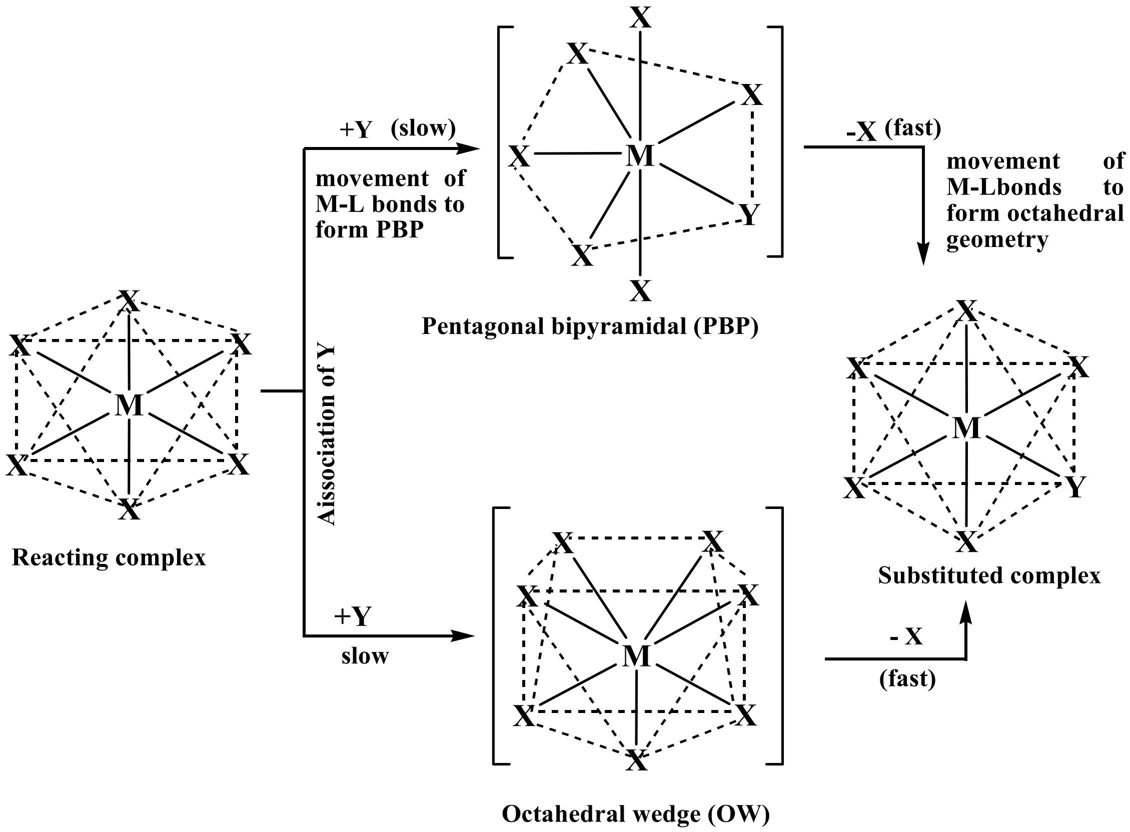


Figure 1.4 Mechanism of substitution reaction in octahedral complexes via associative path. The formation of octahedral wedge intermediate requires comparatively less shifting of metal ligand bonds thus there is not much alteration in ligand-metal-ligand bond angles. Therefore, in octahedral wedge (OW) intermediate the ligand –ligand repulsion and bond pair-bond pair repulsions are comparatively less than that of observed in pentagonal bipyramidal (PBP) intermediate. Hence, the octahedral wedge (OW) intermediate is more stable than pentagonal bipyramidal (PBP) intermediate in S_N2 reaction mechanism. The bimolecular nucleophilic substitution reaction (S_N2) or Associative substitution reaction (A), thus, preferably proceeds through the octahedral wedge (OW) intermediate rather than pentagonal bipyramidal (PBP) intermediate.

1.4 STABILITY AND LABILITY OF COORDINATION COMPOUNDS

Stability of coordination compounds or complex refers the ability of a complex to sustain their existence for a period of time. Thus, the complexes those can be stored for longer period of time under suitable conditions are known as stable complex. Since, different complexes shows variation in their stabilities with respect to different reagents, therefore the term stability is considered as a relative term. However, the stability of complexes can be evaluated in reference to the action of light or heat on them. Thus, based on above factors there are two most important parameters (thermodynamic and kinetic) must be considered during the formation of a complex.

1. **Thermodynamic stability:** The thermodynamic stability of a complex is a measurement of the extent to which the complex will form or will be transformed into another species under given set of conditions at equilibrium. Thus, thermodynamically stable complex does not undergo any reactions readily; however, the complexes that are relatively unstable thermodynamically are considered to be reactive. However, it should be noted that the thermodynamic stability does not give any idea about how fast the reaction will take place. The thermodynamic stability is directly related to metal ligand bond energies. On the basis of thermodynamic stability, the stability of complexes in solution, Biltz (1927) has classified the complex compounds into stable and unstable complexes. Stable complexes are those which posses 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:** This kind of stability refers with the rate of reactions (i.e., reactivity) of complexes in solution, the mechanism of chemical reactions, formation of intermediate complexes etc. On the basis of kinetic stability (i.e., reactivity) of the complex in solution, Taube (1950) has classified the complexes into labile and inert complexes. Labile complexes are those whose one or more ligands in the coordination 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 ligands can either not be replaced or can be replaced with difficulty by other ligands.

Thus if the reacting complex for a proposed reaction is thermodynamically stable, it will not undergo transformation under normal conditions; however, it may be transformed to another species under forcing conditions. If the reacting complex is thermodynamically unstable it can be easily transformed to other species. The kinetic study for such reaction will provide information about the rate at which the proposed transformation will occur.

1.4.1 Stepwise formation of complexes:

According to J Bjerrum (1941) the formation of a complex in solution proceeds by the stepwise addition of the ligand to the metal ion. Thus the formation of the complex MLn (M = central metal ion, L = monodentate ligand and n = maximum coordination number of the metal ion M for the ligand L) may be supposed to take place by the following n consecutive steps and equilibrium constant:

$$M + L \xrightleftharpoons{K_1} ML, \qquad K_1 = \frac{[ML]}{[M]\ [L]}$$

$$M + L \xrightleftharpoons{K_2} ML_2, \qquad K_2 = \frac{[ML_2]}{[M]\ [L]}$$

$$M_{n-1} + L \xrightleftharpoons{K_n} ML_n, \qquad K_n = \frac{[ML_n]}{[M_{n-1}]\ [L]}$$

The equilibrium constants K_1, K_2………K_n are called stepwise formation constant or stepwise stability constants.

The formation of the complex MLn may also be expressed by the following steps and equilibrium constant:

$$M + L \xrightleftharpoons{\beta_1} ML, \qquad \beta_1 = \frac{[ML]}{[M]\ [L]}$$

$$M + 2L \xrightleftharpoons{\beta_2} ML_2, \qquad \beta_2 = \frac{[ML_2]}{[M]\ [L]^2}$$

$$M + nL \xrightleftharpoons{\beta_n} ML_n, \qquad \beta_n = \frac{[ML_n]}{[M]\ [L]^n}$$

The equilibrium constants β_1, β_2 ……….. β_n are called overall or cumulative formation constants or overall or cumulative stability constants. β_n is termed as nth overall or cumulative formation constant or overall or cumulative stability constant.

Trends in stepwise (or successive) formation constants

With a few exception, it is commonly observed that the magnitude of stepwise formation constant decrease steadily from K_1 to Kn.

$$K_1 > K_2 > K_3 > \ldots\ldots\ldots\ldots\ldots\ldots > K_{n-1} > K_n$$

The above order is illustrated by the data for the $Cd^{2+} – NH_3$ system where the ligands are neutral molecules and by $Cd^{2+} – CN^-$ system where the ligands are charged.

$$Cd^{2+} + NH_3 \longrightarrow [Cd(NH_3)]^{2+} \qquad K_1 = 10^{2.65}$$

$$[Cd(NH_3)]^{2+} + NH_3 \longrightarrow [Cd(NH_3)_2]^{2+} \qquad K_2 = 10^{2.10}$$

$$[Cd(NH_3)_2]^{2+} + NH_3 \longrightarrow [Cd(NH_3)_3]^{2+} \qquad K_3 = 10^{1.44}$$

$$[Cd(NH_3)_3]^{2+} + NH_3 \longrightarrow [Cd(NH_3)_4]^{2+} \qquad K_4 = 10^{0.93}$$

$$\beta_4 = K_1 . K_2 . K_3 . K_4 = 10^{2.65} . 10^{2.10} . 10^{1.44} . 10^{0.93}$$
$$= 10^{7.12}$$

$$Cd^{2+} + CN^- \longrightarrow [Cd(CN)]^+ \qquad K_1 = 10^{5.48}$$

$$[Cd(CN)]^+ + CN^- \longrightarrow [Cd(CN)_2] \qquad K_2 = 10^{5.12}$$

$$[Cd(CN)_2] + CN^- \longrightarrow [Cd(CN)_3]^- \qquad K_3 = 10^{4.64}$$

$$[Cd(CN)_3]^- + CN^- \longrightarrow [Cd(CN)_4]^{2-} \qquad K_4 = 10^{3.55}$$

$$\beta_4 = 10^{5.48} . 10^{5.12} . 10^{4.64} . 10^{3.55}$$
$$= 10^{18.8}$$

The steady decrease in the values of K_1, K_2,……..K_n with increasing number of ligands is due to the fact that as more and more ligands move into the coordination zone, less and less aqua-molecules are available to fresh ligands for replacement. With progressive intake of ligands the metal ion becomes fewer electrons greedy.

1.4.2 Factor affecting the stability of metal complexes

The stability or stability constant of metal complexes depends on the following factors:

1. **Nature of central metal ion:** The following properties of central metal ion affect the stability.

i. Size of central metal ion: For a given ligand and metal ion of same oxidation state, stability of the complexes increases with decrease in size of metal ions. For M^{2+} ions, the general trend in stability for complexes is:

$$Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$

This order in stability is consistent with charge to radius ratio concept because the radii decrease from Ba^{2+} to Cu^{2+} and then increases to Zn^{2+}. The order of size of dipositive ions is:

$$Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$

The inverse relation between the size of the metal ion and the stability of the complexes formed is also confirmed, when we see that the stability of the complexes of Mn^{2+}, Fe^{2+}, Co^{2+},

Ni^{2+}, Cu^{2+} and Zn^{2+} ions with a given ligand increases from Mn^{2+} to Cu^{2+} and then decreases at Zn^{2+}.

Ions	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
Ionic radii (Å)	0.91	0.83	0.82	0.78	0.69	0.74
Order of stability of complexes	Mn^{2+} <	Fe^{2+} <	Co^{2+} <	Ni^{2+} <	Cu^{2+} >	Zn^{2+}

This trend in stability is known as Irving-Williums series of stability of Complexes of M^{2+}ions.

ii. Charge on the central metal ion: For a given ligand, the stability of the complexes of metal ion having almost same size but different charge on them decreases with the decrease of the charge on them. Thus the stability of complexes given by following metal ions with the same ligand is in the order:

$La^{3+} > Sr^{2+} > K^{+}$

$Co^{3+} > Co^{2+}$

$Fe^{3+} > Fe^{2+}$

$Th^{4+} > Y^{3+} > Ca^{2+} > Na^{+}$

iii. Electronegativity of the central metal ion: Electronegativity of the central metal ion also influences the stability of its complexes. The greater the electronegativity of the metal ion, greater will be the stability of the complexes formed by it. This is because the bonding between a metal ion and a ligand is due to the donation of electron pairs by the ligands. Hence, a strong electron attracting central metal ion will give stable complexes.

Conclusion: The greater the positive charge density (i.e., charge/size) and the greater the electronegativity of the central metal ion, the greater is the stability of the complex formed by it.

2. **Nature 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 high 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 as a ligand, is in the order: $F^- > Cl^- > Br^- > I^-$.

ii. Basic character of ligands: The more basic is the ligand, more easily it can donate electron pairs to the metal ion and hence more easily it can form complexes of greater stability. The ligands that bind H^+ firmly form more 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.

iii. 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 central metal ions, gives more stable complexes.

1.5 INTERPRETATION OF LABILITY AND INERTNESS OF TRANSITION METAL COMPLEXES:

Generally, complexes in which the ligands from the coordination sphere can be easily replaced by other ligands are called labile complexes. On the other hand, complexes in which such exchange of ligands either do not occur or occurs with very slow rate are called inert complexes. It should be noted that the inertness of the complexes no relation with its thermodynamic stability. For example, the complex $[Ni(CN)_4]^{-2}$ is thermodynamically stable but kinetically it is labile.

$$[Ni(CN)_4]^- + {}^{14}CN^- \xrightarrow[\text{in aqueous medium}]{\text{fast}} [Ni(CN)_3{}^{14}CN]^{2-} + CN^-$$

Similarly, the complex $[Co(NH_3)_6]^{+3}$ is thermodynamically unstable but kinetically it is inert. Thus the complex is quite stable and remains undecomposed in aqueous solution even over the period of several days. The ligand NH_3 could not be replaced by ligand H_2O.

$$[Co(NH_3)_4]^{+2} + H_2O \xrightarrow{\times} \text{No reaction}$$

The lability and inertness of transition metal complexes can be explained on the basis of valance bond theory (VBT) and crystal field theory (CFT) of coordination compounds.

1.5.1 Lability and inertness of transition metal complexes and VBT:

The valence bond theory has explained the lability and inertness of a transition metal complex is a very simple manner, however, this offers only a partial explanation for it. The crystal field theory, however, explains the lability and inertness of a transition metal complex more satisfactorily.

According to the valance bond theory, those transitional metal complexes which give substitution reactions through the dissociative SN^1 mechanism would be labile if the metal-ligand bonds are comparatively weak and they would be inert if the metal-ligand bonds are comparatively strong. Those transition metal complexes in which formation of metal-ligand bonding involve metal hybrid orbitals with outer *d*-orbitals would be less stable than those transition metal complexes in which formation of metal-ligand bonding involve metal hybrid orbitals with inner *d*-orbitals. Since, the outer *d*-orbitals are associated with high energy than the inner *d*-orbitals. Thus, according to the valance bond theory the outer orbital octahedral complexes using sp^3d^2 hybridized orbital for metal-ligand bonding would allow relatively easier exchange of ligands than the inner orbital octahedral complexes using d^2sp^3 hybridized orbital for metal-ligand bonding. Thus according to the above interpretation all outer orbital octahedral complexes are labile and all inner orbital octahedral complexes would be inert if substitution reaction proceeds through SN^1 mechanism. Since, the metal-ligand bonds in inner orbital octahedral complex are quite strong; therefore, considerable amount of energy is required to dissociate these bonds. This is because the inner orbital octahedral complexes prefer to follow an associative SN^2 reaction mechanism rather than the dissociative SN^1 reaction mechanism in their respective substitution reactions. In contrast, due to comparatively weaker metal-ligand bonds, the outer orbital octahedral complexes prefer to follow the dissociative SN^1 reaction mechanism rather than the associative SN^2 reaction mechanism. Although, inner orbital octahedral complexes are quite stable for dissociative SN^1 reaction mechanism; however, there are some exceptions too. Some inner orbital octahedral complexes with at least one empty inner orbital which can accommodate electrons from incoming nucleophile would facilitate the formation of seven coordinated intermediates. Such complexes are therefore referred as labile complexes. Some examples of such type of complexes are octahedral complexes of all d^0 systems such as Sc^{+3}, Y^{+3}, Zr^{+4}, Ce^{+4} etc.; octahedral complexes of all d^1 systems such as Ti^{+3}, V^{+4}, Mo^{+5} etc., and octahedral complexes of all d^2 systems such as Ti^{+2}, V^{+3}, Nb^{+3}, Mo^{+4} etc. However, it is difficult to accommodate the electrons from incoming nucleophile for those inner orbital complexes in which at least one electron in each of the three inner orbitals *[i.e. (n-1)d orbitals]* which do not participate in hybridization. Therefore, such complexes could not be able to form seven coordinated intermediate easily hence are considered as inert complexes. The octahedral complexes of

d^3,$d^4$$d^5$ and d^6 systems are examples of such complexes. Although, valence bond theory (VBT) has put its great efforts to explain lability and inertness of transition metal complexes; however, it could not able to explain the lability or inertness of some octahedral complexes, for example according to valence bond theory (VBT) the octahedral complexes of Ni(II) with d^8 system are labile since according to VBT Ni(II) system involve its sp^3d^2 hybrid orbitals (outer *d* orbitals) to form metal-ligand bonding. However, experimentally it is observed that these octahedral complexes of Ni (II) with d^8 system are inert. To understand this Crystal Field Theory is very helpful and play a crucial role to explain these phenomenon.

1.5.2 Lability and inertness of transition metal complexes and CFT:

This interpretation of lability and inertness of transition metal complexes is based on crystal field stabilization energy, crystal field activation energy.

As, the crystal field stabilization energy is the decrease in energy of transition metal ion in a given environment of ligand because of the splitting of d orbitals of metal ion due to electrostatic crystal field potential of ligand.

The activation energy is defined as the energy required for transforming the reacting complex in to the intermediate at transition state. Similarly, the crystal field activation energy is the energy change in the crystal field stabilization energy when a reacting complex is transformed in to the intermediate. Thus,

Crystal Field Activation Energy = (Crystal Field Stabilization Energy of intermediate)
– (Crystal Field Stabilization Energy of complex)

or, CFAE = CFSE of intermediate – CFSE of complex

Since, the geometries of reacting complex and the intermediate complex is different therefore the order of extent of splitting of d-orbitals of metal ion in both the geometries would also be different. Hence, the CFSE of reacting complex is different than that of intermediate complex. Thus according to crystal field theory

- Those complexes for which the value of CFAE is low or zero or negative are labile because the reacting complex would require less energy for its transformation into intermediate.
- Those complexes for which the value of CFAE is high are inert because the reacting complex would require more energy for its transformation into intermediate.

It must be noted that since CFAE is only a part of total activation energy, a valid comparison of lability or inertness of complex on the basis of CFAE can be made only when all other factors that contribute to the activation energy are almost same. It means, the complex must be more or less identical except the configuration of metal ions and those should be involved in the similar types of reactions. Since, the nature of ligands also affects the CFSE of a complex. The strong field octahedral complexes have more CFSE value than those of weak field octahedral complexes. For example, the CFSE value of $[CoF_6]^{-3}$ is 13100 cm^{-1}; CFSE value of $[Co(NH_3)_6]^{+3}$ is 22870 cm^{-1}; CFSE value of $[CrF_6]^{-3}$ is 15060 cm^{-1}; and CFSE value of $[Co(CN)_6]^{-3}$ is 26600 cm^{-1}. Thus, to justify the lability and inertness of octahedral complexes the CFSE of reacting complex and the intermediate must be known. As discussed earlier that the unimolecular or dissociative nucleophilic substitution reaction (S_N^1) proceeds through a square pyramidal (SP) intermediate and the bimolecular or Associative nucleophilic substitution reaction (S_N^2), proceeds through the octahedral wedge (OW) intermediate. Thus the difference between CFSE of reacting complex and the respective intermediate would give the CFAE for the respective transformation.

The crystal field activation energies (CFAE) of octahedral complexes corresponding to S_N^1 reactions with square pyramidal intermediate are given in table 1.1 and 1.2.

Table 1.1: CFAE of strong field octahedral complexes undergoing S_N^1 reactions with square pyramidal intermediate

System	**Strong field complexes**		
	CFSE for (*Dq*)		**CFAE**
	Octahedral Complex (reacting complex)	**Square pyramidal Complex (intermediate)**	
d^0	0	0	0
d^1	-4.0	-4.57	-0.57
d^2	-8.0	-9.14	-1.14
d^3	-12.0	-10.0	2.0
d^4	-16.0	-14.57	1.43
d^5	-20.0	-19.14	0.86
d^6	-24.0	-20.0	4.0
d^7	-18.0	-19.14	-1.14
d^8	-12.0	-10.0	2.0
d^9	-6.0	-9.14	-3.14
d^{10}	0	0	0

Table 1.2: CFAE of weak field octahedral complexes undergoing S_N^1 reactions with square pyramidal intermediate

System	**Weak field complex**		
	CFSE for (*Dq*)		**CFAE**
	Octahedral Complex (reacting complex)	**Square pyramidal Complex (intermediate)**	
d^0	0	0	0
d^1	-4.0	-4.57	-0.57

d^2	-8.0	-9.14	-1.14
d^3	-12.0	-10.0	2.0
d^4	-6.0	-9.14	-3.14
d^5	0	0	0
d^6	-4.0	-4.57	-0.57
d^7	-8.0	-9.14	-1.14
d^8	-12.0	-10.0	2.0
d^9	-6.0	-9.14	-3.14
d^{10}	0	0	0

From table 1.1 and table 1.2 the following conclusions can be made.

1. For strong field octahedral complexes (table 1.1), the d^0 d^1 d^2 d^7d^9 and d^{10} systems have either negative or zero CFAE value and therefore these complexes would be labile; however, the strong field octahedral complexes with d^3d^4 d^5 d^6 and d^8 configurations of metal ions have positive CFAE values, hence, these octahedral complexes would be inert and therefore would react slowly. The on the basis of CFAE the order of reactivity of these inert complexes is $d^6 > d^3 \sim d^8 > d^4 > d^5$.
2. For weak field octahedral complexes (table 1.2), the d^0 d^1 d^2 d^4 d^5 d^6 d^7d^9 and d^{10} systems have either negative or zero CFAE value and therefore these complexes would be labile; however, the weak field octahedral complexes with d^3 and d^8 configurations of metal ions have positive CFAE values, hence, these octahedral complexes would be inert and therefore would react slowly.

Similarly, the crystal field activation energies (CFAE) of octahedral complexes corresponding to S_N^2 reactions with octahedral wedge intermediate are given in table 1.3 and 1.4.

Table 1.3: CFAE of strong field octahedral complexes undergoing S_N^2 reactions with octahedral wedge intermediate

System	**Strong field complexes**		
	CFSE for (*Dq*)		**CFAE**
	Octahedral Complex (reacting complex)	**Square pyramidal Complex (intermediate)**	
d^0	0	0	0
d^1	-4.0	-6.08	-2.08
d^2	-8.0	-8.68	-0.68
d^3	-12.0	-10.20	1.80
d^4	-16.0	-16.26	-0.26
d^5	-20.0	-18.86	1.14
d^6	-24.0	-20.37	3.63
d^7	-18.0	-18.98	-0.98
d^8	-12.0	-10.20	1.80
d^9	-6.0	-8.79	-2.79
d^{10}	0	0	0

Table 1.4: CFAE of weak field octahedral complexes undergoing S_N2 reactions with octahedral wedge intermediate

System	Weak field complex		
	CFSE for (*Dq*)		CFAE
	Octahedral Complex (reacting complex)	Square pyramidal Complex (intermediate)	
d^0	0	0	0
d^1	-4.0	-6.08	-2.08
d^2	-8.0	-8.68	-0.68
d^3	-12.0	-10.20	1.80
d^4	-6.0	-8.79	-2.79
d^5	0	0	0
d^6	-4.0	-6.08	-2.08
d^7	-8.0	-8.68	-0.68
d^8	-12.0	-10.20	1.80
d^9	-6.0	-8.79	-2.79
d^{10}	0	0	0

From table 1.3 and table 1.4 the following conclusions can be made.

1. For strong field octahedral complexes (table 1.1), the d^0 d^1 d^2 d^4 d^7d^9 and d^{10} systems have either negative or zero CFAE value and therefore these complexes would be labile; however, the strong field octahedral complexes with d^3 d^5 d^6 and d^8 configurations of metal ions have positive CFAE values, hence, these octahedral complexes would be inert and therefore would react slowly. The on the basis of CFAE the order of reactivity of these inert complexes is $d^6 > d^3 \sim d^8 > d^5$.
2. For weak field octahedral complexes (table 1.2), the d^0 d^1 d^2 d^4 d^5 d^6 d^7d^9 and d^{10} systems have either negative or zero CFAE value and therefore these complexes would be labile; however, the weak field octahedral complexes with d^3 and d^8 configurations of metal ions have positive CFAE values, hence, these octahedral complexes would be inert and therefore would react slowly.

1.6 MECHANISTIC AND KINETIC STUDIES OF SUBSTITUTION REACTIONS:

Ligand substitution is an important step on many reactions of coordination complexes. The proper justification and explanation of these reactions needs extensive mechanistic and kinetic studies.

For mechanistic consideration, we have already discussed in previous section of this chapter, the substitution reactions may precede either through dissociative (D), associative (A) and interchange (I) reaction mechanism. Between the dissociative and associative reaction mechanism the interchange reaction mechanism takes place when the incoming ligand assists in the reaction but no intermediate is detected. When the extent of such assistance is small and the reaction primarily follow the dissociative mechanism the reaction is known as dissociative interchange (I_d). However, when the incoming ligand begins forming a bond to the central metal before departing ligand bond is weakened, the mechanism is called associative interchange (I_a) mechanism. In many cases the substitution reaction in transition metal complex are described by dissociative interchange (I_d) or associative interchange (I_a), rather than the simple dissociative (D) or associative (A) mechanism when no detection of intermediates is observed, however, the kinetic evidences indicated the reaction as dissociative or associative. These categories (dissociative (D); associative (A) and interchange (I) reactions) are called the stoichiometric mechanism. The energy profile diagrams for dissociative (D), associative (A) and interchange (I) reactions are shown below (Figure 1.3).

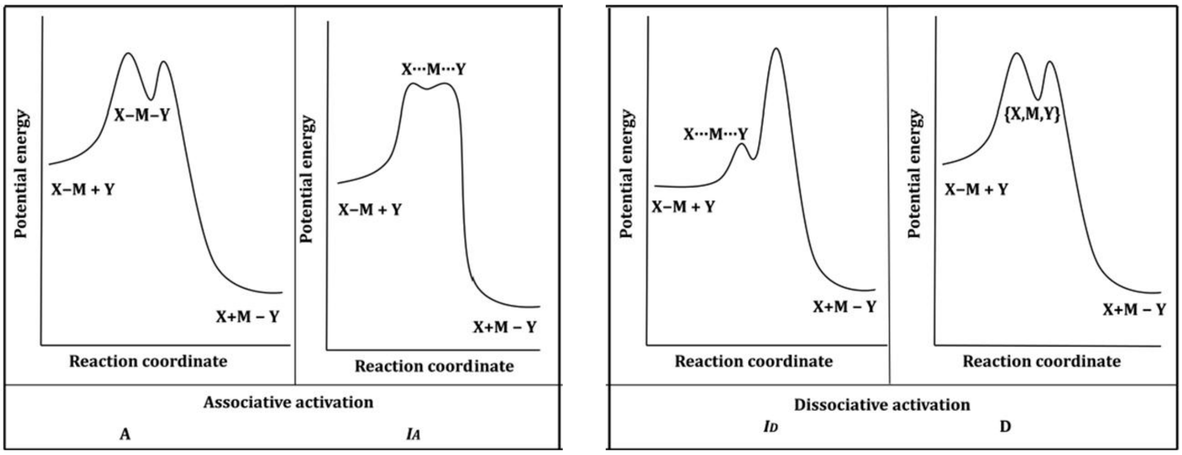


Figure 1.5: Energy profile diagram for dissociative (D), associative (A) and interchange (I) reactions

For kinetic consideration deals with the rate law of the various types of substitution reaction which is used to propose their respective reaction mechanism. The detail discussion on the kinetics of individual type of reaction is as follow:

1.6.1 Kinetics of unimolecular nucleophilic substitution reaction (SN^1) or dissociative substitution reaction (D):

In unimolecular nucleophilic substitution reaction (S_N1) or dissociative substitution reaction (D), the first step involves cleavage of metal ligand bond in reacting complex; the loss of ligand leads the formation of a pentavalent intermediate (intermediate with lower coordination number). The subsequent additions of either the incoming ligand or the leaving group are two possible reactions for this mechanism. Let us consider an example of a reacting complex ML_5X (where M is central metal, L is ligand and X is leaving ligand) which undergoes the ligand substitution reaction with a new ligand (Y). The possible reaction mechanism is shown as follow:

$$[ML_5X] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [ML_5] + X \quad \text{.................. 1}$$

$$[ML_5] + Y \xrightarrow{k_2} [ML_5Y] \quad \text{..................2}$$

The rate of above reactions (1 and 2) can be explained using steady state approximation. According to this approximation it is assumed that the concentration of highly reactive intermediate $[ML_5]$ is almost constant (since it is rapidly vanishing with time) since the rates of formation and consumption of the intermediate are equal. If these rates are same then the change in concentration of $[ML_5]$ must equal to zero; and hence it concludes that this species cannot accumulate during the reaction. The rate law equation for above reaction is as follow:

$$\frac{d[ML_5]}{dt} = k_1[ML_5X] - k_{-1}[ML_5][X] - k_2[ML_5][Y] \ldots\ldots.(i)$$

Applying steady state approximation to equation (i) we have

$$\frac{d[ML_5]}{dt} = k_1[ML_5X] - k_{-1}[ML_5][X] - k_2[ML_5][Y] = 0 \ldots\ldots.(ii)$$

Or

$$k_1[ML_5X] - k_{-1}[ML_5][X] - k_2[ML_5][Y] = 0 \ldots\ldots.(iii)$$

Or

$$k_1[ML_5X] - [ML_5]\{k_{-1}[X] + k_2[Y]\} = 0 \ldots\ldots.(iv)$$

$$k_1[ML_5X] = [ML_5]\{k_{-1}[X] + k_2[Y]\} \ldots\ldots.(v)$$

Or

$$[ML_5] = \frac{k_1[ML_5X]}{k_{-1}[X] + k_2[Y]} \ldots\ldots.(vi)$$

The rate law expression for the formation of product $[ML_5Y]$ may be written as

$$\frac{d[ML_5Y]}{dt} = k_2[ML_5][Y] \ldots\ldots.(vii)$$

Substituting the value of *$[ML_5]$* from equation (vi) to equation (vii), the rate law expression

for formation of product would be

$$\frac{d[ML_5Y]}{dt} = \frac{k_1k_2[ML_5X][Y]}{k_{-1}[X] + k_2[Y]} \ldots\ldots.(viii)$$

The mechanism of unimolecular nucleophilic substitution reaction ($S_N{}^1$) or dissociative substitution reaction (D) on the basis of derived rate law expression (viii) will exhibit a complicated dependence upon [X] and [Y]. The above expression may be simplified since it has two limiting cases. Systematic variations of both X and Y would provide the best evidences for dissociative mechanism.

Case 1: At very high concentration of [Y]; the

$$[Y] >> [X]$$

$$k_2[Y] >> k_{-1}[X]$$

$$\text{or } k_2[Y] + k_{-1}[X] \approx k_2[Y]$$

hence, equation (viii) may be written as

$$\frac{d[ML_5Y]}{dt} = \frac{k_1k_2[ML_5X][Y]}{k_2[Y]} \ldots\ldots.(ix)$$

Or

$$\frac{d[ML_5Y]}{dt} = k_1[ML_5X] \ldots\ldots.(x)$$

From equation (x), it is evident that at very high concentration of [Y], the rate of formation of $[ML_5Y]$ would have dependence upon the concentration of $[ML_5X]$ and reaction is of first order.

Case 2: At very high concentration of [X]; the

$$[X] >> [Y]$$

$$k_{-1}[X] >> k_2[Y]$$

$$\text{or } k_2[Y] + k_{-1}[X] \approx k_{-1}[X]$$

hence equation (viii) may be written as

$$\frac{d[ML_5Y]}{dt} = \frac{k_1k_2[ML_5X][Y]}{k_{-1}[X]} \ldots\ldots.(xi)$$

From equation (xi), it is evident that at very high concentration of [X], the rate of formation of $[ML_5Y]$ would have dependence upon both the concentration of $[ML_5X]$ and [Y].

1.6.2 Kinetics of bimolecular nucleophilic substitution reaction (S_N^2) or associative substitution reaction (a):

In bimolecular nucleophilic substitution reaction (S_N^2) or associative substitution reaction (A), the first step involves association of incoming ligand to the central metal atom of reacting complex; this association of incoming ligand leads the formation of a heptavalent intermediate (intermediate with higher coordination number). The first step in which formation of seven coordinated (heptavalent) intermediate takes place is the rate determining step of the reaction. This first step is followed by a faster reaction in which the leaving group depart and product formation takes place.

$$[ML_5X] + Y \xrightleftharpoons[k_{-1}]{k_1} [ML_5XY] \qquad \ldots\ldots\ldots\ldots\ldots\ldots 3$$

$$[ML_5XY] \xrightarrow{k_2} [ML_5Y] + Y \qquad \ldots\ldots\ldots\ldots\ldots\ldots 4$$

Similar to above discussed process to calculate the rate law expression for dissociative ligand substitution reactions; the rate of above reactions (3 and 4) can also be derives by using steady state approximation. The rate law equation for above reactions (3 and 4) is as follow:

$$\frac{d[ML_5XY]}{dt} = k_1[ML_5X][Y] - k_{-1}[ML_5XY] - k_2[ML_5XY] \ldots\ldots.(i)$$

Applying steady state approximation to equation (i) we have

$$\frac{d[ML_5XY]}{dt} = k_1[ML_5X][Y] - k_{-1}[ML_5XY] - k_2[ML_5XY] = 0 \ldots\ldots.(ii)$$

Or

$$k_1[ML_5X][Y] - k_{-1}[ML_5XY] - k_2[ML_5XY] = 0 \ldots\ldots.(iii)$$

Or

$$k_1[ML_5X][Y] - [ML_5XY]\{k_{-1} + k_2\} = 0 \ldots\ldots.(iv)$$

$$k_1[ML_5X][Y] = [ML_5XY]\{k_{-1} + k_2\} \ldots\ldots.(v)$$

Or

$$[ML_5XY] = \frac{k_1[ML_5X][Y]}{k_{-1} + k_2} \ldots\ldots.(vi)$$

The rate law expression for the formation of product [ML_5Y] may be written as

$$\frac{d[ML_5Y]}{dt} = k_2[ML_5XY] \ldots\ldots.(vii)$$

Substituting the value of *[ML₅XY]* from equation (vi) to equation (vii), the rate law expression for formation of product would be

$$\frac{d[ML_5Y]}{dt} = \frac{k_1k_2[ML_5X][Y]}{k_{-1} + k_2} \ldots\ldots.(ix)$$

Or

$$\frac{d[ML_5Y]}{dt} = k[ML_5X][Y] \ldots\ldots.(x)$$

The rate law expression (x) shows that the bimolecular nucleophilic substitution reaction (S_N^2) or associative substitution reaction (A), follows the second order kinetics. The rate of reaction depends upon the concentration of both the reacting complex and the incoming ligand.

1.6.3 Kinetics of interchange nucleophilic substitution reaction (I):

The interchange substitution reaction can simply defined as a direct replacement of the leaving group in a reacting complex with the incoming ligand without formation of any intermediate. The reaction proceeds through the formation of transition state to the conversion of reactants to products. The interchange reaction either may be reversible or it may be irreversible.

Case 1: The irreversible interchange substitution reaction is written as:

$$[ML_5X] + Y \xrightarrow{k_1} [ML_5Y] + X \ldots\ldots\ldots\ldots 5$$

The rate of irreversible interchange reaction may be written as

$$\frac{d[ML_5Y]}{dt} = k_1[ML_5X][Y] \ldots\ldots.(i)$$

It is evident from the equation (i) that the irreversible interchange reaction will exhibit second order kinetics. The reaction is of first order with respect to [ML_5X] and first order with respect to [Y] too.

Case 2: The reversible interchange substitution reaction is written as:

$$[ML_5X] + Y \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [ML_5Y] + X \ldots\ldots\ldots\ldots\ldots\ldots 6$$

The rate law expression for equation (6) may be written as

$$\frac{d[ML_5Y]}{dt} = k_1[ML_5X][Y] - k_{-1}[ML_5Y][X] \ldots\ldots.(ii)$$

The reversible interchange reaction requires a more complicated treatment to deal with the approach towards the resulting equilibrium. To solve the above equation (ii) steady state approximation is employed by assuming very high concentrations of [Y] and [X] (a common experimental condition) and also assuming the reaction as a pair of opposing pseudo first order reaction. Since the concentrations of [Y] and [X] very high therefore change in concentration of [Y] and [X] almost constant; hence, [X] = [Y] = 1; Thus the rate law expression (ii) may be written as

$$\frac{d[ML_5Y]}{dt} = k_1[ML_5X] - k_{-1}[ML_5Y] \ldots\ldots.(iii)$$

Equation (iii) is the rate law expression for reversible interchange substitution reaction.

1.7 SUBSTITUTION REACTIONS OF OCTAHEDRAL COMPLEXES :

The kinetic studies of most of the ligand substitution reactions of octahedral complexes have been carried out in aqueous medium. Let us consider a substitution reaction of octahedral complex $[ML_5X]^{+n}$ in the presence of incoming ligand Y^- in aqueous medium. Since water also acts as a ligand and its concentration is much more in comparison to the incoming ligand Y^-; thus there is always hydration of reacting complex occurs first. The hydration of reacting complex is known as **aquation of the complex.** The reaction is known as aquation reaction or **acid hydrolysis**.

$$[ML_5X]^{n+} + H_2O \longrightarrow [ML_5(H_2O)]^{(n+1)+} + X^-$$

$$[Co(NH_3)_5Cl]^{2+} + H_2O \xrightarrow[\text{hydrolysis}]{\text{acid}} [Co(NH_3)_5H_2O]^{3+} + Cl^-$$

If the incoming ligand (say Y^-) present in an appreciable amount in the reaction medium then it would replace the water ligand from aquated complex to give $[ML_5Y]^{+n}$. Thus the reaction in aqueous medium in which the anion (it may be anion of water or any other ligand) replaces a coordinated ligand from the reacting complex is known as **anation of the complex** and the reaction is known as anation reaction. The anation reaction may also consider the reversal of acid hydrolysis. When the anion from water *i.e.* OH^- ion, replaces a coordinated ligand from reacting complex, the reaction is known as a **base hydrolysis**. Base hydrolysis is also a part of anation reaction.

$$[ML_5(H_2O)]^{(n+1)+} \quad + \quad Y^- \longrightarrow [ML_5Y]^{n+} + H_2O$$

$$[Co(NH_3)_5H_2O]^{3+} + Cl^- \xrightarrow[\text{reaction}]{\text{anation}} [Co(NH_3)_5Cl]^{2+} + H_2O$$

$$[Co(NH_3)_5Cl]^{2+} + OH^- \xrightarrow[\text{hydrolysis}]{\text{base}} [Co(NH_3)_5OH]^{2+} + Cl^-$$

Since, due to auto ionization of H_2O, some OH^- ions are always present in the reaction medium hence, some $[ML_5OH]^{+n}$ complexes are always formed along with $[ML_5(H_2O)]^{+(n+1)}$ during the hydrolysis of $[ML_5X]^{+n}$ even in neutral aqueous medium.

1.7.1 Acid hydrolysis of octahedral complexes:

The substitution reaction in which an aqua complex is formed due to the replacement of a ligand by water molecule is called acid hydrolysis or aquation reaction. Acid hydrolysis reactions take place in neutral and in acidic medium (pH < 3).

Mechanism of acid hydrolysis: The aquation reactions are carried out in aqueous medium, where water plays a crucial role as it can behave both as solvent and as nucleophile. To understand the mechanism of acid hydrolysis of octahedral complexes following considerations may be adopted. Both, the S_N1 and S_N2 reaction mechanism may be considered to study the progress of acid hydrolysis.

In S_N1 mechanism of acid hydrolysis, the first step in which metal-ligand bond get dissociates is the slowest step and it is the rate determining step too. In the first step the five coordinated complex is formed as intermediate which then quickly reacts with water to form the product. Let us consider a acid hydrolysis of reacting complex $[ML_5X]^{+n}$. If the reaction follows the S_N1 mechanism, the various steps involved in this reaction are as follow:

$$[ML_5X]^{+n} \xrightarrow{\text{slow}} [ML_5]^{+(n+1)} + X^-$$

$$[ML_5]^{+(n+1)} + H_2O \xrightarrow{\text{fast}} [ML_5(H_2O)]$$

Rate of aquation (or hydrolysis) = k $[ML_5X]^{+n}$

If the acid hydrolysis proceeds through S_N2 mechanism; the first step of reaction is associative and it results the formation of seven coordinated complex as an intermediate, this seven coordinated complex then readily gives up the leaving group (ligand) to yield the product. The various steps involved in the reaction are as follow:

$$[ML_5X]^{+n} + H_2O \xrightarrow{slow} [ML_5\,X(H_2O)]^{+n}$$

$$[ML_5\,X(H_2O)]^{+n} \xrightarrow{fast} [ML_5(H_2O)]^{+(n+1)} + X^-$$

Rate of aquation (hydrolysis) = $k\{[ML_5X]^{+n}[H_2O]\}$

Since during hydrolysis water is present in large amount therefore the change in concentration of water (*i.e.* $[H_2O]$) during hydrolysis is almost constant. The rate expression for above S_N^2 mechanism may be written as

Rate of aquation (hydrolysis) = $k[ML_5X]^{+n}$

Thus from the above discussion it is evident that, both S_N^1 and S_N^2 pathways of acid hydrolysis of an octahedral complex predict that the rate of reaction would be dependent only on the concentration of the complex $[ML_5X]^{+n}$. Therefore, the kinetic measurement of the acid hydrolysis of octahedral complex would fail to establish whether the reaction follows S_N^1 and S_N^2 mechanism. Hence, we must consider some other factors which can help to establishing the mechanism through which the acid hydrolysis reaction proceed.

1.7.2 Factors that influence the rate of acid hydrolysis:

The following are the factors which affect the rate of acid hydrolysis.

1) Charge on the reacting complex
2) The nature of leaving group
3) Inductive effects of inert ligands
4) Stability constant
5) Presence of chelating ligands
6) Substitution on chelating ligand (Steric effect)

(1). Charge on the complex: It has been observed that in acid hydrolysis of several octahedral complexes of Co(III) and some other metal ions that an increase in the positive charge on the complex on the reacting complex decreases the rate of acid hydrolysis. For example, the reaction rate of divalent monochloro complexes is about 100 times less than that of monovalent dichloro complexes. Therefore, a S_N^1 mechanism is proposed for such conversions. The proposed mechanism of hydrolysis of monovalent dichloro octahedral complex and divalent monochloro octahedral complex is shown below:

Mechanism of acid hydrolysis of monovalent dichloro complex is shown as

$$\underset{\mathrm{CN} = 6}{[Co(en)_2Cl_2]^+} \xrightarrow{\text{slow}} \underset{\mathrm{CN} = 5}{[Co(en)_2H_2O]^{3+}} + Cl^-$$

$$\underset{\mathrm{CN} = 5}{[Co(en)_2H_2O]^{3+}} + H_2O \xrightarrow{\text{fast}} \underset{\mathrm{CN} = 6}{[Co(en)_2(H_2O)_2]^{3+}}$$

Mechanism of acid hydrolysis of divalent monochloro complex is shown as

$$\underset{\mathrm{CN} = 6}{[Co(en)_2Cl(H_2O)]^{2+}} \xrightarrow{\text{slow}} \underset{\mathrm{CN} = 5}{[Co(en)_2Cl]^{2+}} + Cl^-$$

$$\underset{\mathrm{CN} = 5}{[Co(en)_2Cl]^{2+}} + H_2O \xrightarrow{\text{fast}} \underset{\mathrm{CN} = 6}{[Co(en)_2Cl(H_2O)]^{2+}}$$

Where, ligand (en) is the ethylenediamine [$H_2N-CH_2-CH_2-NH_2$], a bidentate ligand. The rate of aquation of cis$[Co(en)_2Cl_2]^+$ is more than 100 times faster than the rate of aquation of cis$[Co(en)_2Cl(H_2O)]^{2+}$. Similarly, the rate constant of aquation reactions of various complexes of Ruthenium (Ru) are shown as:

$$[RuCl_6]^{-3} + H_2O \longrightarrow [RuCl_5(H_2O)]^{2-} + Cl^-$$

$$k = 1.0\ s^{-1}$$

$$[RuCl_3(H_2O)_3]^0 + H_2O \longrightarrow [RuCl_2(H_2O)_4]^{1+} + Cl^-$$

$$k = 2.1 \times 10^{-6}\ s^{-1}$$

It can be easily observed that the rate of aquation process is decreases with increase in the positive charge on the complex. The above observation also favour the dissociative S_N1 path for the aquation process since the increase in positive chare on the complex would obviously make the dissociation of the leaving group from the metal M more difficult; and thus the rate of aquation process decreases.

(2). The nature of leaving group: The rate of aquation reaction also depends upon the bond strength of leaving group to the central metal in a reacting complex.

Let us consider an example of aquation or acid hydrolysis of a divalent $[Co(NH_3)_5L]^{+2}$ complex. The rate of acid hydrolysis of this complex depends upon the ease of departure of leaving group L, *i.e.* the M-L bond strength. The experimental rate constant of different aquation reactions for the acid hydrolysis of divalent $[Co(NH_3)_5L]^{+2}$, considering L as a carboxylate ligand, are as

$$[Co(NH_3)_5L]^{2+} + H_2O \xrightarrow[\text{hydrolysis}]{\text{acid}} [Co(NH_3)_5H_2O]^{3+} + L^-$$

when

$L = CH_3CH_2COO^-$	$k = 0.3 \times 10^{-3}$
$L = ClCH_2COO^-$	$k = 0.6 \times 10^{-3}$
$L = Cl_2CHCOO^-$	$k = 1.6 \times 10^{-3}$
$L = Cl_3CCOO^-$	$k = 5.4 \times 10^{-3}$
$L = F_3CCOO^-$	$k = 5.5 \times 10^{-3}$

It is well understood from the above rate constant data that the rate of acid hydrolysis increases with the decreasing basicity of the leaving group L. As the strength of M-L (metal-leaving group) bond is directly proportional to the basicity of L; more basic is the ligand stronger the M-L bond. This indicates that the rate of aquation reaction proceed through the dissociation of the M-L bond. The above observations also support a dissociative S_N1 path for the aquation process of the octahedral complexes in acidic medium. Similarly, the rate of acidic aquation of octahedral complexes also depends upon the reactivity of leaving group (L). Higher the reactive the leaving group lesser the M-L bond strength. The reactivity of some of the ligands (leaving groups) in their decreasing order is shown below:

$$HCO_3^- > NO_3^- > I^- > Br^- > Cl^- > SO_4^{2-} > F^- > CH_3COO^- > SCN^- > NO_2^-$$

(3). Inductive effects of inert ligands: The ligands which remain unaffected during the substitution reaction are called inert ligands. Inert ligands do not participate in substitution reactions. Let us consider an example of aquation of octahedral complex $[Co(en)(subtd.\ py)Cl]^{+2}$ where (subtd. py) stands for substituted pyridine in which one H atom of pyridine is replaced by any other substituent. The pyridine (py) is an inert ligand thus the Co-py bond is stronger than the Co-Cl bond.

$$[Co(en)(subtd.\ py)Cl]^{2+} + H_2O \longrightarrow [Co(en)(subtd.\ py)H_2O]^{3+} + Cl^-$$

The substituent on pyridine with electronic effect increases the basicity of pyridine or electron donating power of pyridine ligand. This will accumulate more negative charge on the central metal Co, which weakens the Co-Cl bond it would result in easier heterolytic dissociation of Co-Cl bond. This also supports the S_N1 mechanism of acid hydrolysis.

(4). Stability Constant: The study of stability constants of a complex with different leaving groups revealed that during acid hydrolysis the leaving group is present in both, the product and the intermediate in the form of solvated anion. The presence of such solvated anion indicates that the dissociation of metal-leaving group bond which get solvated immediately. For example, when stability constants of aquation of $[Co(NH_3)_5X]^{+2}$ complex with different leaving groups was calculated, it was observed that the leaving was present in both, intermediate and the product. The dissociation of Co-L bond results the formation of intermediate. Thus the solvation assisted dissociation mechanism ($S_N{}^1$ mechanism) leads the aquation of $[Co(NH_3)_5X]^{+2}$ complex. The solvation lowers the energy of intermediate and makes the process more facile.

$$[Co(NH_3)_5Cl]^{2+} + H_2O \longrightarrow [Co(NH_3)_5]^{3+}{}_{solvated} + Cl^-{}_{solvated}$$

$$[Co(NH_3)_5]^{3+}{}_{solvated} + H_2O \longrightarrow [Co(NH_3)_5H_2O]^{3+}{}_{solvated}$$

(5). Presence of chelating ligands and size of chelate: To understand the effect of chelating ligands and the size of chelates on the acid hydrolysis of octahedral complexes, let us consider the aquation of $[Co(NH_3)_5Cl]^{+2}$, $[Co(en)(NH_3)_3Cl]^{+2}$, $[Co(en)_2(NH_3)Cl]^{+2}$, $[Co(en)(diene)Cl]^{+2}$ and $[Co(tetraene)Cl]^{+2}$ complexes. It was observed that the rate of aquation of these complexes follow the order as

$[Co(NH_3)_5Cl]^{+2}$ > $[Co(en)(NH_3)_3Cl]^{+2}$ > $[Co(en)_2(NH_3)Cl]^{+2}$ > $[Co(en)(diene)Cl]^{+2}$ > $[Co(tetraene)Cl]^{+2}$

Where; en = ethylenediamine; diene = diethylenetriamine; teraene = tetraethylenepentamine.

The above order signifies that the rate of aquation goes on decreasing with the increase in extent of chelation in the reacting complex. The aquation of $[Co(NH_3)_5Cl]^{+2}$ (smaller size) complex and $[Co(en)(NH_3)_3Cl]^{+2}$ (bigger size) complex can be represented as follow, assuming that the process involves the $S_N{}^1$ path. The aquation process of these complexes can be explained satisfactorily by solvation theory. According to it, in aqueous medium, the reacting species, the intermediates and the products are all present in the hydrate state. The hydration of any species reduces its energy and thus stabilise it; thus the extent of stabilization related to the extent of hydration of the species. The extent of hydration is depends upon the charge and the size of the complex; greater the charge and smaller the size of the species, the greater would be the extent of hydration and hence the extent of its stabilization.

Aquation process for $[Co(NH_3)_5Cl]^{+2}$ (smaller size) complex is as

$$[Co(NH_3)_5Cl]^{2+} + H_2O \longrightarrow [Co(NH_3)_5]^{3+}{}_{hydrated} + Cl^-{}_{hydretaed}$$

$$[Co(NH_3)_5]^{3+}{}_{hydrated} + H_2O \longrightarrow [Co(NH_3)_5H_2O]^{3+}{}_{hydrated}$$

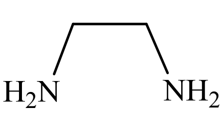
Aquation process of $[Co(en)(NH_3)_3Cl]^{+2}$ (bigger size) complex is as

$$[Co(en)(NH_3)_3Cl]^{2+} + H_2O \longrightarrow [Co(en)(NH_3)_3]^{3+}_{hydrated} + Cl^{-}_{hydretaed}$$

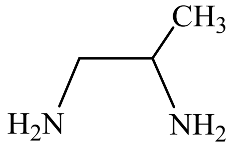
$$[Co(en)(NH_3)_3]^{3+}_{hydrated} + H_2O \longrightarrow [Co(en)(NH_3)_3H_2O]^{3+}_{hydrated}$$

As it can be evident that the intermediate $[Co(en)(NH_3)_3]^{+3}$ of the chelated complex $[Co(en)(NH_3)_3Cl]^{+2}$ is bigger in size than the intermediate $[Co(NH_3)_5]^{+3}$ of a non chelated complex $[Co(NH_3)_5Cl]^{+2}$. Thus the extent of hydration of intermediate $[Co(en)(NH_3)_3]^{+3}$ is lesser than that of $[Co(NH_3)_5]^{+3}$ and hence intermediate $[Co(en)(NH_3)_3]^{+3}$ is stable than that of $[Co(NH_3)_5]^{+3}$; therefore, the intermediate $[Co(en)(NH_3)_3]^{+3}$ requires more energy to form in comparison to $[Co(NH_3)_5]^{+3}$. Thus the rate of aquation of chelated complex $[Co(en)(NH_3)_3Cl]^{+2}$ is slower than that of non chelated complex $[Co(NH_3)_5Cl]^{+2}$. Similarly, it can also be concluded that the chelate complex of larger size would have the slower rate of aquation than the chelate complex of smaller size (provided increasing the chelate ring size do not bring any appreciable change in the steric environment around the central metal ion).

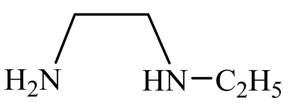
(6). Substitution on chelating ligand (Steric effect): It has been observed that the rate of dissociative acid hydrolysis of octahedral complexes having chelating ligands is also depends upon the steric crowding around the central metal ion. An increase in bulk of ligands which can cause an increase in steric overcrowding around the central metal ion favours the dissociative S_N1 mechanism. Let us consider aquation reactions of some chelate complexes of Cobalt (Co) in which there is an increase in overcrowding around the metal ion due to an increase in substitution on chelating ligand. The reacting complex can be represented as $[Co(subtd.\ en)_2Cl_2]^+$ where (subtd.en) stands for substituted ethylene diamine ligands. The substituted ethylenediamine ligands are such as:



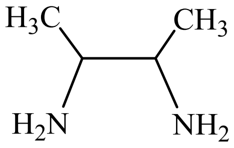
ethylenediamine



propane-1,2-diamine

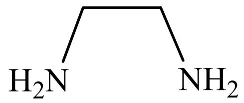
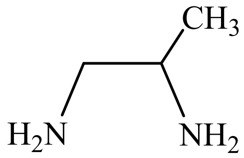
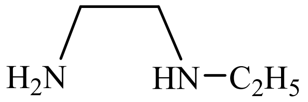
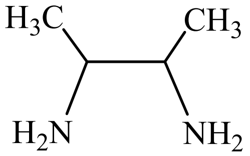


*N*¹-ethylethane-1,2-diamine



butane-2,3-diamine

In above chelating ligands the steric crowding is increases from ethylenediamine to butane-2,3-diamine. The rate constants for the aquation process of complexes $[Co(subtd.\ en)_2Cl_2]^+$ are obtained as shown below:

Chelating Ligand (subtd. en)	**Rate constant (*k*)**
 ethylenediamine	$3.2 \times 10^{-5}\ s^{-1}$
 propane-1,2-diamine	$6.0 \times 10^{-5}\ s^{-1}$
 *N*^{1}-ethylethane-1,2-diamine	$6.0 \times 10^{-5}\ s^{-1}$
 butane-2,3-diamine	$42.0 \times 10^{-5}\ s^{-1}$

It is clear from above observation that the rate of aquation is increases with increase in the steric crowding. This observation clearly supports a dissociative S_N^1 mechanism for aquation reaction. Thus greater the steric crowding around the central metal higher the rate of dissociative S_N^1 mechanism. It has also been observed that, for similar types of complexes if the coordinated ligands are differ in size but they could not able to produce any appreciable change in steric environment around the central metal ion the rate of aquation reaction would depend upon the extent of solvation rather than the steric effects.

1.7.3 Base hydrolysis of octahedral complexes:

As discussed above, the hydrolysis of octahedral complexes in presence of OH^- ions is known as base hydrolysis. Generally, the base hydrolysis reactions of octahedral complexes are known to proceed with a faster rate in comparison to the acid hydrolysis of octahedral complexes. Experimental evidences revealed that the base hydrolysis of octahedral complex is a second order reaction; *i.e,* reaction is of first order with respect to the reacting complex and it is of first order with respect to OH^- ions. Thus the rate law expression for base hydrolysis of an octahedral complex is shown as:

$$\textbf{Rate} = k[\textbf{reacting complex}][OH^-]$$

Since base hydrolysis of amine complexes of Co(III) have been studied extensively, therefore for better understanding of the learners, our discussion on the mechanism and other related study of base hydrolysis is based on amine complexes of Co(III) ion.

Mechanism of Base hydrolysis:

There are two mechanism $S_N{}^2$ (i.e. bimolecular substitution mechanism) and $S_N{}^1$(CB) (i.e. unimolecular substitution mechanism with conjugate base) have been proposed to explain the mechanism of base hydrolysis of octahedral complexes. The detailed discussion on $S_N{}^2$ and $S_N{}^1$(CB) of amine complexes of Co(III) is given as:

$S_N{}^2$ mechanism or associative mechanism of base hydrolysis of octahedral amine complexes of Co(III): To discuss the $S_N{}^2$ mechanism or associative mechanism of base hydrolysis of octahedral complexes, let us consider the hydrolysis of $[Co(NH_3)_5Cl]^{+2}$ under basic condition. According to this mechanism, being a good nucleophile, the incoming ligand OH^{-} ion attacks the reacting complex in first step (which is the slow step of the reaction) to form a seven coordinated complex as an intermediate; in second step the seven coordinated intermediate rearranges to six coordinated substituted product by eliminating the leaving group as shown below:

$$[Co(NH_3)_5Cl]^{2+} + OH^- \xrightarrow{\text{slow}} [Co(NH_3)_5Cl(OH)]^+$$

$$[Co(NH_3)_5Cl(OH)]^+ \xrightarrow{\text{fast}} [Co(NH_3)_5OH]^{2+} + Cl^-$$

The kinetic study of above hydrolysis provided the rate law expression as

$$\textbf{Rate} = k\{[Co(NH_3)_5Cl]^{+2}[OH^{-}]\}$$

Thus this reaction is follows the second order kinetics. However, the above proposed mechanism fails to explain following observations:

a) The above reaction is fails to follow the second order kinetics at high concentration of $[OH^{-}]$ ions. At high concentration of $[OH^{-}]$ ion, the reaction rate becomes almost independent of the concentration of $[OH^{-}]$ ion, and it appears to follow the first order kinetics. This observation could not be explained by simple $S_N{}^2$ mechanism.

b) According to $S_N{}^2$ mechanism the rate of base hydrolysis is directly related to the nucleophilic strength of incoming ligand. However, when the base hydrolysis of the $[Co(NH_3)_5Cl]^{+2}$ complex is performed in the presence of ligands like NCS^{-}, $NO_2{}^{-}$, $NO_3{}^{-}$ etc. (which are as strong as OH^{-}); the rate of base hydrolysis was not affected by the concentration of those ligands. In other words, the rate of hydrolysis of $[Co(NH_3)_5Cl]^{+2}$ is independent of concentration of these nucleophiles and thus reactions are appear to follow first order kinetics. This fact also could not be explained by the simple S_N^2 mechanism.

Thus there must be some other mechanism that could able to explain the above observations for which the S_N^2 mechanism was failed to explain. The other mechanism, that could satisfactorily explained the above mentioned facts along with many other such observations was S_N^1(CB) (i.e. unimolecular substitution mechanism with conjugate base).

S_N^1 (CB) mechanism or (dissociative mechanism with conjugate base) of base hydrolysis of octahedral amine complexes of Co(III): The S_N^1(CB) (i.e. unimolecular substitution mechanism with conjugate base) mechanism was proposed by the ***Garrik***. The mechanism takes place through following step:

Step 1: In this step the basic nature of OH^- ion dominates the reaction and it leads the deprotonation of reacting complex which results the formation of conjugate base of reacting complex. Since, the reacting complex looses proton from it hence it behaves like an acid at this instant. The deprotonation step is an equilibrium step and it was proposed by Garrik. It is represented as

$$[Co(NH_3)_5Cl]^{2+} + OH^- \overset{K}{\rightleftharpoons} [Co(NH_3)_4(NH_2)Cl]^{+} + H_2O$$

K = equilibrium constant

conjugate base of amine complex

Step 2: In this during hydrolysis the conjugate base, produced in step 1, get convert itself into five coordinated intermediate more efficiently than the seven coordinated intermediate. This is because in conjugate base the ligand (NH_2^-) acts as a pi ligand which can effectively coordinate with the Co(III) by forming a pi bond to result the more pi-stabilized five coordinated intermediate. The pi-bonding ligand also helps in the dissociation of Cl^- in this step.

$$[Co(NH_3)_4(NH_2)Cl]^{+} \xrightarrow{k_2} [Co(NH_3)_4(NH_2)]^{+} + Cl^-$$

conjugate base of amine complex

five coordinated intermediate

Step 3: In this step the five coordinated intermediate formed in step 2 reacts quickly with H_2O to give the final product of hydration.

$$[Co(NH_3)_4(NH_2)]^{+} + H_2O \xrightarrow{\text{fast}} [Co(NH_3)_5OH]^{2+}$$

five coordinated intermediate

1.7.4 Factors that favour the S_N^1 (CB) mechanism:

Kinetics of S_N^1 (CB) mechanism: From above mechanism following points may take into consideration.

a) In step 1, the equilibrium is established quickly and the amount of conjugate base present at equilibrium is small, i.e. K is small.

b) Since in step 2, the dissociation of Cl^- from the conjugate base takes place; hence, it is supposed to be the slowest step of the reaction. Hence, step 2 is the reate determining step for above reaction.

c) Step 3 involves the abstraction of proton from H_2O by basic $-NH_2$ group. Thus this step is assumed to the fastest step of the reaction.

Therefore the rate of hydrolysis for above reaction is given as

$$\text{Rate} = k \{\text{Conc. of } [Co(NH_3)_4NH_2Cl]^+\}$$

From step 1;

$$K = \frac{\text{Conc. of } [Co(NH_3)_4NH_2Cl]^+}{\text{Conc. of } [Co(NH_3)_5Cl]^{2+}\,[OH^-]}$$

$$\text{or} \quad \text{Conc. of } [Co(NH_3)_4NH_2Cl]^+ = K\,(\text{Conc. of } [Co(NH_3)_5Cl]^{2+}\,[OH^-])$$

Thus rate of hydrolysis may be written as:

$$\text{Rate} = kK \{\text{Conc. of } [Co(NH_3)_5Cl]^{+2} \text{ x } [OH^-]\}$$

$$\text{Rate} = k' \{\text{Conc. of } [Co(NH_3)_5Cl]^{+2} \text{ x } [OH^-]\}$$

Where, $k' = kK$ (a constant value)

It is clear from the above rate law expression that, although the base hydrolysis involves the S_N^1 mechanism (formation of five coordinated intermediate) but the order of reaction is two. The S_N^1(CB) (i.e. unimolecular substitution mechanism with conjugate base) mechanism has also explained those observations which could not be justified by S_N^2 mechanism. The justifications of those observations are as follow:

It was observed that, **when the concentration of OH^- ion is very high** then the rate of base hydrolysis will be almost independent of the concentration of OH^- ion. If the amount of OH^- ion is very large, there would be very little change in the concentration of OH^- ion. In other words the concentration of OH^- can be taken as constant. Thus from the rate law expression for S_N^1(CB) mechanism may be written as

$$\text{Rate} = k' \{\text{Conc. of } [Co(NH_3)_5Cl]^{+2} \text{ x } [OH^-]\}$$

or when $[OH^-]$ ions taken as constant

$$\text{Rate} = k' \{\text{Conc. of } [Co(NH_3)_5Cl]^{+2} \text{ x constant}\}$$

$$\text{Rate} = k'' \{\text{Conc. of } [Co(NH_3)_5Cl]^{+2}\}$$

Thus at very high concentration of OH^{-} ion the rate of base hydrolysis would depend only upon the concentration of the reacting complex.

Acid –Base behaviour of the reacting complex: According to S_N1(CB) mechanism, the reacting complex acts as Bronsted acid and hence it is necessary that the reacting complex must have at least one acidic hydrogen on a non leaving ligand so that the base (OH^{-} ion) could deprotonated the reacting complex to form the conjugate base of reacting complex and conjugate acid of OH^{-} ion. The rate of abstraction of proton must be fast as compared to the rate of ligand substitution reaction. It has been observed that the rate of deprotonation of complexes like $[Co(NH_3)_5Cl]^{+2}$, $[Co(en)_2(NH_3)Cl]^{+2}$ is nearly 10^5 times faster than the rate of hydrolysis reaction. Thus a reacting complex with no acidic hydrogen should reacts with OH^{-} ion more slowly and also the rate of reaction would be independent of the concentration of OH^{-} ion. For example, in basic hydrolysis of complexes like $[Co(CN)_5Br]^{-3}$ and $[Co(CN)_5Br]^{-3}$ hydrolyses slowly to yield $[Co(CN)_5OH]^{-3}$, and their rates of hydrolysis are also independent of the concentration of OH^{-} ion. Similarly, the rate of hydrolysis of complexes like $[Co(py)_4Cl_2]^{+}$ and $[Co(dipy)_4(OAc)_2]^{+}$ is also independent of the concentration of OH^{-} ion. These observations indicate that the hydrolysis of complex lacking acidic hydrogens do not proceed through the S_N1(CB) mechanism.

Similarly, those complexes which do contain the acidic hydrogen but their deprotonation is very difficult due to high negative charge on the reacting complex would fnd it extremely difficult to form their conjugate base. Hence hydrolysis of such complexes also would not proceed through the S_N1(CB) mechanism. The $[Fe(CN)_5NH_3]^{-3}$ is one of the examples of such complexes.

Basicity of incoming ligands: Similarly, when the hydrolysis of octahedral amine complex of Co(III) is performed in the presence of ligands like NCS^{-}, NO_2^{-}, NO_3^{-} etc. (which are as strong as OH^{-}); the rate of base hydrolysis was not affected by the concentration of those ligands. The explanation of this observation can be as follow:

The strong nucleophilic ligands like NCS^{-}, NO_2^{-}, NO_3^{-} etc. are equally strong nucleophile as OH^{-} ion; however, these ligand are not strong base as the OH^{-}. These nucleophiles are much weaker base than OH^{-} ion, and hence, they could not able to deprotonated the reacting complex to yield the conjugate base of the reacting complex. Thus in the absence of the formation of conjugate base the hydrolysis of reacting complex cannot be proceed through the S_N^1(CB). The hydrolysis of octahedral ammine complexes in presence of NCS^-, NO_2^-, NO_3^- etc. however, can be explained by the conventional associative S_N^2 or dissociative S_N^1 mechanism as follow:

During the hydrolysis of octahedral amine complex of Co(III), the water (H_2O) molecules are present in excess than the nucleophiles NCS^-, NO_2^-, NO_3^- etc., thus there would be more possibility of H_2O molecule to attack the complex ion or its intermediate rather than the nucleophilic anions NCS^-, NO_2^-, NO_3^- etc. Therefore, in general, the aquated complex is the resultant product of such hydrolysis. The associative S_N^2 or dissociative S_N^1 mechanism of hydrolysis are thus represented as follow:

Associative S_N^2 path:

$$[Co(NH_3)_5Cl]^{2+} + H_2O \xrightleftharpoons[\text{slow}]{\text{anionic ligand}} [Co(NH_3)_5(H_2O)Cl]^{+2} \xrightarrow{\text{fast}} [Co(NH_3)_5(H_2O)]^{+3} + Cl^-$$

anionic ligand = NCS^-, NO_2^-, NO_3^- etc.

Dissociative S_N^1 path:

$$[Co(NH_3)_5Cl]^{2+} + H_2O \xrightleftharpoons[\text{slow}]{\text{anionic ligand}} [Co(NH_3)_5]^{+3} + Cl^- \xrightarrow[\text{fast}]{H_2O} [Co(NH_3)_5(H_2O)]^{+3}$$

anionic ligand = NCS^-, NO_2^-, NO_3^- etc.

According to both the above mechanism the rate of hydrolysis is given as

$$\text{Rate} = k\ \{\text{Conc. of } [Co(NH_3)_5Cl]^{+2}\}$$

Thus the rate is independent from the concentration of nucleophilic anions NCS^-, NO_2^-, NO_3^- etc.

1.8 ANATION REACTIONS:

Let us consider the following ligand substitution reaction

$$[Co(NH_3)_5Cl]^{2+} + H_2O \xrightarrow[\text{hydrolysis}]{\text{acid}} [Co(NH_3)_5H_2O]^{3+} + Cl^-$$

$$[Co(NH_3)_5H_2O]^{3+} + L \xrightarrow{\text{anation}} [Co(NH_3)_5L]^{2+} + H_2O$$

L = any anionic ligand; or anion from H_2O

During the process of aquation if the anionic ligand present in an appreciable amount in the reaction medium then it would replace the water ligand from aquated complex to give back the reacting complex. Thus the reaction in aqueous medium in which the anion (it may be anion of water or any other ligand) replaces a coordinated ligand from the reacting complex is known as **anation of the complex** and the reaction is known as anation reaction.

Anation reactions are considered as the reverse of acid hydrolysis reaction or aquation reaction. The rate of anation reaction is slower than that of the aquation reaction. This kind of reverse reactions makes the rate law expression more complicated hence distinction between associative S_N2 or dissociative S_N1 mechanism could become more difficult. To understand the anation reactions let us consider the anionic complex $[Co(CN)_5(H_2O)]^{-2}$.

It has been observed that the anation reaction proceed through the dissociative S_N1 mechanism with the formation of stable five coordinated intermediate species $[Co(CN)_5]^{-2}$ in reversible first step. The fast second step involved the attack of anionic ligand to the five coordinated intermediate to form the anated product.

$$[Co(CN)_5(H_2O)]^{-2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Co(CN)_5]^{-2} + H_2O$$

$$[Co(CN)_5]^{-2} + X^- \xrightarrow{k_2} [Co(CN)_5(X)]^{-3}$$

According to the derivation of rate law expression for dissociative mechanism discussed in section 1.6.1 of this unit, the rate law expression for given anation reaction can be written as

$$\frac{d[Co(CN)_5X]}{dt} = \frac{k_1k_2[Co(CN)_5H_2O][X]}{k_{-1}[H_2O] + k_2[X]}$$

For the anionic complex $[Co(CN)_5(H_2O)]^{-2}$ the value of k_1 was found almost constant at constant ionic strength. However, the values of (k_2/k_{-1}) allows to make the comparison of the reactivity of all the ligands studied towards the five coordinated intermediate species $[Co(CN)_5]^{-2}$ and the following reactivity order of anionic ligands was observed:

$$OH^- > N_3^- > SCN^- > I^- > NH_3 > Br^- > S_2O_3^{2-}$$

1.9 SUBSTITUTION REACTION OF OCTAHEDRAL COMPLEXES WITHOUT BREAKING OF METAL-LIGAND BOND:

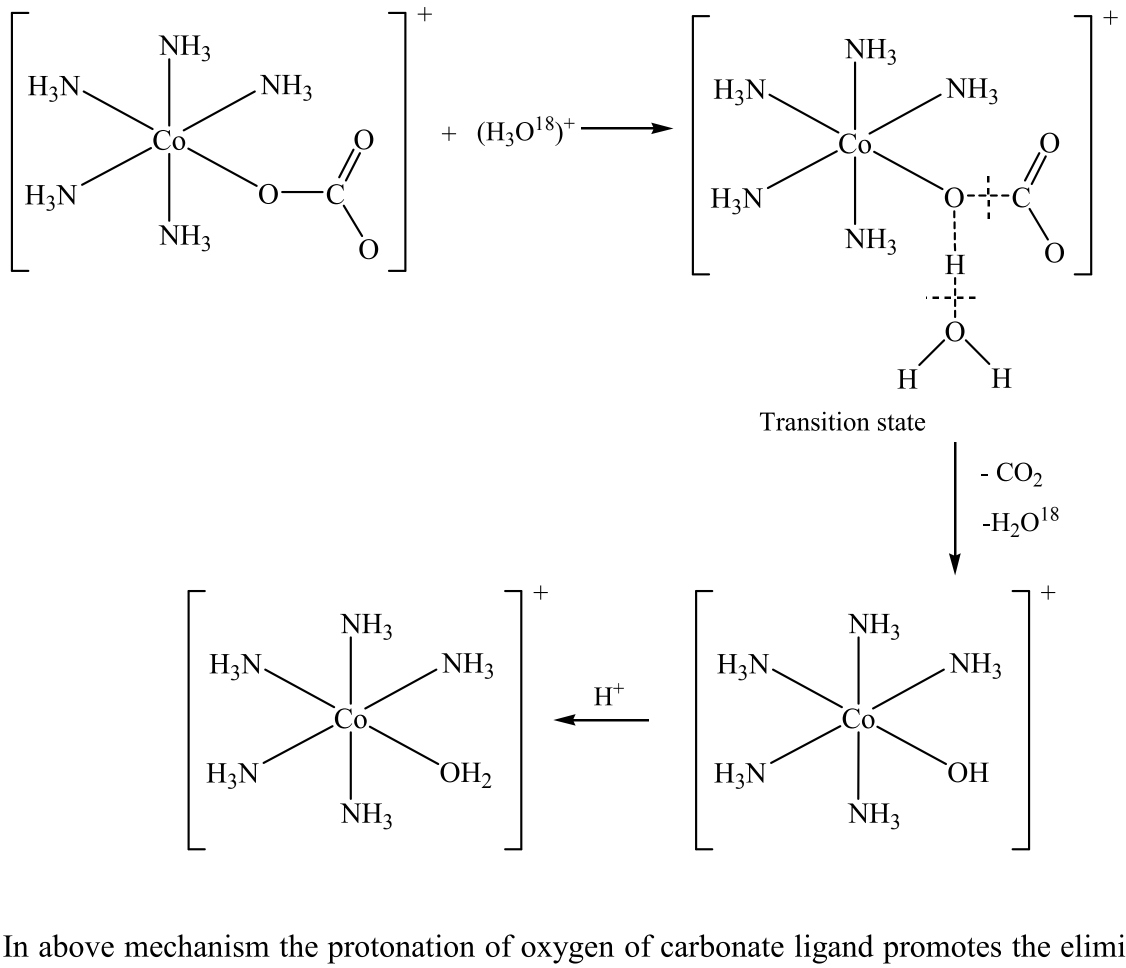
In previous sections of this unit we have discussed various ligand substitution reactions in which nucleophilic ligands reacts with reacting complex to form substituted product.

However, in this section we would be discussing the reactions in which an electrophilic attack on ligand takes place. In these reactions the ligand exchange does not involve the breaking of metal-ligand bonds; instead of it the bonds within the ligands themselves are broken and reformed. The classical example of this kind of reaction is the aquation of carbonato complex through its decarboxylation. The aquation of carbonato complex $[Co(NH_3)_5CO_3]^+$ is shown as follow:

$$[Co(NH_3)_5CO_3]^+ \quad + \quad H_3O^+ \longrightarrow [Co(NH_3)_5H_2O]^{+3} \quad + \quad CO_2 \quad + \quad H_2O$$

Initial observation shows that the above reaction is an acid hydrolysis; however, when the hydrolysis of above carbonato complex is performed in the presence of H_2O^{18} with labelled oxygen, it is observed that the oxygen atom from the nucleophile (i.e. H_2O^{18}) does not enter into the product. This can be easily understood by the following mechanism.

Mechanism: The most probable mechanism for above reaction is shown as



In above mechanism the protonation of oxygen of carbonate ligand promotes the elimination of carbon dioxide along with the water molecule. This decarboxylation leads the formation of a hydroxo complex which readily abstracts the proton from the medium to give the resultant aquo complex. The absence of isotopic oxygen O^{18} in the product can be easily justified by this mechanism.

Another example of this kind of reaction is the anation reaction of Co(III) ammine aquo complex using $(NO_2)^-$ as an anionic ligand.

$$[Co(NH_3)_5(H_2O^{18})]^{+3} + NO_2^- \xrightarrow{\text{anation}} [Co(NH_3)_5(O^{18}NO)]^{+2} + H_2O$$

The presence of isotopic oxygen (O^{18}) in the product confirms that the Co-O^{18} bond is not broken during the anation reaction.

1.10 SUMMARY:

The above unit comprises of the various fundamental aspect of reaction mechanism of transition metal complexes. The unit may be summarized as follow:

1. Importance of the synthesis of coordination compounds in modern chemistry is discussed briefly in this unit.
2. The energy consideration for a reaction is an important parameter for its successful completion.
3. All chemical reaction occurs with migration from one energy minimum (the reactants) through a high energy transition state (TS) to next energy minimum (the product).
4. Depending on the energy of reaction (*i.e.* energy difference between reactants and products), reactions can be classified in to two category; 1) exothermic reaction and 2) endothermic reaction.
5. An exothermic reaction is that in which energy of reaction (*i.e.* energy difference between reactants and products) ΔH is negative (-ve).
6. An endothermic reaction is that in which energy of reaction (*i.e.* energy difference between reactants and products) ΔH is positive (+ve).
7. The reactions of transition metal complexes may be divided as; a) Substitution reactions at the metal center; b) Oxidation-reduction reactions; and c) Reactions of ligands that do not change the attachments to the central metal atom.
8. Nucleophilic substitution reactions may be associative, dissociative or interchanged substitution reactions.
9. Dissociative nucleophilic substitution reactions are following the first order kinetics hence known as S_N1 reaction or unimolecular nucleophilic substitution reactions.

10. Associative nucleophilic substitution reactions are following the second order kinetics hence known as S_N^2 reaction or bimolecular nucleophilic substitution reactions.
11. S_N^1 reaction proceeds through the formation of square pyramidal intermediate; whereas the S_N^2 reaction proceeds through the formation of octahedral wedge intermediate.
12. The lability and inertness of transition metal complexes with different *d*-systems is discussed in detail based on VBT and CFT.
13. The mechanistic and kinetic studies of different types of ligands substitution reactions have also been discussed in the present unit.
14. The mechanism and kinetic studies of acid and base catalyzed hydrolysis of octahedral complexes has also been explained. Various factors that affect the rate of acid and base catalyzed hydrolysis of octahedral complexes have also been discussed.
15. A comprehensive note on anation reaction is also given in this unit.
16. At the end of this unit mechanism of substitution reaction of octahedral complexes without breaking of metal-ligand bond is also discusses in brief.

1.11 SAQs TYPE QUESTIONS:

A. Multiple choice questions

1) The correct relation is

a) $\Delta G^0 = RTlog\beta_n$ b) $\Delta G^0 = -RTlog\beta_n$

c) $\Delta G^0 = 2.303RTlog\beta_n$ d) None the above

2) Value of stepwise stability constant generally

a) Increases b) Decreases

c) remains constant d) remains zero

3) The most stable complex among given is

a) $[Cu(NH_3)_4]^{+2}$ b) $[Cu(en)_2]^{+2}$

c) $[Cu(trien)]^{+2}$ d) $[Cu(en)(NH_3)_2]^{+2}$

4) Replacement of monodentate ligands by cyclic polydentate ligands leads to

a) Increase in stability b) Decrease in stability

c) Increase in lability d) Increase in entropy

5) Thermodynamic stability is related to

a) Rate of reaction b) Activation energy

c) Stability constant d) All the above

6) Complexes with chelating ligands are comparatively

   a) Less stable b) More stable

   c) Highly reactive d) All the above

7) $[Co(NH_3)_6]^{+3}$ complex is

   a) Inert b) Labile

   c) Both (a) and (b) d) none the above

8) With the decrease in the CFSE value, the activation energy

   a) Decreases b) Increases

   c) Does not changes d) none the above

9) The order of inertness of low spin complexes is

   a) $d^3 > d^6 > d^4 > d^5$ b) $d^6 > d^3 > d^4 > d^5$

   c) $d^4 > d^3 > d^6 > d^5$ d) $d^6 > d^4 > d^3 > d^5$

10) The $Ni(CN)_4$ complex is

    a) Inert b) Labile

    c) Both (a) and (b) d) none the above

11) Conjugate base mechanism for base hydrolysis was proposed by

    a) M. Faraday b) Marcus

    c) Garrick d) Kerr

12) Electrostatic polarization theory was proposed by

    a) Garrick b) Grinberg

    c) Chatt d) Pauling

13) In an exothermic reaction the free energy of the reaction is

    a) Positive b) Negative

    c) Zero d) None the above

14) Most of the nucleophilic substitution reactions in octahedral complexes follow

    a) only S_N^1 mechanism b) only S_N^2 mechanism

    c) both S_N^1 and S_N^2 mechanism d) None the above

15) The geometry of intermediate formed in S_N^1 nucleophilic substitution reactions of octahedral complexes is

    a) Trigonal bipyramidal (TBP) b) Square pyramidal (SP)

    c) Tetrahedral d) Octahedral

16) The geometry of intermediate formed in S_N^2 nucleophilic substitution reactions of octahedral complexes is

    a) Octahedral Wedge (OW) b) Square pyramidal (SP)

c) Pentagonal bipyramidal d) Trigonal bipyramidal

B. Fill in the bling

(i) The substitution reaction in which an aqua complex is formed due to the replacement of a ligand by water molecule is called………….. or ………..

(ii) The reaction in aqueous medium in which the anion (it may be anion of water or any other ligand) replaces a coordinated ligand from the reacting complex is known as………………. and the reaction is known as……….. .

(iii) The ligands which remain unaffected during the substitution reaction are called….. ligands.

(iv) The rate of reaction depends only on the concentration of one molecule hence this reaction is also known as……………..

C. True/False

(i) The rate of reaction depends only on the concentration of one molecule hence this reaction is also known as Bimolecular Nucleophilic Substitution reaction True/False

(ii) In octahedral complexes, nucleophilic substitution reaction occurs through association, True/False

(iii) Trigonal bipyramidal is more stable transition then Square pyramidal True/False

(iv) Substitution reaction occurs more rapidly is known as inert complexes True/False

(v) In acid hydrolysis conjugate base is formed intermediate True/False

D. Match the following

i. Cumulative stability constant	a. Kn
ii. Stepwise formation constant	b. βn
iii. Chelate complex	c. $[Co(NH_3)_4(NH_2^-)\ Cl]^+$
iv. Conjugate base	d. $[Co(en)_3]^{3+}$

Answer Keys:

A.

1. a 2. b 3. a 4. a 5. c 6. b 7. a 8. a
9. b 10. b 11. c 12. c 13. b 14. c 15. b 16. a

B.

i. acid hydrolysis, aquation reaction ii. anation of the complex, anation reaction
iii. Inert iv. Unimolecular Nucleophilic Substitution Reaction

C.

i. True ii. False iii. True iv. True v. True

D.

i b, ii a iii d iv c

1.12 GLOSSARY:

OW = Octahedral Wedge

TBP = Trigonal Bipyramidal

CFSE = Crystal Field Stabilisation Energy

S_N1 = Unimolecular Nucleophilic Substitution

S_N2 = Bimolecular Nucleophilic Substitution

TS = Transition State

SP = Square pyramidal

CB = Conjugate Base

1.13 REFERENCES :

1. Huheey J. E., Keiter E. A., Keiter R. L., (1997), *Inorganic chemistry- Principles of structure and reactivity(Fourth Edition)*, Pearson, 964.
2. Puri B. L. Sharma L. R. Kalia K. C.,(2020), *Principles of Inorganic Chmistry, (33rd Edition)*, Vishal Publishing.
3. Miessler G. L. , Fischer P. J., Tarr D. A., (2014) *Inorganic Chemistry(5th edition),* 696.
4. Banerjea D., (2009), *Coordination Chemistry" (second edition),* Asian Books, 4, 874.
5. House J. E., (2009), *Inorganic Chemistry*, Elsevier,

1.14 SUGGESTED READING

1. C. E. Housecroft, A. G. Sharpe, (2018), *Inorganic chemistry*, Pearson (Fifth edition), 1256.
2. F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, (1999), *Advanced inorganic chemistry*, Wiley-Interscience (Six Edition), 1376.
3. J. D. Lee, (1999), *Concise inorganic chemistry*, Wiley-Blackwell (Fifth edition), 1072.

1.15 TERMINAL QUESTIONS:

1. What is natural order of stability?
2. Explain the differences between stepwise and overall stability constant.
3. Write the relation between stepwise and overall stability constants.
4. Discuss trends in stepwise stability constants.
5. Explain chelate effect.
6. Give any two factors affecting thermodynamic stability of complexes. Explain the reason too.
7. What are labile and inert complex? Explain with suitable examples.
8. Discuss different types of stability constants of complexes.
9. Write short note on Molar ratio method.
10. Explain the effect of charge and size of metal ion on stability of complexes.
11. Explain how the stability constant is related to the crystal field stabilization energy?
12. Write a note on limiting logarithmic method.
13. The rate of water exchange for $[Mo(H_2O)_6]^{+3}$ is very slow. Explain why?
14. The rate constant for the reaction $[Co(NH_3)_6]^{+2} \rightarrow [Co(NH_3)_6]^{+3}$ is 10^{-4} why?
15. Write the mechanism of reaction of $[Co(NH_3)_5Cl]^{+2}$ with $[Cr(H_2O)_6]^{+2}$.
16. Arrange the following in order of increasing rate of water exchange:

    $[V(H_2O)_6]^{+2}$, $[Cr(H_2O)_6]^{+3}$, $[Mg(H_2O)_6]^{+2}$, $[Al(H_2O)_6]^{+3}$
17. The hydrolysis of chelate carbonato complexes of cobalt (III) is much faster in acid than in neutral solution. Explain why?
18. What do you understand by nucleophilic substitution reactions for octahedral complexes?
19. Discuss the $S_N{}^1$ and $S_N{}^2$ mechanism for octahedral complexes.
20. Discuss in detail the mechanism involved in the base hydrolysis of $[Co(en)_2NH_3Cl]^{+2}$.
21. What do you understand by $S_N{}^1$(CB) mechanism? Give suitable examples.
22. Discuss the mechanism of aquation of cis and trans $[Co(en)_2(OH)Cl]^{+1}$ complexes.
23. Discuss briefly $S_N{}^1$(CB) mechanism for the reaction:

    $$[Co(en)_2NH_3Cl]^{+2} + OH^{-} \rightarrow [Co(en)_2NH_3(OH)]^{+2}$$
24. Explain the cause of lability on the basis of valence bond theory.
25. Discuss the nucleophilic substitution reactions of octahedral complexes occur without breaking of metal-ligand bond.
26. What are anation reactions? Explain with suitable example.
27. What are the factors that favour the $S_N{}^1$(CB) mechanism?

28. Discuss base hydrolysis of octahedral complexes in detail.
29. What the factors that influences the rate of acid hydrolysis of octahedral complexes. Discuss in detail.
30. Write a note on acid hydrolysis of octahedral complexes.
31. Discuss the types of intermediates that are formed in S_N^1, S_N^2 and S_N^1(CB) mechanism with suitable examples.
32. What types of octahedral complexes undergo the acid hydrolysis by S_N^2 mechanism? What type of intermediate and product would be formed? Illustrate with suitable examples.
33. Comment on the role of pi bonding in determining the geometry of the product formed during the acid hydrolysis of octahedral complexes.
34. Discuss the kinetics of S_N^2 mechanism via associative and interchange reaction.
35. Discuss the kinetics of S_N^1 mechanism via dissociative reaction.
36. Explain the lability and inertness of transition metal complexes based on CFT.
37. Explain the lability and inertness of transition metal complexes based on CFT.
38. Explain the following:
    a) Anation reactions
    b) Lability and inertness of transition metal complexes
    c) Acid hydrolysis of octahedral complexes
    d) Base hydrolysis of octahedral complexes
39. Explain how the acid hydrolysis of cis $[Co(en)_2(OH)Cl]^{+1}$ complex differ from that of the trans $[Co(en)_2(NO_2)Cl]^{+1}$ complex.
40. Discuss all the factors that evidence that establish the S_N^1(CB) mechanism for base hydrolysis of octahedral complexes.

UNIT : SECOND

REACTION MECHANISM OF TRANSITION METAL COMPLEXES - II

Structure of the unit :

Unit- second

REACTION MECHANISM OF TRANSITION METAL COMPLEXES - II

2.1 INTRODUCTION:

In unit first we have discussed about various fundamental aspect of ligand substitution reactions of transition metal complexes such as; the energy consideration of various chemical reactions; types of reactions of transition metal complexes; types of ligand substitution reactions; concept of lability and inertness of a transition metal complex, etc. However, the unit 1 is mainly dealt with the reaction mechanism and kinetic studies of ligand substitution reactions of octahedral complexes.

The present unit will be focusing on the various aspects of ligand substitution reactions of square planar complexes; redox reactions and electron transfer reactions of transition metal complexes. The present unit will be subdivided in to three main part *i.e.* Ligand substitution reactions of square planar complexes; Redox reactions of transition metal complexes; and the electron transfer reactions of transition metal complexes.

2.2 OBJECTIVES:

At the end of this unit learner would be able to

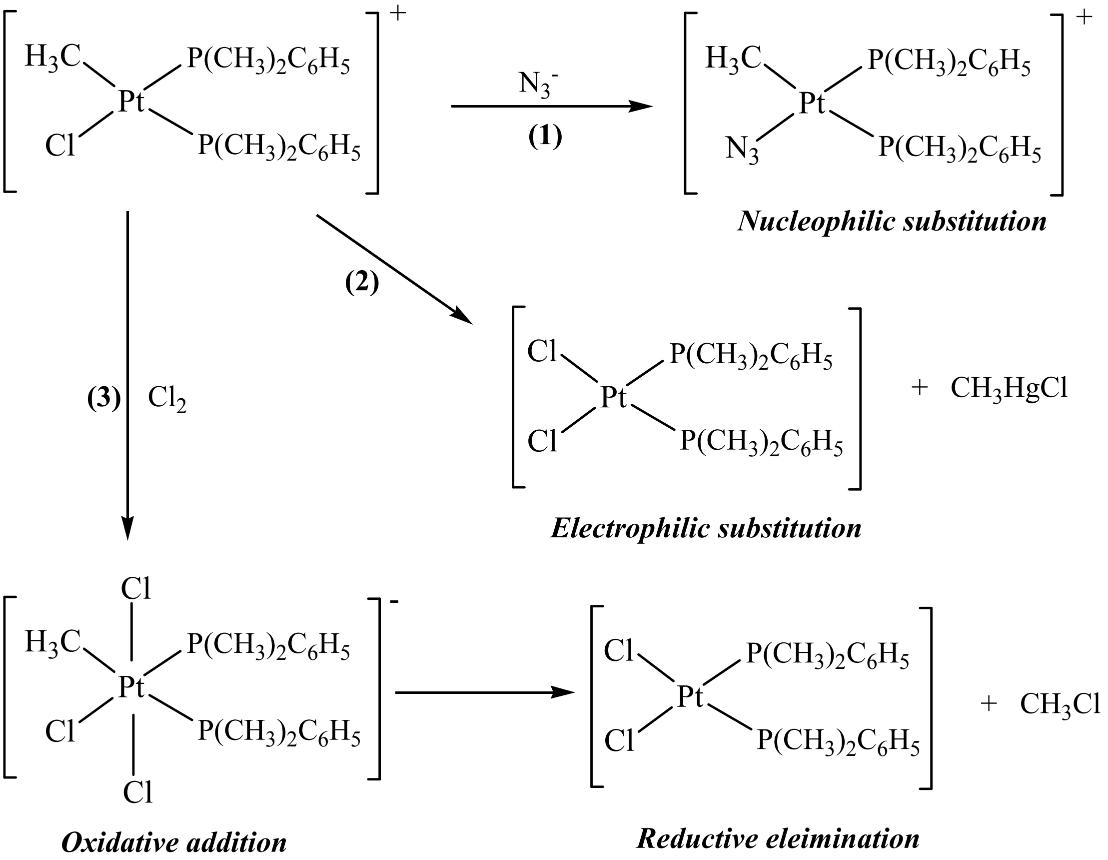
- Learn how the ligand substitution reactions occur in square planar complexes
- Know the mechanisms by which these ligand substitution reactions occur in square planar complexes
- Learn about the dependence of ligand substitution reactions on reacting complexes
- Know the kinetics of nucleophilic substitution reactions of square planar complexes
- Learn about the effect of ligands present at *trans* position on the rate of substitution reactions of square planar complexes (*i.e.* the *trans* effect)
- Know about the theories that support the *trans* effect
- Learn about the factors affect the rate of ligand substitution reactions in square planar complexes
- Learn about the redox reactions take place in transition metal complexes
- Know how the redox reactions occur through electron transfer mode

- Know the outer sphere and inner sphere redox reactions
- Know the type of barriers that require energy in outer sphere and inner sphere electron transfer
- Learn about the Marcus- Hush theory
- Know about the factors affecting the rate of electron transfer reactions

2.3 LIGAND SUBSTITUTION REACTIONS OF SQUARE PLANAR COMPLEXES:

Square planar complexes are the complexes with coordination number 4. Since, the coordination number 4 complexes have both tetrahedral and square planar geometries in which tetrahedral geometry is generally favoured. The square planar geometry is less favoured sterically than the tetrahedral geometry when the ligands are large. However, if the ligands are small enough to form a square planar complex, then instead of forming square planar complex it is preferred to form the octahedral complex with the formation of two additional sigma bonds without any additional steric repulsion. This is the reason that the square planar complexes are formed only by a few metal ions. The metal ions with d^8 configuration such as Ni(II), Pt(II), Pd(II), Au(III), Rh(I) and Ir(I) usually forms the square planar complexes. There are also complexes of Cu (II) with d^9 configuration, Co (II) with d^7 configuration, Co (III) with d^6 configuration and Cr (II) with d^4 configuration, that are square planar, however, such complexes are not very common. The essential requirement for the stability of square planar complexes is the presence of non-bulky, strong field ligands. The stability of square planar complexes would be more if the strong field ligand having π–bonds is used for the complex formation; the π–bond of ligand sufficiently compensate the energy loss during the formation of square planar complexes rather than octahedral complexes. For example, with Ni^{+2} metal ion the cyanide (CN^-) ligand forms a square planar complex, whereas the ligands like ammonia (NH_3) and water (H_2O) always form the octahedral complexes, and the ligands like chloride (Cl^-), bromide (Br^-), and iodide (I^-) form tetrahedral complexes.

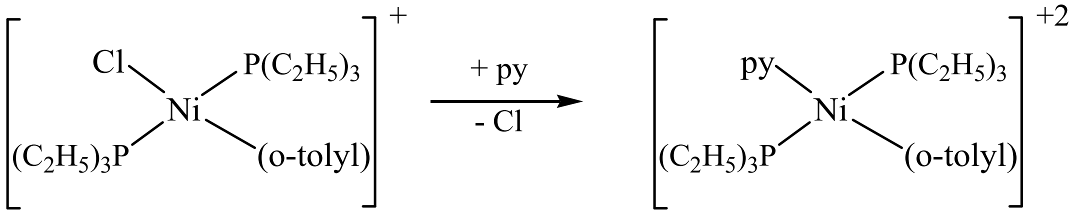
Ligand substitution reactions of square planar complexes have been extensively studies for the complexes of Pt(II), because they are stable, relatively easy to synthesize and undergo ligand substitution reactions with relatively slow rates that allow easy monitoring. Reaction rates for Pt(II):Pd(II):Ni(II) are approximately $1:10^5:10^7$. Apart from it, the isomerization of less stable Pt(II) complexes to their respective more stable is also very slow. The ligand substitution reactions of square planar complexes may take place either by nucleophilic substitution, electrophilic substitution and oxidative addition followed by reductive elimination. Following are the examples of all three classes of ligand substitution reactions considering the $[Pt(CH_3)Cl(P(CH_3)_2C_6H_5)_2]$ complex as reacting species.



The route (1) is simple nucleophilic substitution reaction; route (2) is as an electrophilic attack by Hg(II) on the platinum-carbon bond. In route (3) the oxidative addition reaction shows oxidative of Pt(II) to Pt(IV) with simultaneous expansion of the coordination number of Pt from 4 to 6. Elimination of methyl chloride reduces the Pt(IV) to Pt(II) to lead the substituted product.

However, ligands substitution reactions of square planar complexes through nucleophilic path have been of great interest and therefore studied extensively. This is the reason; in present unit we will also confine our attention to those proceeding by a nucleophilic path. The mechanism of ligand substitution reactions of square planar complexes through nucleophilic path can be assumed to be associative S_N2 or dissociative S_N1; however, experimental observations revealed that the ligand substitution reaction of square planar complexes through nucleophilic path appears to be associative S_N^2 rather than dissociative S_N^1. The following observations may consider in favour of S_N^2 mechanism.

1. In the case of square planar complexes of Ni(II), Pd(II) and Pt(II) metals ions, there are 5 empty orbital (viz. one inner *d*, one *s* and 3 *p* orbitals) of comparable energies are available on metal ion for the formation of sigma bond. Since, only four orbitals are utilized for the formation of four sigma bonds. Thus the unutilized fifth orbital can easily accommodate the electrons form incoming ligand. In other words, a five-coordinated intermediate or an activated complex thus formed from a four coordinated square planar complex through associative S_N^2 mechanism.
2. The rates of ligand substitution reactions of square planar complexes also sensitive to the nature of reacting complex. Let us consider the ligands substitution reactions of square planar complexes of Ni(II), Pd(II) and Pt(II) with same ligand (*i.e.* py) as follow:



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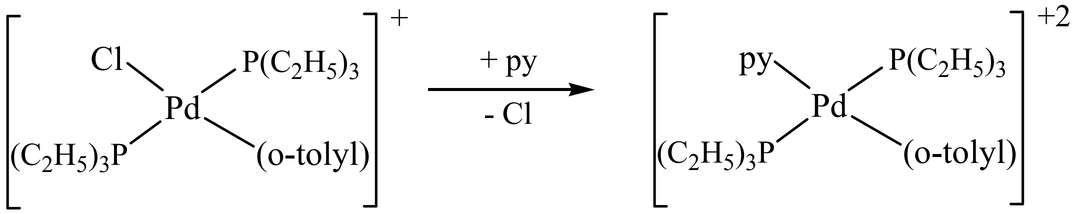

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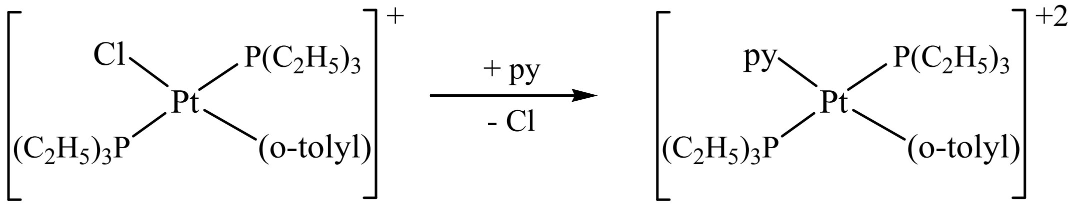

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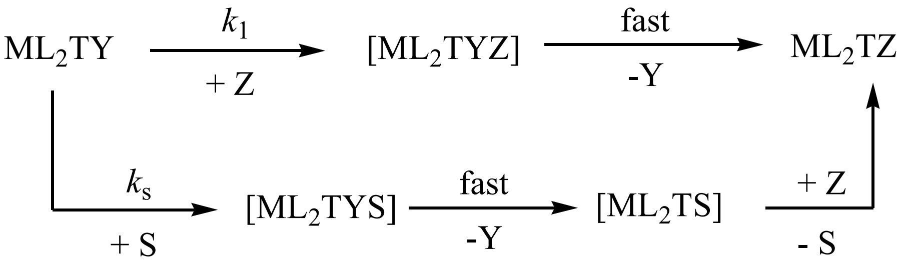
The experimental study revealed that the rate of reaction (1) is 50 times more than the reaction (2), and 100,000 times more than the reaction (3). This is because the square planar Ni(II) expands its coordination number more easily than the square planar Pd(II), similarly, the square planar Pd(II) expands its coordination number more easily than the Pt(II). The complexes that can expand their coordination number more easily are relatively more reactive. This clearly indicates that the ease of formation of an intermediate or an activated complex with higher coordination number during the substitution reaction of square planar will be in the order of Ni(II) > Pd(II) > Pt(II). This kind of associative intermediate thus can be formed only through an associative S_N^2 mechanism.

2.3.1 Determination of rate law for nucleophilic substitution reaction of square planar complex:

Let us consider the ligand substitution reaction of a square planar complex (say complex ML_2TY and substituting ligand is Z).

$$ML_2TY + Z \longrightarrow ML_2TZ + Y \quad ....\ 1$$

In order to explain the mechanism of the above substitution reaction the first step is the experimental determination of rate law expression. The mechanism of the reaction is appears associative $S_N{}^2$ rather than $S_N{}^1$. The reaction takes place via two parallel associative steps as shown below:



Where S is the solvent

The first step (with rate constant k_1) corresponds to an $S_N{}^2$ reaction of Z with the formation of penta coordinated intermediate species, while the second step (with rate constant k_s) corresponds to a two step reaction in which leaving group is first coordinated with solvent (S) probably via $S_N{}^2$ mechanism as the rate determining step followed by the relatively fast replacement of solvent by incoming ligand Z. The rate law expression was determined by performing the reaction under pseudo first order reaction conditions. It implies that the the concentration of Z is made large in comparison to that of reacting complex, so that the change in concentration of Z (i.e. [Z]) can be considered as almost constant during the course of reaction.

The experimental rate law expression for the above transformation is written as:

$$Rate = \frac{-d[ML_2TY]}{dt} = K_1[ML_2TY][Z] + K_s[ML_2TY][S]$$

or

$$= (K_1[Z] + K_s[S])[ML_2TY]$$

$$= (K_1[Z] + K_2)[ML_2TY]$$

Where $K_2 = K_s$

$$= K_{obs}[ML_2TY]$$

Where $K_{obs} = K_1\,[Z] + K_2$

Thus

$$Rate = \frac{-d[ML_2TY]}{dt} = K_{obs}[ML_2TY]$$

The rate is measured at several values of [Z] and the rate constant K_{obs} is plotted against [Z]. The plot is linear in nature with an intercept. The intercept of the plot gives the value of K_2, while that of K_1 is obtained from the slope. The values of K_1 differ for different nucleophiles Z, but the value of K_2 remains unchanged for all nucleophiles except for the solvent present in the reaction. Hence the K_1 term originates due to nucleophilic attack by Z and K_2 term originates due to nucleophilic attack of the solvent. The K_1 is related to nucleophilic path and K_2 is related to solvent path. The stoichiometric mechanisms involved in different nucleophilic substitutions concerning either solvent or nucleophilic or both paths are different and present different rate expressions as different solvent paths are involved.

Four different mode of mechanism have been proposed for the substitution reactions based on relative importance of bond breaking and bond formation in the rate determining steps.

1. Associative mechanism, A: The M-Z bond is fully formed before the breaking of M-Y bond.
2. Interchange associative mechanism, *I*a: The M-Y bond begins to break before the M-Z bond is fully formed, but bond formation is more important than bond breaking.
3. Dissociative mechanism, *D*: The M-Y bond is fully broken before the M-Z bond begins to form.
4. Interchange dissociative, I_d: The M-Z bond begins to form before the M-Y bond is fully broken, but bond breaking is more important than bond making.

If the values of K_1 and K_2 are found non zero, it clearly indicates that the reacting complex [ML_2TY] reacts with two different mechanism. For step 1 the term K_1 is first order with respect to both reacting complex and the incoming ligand and follow an associative mechanism. However, for step 2 the term K_2, is first order with respect to reacting complex and independent of the concentration of incoming ligand Z, would suggest the dissociative path way for the reaction. The experimental evidences shows that the step 2 is also follow the associative path. In second step the solvent acts as nucleophile therefore, a competition is set with Z for [ML_2TY] and [ML_2TS] as shown in the above mechanism.

As mentioned, the K_2 term of the rate law shown in above rate law expression could also arise from dissociation of Y to give three coordinated complex which then reacts with Z to give the substituted product.

$$ML_2TY \xrightarrow{-Y} ML_2T \xrightarrow{+Z} ML_2TZ$$

Thus the form of rate law expression does not help to distinguish between associative (or interchange associative) and dissociative (or interchange dissociative) mechanism for the K_2 pathway. It is observed that nucleophilic substitution reaction proceeds faster in more nucleophilic solvent, suggesting that solvent molecule plays an important role in reaction. Also, the rate of dissociative reaction can be accelerated in the presence of bulky ligands.

The thermodynamic study of the ligand substitution reactions of square planar complex also revealed that the substitution takes place via associative mechanism rather than dissociative mechanism. Let us consider the ligand substitution reaction of a square planar complex (trans-$[Pt(PEt_3)_2(R)Br]$ in which substitution of bromide takes place by either iodide or Thiourea. Thermodynamically the rate of nucleophilic substitution reaction of square planar complex is usually determined by the enthalpy of activation ($\Delta H^{\#}$), entropy of activation ($\Delta S^{\#}$) and volume of activation ($\Delta V^{\#}$), respectively. For above reactions the values of entropy of activation ($\Delta S^{\#}$) and volume of activation ($\Delta V^{\#}$) are negative for both the K_1 and K_2 steps. The decrease in entropy is a usual process when two particles come together to give an activated complex. However, the volume of activation ($\Delta V^{\#}$) is determined by doing the reaction under high pressure (as shown in following expression).

$$\Delta V^{\ddagger} = \frac{RTln(\frac{k_1}{k_2})}{(P_1 - P_2)}$$

An activated complex with smaller volume than the reacting complex will give rise the negative $\Delta V^{\#}$, which is the characteristic of an associative reaction.

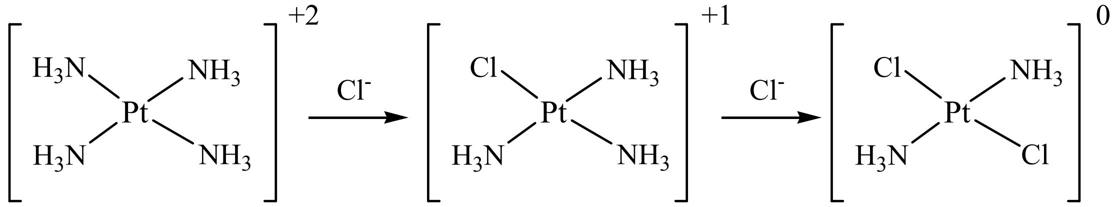
Thus from above discussion it is believed that square planar nucleophilic substitution reactions proceed by associative mechanism rather than dissociative mechanism.

Although, various experiments have been carried out to have the better understanding of the associative mechanism, however, there are still some questions to be answered: such as: what will be the effect of incoming ligand on the rate of reaction and how it affects the mechanism of the reaction. Similarly, some other question, such as the effect of stereochemistry of the complex on the rate of substitution reaction, *i.e.* the effect of the ligands, which are *cis*- or *trans*- to the leaving group, on the rate of reaction and consequently their effect on the mechanism of the reaction. To address the above stereochemical aspect following theory was proposed.

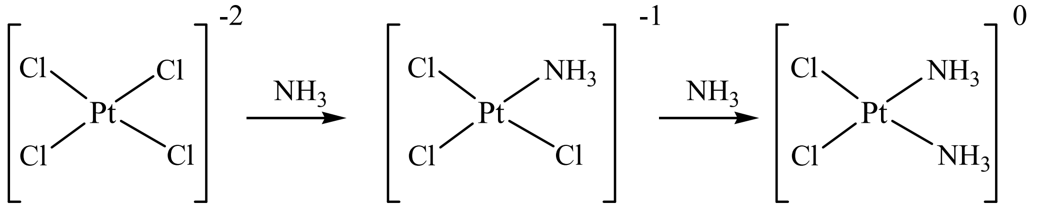
2.3.1a Trans effect:

It was observed that the ligands that are *trans* to leaving group in square planar complexes influences the rate of substitution reaction. This phenomenon is known as *trans* effect. Thus, in substitution reactions the ability of an attached ligand to direct the incoming ligand into a position trans to itself is known as *trans* effect. The *trans* effect was first observed by Werner and further studied by Ilya Ilich Chernyaev (1926). This effect greatly helped to understand the kinetics behaviour of the substitution reactions of square planar complexes in particular. However, this effect is less important in nucleophilic reactions of octahedral complexes except in some complexes where carbonyl or nitrosyl is present as a ligand or where M=O or M≡N bonds are present.

Chernyaev studied the *trans* effect mainly in square planar complex of platinum (II) compounds. According to it, the ligands *trans* to chloride ligand in Pt(II) complex are more easily replaced than those are trans to ammonia; the chloride has stronger *trans* effect than ammonia. The *trans* effect allows the formation of isomeric Pt complexes. Let us consider the following ligands substitution reactions of Pt(II) complexes.



(A)



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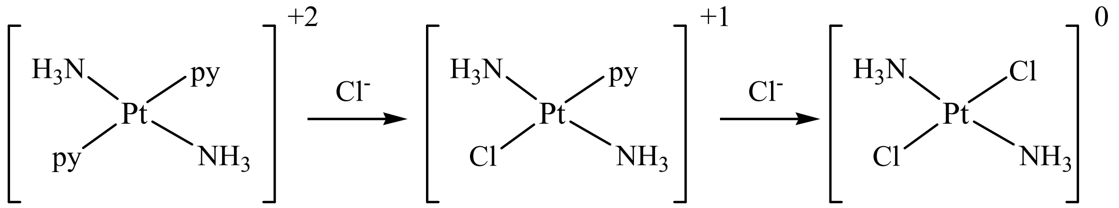
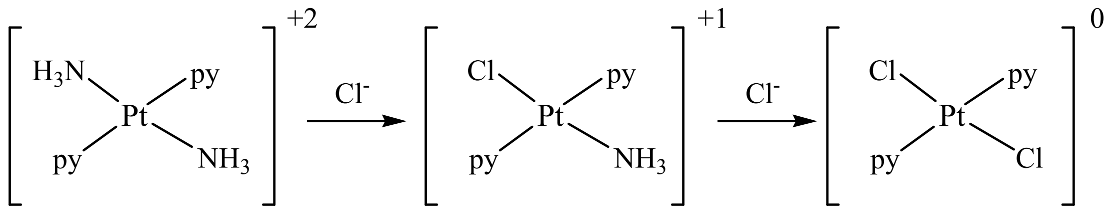


(C)



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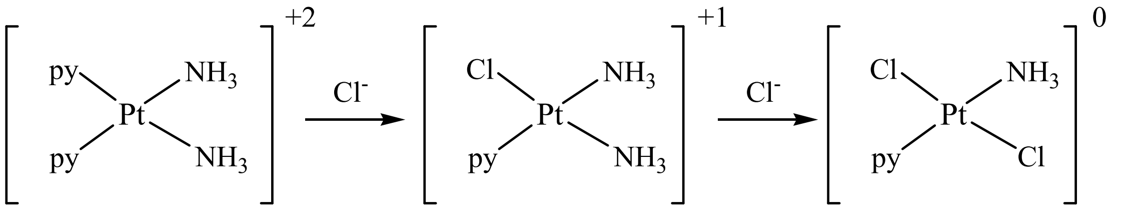
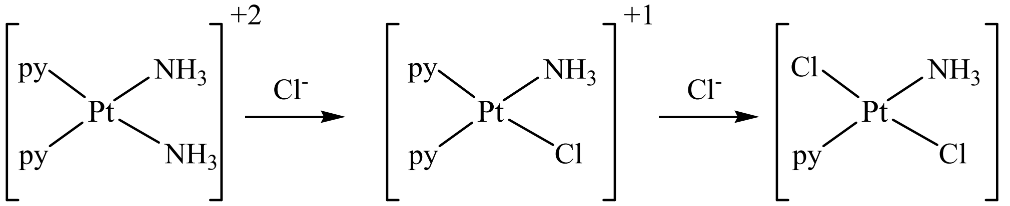


(E)



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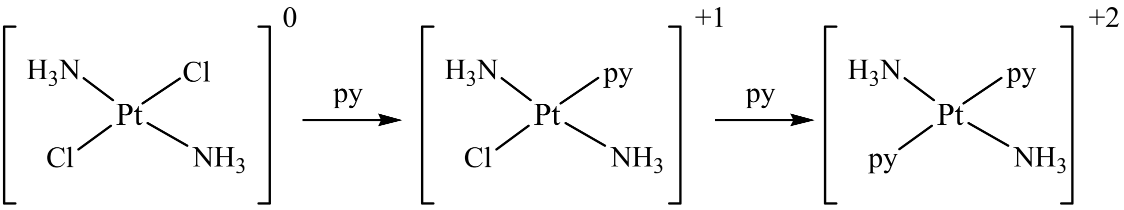
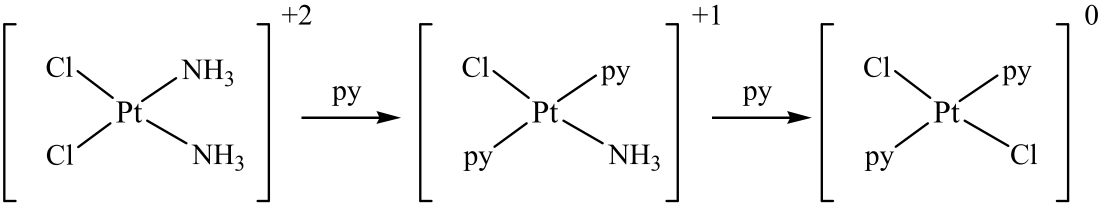


(G)



(H)

Reactions (A) to (H) are the different examples of ligand substitution reactions of different square planar complexes of Pt(II). In example (A), after the first ammonia is replaced, the second ligand is which is *trans* to the first Cl^- ligand. Since the replacement of ammonia by chloride ion is also possible; hence, in example (B), the chloride ligand is replaced by ammonia in first step; however, in second step the replacement of that ligands is takes place which is *trans* to Cl^- ligand. In examples (C) to (F) are the possible replacements, with nearly equal probabilities for replacement of ammonia of pyridine. The second steps of examples (C) to (F) depend on the *trans* effect of Cl^- ligand. Similar, *trans* effect is also observed in examples (G) and (H) in which the first replacement of ligand depends on the greater lability of chloride. Based on such observations, Chernyaev prepared a wide variety of compounds and established the order of *trans*-effect ligands.

$H_2O < OH^- < NH_3 \sim RNH_2 \sim Py < Cl^- < Br^- < SCN^- < I^- < SO_3H < NO_2 < H^- < SH_2 \sim PH_3 < C_2H_4 < CO \sim CN^-$

The CN^-, CO and NO are strong *trans* directing groups, while OH^-, H_2O are *trans* directing groups.

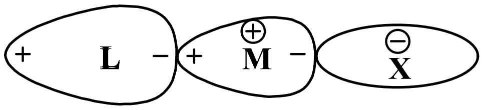
2.3.1b Theories in support to explain the trans effect:

Several theories have been proposed to explain the *trans* effect of ligand in substitution reaction. Since the *trans* effect is a kinetic phenomenon affecting the magnitude of activation energy of a reaction. Thus it depends upon the activation energy, and the stability of both ground state complex and the activated complex (or intermediate). Therefore, any factor that can changes the stability of ground state complex and/or changes the stability of activated complex (or intermediate) would be contributor to the *trans* effect shown by attached ligand. There are two theories of *trans* effect of which one relates the ground state and the other to the activated complex. These two theories are discussed below:

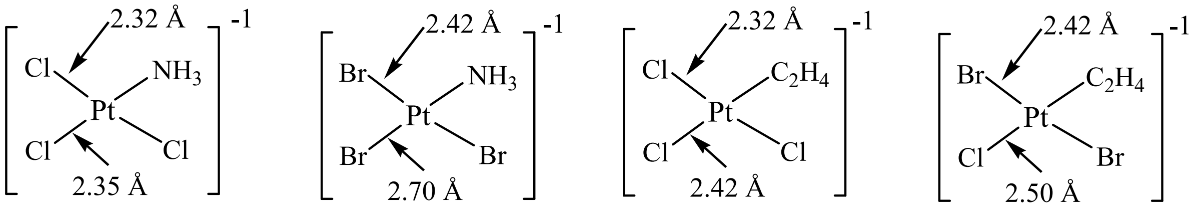
1. The Polarization theory: This theory was put forward by Grinberg in 1927 to rationalize the *trans* effect based on the change in charge distribution among the transition metal and ligands. This theory is primarily concerned with the effect on ground state. In order to explain this theory, let us consider two different types of square planar complexes (*i.e.* $[PtX_4]^{-2}$ and $[PtLX_3]^{-1}$.

$[PtX_4]^{-2}$ Type complexes: Since, all the ligands in the complex $[PtX_4]^{-2}$ are identical, thus the magnitude of induced dipole on ligands by positive charge of Pt(II) will also be identical. Therefore the dipole induced by metal ion on ligands will cancel each other and hence the resultant dipole will be zero. Thus none of the four ligands will show *trans* effect.

$[PtLX_3]^{-1}$ Type complexes: In this kind of complexes where L is different from X's ligand the primary positive charge on Platinum (II) induces a dipole in all ligands. Since, ligands are different therefore the resultant dipole will not be zero. Two similar ligands (two X's) which are placed *trans* to each other will cancel the induced dipole, while other two different ligands placed trans to each other will result a non-zero dipole. Let us assume that ligand L has larger size than X, therefore, L has greater polarizability than ligand X. The orientation of this dipole on the metal ion is such that is repels the negative charge in the ligand X which is *trans* to L. Hence, the ligand X would be less attracted by the metal ion because of the presence of L. The weakening of Pt-X bond *trans* to L make it easy the substitution of ligand X trans to L by the incoming ligand. According to this theory, the polarizability of a ligand should be directly related to this *trans* effect. Thus the ligand with larger polarizability also has greatest *trans* effect. Similarly, the *trans* effect will be important only if the metal is also polarisable. As the *trans* effect of L increases, the bond length of Pt-X decreases hence rate of substitution increases. This is largely true for ligands which do not form π-bonds with the metal ions. This theory does not able to discuss the *trans* effect of ligands present in the activated complex.

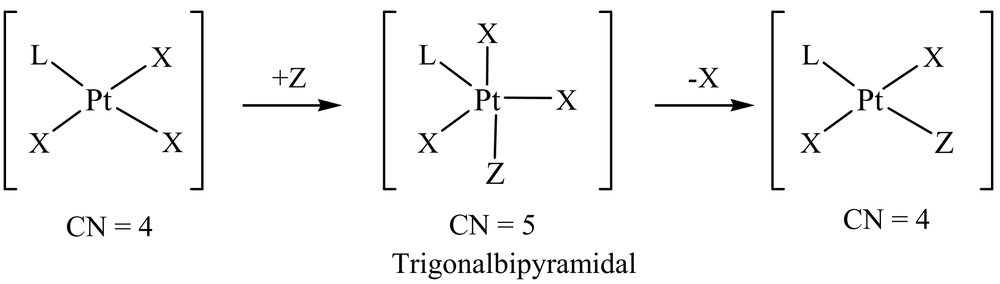


Following are the examples which shows trans effect of ligands trance to each other because of the difference in bond length of metal ligand in complex of $[PtLX_3]^{-1}$ type.



The polarization theory can satisfactory give an explanation of trans effect of the ligands which find place at low end of trans series such as water, hydroxide ion, ammonia etc., but this theory is unable to explain the high trans effect of the π-bonding ligands such as PR_3, NO, CO, C_2H_4, CN^{-} etc.

2. The π-bonding theory: This theory was proposed by Chatt and Orgel to explain the *trans* effect of ligands placed on high end of the trans series. These ligands are either π-acceptor or π-acids like phosphine, CO, olefins etc. According to this theory the empty π or π^* orbitals of the π bonding ligands receive a pair of electrons from the filled d-orbitals of the metal to form metal-ligand π-bond ($d\pi$-$d\pi$ *or* $d\pi$-$p\pi$). Let us consider a square planar complex of Pt(II) (*i.e.* $[PtLX_3]^{-1}$, where L is π–bonding ligand), the d_{yz} orbital of platinum (II) containing a pair of electrons overlaps with the empty P_z orbital of the π–bonding ligand L to form the $d\pi$-$p\pi$ bond between platinum(II) and ligand L. Due to the formation of π–bond between Pt(II) and ligand L in the complex, electron density is increased in the direction of L but reduces in the direction of ligand X placed trans to ligand L. the weakening of the Pt-X bond trans to ligand L make it easy the approach of the incoming ligand (Z) with its lone pair of electrons in the direction of reduced electron density to form the penta-coordinated intermediate species $[PtLX_3Z]^{-2}$ which, loses the ligand X to give the product $[PtLX_2Z]^{-2}$. The intermediate species has distorted trigonal bipyramidal geometry in which two X's ligands, which are *cis* to ligand L, are placed in the apical position.



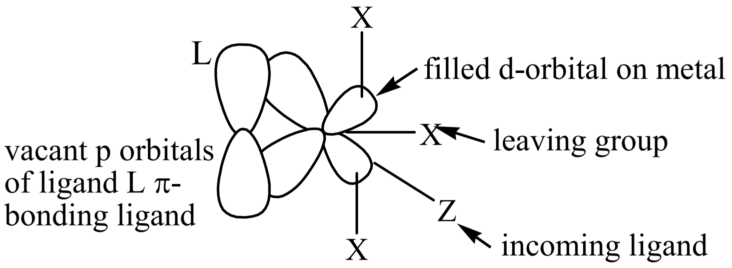
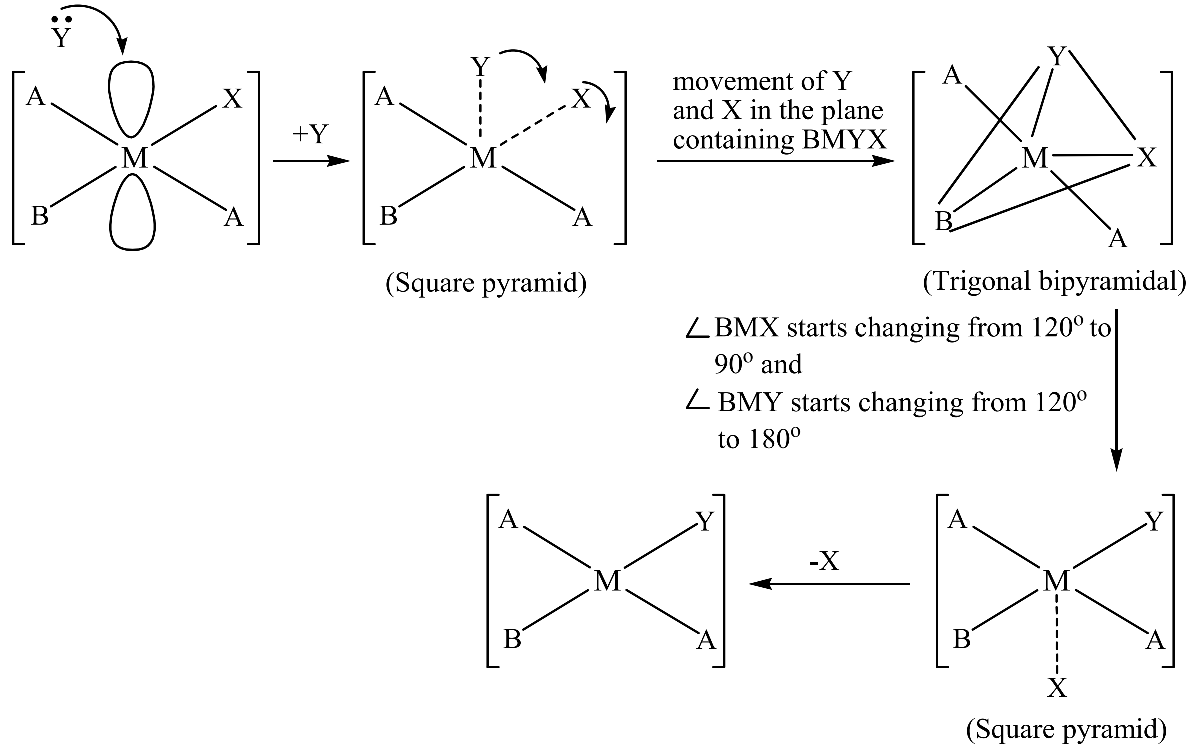


Figure 2.1: Formation of *dπ-pπ* bond in trigonal bipyramidal 5-coordinated intermediate species

Although the π-bonding theory proposes stabilization of the trigonal bipyramidal state, there is evidence that the M-X bonds are longer when they are placed *trans* to a ligand with a strong trans effect than when they are placed cis to such group even in ground state. Therefore, ligand with a strong *trans* effect, affects the ground state as well as the transition state. The present view therefore is that both effects, namely, polarization which weakens the bonds in the ground state and π-bonding which stabilizes trigonal bipyramidal transition state contribute towards the *trans* effect shown by an attached ligand. The extent of contribution by each depends upon the nature of the ligand. The *trans* effect has been made use of in synthesizing certain specific (*cis* or *trans*) complexes. For example, the *cis* and *trans* diamminedichloroplatinum(II) complexes have been synthesized separately keeping in view the trans of Cl^- and NH_3 as illustrated in above equation (A) and (B).

2.3.2 Mechanism of nucleophilic substitution reactions in square planar complexes:

As discussed above that the nucleophilic substitution reaction of square planar complexes occurs through associative (*i.e.* S_N^2) mechanism which involve either the solvent or the incoming ligand as the nucleophilic reagent. In this mechanism the substitution takes place through the formation of penta coordinated intermediate which involve the association of reacting complex with either the solvent or the incoming ligand. The square planar geometry of complex allows the incoming ligand (or solvent) to approach from either above or below the plane of complex. During this approach the incoming ligand faces attraction from the electron deficient central metal ion and repulsion from the filled *d*-orbitals of metal and from the bonding electrons.

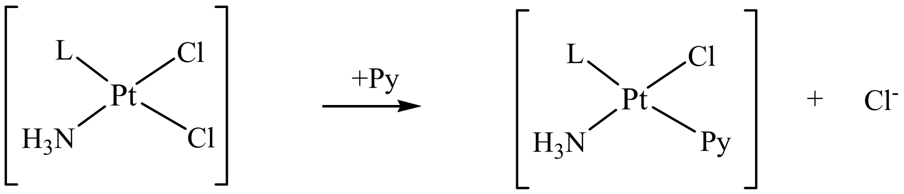


After the association of square pyramidal intermediate is formed which then undergo a transformation to a trigonal bipyramidal structure. In trigonal bipyramidal intermediate geometry, the three ligands, *i.e.* the incoming ligand, leaving ligand and the ligand *trans* to leaving ligand are positioned at equatorial position; whereas, the rest two ligands which are trans to each other in reacting complex are positioned at axial position. As the leaving group departs from the trigonal plane, the trigonal bipyramidal geometry open up and the geometry will again pass through a square pyramidal geometry to form square planar complex. This process is entirely stereospecific, *cis* and *trans* reacting complex lead *cis* and *trans* products.

2.3.3 Factors affecting the rate of ligand substitution reactions in square planar complexes:

The factors which affect the rate of nucleophilic substitution reactions are discussed below:

(1) The *trans* effect: As discussed above the rate of ligands substitution in a square planar complex is affected by the ligand trans to the leaving group. Let us consider the nucleophilic substitution reaction of complex [Pt(NH_3Cl_2L)], the rate of substitution of leaving group (Cl^-) placed trans to ligand L decreases with the decrease in *trans* effect of ligand L.



In this reaction, it has been observed that when L is replaced by ligand such as C_2H_4, NO_2, Br^-, Cl^- in the reacting complex $[Pt(NH_3Cl_2L]$, the relative rate of reaction decreases with the decrease of relative *trans* effect of these trans ligands while the activation energy shows an increase with decease in relative *trans* effect in this order. The kinetic data are shown below:

Relative *trans* effect	$C_2H_4 > NO_2 > Br^- > Cl^-$
Relative rates of substitution reactions	$100 > 90 > 3 > 1$
Activation energy Ea (kcal/mol)	$-11 < 17 < 19$

(2) Effect of the incoming group (nucleophilicity of incoming group): It was mentioned above that the nucleophilic substitution reaction of square planar complex follow the associative mechanism. In an associative mechanism the incoming group plays a crucial role in determining the rate of reaction. The effectiveness of incoming group is a measure of the rate constant. Greater the effectiveness of incoming group, greater will be the value of rate constant for a particular reaction. Let us consider a reacting complex $[Pt(dien)Br]^{+1}$ in which Br is a leaving group.

$$[Pt(dien)Br]^+ + Y^- \xrightarrow{k_2} [Pt(dien)Y]^+ + Br^-$$

When ligand substitution reactions of above complex are performed using different incoming groups at 25°C in aqueous medium, it established the following observations.

The decreasing order of rate constant for various incoming groups is arranged in order to decrease in their nucleophilicity

$$SC(NH_2)_2 > SCN^- > I^- > N_3^- > NO_2^- > py > Cl^- > OH^-$$

(3) Effect of the leaving group: The effect of the leaving group is very difficult to qualify as it is very closely connected with the nature of the incoming nucleophile and the trans ligand. In a dissociative reaction the bond between the leaving group and the metal breaks in the transition state and therefore in these reactions there is a large dependence on the nature of the leaving group. However, for an associative reaction, the effect of the leaving group is dependent on the degree to which bond breaking occurs in the transition state. Each reaction differs in the extent to which bond breaking occurs in their respective transition states.

$$[Pt(dien)Y]^{+} + py \longrightarrow [Pt(dien)py]^{+2} + Y^{-}$$

In above example the rates of reaction using different leaving ligands was calculated and the order of decreasing rate of reaction was observed as

$$NO_3 > H_2O > Cl^{-} > Br^{-} > I^{-} > N_3^{-} > SCN^{-} > NO_2^{-} > CN^{-}$$

It has been observed that H_2O departs about 10^5 times faster than CN^{-}. This indicates that the leaving group has a substantial effect on the rate of the reaction and Pt-X bond breaking make a significant contribution comparable to that of Pt-py bond formation. Generally a good incoming group is a poor leaving group with very few exceptions. The OH^{-} is a very poor nucleophile for Pt(II), but it is replaced very slowly.

(4) Effect of the solvent: The solvent of the reaction medium often influences the energies of the ground state and the transition state through solvation. The degree of solvation of the reactants and the activated complex has a very pronounced influence on the rate of a reaction. The solvent may acts as nucleophile and give rise to parallel path for substitution reaction. The associative substitution reaction mechanism of square planar complex is supported by the involvement of solvent molecule in the transition state. It was observed that the overall rate of substitution reaction increases with increase in the coordinating ability of solvent molecule with central metal ion. This is in consistent with the experimental results of the solvent on the rate of $^{35}Cl^{-}$ exchange with trans-$[Pt(py)_2Cl_2]$, at moderately low concentration of Cl^{-} ions the solvent can be classified into two categories. The first type of solvents is those which have greater coordination ability with central metal as a result the solvent path is exclusively favoured for substitution reactions. Therefore, the rate of such reaction does not depend on the concentration of chloride ion.

$$(K_S >> K_{Cl})$$

Thus for good coordinating solvents, the value of K_{obs} increases in the order of

Solvent	$ROH < H_2O < CH_3NO_2 < (CH_3)_2SO$
K_{obs}	$10^{-4} < 2.1 \times 10^{-3} < 1.9 \times 10^{-3} < 2.3 \times 10^{-2}$

The series shows that the rate of ligand substitution in faster in dimethyl sulphoxide $(CH_3)_2SO$ than in water (H_2O).

The second type of solvents is those which have poor coordinating ability like CCl_4, C_6H_6 etc., and they contribute little to the overall rate of reaction. Therefore, the rate of such reaction does not depend much on the solvent it depends on the concentration of chloride ion.

$$(K_S << K_{Cl})$$

Thus for poor coordinating solvents, the value of K_{obs} increases in the order of

Solvent $CCl_4 < C_6H_6 <$ *m*-Cresol $<$ *t*-C_4H_9OH

K_{obs} $1 \times 10^{-4} < 2 \times 10^{-4} < 2 \times 10^{-4} < 2.3 \times 10^{-3}$

2.4 OXIDATION-REDUCTION (REDOX) REACTIONS

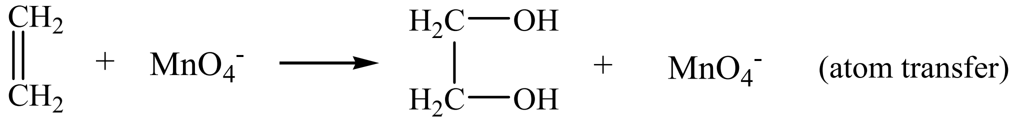
Oxidation-reduction reactions of transition metal complexes involve either atom/group transfer or electron transfer. Reactions of both categories are discussed below:

1. Oxidation-Reduction Reactions through Atom or Group Transfer:

In most of the cases, oxidation-reduction reactions \\can be explained in terms of atom or group transfer. For example, MnO_4^- acts as an oxidant through atom transfer while oxidizing organic compounds. For example

$$RH + MnO_4^- \longrightarrow HMnO_4 + R^- \quad \text{(transfer of H atom)}$$

$$R_2CH_2OH + MnO_4^- \longrightarrow HMnO_4 + R_2CO \quad \text{(transfer of H atom)}$$



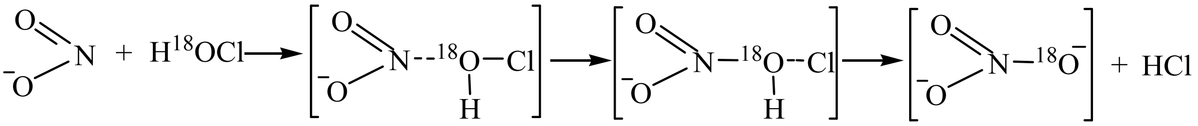
$$CH_2{=}CH_2 + MnO_4^- \longrightarrow H_2C(OH){-}CH_2(OH) + MnO_4^- \quad \text{(atom transfer)}$$

Similarly, Fe^{+2}(aq) acts as a reducing agent if it transfers an H atom from its inner hydration shell to an organic free radial whereas Fe^{+3}(aq) acts as an oxidizing agent if it transfers OH from inner hydration shell to an organic free radical. Thus,

$$[Fe(H_2O)_6]^{+2} + R^{\bullet} \longrightarrow [Fe(H_2O)_5OH]^{+2} + RH \quad \text{(Transfer of H)}$$

$$[Fe(H_2O)_6]^{+2} + R^{\bullet} \longrightarrow [Fe(H_2O)_5]^{+2} + H^+ + ROH \quad \text{(Transfer of OH)}$$

The atom or group transfer reactions have also been studies by NMR and Isotopic exchange Techniques. For example, the oxidation of NO_2^- by HOCl has been shown to occur through the transfer of oxygen atom of HOCl and NO_2^-, by using ^{18}O isotopic exchange.



Atom or group transfer reactions are generally proceeds through inner sphere mechanism, where, the atoms or group under transfer first forms a bridge between the two reacting species which then breaks to affect the transfer of atoms or groups from one reacting species to the other. The oxidation-reduction in such atoms or group transfer reactions does not, necessarily require the transfer of electrons other than those which were already present with the atom or group being transferred.

2. Oxidation-Reduction Reactions through Electron Transfer:

Electron transfer reactions can be further subdivided in to two categories:

(1). The first type include those electron transfer reactions in which electron transfer results in to net chemical change and called simply electron exchange reaction. Examples of such reactions are as follows:

$$\begin{array}{lll|lll}
[Fe(CN)_6]^{-4} & \longrightarrow & [Fe(CN)_6]^{-3} & [Mn(CN)_6]^{-4} & \longrightarrow & [Mn(CN)_6]^{-3} \\
[Fe(H_2O)_6]^{+2} & \longrightarrow & [Fe(H_2O)_6]^{+3} & [Co(NH_3)_6]^{+2} & \longrightarrow & [Co(NH_3)_6]^{+3} \\
[Co(H_2O)_6]^{+2} & \longrightarrow & [Co(H_2O)_6]^{+3} & [Co(CN)_6]^{-4} & \longrightarrow & [Co(CN)_6]^{-3} \\
[Mn(H_2O)_6]^{+2} & \longrightarrow & [Mn(H_2O)_6]^{+3} & [Ce(NH_3)_6]^{+2} & \longrightarrow & [Ce(NH_3)_6]^{+3}
\end{array}$$

Since, in above reactions there is no chemical change; hence these reactions can be studies only by isotopic exchange methods (isotopic labelling) or nuclear magnetic resonance (NMR) spectroscopy.

(2) The second type includes those electron transfer reactions in which there is net chemical change and these are usual redox reactions that which occur and hence these can be studied by various standard chemical and physical methods.

$$[Cr(NH_3)_5X]^{+2} \longrightarrow [Cr(NH_3)_6]^{+3}$$

$$[Cr(NH_3)_5Cl]^{+2} \longrightarrow [Cr(NH_3)_5H_2O]^{+3}$$

Mechanism of Electron Transfer Reactions in Solution Phase:

The electron transfer reactions involving metal complexes have been divided into broad mechanism classes called the outer sphere and inner sphere mechanism. Generally, two types of transition state or intermediates are formed during the electron transfer reactions which are **outer sphere transition states** and **inner sphere transition states**.

The outer sphere transition states appear when the inner coordination spheres of two reacting complex ions remain intact in the transition state (or intermediate) of an electron transfer reaction, it is called an outer sphere transition state. The mechanism of electron transfer reaction through outer sphere transition state is called **outer sphere mechanism**.

Similarly, the inner sphere transition states appear when the coordinated ligand of one complex ion forms a bridge (or linkage) with the other complex ion in the transition state of an electron transfer reaction is known as inner transition state. The mechanism of electron transfer reaction through inner sphere transition state is called **inner sphere mechanism**.

Both, the outer sphere mechanism and the inner sphere mechanism of electron transfer reaction are discussed below separately.

2.4.1. The outer sphere mechanism:

If the reacting complexes (reductant and oxidant complex ions) are inert and if their inner coordination spheres are saturated, the rate of ligand exchange would be very small and the possibility of the formation of a ligand bridge between reacting complexes would be negligible. However, the observed rate of electron transfer between such pairs of complex ions is quite fast. This cannot be explained by any mechanism involving the dissociation of an atom or a group, or exchange of a coordinated ligand, since both the complex ions are inert. Such electron transfer reaction would obviously occur through outer sphere mechanism. Let us consider the following example to understand the electron transfer reactions occur through outer sphere mechanism.

$$[Fe(CN)_6]^{-4} + [Ir(Cl)_6]^{-2} \longrightarrow [Fe(CN)_6]^{-3} + [Ir(Cl)_6]^{-3}$$

In above reaction both electron transfer and ligand exchange occurs but the rate of electron transfer process is faster than ligand exchange for both the reactant. In this type of reactions, both complexes participating in the reaction undergo substitution reactions more slowly than the rate of electron transfer. In the electron transfer process both the reactants (oxidant and reductant) come closer and the coordination spheres stay intact and transfer of an electron takes place from reductant to oxidant. Thus and outer sphere mechanism involves electron transfer from reductant to oxidant when the coordination sphere of both the complexes are in contact at their outer edges (*i.e.* the distance between two metals is minimum).

An outer sphere electron transfer reaction may occur in the following elementary steps:

In first step the oxidants and reductant come closer and form a precursor complex

$$\text{Oxdt} + \text{Redt} \longrightarrow \underset{\text{Precursor complex}}{\text{Oxdt}\,\|\,\text{Redt}}$$

In second step, there is activation of precursor complex which includes recognition of the solvent molecules and changes in M-L bond lengths which occurs before electron transfer.

$$\underset{\text{Precursor complex}}{\text{Oxdt}\,\|\,\text{Redt}} \longrightarrow \underset{\text{Activated complex}}{[\text{Oxdt}\,\|\,\text{Redt}]^{\ddagger}}$$

The activated complex then transformed into ion pair

$$\underset{\text{Activated complex}}{[\text{Oxdt}\|\text{Redt}]^{\ddagger}} \longrightarrow \underset{\text{Ion pair}}{\overset{-}{[\text{Oxdt}}\|\overset{+}{\text{Redt}]}}$$

In final step, the ion pair formed in the third step get dissociated into products.

$$\underset{\text{Ion pair}}{\overset{-}{[\text{Oxdt}}\|\text{Redt}]} \longrightarrow \underset{\text{Products}}{\text{Oxdt}^{-} + \text{Redt}^{+}}$$

After activation of the precursor complex, electron transfer takes place from reducing to oxidizing agents. Reorganization of solvent molecules and changes in metal-ligand bond length must occur before electron transfer takes place.

2.4.2 Salient Features of Outer Sphere Mechanism:

Following are the salient features of outer sphere mechanism.

1. For outer sphere mechanism both the reactants should be kinetically inert. However, if one of the reactant is labile, then the inert complex should not possess a donor ligand which can be used to form a bridge with the labile complex.

   For example: reduction of $[Fe(CN)_6]^{-3}$ by $[Cr(H_2O)_6]^{+2}$

   However, in case, if both the reactants are labile and there is a possibility of electron transfer from π* of reductant to the π* of oxidant, then the reaction proceeds through outer sphere mechanism.

   Example:

$$[Fe(H_2O)_6]^{+2} + [\overset{*}{Fe}(H_2O)_6]^{+3} \longrightarrow [Fe(H_2O)_6]^{+3} + [\overset{*}{Fe}(H_2O)_6]^{+2}$$

2. When both the reactants are inert with respect to ligand exchange, a close approach of the metal ions is impossible and the electron transfer takes place by a tunneling or outer sphere mechanism. The rate of electron transfer depends upon the ability of electrons to tunnel through the ligands.
3. The rate constant of electron transfer reactions via outer sphere mechanism are found to vary over a wide range from 10^{-4} to $\sim 10^{9}$. The difference in rate constant of electron transfer reactions can best be explain in terms of second contribution to the activation energy (*i.e.* energy needed for changing the bond length). The explanation of such wide range of rate constant is discussed below:

According to the Frank-Condon principle, the electronic transition occurs very rapidly than the rearrangement of atoms so that bond distances do not change during such very short period of electronic transition. The electron transfer is very fast when both the reacting complexes are low spin. The electron transfer takes place from π* (t_{2g}) of reductant to the π* (t_{2g}) of oxidant due to their same energy levels and there is no appreciable change in M-L bond length due to such electron transfer. However, if reacting complexes have π acceptor ligands (such as CN^-, Phen, bpy etc.) then the electron transfer is comparatively faster than those reacting complexes having σ donor ligands (such as H_2O, NH_3, en etc.). The vacant π* orbital of π acceptor ligands can accept electrons then pass them to the oxidant. Thus for those reacting complexes having π-donor ligands the outer sphere electron transfer is direct from one metal to another metal. However, for those reacting complexes having π-acceptor ligands the outer sphere electron transfer occurs indirectly.

If the electron transfer from reductant to oxidant occurs from e_g (or σ*) the rate of electron transfer is slow, because the e_g orbitals are shielded by the ligands and thus transfer of electron is sterically slow.

Also, the electron transfer between high spin and low spin complexes occurs with slow rate, because in such reacting complexes the electron transfer occurs from e_g of reductant to vacant e_g of the oxidants resulting the large change in M-L bond length.

4. Outer sphere electron transfer reactions between complexes of different metal ions are faster than that of electron transfer between complexes of similar metal ions. Electron transfer reactions occurring between the complexes having same metal ions are called self exchange reactions in which no net chemical change occurs because the products are indistinguishable from the reactants; however, the elecyron transfer reactions between complexes having different metal ions are called cross reactions in which net chemical change occurs because the reactants and products are distinguishable.

$$[Fe(H_2O)_6]^{+2} + [\overset{*}{Fe}(H_2O)_6]^{+3} \longrightarrow [Fe(H_2O)_6]^{+3} + [\overset{*}{Fe}(H_2O)_6]^{+2}$$

Self exchange reaction

$$[Fe(CN)_6]^{-4} + [Mo(CN)_8]^{-3} \longrightarrow [Fe(CN)_6]^{-3} + [Mo(CN)_8]^{-4}$$

Cross reaction

5. In outer sphere mechanism bonds are neither broken nor formed.
6. In outer sphere mechanism the spin forbidden reactions are slow because these reactions require high activation energy.

The above factors can be made more clear by the following examples and discussion.

1. Consider the given reaction

$$[Fe(CN)_6]^{-4} + [\overset{*}{Fe}(CN)_6]^{-3} \longrightarrow [Fe(CN)_6]^{-3} + [\overset{*}{Fe}(CN)_6]^{-4}$$

Low spin	Low spin
$t_{2g}^6 e_g^0$	$t_{2g}^5 e_g^0$
Inert	inert
Fe^{+2}	Fe^{+3}
BL = 195 pm	BL = 192 pm

The rate of reaction is fast due to following reasons:

(a) Both the reactants are inert hence the electron transfer is faster than the ligand exchange.

(b) Electron transfer is spin allowed.

(c) The electron transfer occurs through t_{2g} of reductant to t_{2g} of oxidants.

(d) Since t_{2g} orbitals are pointed between the ligands hence M-L bond length do not change appreciably.

(e) The ligand CN^- is π-acceptor which facilitates the electron tunneling and also the π-acceptor ligand CN^- is stabilizes the complex with lower oxidation state by forming back π-bonding.

2. Consider the following example

$$[Fe(H_2O)_6]^{+2} + [\overset{*}{Fe}(H_2O)_6]^{+3} \longrightarrow [Fe(H_2O)_6]^{+3} + [\overset{*}{Fe}(H_2O)_6]^{+2}$$

high spin	high spin
labile	labile
Fe^{+3}	Fe^{+2}
$t^3_{2g}e^2_g$	$t^4_{2g}e^2_g$
BL = 78pm	BL = 92pm

In this reaction, the reactants and products are the same except the position of radioactive label. The energy of activation for this reaction is 32 $kJmol^{-1}$, this indicates that the rate of electron transfer is slow (the second order rate constant $4Lmol^{-1}s^{-1}$). Since, the energy levels of the reacting complexes are not equal for electron transfer process; hence the electron transfer process is very slow. The electron transfer occurs through t_{2g} of reductant (FeII) to t_{2g} (FeIII) of oxidants, both have different energy levels.

3. Consider another example

$$[Co(NH_3)_6]^{+3} + [\overset{*}{C}o(NH_3)_6]^{+2} \longrightarrow [Co(NH_3)_6]^{+2} + [\overset{*}{C}o(NH_3)_6]^{+3}$$

Low spin	High spin	Co^{+2}	Co^{+3}
Co^{+3}	Co^{+2}	$t^6_{2g}e^1_g$	$t^5_{2g}e^1_g$
$t^6_{2g}e^0_g$	$t^5_{2g}e^2_g$	BL = 231pm	BL =177pm
BL = 196pm	BL = 211pm		

The two reacting complexes (in given reaction) have almost equal metal ligand bond length hence it is expected that the electron transfer reaction is fast. However, the two reacting complexes have different electronic configuration (before and after electron transfer). These different electronic configurations represent state with a much higher energy. This additional energy can be released in the form of radiation or thermal energy. But the additional energy is involved in the activation energy of the reaction. This could affects the rate of reaction hence the rate of electron transfer between reacting complexes is much slower with a second order rate constant 10^{-4} $m^{-1}s^{-1}$.

(1). Consider another example

$$[Ru(NH_3)_6]^{+3} + [Ru(NH_3)_6]^{+2} \longrightarrow [Ru(NH_3)_6]^{+2} + [Ru(NH_3)_6]^{+3}$$

Low spin	Low spin	Low spin	Low spin
Ru^{+3}	Ru^{+2}	Ru^{+2}	Ru^{+3}

The electron exchange rate of the above reaction is 8.2 X 10^2 $mol^{-1}s^{-1}$. The metal ligand bond length difference between both the reacting complexes is very small (*i.e.* 4pm). As a result much faster electron exchange rate for the above reaction is expected because of small bond length adjustment before electron transfer. Also, the ruthenium complexes remain low spin in both the reduced and oxidized form.

(2). The electron transfer reaction

$$[MnO_4]^{-2} + [MnO_4]^{-} \longrightarrow [MnO_4]^{-} + [MnO_4]^{-2}$$

is fast with second order rate constant of approximately 10^3 (at 0°C).

2.4.3 Marcus-hush theory:

Marcus-Hush theory (M-H) was developed in 1956 by Rudolph A. Marcus which explains the fundamentals of the redox/ electron transfer reactions in terms of the rate of jumping/moving an electron from oxidant species (electron donor) to the reductant (electron acceptor). M-H theory works as alternative Eyring's transition state theory for electron transfer reactions where bond making or bond breaking does not occur. For electron transfer processes there are some important facts associated with this theory which influence the electron transfer process in redox reactions.

2.4.3.1 Vibration barrier: According to M-H theory vibration barrier exists that slows down the redox/ electron transfer reactions. The equilibrium structures for both the reacting complexes are dissimilar and the oxidation state to be changed during the course of reaction. If electron transfer should occur the Franck Condon Principle must be fulfilled (it says that the movement of the nuclei is slow compared to the movement of the electrons. The nuclear positions do not change during the reaction, which is characteristic for a vertical process). Under energy conservation the electron transfer can only take place on the cut surface of the two potential curves.

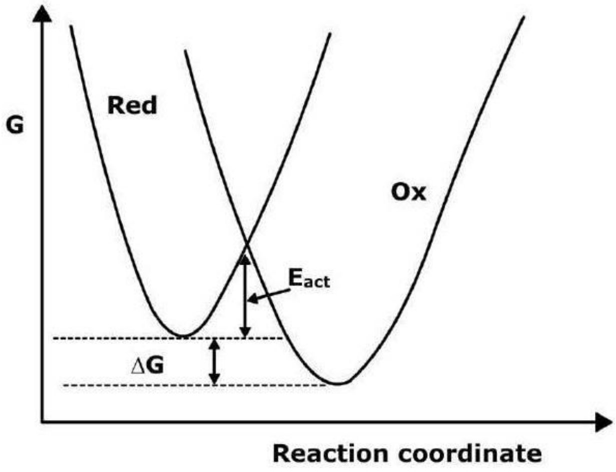


Figure 2.2

The energy on this surface is equal to the thermal activation energy. For an electron transfer to take place, the electronic movement must be faster relative to that of nuclear movement. The vertical process feature suggests that nuclear locations do not change at the time of reaction. According to the energy conservation law, the transfer of electron can merely occur on the cut surface of two potential curves whose energy is equal to that of thermal activation energy. The structural reorganization of each complex takes place by bringing the distant ligand closer and the closer to distant by adjusting all the M-L bond lengths to be equal (λi inner reorganisation energy). This reorganization is associated to facilitate the electron transfer that requires both redox centres must have a alike structure during the course of electron transfer. As the vibration barrier is proportional to the distance between redox centres the closer attachment of both the redox partners is desired to make the redox barrier low and thus electron transfer to be faster.

2.4.3.2 Solvation barrier: Another factor that influences redox process is solvation barrier which is related to the organization of solvent molecules. During the complete electron transfer reaction the solvent shell around the complexes will change and this change needs energy which is related to the outer reorganisation energy λ_o. Before the electron can be transferred the solvent shells must change into similar structures.

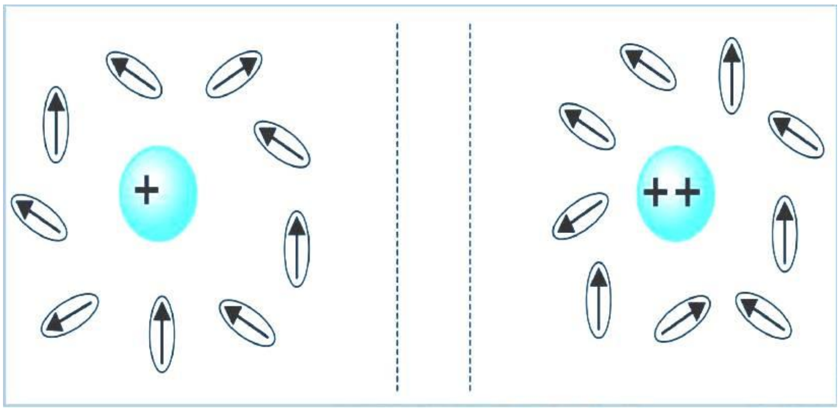


Figure 2.3

The Marcus –Hush theory calculated the free energy change $\Delta G^{\#}$ for outer sphere reaction. In this model outer sphere reactions are regarded as involving the following five steps.

1. The oxidizing and reducing agents combine together to form an outer sphere complex i.e. precursor complex in which both metal coordination spheres remains intact.

$$\text{Oxdt} + \text{Redt} \longrightarrow \underset{\text{Precursor complex}}{\text{Oxdt}\,\|\,\text{Redt}}$$

2. Bond distances around each metal change to become product like structure. In the transition state for electron exchange both species has the same dimensions. The bond length of the M-L bond must be the same in both oxidizing and reducing agents and therefore contribution to the activation energy of bond stretching and contracting should be small.
3. The solvent shell around the outer sphere complex reorganizes. The activation energy includes the energy required for the reorganization of solvent shell outside the first coordination sphere.

$$\underset{\text{Precursor complex}}{\text{Oxdt}\,\|\,\text{Redt}} \longrightarrow \underset{\text{Activated complex}}{[\text{Oxdt}\,\|\,\text{Redt}]^{\ddagger}}$$

4. The electron is transferred from reducing agent to oxidizing agent and ion pair is formed.

$$[\text{Oxdt}\|\text{Redt}]^{\ddagger} \longrightarrow \overset{-}{[}\text{Oxdt}\|\text{Red}\overset{+}{\text{t}}]$$

Activated complex Ion pair

5. The ion pair dissociated in to product which diffuses away, this step is generally fast.

$$\overset{-}{[}\text{Oxdt}\|\text{Redt}] \longrightarrow \text{Oxdt}^{-} + \text{Redt}^{+}$$

Ion pair Products

The activation energy for the electron transfer reaction is made of three parts

$$\Delta Ea = \Delta Et + \Delta Ei + \Delta Eo$$

Where

ΔEt = Energy needed to bring the oxidizing and reducing agents into configuration in which they are separated by the required distance

ΔEi = Energy needed for compression and stretching of bonds to get orbitals of same energy (energy needed to change the bond length)

ΔEo = Energy needed for reorganization of solvent shell outside the first coordination sphere

Similarly, the various contributing factors for $\Delta G^{\#}$ can be expressed as given below

$$\Delta G^{\#} = \Delta G^{\neq}_{inner\ sphere} + \Delta G^{\neq}_{solvation} + \Delta G_{r^{o}} + \frac{(\Delta G_{r}o)^{2}}{16(\Delta G^{\neq}_{inner\ sphere} + \Delta G^{\neq}_{solvation})}$$

Where $\Delta G_{r^{o}}$= Overall free energy change of the reaction

$\Delta G^{\neq}_{inner\ sphere}$ = Energy require to change the bond length

$\Delta G^{\neq}_{solvation}$ = Energy require for solvent reorganization

Solving the above relation we obtained

$$\Delta G^{\neq} = \frac{\lambda}{4}\left[1 + \frac{\Delta G^{0}}{\lambda}\right]^{2}$$

$$\Delta G^{\neq} = \left[\frac{\lambda + \Delta G^{0}}{4\lambda}\right]^{2}$$

This equation express the barrier hight or free energy activation for crossing two curves in terms of the overall free energy of reaction ΔG^{o} and the reorganization energy λ. The expression for the rate constant k_{et} of the reaction is given from the standard Arrhenius relationship

$$k_{et} = A\exp\left[\frac{-\Delta G^{\neq}}{K_{B}T}\right]$$

The prefactor *A* in above equation depends on the nature if the electron transfer reaction. ΔG^0 is the standard free energy for the reaction (and equal to zero for the self exchange reaction) and λ is a reorganization term.

The reaction profiles can be discriminated by following three ways:

a) $(\lambda+\Delta G^0) > 0$: Marcus's normal region, rate of reaction enhances with increase in ΔG^0

b) $(\lambda+\Delta G^0) = 0$: reaction rate reaches to maximum since there is no activation barrier for electron transfer to occur (diffusion controlled reaction)

c) $(\lambda+\Delta G^0) < 0$: Marcus's inverted case and rate reaction diminishes since activation barrier increases.

2.4.4 Cross reactions:

The electron transfer reactions that take place between two complexes having different metal ions are known as cross reactions. In cross reactions net decrease in free energy is observed. Hence the rates of electron transfer reactions are generally higher than those observed fro comparable exchange reactions. Some examples are

$$[Fe(CN)_6]^{-4} + [Ir(Cl)_6]^{-2} \longrightarrow [Fe(CN)_6]^{-3} + [Ir(Cl)_6]^{-3}$$

$$[Fe(CN)_6]^{-4} + [Mo(CN)_8]^{-3} \longrightarrow [Fe(CN)_6]^{-3} + [Mo(CN)_8]^{-4}$$

The rate of electron transfer reaction is faster than ligand exchange for either reacting complexes which means that both reacting complexes undergo ligand exchange reactions more slowly than they participate in the electron transfer process. In these reactions both reacting complexes are termed as inert complexes because the rate of electron transfer process has a second order rate constant of 10^5 $mol^{-1}s^{-1}$ at 25°C. Since both reacting complexes are inert, so the process of electron transfer from reducing agent to oxidizing agent with bond breaking is not considered. In these reaction also, bond are neither broken nor formed. Thus the mechanism of cross reaction involves electron transfer from reducing agent to oxidizing agent without breaking of metal ligand bond. In these reactions also the bond length and the solvent molecules reorganized in the transition state and proceeds to products. When the excited states of product revert to ground state, the lowering in energy can appear as the free energy of the reaction.

2.4.5 Inner sphere reactions:

The inner sphere reactions are those which incorporate "sharing/bridging" of at least one ligand for electron transfer and the reactants undergo change in complementary oxidation state. The reactants join together to result a single primary bond system through adopting ligand bridging pathway. There are two significant points for inner sphere reactions to take place; 1) The complex having at least one ligand with secondary binding site that is sterically favorable to the second metal ion is desirable (not compulsory) condition for inner sphere reactions; 2) Complex receiving the ligand must be labile in terms of expanding its coordination number at the time of electron transfer. Therefore, such reactions can be considered to be mediated by bridging ligand. Unlike to that for outer sphere mechanism, the coordination sphere of the complex participates in the inner sphere mechanism and atom/group/ion transfer occurs. Despite satisfying above mentioned terms and conditions, the reactants may still adopt a lower energy pathway that is outer sphere mechanism therefore a convincing evidence for inner sphere route is required. Although, the variation in mechanistic plausibility has been numerously argued to support inner sphere pathway but direct evidences are still lacking. Inspite of this the inner sphere reactions are of considerable importance owing to its widespread applications.

In inner sphere reactions two reacting complexes *i.e.* oxidizing and reducing combine to form bridged intermediate in which one ligand is shared. The bridging/sharing ligand mediates inner sphere electron transfer process. Both the reacting metal complexes should connect with a bridging ligand during the course of substitution. One of the reacting species should have a ligand that can form a bridge between both the metal complexes. The bridging ligand formation is basically intermediate therefore it is occasionally called a ligand-bridged mechanism. The transfer of electron as well as sometimes transfer of ligand occurs depending upon the groups or ligands attached with the reactants. However, inner-sphere redox reactions are slower relative to that of outer-sphere reactions. The mechanism of an inner-sphere electron transfer reaction involves the following four steps which can be represented as:

1. In the first step of the reaction, substitution by the bridging group into coordination sphere of a labile complex (generally a reducing agent) takes place and hence a bridged intermediate binuclear species known as precursor complex is formed.

$$\mathrm{Ox{-}X} \quad + \quad \mathrm{R - OH_2} \rightleftharpoons [\mathrm{Ox{-}X{-}R}] \quad + \quad \mathrm{H_2O}$$

2. In second step, precursor complex species gets activated which include reorganization of solvent molecules and changes in metal ligand bond length.

$$[Ox—X—R] \rightleftharpoons [Ox—X—R]^*$$

3. In third step electron transfer from reducing agent to oxidizing agent takes palce as a result the ion pair (successor complex) is formed

$$[Ox—X—R]^* \rightleftharpoons [\overset{-}{Ox}—X—\overset{+}{R}]$$

4. Decomposition of ion pair (successor complex) leads to the formation of product

$$[\overset{-}{Ox}—X—\overset{+}{R}] \rightleftharpoons Ox(H_2O)^- + X—R^+$$

The rate law for the overall reaction

$$Ox-X + R-OH_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [Ox—X—R] \underset{k_4}{\overset{k_3}{\rightleftharpoons}} Ox(H_2O)^- + X—R^+$$

is

$$Rate = \frac{k_1 k_3}{k_2 + k_3}[Ox - X][R - OH_2]\text{.........(1)}$$

Where k_3 is the overall rate constant for 2nd and 3rd step/

If $k_3 >> k_2$ then the rate determining step is the precursor complex and the rate law will be:

$$Rate = k_1[Ox - X][R - OH_2]\text{.........(2)}$$

If $k_2 >> k_3$ then the rate determining step will be rearrangement and electron transfer within the intermediate. Thus rate law will be

$$Rate = \frac{k_1 k_3}{k_2}[Ox - X][R - OH_2]\text{.........(3)}$$

Some examples of inner sphere electron transfer reactions are discussed below:

(1). This is the first reaction reported which occurs theough inner sphere mechanism

$$[Co(NH_3)_5Cl]^{+2} + [Cr(H_2O)_6]^{+2} + 5H_3\overset{+}{O} \longrightarrow [Co(H_2O)_6]^{+2} + [Cr(H_2O)_5Cl]^{+2} + 5\overset{+}{N}H_4$$

Low spin	High spin	High spin	-
Co^{+3}	Co^{+2}	Co^{+2}	Co^{+3}
$t^6_{2g}e^0_g$	$t^3_{2g}e^1_g$	$t^5_{2g}e^2_g$	$t^3_{2g}e^0_g$
Inert	Labile	Labile	Inert

In this reaction Co^{+3} is reduced by Cr^{+2} and the bridging ligand Cl^- is transferred from coordination sphere of cobalt to that of chromium. Following points may be considered in respect of the above reaction.

(a). $[Co(NH_3)_5Cl]^{+2}$ is kinetically inert and $Cl^-$is the bridging ligand.

(b). Electron transfer takes place from $e_g(\sigma^*)$ of $[Cr(H_2O)_6]^{+2}$ to $e_g(\sigma^*)$ of $[Co(NH_3)_5Cl]^{+2}$.

Thus, electron transfer by inner sphere mechanism is fast (k = 6 x 10^5 $Lmol^{-1}s^{-1}$).

(2). In the following reaction, no ligand transfer occurs because both the reacting complexes are inert.

$$[Fe(CN)_6]^{-3} + [Co(edta)]^{-2} \longrightarrow [Fe(CN)_6]^{-4} + [Co(edta)]^{-}$$

The comparative inner sphere and outer sphere reaction pathways strongly recommend the presence of a bridging ligand in one of the metal complex reactants to precede the reaction through inner sphere pathway.

The bridging ligands are usually negatively charges monodentate ligands i.e.:

Cl^-, Br^-, I^-, OH^-, NCS^-, SCN^-, N_3^-, CN^-, etc.

There are some other ligands as well which can act as bridging ligands in the course of electron transfer reaction through inner sphere path such as:

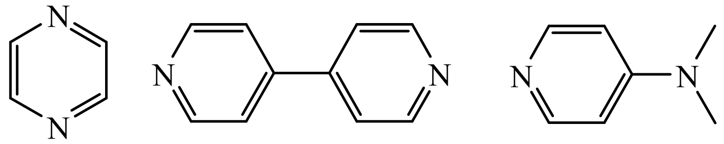


Figure 2.4

2.4.6 The basic requirement for inner sphere mechanism:

Following are the basic requirements for a redox reaction to proceed via inner sphere electron transfer process:

1. One of the reacting metal complexes (generally oxidant) has at least one ligand which can bridge concurrently to both the metals (in the oxidant and reductant).
2. The metal complex (usually reductant) must be labile for substitution so that one of the ligand from it can be displaced by the incoming bridging ligand.

2.5 FACTORS AFFECTING THE RATES OF ELECTRON TRANSFER REACTIONS:

The factors affecting the rate of electron transfer reactions are explained below:

1. Electrostatic repulsion between ions of like charges: Energy is needed to bring both the reacting complexes to a required distance for charged reactants; this includes also the energy to overcome columbic repulsion. This energy factor contributes to the activation energy of reactions. Due to electrostatic repulsion, the activation energy also increases which slow down the rate of reaction.

2. Nature of Ligands: Outer sphere electron transfer reactions are found to be more rapid for those reacting complexes containing ligands with π-electron system which provide easy passage of electrons. Electron transfer reactions for reacting complexes containing ligands like water or ammonia are much slower than complexes containing cyanide ligand.

$[Co(NH_3)_6]^{+2} – [Co(NH_3)_6]^{+3}$	10^{-4} $mol^{-1}s^{-1}$
$[Co(en)_3]^{+2} – [Co(en)_3]^{+3}$	10^{-4} $mol^{-1}s^{-1}$ (at 25° C)
$[Fe(CN)_6]^{-3} – [Fe(CN)_6]^{-4}$	10^{-5} $mol^{-1}s^{-1}$ (at 25° C)

3. Conductivity of ligands: The greater the conductivity of bridging ligands, the faster will be the electron transfer reaction between two reacting complexes. For example, the electron transfer between different complexes of cyanide ligand has been found to be rapid.

4. Polarizability of bridging ligands: The ability of bridging mono atomic ligand to carry the transferred electrons can be related to the polarizability of bridging group. In a reaction between Cr^{+2} and CrX^{+2} and than between Cr^{+2} and $[Co(NH_3)_5X]^{+2}$, the rate of electron transfer decreases as the bridging ligand X is changed in the order

$$F^{-} < Cl^{-} < Br^{-} < I^{-}$$

However, for the reactions Fe(II) – $[Co(NH_3)_5X]^{+2}$ and Eu(II) - $[Co(NH_3)_5X]^{+2}$, the reverse order is obtained (i.e. $F^{-} > Cl^{-} > Br^{-} > I^{-}$).

5. Reorganization energy or Frank-Condon energy: The bond length in $[MnO_4]^{-}$ and $[MnO_4]^{-2}$ system differs as in the activated complex a compressed Mn-O bond in $[MnO_4]^{-2}$ and a stretched Mn-O bond in $[MnO_4]^{-}$ is observed. The rate constant for this reaction is second order with nearly 10^{3}. If the reacting complexes has different M-L bond length, different geometry or solvation shell or electronic configuration, a slow rate of electron transfer reaction is expected. For octahedral complexes, bond lengths are changed more drastically when e_g-electrons are involved in the electron transfer as compared to t_{2g} electrons in the *d*-orbitals. Thus, energy needed for bond compression and stretching to accomplish orbitals of same energy will be large, the activation energy for the electron transfer reaction also increases significantly.

6. Free energy of the reaction ($\Delta G^{\#}$): The greater the negative free energy change for the overall reactions, the greater will be the rate of reaction.

2.6 SUMMARY

The present unit may be summarized as follow:

- The unit begins with the discussion on ligands substitution reactions occur in square planar complexes.
- Further unit explains the determination of rate law for nucleophilic substitution reactions of square planar complexes
- Various mode of mechanism proposed (associative, interchange associative, dissociative and interchange dissociative) for the substitution reactions in square planar complexes have also been elaborated in this unit.
- The effect of ligands that are *trans* to the leaving group on substitution reactions (*trans* effect) is discussed in detail along with the theories supporting the *trans* effect are also elaborated in the present unit.
- The unit also well explained the factors affecting the rate of ligand substitution reactions in square planar complexes.
- The fundamentals of oxidation-reduction (redox) reactions of the transition metal complexes also discussed like group transfer redox reactions, electron transfer redox reactions etc.
- The mechanism of electron transfer reactions i.e. outer sphere mechanism and inner sphere mechanism along with their salient features also explained in the unit.
- The fundamentals of Marcus-Hush theory for the explanation of redox reactions are also discussed.
- The vibration barrier and salvation barriers which need surplus energy to facilitate electron transfer process is also incorporated.
- The fundamental understandings on cross reaction are obtained from the later section of unit.
- Contributions of diverse free energies on reorganizations of reactants is discussed and summations of all free energy gives total energy of activation for cross reactions
- Detailed introduction about inner sphere reactions is given with deciding parameters to distinguish them from outer sphere reactions.
- The stability of the reacting partners which is also responsible whether formation of precursor complex will be faster or slower has been discussed.
- The stability of the precursor complex (bridged complex) has also been discussed since it facilitates/not facilitates the electron transfer depending on stability.
- Importance of bridging/sharing ligands on the rate of inner sphere reactions is also discussed briefly.

- At the end of the unit the factors affecting the rate of redox reactions in transition metal complexes is discussed.

2.7 SQAs TYPE QUESTIONS

(a) Multiple choice questions

1. The Ni$(CN)_4$ complex is

a) Inert b) Labile

c) Both (a) and (b) d) none the above

2. $[Pt(Cl)_4]^{-2}$ reacts with ammonia to form

a) *cis*-$[Pt(Cl)_2(NH3)_2]$ b) *trans*-$[Pt(Cl)_2(NH3)_2]$

c) both (a) and (b) d) none the above

3. Ligand group with minimum *trans* effect

a) CN^- b) C_2H_4

c) NH_3 d) H_2O

4. Substitution of *X* is very rapid in square planar complexes when *X* is

a) NO_3^- b) Cl^-

c) Br^- d) I^-

5. Substitution reactions in square planar complexes is

a) SN1 b) SN2

c) SE1 d) SE2

6. If two complexes form a bridged intermediate the mechanism will be

a) Inner sphere b) Outer sphere

c) SN1 d) Sn2

7. Theorie(s) in support of the *trans* effect is (are):

a) The Polarization theory b) The π-bonding theory

c) Both (a) and (b) d) none the above

8. In associative ligand substitution reaction of square planar complex the square pyramidal complex transformed in to:

a) trigonal bipyramidal b) pentagonal

c) Both (a) and (b) d) none the above

9. The decreasing order of rate constant for various incoming groups (Y) for following ligand substitution reactions will be

$$[Pt(dien)Br]^{+} \quad + \quad Y^{-} \xrightarrow{k_2} [Pt(dien)Y]^{+} \quad + \quad Br^{-}$$

a) $SCN^{-} > I^{-} > N_3^{-} > NO_2^{-}$ b) $SCN^{-} > N_3^{-} > I^{-} > NO_2^{-}$

c) $SCN^{-} > I^{-} > NO_2^{-} > N_3^{-}$ d) $SCN^{-} > N_3^{-} > NO_2^{-} > I^{-}$

10. The decreasing order of rate constant for various leaving groups (Y) for following ligand substitution reactions will be

$$[Pt(dien)Y]^{+} \quad + \quad py \longrightarrow [Pt(dien)py]^{+2} + \quad Y^{-}$$

a) $NO_3 > Cl^{-} > Br^{-} > H_2O > I^{-}$ b) $NO_3 > H_2O > Cl^{-} > Br^{-} > I^{-}$

c) $NO_3 > I^{-} > H_2O > Cl^{-} > Br^{-}$ d) $NO_3 > Cl^{-} > Br^{-} > H_2O > I^{-}$

11. In outer sphere mechanism the first step involves the formation of

a) Ion pair b) Activated complex

c) Precursor complex d) Products

12. The best condition for outer sphere mechanism

a) Both reactants must be inert b) Both reactants must be labile

c) One reactant labile other inert d) None the above

13. The electron transfer reactions via outer sphere mechanism have rate constant in the range of

a) 10^{4} to ~10^{9} b) 10^{-9} to ~10^{9}

c) 10^{-4} to ~10^{-9} d) 10^{-4} to ~10^{9}

14. The best condition for outer sphere mechanism

a) Both reacting complexes must have same metal ions b) Both reacting complexes must have different metal ions

c) Both (a) and (b) d) None the above

15. In outer sphere mechanism

a) Bonds are neither broken nor formed b) Bonds are formed but not broken

c) Bonds are broken but not formed d) Both (b) and (c)

16. The electron transfer reaction that takes place between two complexes having different metal ions in known as

a) Cross reaction b) Remote reaction

c) Spin cross over reaction d) Group transfer reaction

17. In inner sphere mechanism the reductant complex must be

a) Inert b) Labile

c) Both (a) and (b) d) none the above

B. Fill in the bling

(i) The ligands that are *trans* to leaving group in square planar complexes influences the rate of substitution reaction. This phenomenon is known as ………..

(ii) The square planar geometry is less favoured sterically than the…………. geometry when the ligands are large.

(iii) Outer sphere electron transfer reactions between complexes of …………different metal ions are faster than that of electron transfer between complexes of similar metal ions.

(iv) The electron transfer reactions that take place between two complexes having different metal ions are known as…………..

C. True/False

(i) Chernyaev studied the *trans* effect mainly in square planar complex of platinum (II) compounds True/False

(ii) Marcus-Hush theory (M-H) was developed in 1956 by Rudolph A. Marcus True/False

(iii) H_2O show greater trans effect then NH_3 True/False

(iv) In outer sphere complexes both reactant are oxidant or reductant True/False

D Match the following

i. $[Fe(CN)_6]^{-4}$	a. $t_{2g}^3e_g^2$
ii. $[Fe(CN)_6]^{-3}$	b. $t_{2g}^4e_g^2$
iii. $[Fe(H_2O)_6]^{+2}$	c. $t_{2g}^6e_g^0$
iv. $[Fe(H_2O)_6]^{+3}$	d $t_{2g}^5e_g^0$

Answer Keys:

A. 1 (b) 2 (a) 3 (d) 4 (a) 5 (b) 6 (a) 7 (c) 8 (a) 9 (c)
10 (b) 11 (c) 12 (a) 13(d) 14 (b) 15 (a) 16 (a) 17 (b)

B. (i) *trans* effect, (ii) tetrahedral (iii) different metal ions (iv) cross reactions

C. (i) True (ii) True (iii) False (iv) False

D. i c ii d iii b iv a

2.8 GLOSSARY :

Oxdt = Oxidant

Redt = Reductant

t_2g = Triple degenerate state

eg = Doubly degenerate state

Ea = Activation energy

dien = Diethylenetriamine

Phen = Phenanthroline

Edta = Ethylene diamine tetraacertate

2.9 REFERENCES :

1. Huheey J. E., Keiter E. A., Keiter R. L., (1997), *Inorganic chemistry- Principles of structure and reactivity(Fourth Edition)*, Pearson, 964.
2. Puri B. L., Sharma L. R., Kalia K. C., (2020), *Principles of Inorganic Chmistry, (33rd Edition)*, Vishal Publishing.
3. Miessler G. L. , Fischer P. J., Tarr D. A., (2014) *Inorganic Chemistry(5th edition),* 696.
4. Banerjea D., (2009), *Coordination Chemistry" (second edition),* Asian Books, 4, 874.
5. House J. E., (2009), *Inorganic Chemistry*, Elsevier,

2.10 SUGGESTED READING

1. C. E. Housecroft, A. G. Sharpe, (2018), *Inorganic chemistry*, Pearson (Fifth edition), 1256.
2. F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, (1999), *Advanced inorganic chemistry*, Wiley-Interscience (Six Edition), 1376.
3. J. D. Lee, (1999), *Concise inorganic chemistry*, Wiley-Blackwell (Fifth edition), 1072.

2.11 TERMINAL QUESTIONS

1. Discuss the mechanism involved in electron transfer reactions. Give suitable examples.

2. Give examples of oxidation-reduction reactions occurring through the transfer of atoms or groups of atoms.
3. Give examples of oxidation-reduction reactions occurring through the transfer of electrons.
4. What are the conditions for transfer of an electron from M^{+2} to M^{+3} in aqueous medium?
5. Discuss the outer sphere and inner sphere mechanism of electron transfer reactions.
6. Explain why the electron transfer in $[Co(NH_3)_6]^{+2} \rightarrow [Co(NH_3)_6]^{+3}$ slower than the electron transfer in $[Fe(CN)_6]^{-4} \rightarrow [Fe(CN)_6]^{-3}$?
7. Explain the method for determination of rate law for nucleophilic substitution reaction of square planar complex.
8. Discuss the mechanism of nucleophilic substitution reactions in square planar complexes.
9. What do you understand with the *trans* effect? Explain with giving some examples.
10. What are the theories that support the *trans* effect?
11. Discuss the factors affecting the rate of ligand substitution reactions in square planar.
12. What are the Salient features of outer sphere mechanism? Discuss with suitable examples.
13. What do you understand by cross reactions?
14. What is Marcus theory? Explain with examples.
15. What are inner sphere reactions? Discuss the basic requirements for inner transfer reactions.
16. What are the factors that affect the rates of electron transfer reactions?
17. Discuss the mechanism of electron transfer in $[Fe(CN)_6]^{-4} \rightarrow [Fe(CN)_6]^{-3}$ reaction.
18. Explain why the electron transfer in $[Co(NH_3)_6]^{+2} \rightarrow [Co(NH_3)_6]^{+3}$ is quite slow, however, when one ammonia is replaced by a halide group the rate is significantly increases?
19. Write a note on the followings.
    (i) Trans effect (ii) labile and inert complexes
20. Write a note on the followings.
    (i) Cross reactions (ii) Bridging ligands

Block II Electronic Spectra

UNIT : THIRD

METAL-LIGAND BONDING

Structture of unit:

Unit-Third

METAL-LIGAND BONDING

3.1 INTRODUCTION

There are several theories to explain the electronic structure and bonding interactions between mostly transition metals surrounded by electron rich moieties (ion or molecule) known as ligands which donate one or more electrons to the metal ion. After the significant shortcomings of VBT came the molecular orbital theory (MOT) explaining the electronic structure of molecules. In similar way any lapses in previous theories gave rise to new theory and hence Ligand Field Theory (LFT) and crystal field theory (CFT) were developed. These theories also enable us to calculate the stabilization energy of a complex molecule and provide a general understanding about role of ligands in their stability and many other properties such as color of complexes and preference for octahedral, tetrahedral or square planar geometry.

3.2 OBJECTIVE

After end of this unit you will be able to-

- Limitations of Crystal Field Theory.
- Ligand Field Theory or The Delocalized-Molecular Orbital Theory.
- Weak Field and Strong Field Ligands and its importantance in formation of coordination compound.
- Spectrochemical Series and its uses in coordination complexes.
- Crystal Field Stabilization Energy or Ligand Field Splitting Energy (Δo), in Octahedral, Tetrahedral, Square Planar complexes.

  Jahn Teller Distortion and how Jahn Teller Distortion effect the geometry of complexes.
- The chapter will help in building an understanding about difference in absorption of energy by a complex as ligands are changed, stability of one electronic configuration over another.

3.3 LIMITATIONS OF CRYSTAL FIELD THEORY

Crystal field theory was proposed to explain the bonding interactions between ligands and transition metal center. The theory states that when the ligands approach the metal atom the degeneracy of **d** and **f** orbitals is disturbed due to the ligand electron cloud. The theory was able to explain the color of complexes, magnetic properties and hydration energies of the transition metal complexes. Here we will discuss the shortcomings or limitations of CFT which led to the proposal of Ligand field theory. The CFT is based on the assumption that there is electrostatic attraction between the ligand and the metal in the complex molecule. However, this assumption does not seem to be very convincing as is evident now that there is some amount of covalent bonding between the ligand and metal. Nuclear Magnetic Resonance studies on certain complexes has revealed the presence of electron sharing or covalency between the ligand and metal center owing to the presence of unpaired electron density on ligands. It fails to present a convincing picture of how metal and ligands are held together in the complex. It also does not offer any explanation as to why a particular ligand causes pairing of electrons or lies at a certain position in the spectrochemical series.

3.4 LIGAND FIELD THEORY OR THE DELOCALIZED-MOLECULAR ORBITAL THEORY :

Some of the shortcomings of CFT are addressed in delocalized Molecular orbital theory (MOT). This theory considers covalent bonding between metal and ligand in the complex. The failure of valence bond theory to explain bond orders in molecules which lie between that of single and double bond (eg resonance stabilized molecules) also led to MOT which could look into these aspects of bonding. The MOT or Ligand Field theory takes into account the orbitals on the ligands unlike CFT which considered ligands as spherical charge. The MOT uses quantum mechanics to understand electronic structure of molecules which uses the concept of atomic orbitals and molecular orbitals. Quantum mechanics considers electrons in the complex as molecular orbitals (MOs) surrounding the atoms containing the valence electrons in them. The concepts in density functional theory, Hartree Fock theory when applied to Schrodinger equation show that molecular orbitals are linear combination of atomic orbitals (LCAO). The salient features of this theory are discussed below:

1. MOT is based on the assumption that valence electrons of atoms in a molecule become electrons of the molecule as a whole. We know that atomic orbitals (AOs) can be defined by a mathematical equation which predict the maximum probability (square of wave

function) of finding an electron. The molecular orbitals are formed by linear combination of these atomic orbitals and hence total molecular orbitals formed are sum of the atomic orbitals which combine. In a simple molecule such as H_2 the atomic orbitals are same in every aspect however in a complex molecule the atomic orbitals should fulfill certain criterion before they can combine to form MOs. They are: (i) The AOs must have same symmetry (ii) similar energy and (iii) capable of a spatial overlap.

2. Pi bonding and Crystal Field Splitting Energy: Two AOs will combine to form two MOs, one bonding MO and other antibonding. For example, in $[CoF_6]^{3-}$ the six ligand orbitals having σ like symmetry combine with six of the nine metal orbitals (viz. s, p_x, p_y, p_z, dx^2-y^2 and dz^2 orbitals) will give six delocalized bonding molecular orbitals and six anti-bonding orbitals (**Figure 3.1**). The remaining metal d orbitals those are d_{xy}, d_{yz}, d_{xz} orbitals are nonbonding since their symmetry is unlike σ-like ligand orbitals. Electron pairs in these orbitals have no significant effect on keeping the ligands and metal together in the complex and hence also called as *metal lone pair electrons*. The non-bonding level of orbitals and the lowest anti-bonding level of orbitals are the t_{2g} and e_g orbitals which we have studied in CFT as splitting of d orbitals into the two levels. However, there is a difference in how the splitting occurs in these two theories. In CFT the splitting occurs due to electrostatic repulsion while in ligand field theory it occurs due to formation of molecular orbitals.

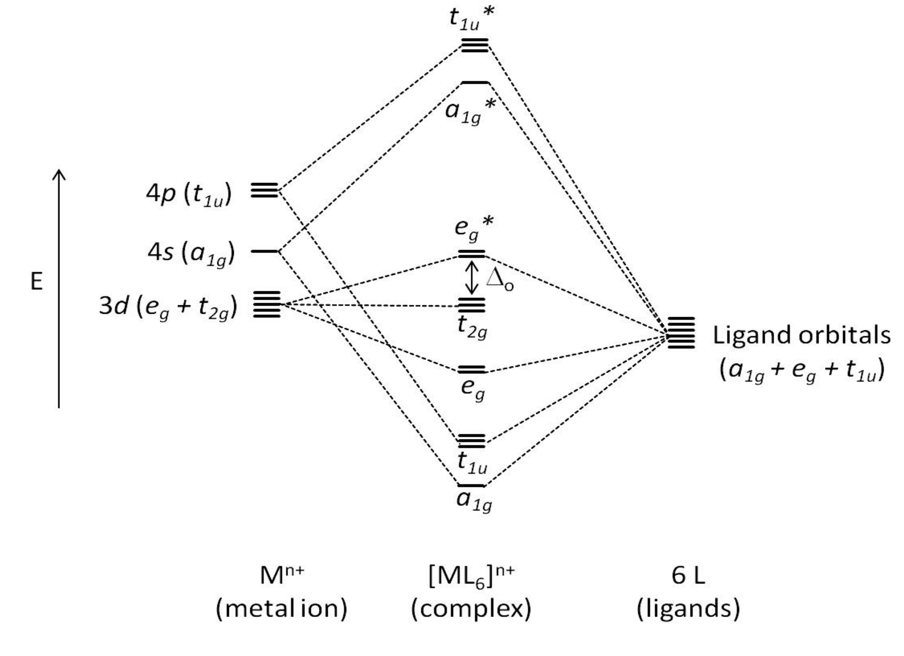


Figure 3.1. Approximate molecular orbital (MO) diagram for the formation of $[ML_6]^{n+}$ considering only sigma bonds.

Through the above example we will also discuss about the ***crystal field splitting energy Δ_o*** as we have read in CFT. The CFT did not consider any ligand orbitals instead considered them as charged spheres whereas the ligand field theory considers ligand orbitals that form bond with the metal and the two unhybridized ligand *p* orbitals at right angle to the metal-ligand bond. These unhybridized orbitals strongly influence the Δ_o which is called the ***ligand field splitting energy***.

3.5 *WEAK FIELD AND STRONG FIELD LIGANDS AND Π BACK BONDING :*

The four chloride *p* orbitals overlap with one of the three t_{2g} *d* orbitals of metal. If there are electrons in these orbitals, repulsion occurs between them and lone-pair electrons in the p orbitals of ligand. Hence, the energy of t_{2g} level is raised and **splitting energy Δ_o is decreased**. Such an interaction is called ligand to metal π interaction. Here we can use the terminology from CFT, ligands such as Cl^-, OH^-, Br^-, I^- will be *weak field ligands*. The fluoride ion holds its electrons very tightly and hence above phenomena does not occur in this case.

In case polyatomic ligands such as CN^- (cyanide ion) the bonding interactions are different. The cyanide ion has a triple bond consisting of one sigma bonding (σ^b) MO and two π bonding MOs (π^b). The π^b MO interacts with metal *d orbitals* similar to that seen in case of Cl^- ($L \rightarrow M\,\pi$ interaction), providing destabilizing effect, hence raising the energy of t_{2g} orbitals. But in case of cyanide ion most of the electron density lies between C and N atoms and not towards metal atom. Here it is the π* antibonding orbitals that interact with metal t_{2g} orbitals affecting them in a manner inverse to that seen in Cl- ligands. Electrons in the metal t_{2g} orbitals are partially delocalized towards the π* antibonding orbitals of CN- which stabilizes the t_{2g} orbitals and lowers its energy, thus **Δo increases**. This process of flow of electron cloud towards ligand π* antibonding orbitals from metal t_{2g} orbitals is known as *π back bonding* ($L \rightarrow M\,\pi$ interaction). Following the CFT terminology ligands which increase the splitting energy are called strong field ligands (CO, CN^-, NO_2^-).

3.6 SPECTROCHEMICAL SERIES :

A series of ligands arranged in order in which they cause splitting of the energy levels of d-orbitals in metal complexes. Weak field ligands have small Δ_o and will form high spin complexes. In high spin complexes the lower energy d orbitals get half-filled first and then move up to higher energy d orbitals and fill them singly according to the number of electrons available. After that pairing starts because these orbitals have low energy difference between them ($P > \Delta_o$). Strong field ligands have large Δ_o and will form low spin complexes. In such complexes the lower energy orbitals get completely filled first only then the remaining electrons are filled in the higher energy d orbitals. This is because the energy gap between the orbitals is large enough and pairing energy (P) is less than splitting energy (Δ_o). In the series given below the ligands towards the left are weak field and those towards right are strong field.

$I^- < Br^- < Cl^- < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < NH_3 \sim py < en < bipy < phen < NO_2^- < PR_3 < CN^- \sim CO < NO^+$

Note that in above series the ligands have elements staring from group 17 donors and moving to 16, 15 and 14, and that Δ_o increases as the electronegativity of the ligand decreases.

3.7 CRYSTAL FIELD STABILIZATION ENERGY OR LIGAND FIELD SPLITTING ENERGY (Δ_o):

For a quick reminder we will discuss the important outcomes of CFSE and its calculation here which is an integral part of crystal field theory. The CFSE (**Δ_o**) is the energy absorbed when one electron is promoted from t_{2g} level to e_g level. This splitting energy accounts for the magnetic properties of transition metal complexes. You should know that pairing energy (P) is the energy required to pair up electrons in the corresponding orbital.

$$\Delta_o = \text{no. of electrons in } t_{2g} \times (2/5)\Delta_o + \text{no. of electrons in } e_g \times (3/5)\Delta_o$$

or

$$\Delta_o = \text{no. of electrons in } t_{2g} \times (-0.4\Delta_o) + \text{no. of electrons in } e_g \times (0.6\Delta_o)$$

If Δ_o is small the electrons tend to spread out more. That is the d orbitals are filled singly. There is saving of energy if as few electrons are paired as possible ($\Delta_o < P$). If the splitting constant is large enough ($\Delta_o > P$) to overcome the energy needed to pair up two electrons in an orbital the more stable arrangement will be the low energy t_{2g} orbitals to contain paired up electrons. Example: (i) $[CoF_6]^{3-}$ is a d^6 system and the six *d* electrons are spread out singly into all the t_{2g} and e_g orbitals. Such a complex is called a ***high spin complex***. (ii) $[Co(NH_3)_6]^{3-}$

In this complex Co^{3+} is again a d^6 system but here the electrons are first filled in pairs in the lower energy t_{2g} orbitals. Only after filling the t_{2g} orbitals completely the remainder electrons move to e_g orbitals. Such complexes are ***low spin.***

We have already discussed above how ligands (discussed example of Cl^{-} and CN^{-}) can affect the energy of t_{2g} orbitals thus lowering or raising the value of Δ_o. We can summarize here that weak field ligands such as chloride show repulsion in ligand to metal-π interaction which raises the energy of t_{2g} orbitals and hence Δ_o decreases. Whereas, strong field ligands such as cyanide ion cause π back bonding polarizing the metal electrons towards ligand orbitals (π* orbitals) hence stabilizing the t_{2g} orbitals which increases the splitting energy Δ_o. The nature of metal also has a strong influence on splitting energy. It has been found experimentally that the metal atoms/ions with 4d and 5d valence electrons cause much larger splitting of d orbitals as compared with metal atom/ions with 3d valence electrons. However, the reason behind it is not fully understood. For example, Δ_o values for $[Co(NH_3)_6]^{3+}$, $[Rh(NH_3)_6]^{3+}$, $[Ir(NH_3)_6]^{3+}$ are 22,900 cm^{-1}, 34,100 cm^{-1} and 40,000 cm^{-1} respectively. It is presumed that the *4d* and *5d* orbitals are more suited for sigma bonding with ligand orbitals than *3d* orbitals. An important outcome of this behavior that is much larger Δ_o for 4d and 5d metal complexes is that all second and third row metal transition metal complexes are low spin even with weak field ligands such as bromide. $[RhBr_6]^{3-}$ is a low spin complex.

Table 1. Crystal Field stabilization energies for octahedral complexes.

No. of d electrons	Configuration	CFSE (Δ_o)	Configuration	CFSE (Δ_o)
1	t_{2g}^1	-0.4		
2	t_{2g}^2	-0.8		
3	t_{2g}^3	-1.2		
4	$t_{2g}^3e_g^1$	-0.6	t_{2g}^4	-1.6
5	$t_{2g}^3e_g^2$	0.0	t_{2g}^5	-2.0
6	$t_{2g}^4e_g^2$	-0.4	t_{2g}^6	-2.4
7	$t_{2g}^5e_g^2$	-0.8	$t_{2g}^6e_g^1$	-1.8
8	$t_{2g}^6e_g^2$	-1.2		
9	$t_{2g}^6e_g^3$	-0.6		
10	$t_{2g}^6e_g^4$	0.0		

3.8 OCTAHEDRAL, TETRAHEDRAL, SQUARE PLANAR COMPLEXES :

The order of energy levels of d orbitals for complexes in different geometrical arrangements around metal ion with a particular ligand from ligand field theory (similar to CFT) is depicted in **Figure 3.2**. The relative order in *tetrahedral (Td) geometry* is reverse of octahedral (Oh) geometry since the ligands in Td geometry approach the metal atom from four out of eight corners of the cube. The dx^2-y^2 and dz^2 orbitals do not lie or do not point towards the corners of the cube around the metal atom. The lobes of the d_{xy}, d_{yz}, d_{xz} orbitals point to the midpoints of the twelve edges of the cube whereas dx^2-y^2 and dz^2 point to the midpoint of the six faces of the cube. The former set of three d orbitals lie closer to the ligands in Td geometry will be less stable and cause splitting of d orbitals which is not as pronounced as in Oh geometry because the ligands do not lie directly in the path of the t_{2g} orbitals.

For ***square planar complexes*** let us take the complex in the x-y plane and assume ligands at equidistance in +- x and +- y directions. Then the dx^2-y^2 orbital points directly at the four ligands and is destabilized. The dz^2 orbitals lie perpendicularly out of the plane of the ligands and is most stable. The d_{xz} and d_{yz} orbitals have more stability than d_{xy} orbital because they are out of the plane of the ligands.

The ***octahedral arrangement*** of ligands is more stable than square planar since six bonds are formed instead of four. Generalizing we can say that the two extra bonds in octahedral complexes give them an energy advantage of 35,000 to 65,000 cm-1. It is observed that d1 to d6 configurations the octahedral coordination is preferred because of the extra bond energy gained. However, seventh and eighth electrons are pushed into higher energy e_g orbitals but for a square planar geometry the d_{xy} orbitals are still available at a lower energy than e_g orbitals. Thus, this extra stability becomes a deciding factor for d^8 configuration which have large ligand-field splitting energy and they are found as square planar complexes. Since the ligand field splitting is higher for high atomic numbers therefore Pt(II) and Pd(II) complexes have square planar complexes and Ni(II) is usually octahedral. At ninth and tenth electron the preference is again shifted to octahedral geometry due to the stability gained by formation of extra bonds.

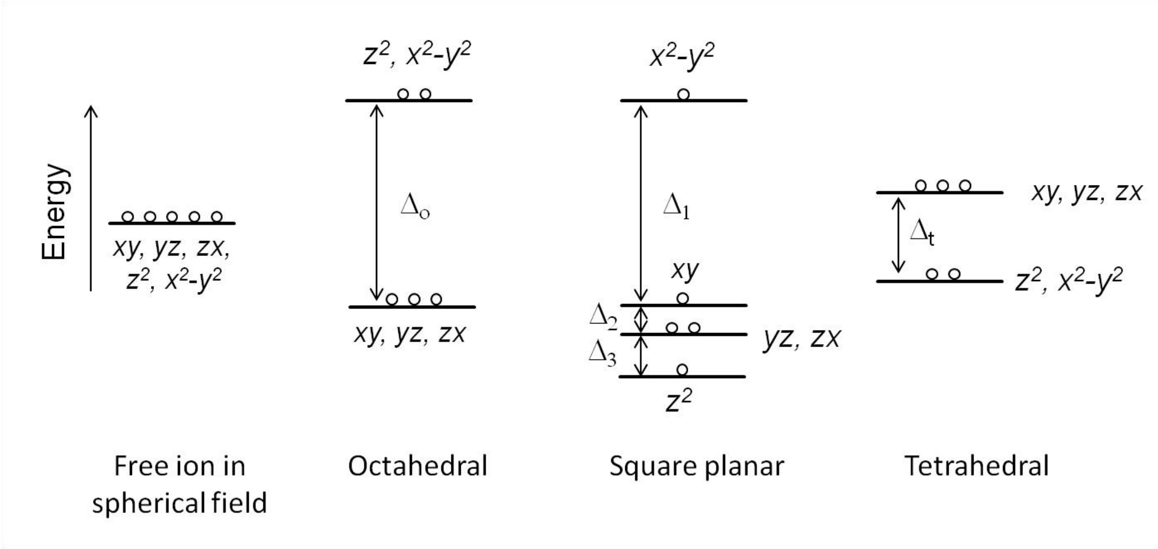


Figure 3.2. Energy level of d orbitals in the free ion in a spherical field of electrical charge, octahedral, square planar and tetrahedral geometries. Δ_o, Δ_1, Δ_2, Δ_3 and Δ_t represent ligand field splitting energies.

3.9 JAHN TELLER DISTORTION:

To understand the Jahn Teller distortion let us look into the absorption spectra (as shown below) of hexa-aquo titanium (III) complex ion (**Figure 3.3**). The choice of this complex is simply because of its simplicity being a d^1 electron system (since Ti^{+3}).

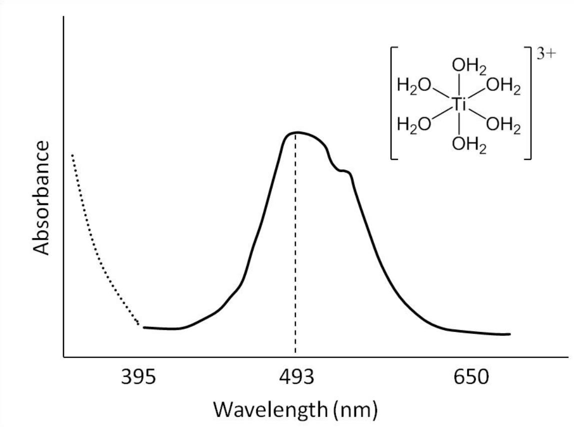


Figure 3.3. Absorption spectra of hexa-aquo titanium (III) ion.

If we observe the spectrum, we notice an absorption maximum (point where absorption is maximum by the complex) is at 493 nm (corresponds to Δ_o = 242.6 kJ mol^{-1}) that is the peak in graph and not the trough if u look at the x axis which shows wavelength at which absorption occurs. We know that longer wavelength means shorter frequency and vice versa.

The spectrum extends into the UV region beyond 395 nm and towards right into IR region up to 650 nm. The solution of this complex will absorb light in the yellow-green region of the spectrum and hence it will appear red-purple in color. The major noticeable point of the spectrum which can be explained by Jahn teller distortion is the appearance of a small hump/shoulder in the main peak. Its presence is interesting given the fact there is only one electron and hence only transition is possible. So, there should be only one main peak.

To explain this shoulder peak in the spectrum let us first consider a d^4 high spin complex such as $[Cr(H_2O)_6]^{2+}$. For a high spin complex when we start filling the four electrons, we place one each in the three t_{2g} orbitals and the remaining one electron goes into the e_g orbitals but here we have a choice (**Figure 3.4**). We can put the remaining one electron in either dx^2-y^2 or dz^2. One may say what difference would it make but actually there is a difference.

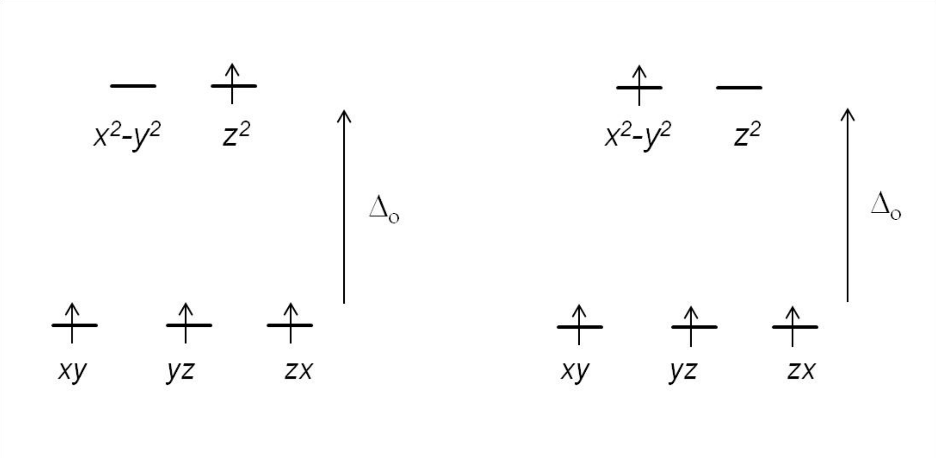


Figure 3.4. Two possibilities of high spin d^4 electronic configurations.

Suppose if we put the electron in dz^2 orbital that lies along the *z* axis. So, the two ligands that lie along the *z* axis will be repelled by this electron and will be pushed little bit outward and the ligands which approach in the *x-y* plane will not feel the repulsion and will be pushed in a little bit. Thus, we now get a slightly distorted octahedral structure with two ligand bonds longer than the other four. This is also called the tetragonal elongation (**Figure 3.5**).

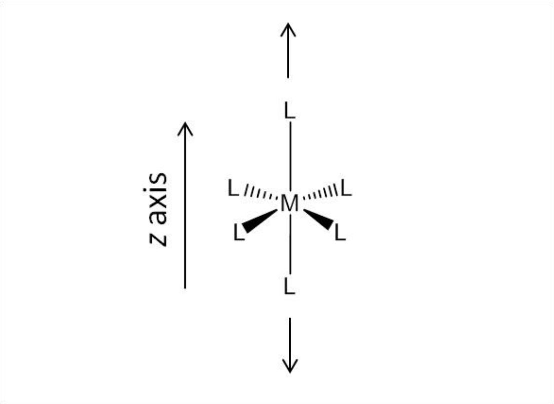


Figure 3.5. Tetragonal elongation of $[ML_6]^{n+}$ complex.

This also effects the orbital energies (**Figure 3.6**). Since the two ligands along *z* axis move out a bit the energy of dz^2 is somewhat lowered. And similarly, since the ligands along the x-y axis have moved in a bit this will raise the energy of $d_{x^2-y^2}$ orbital by some amount. Now we have another small splitting of e_g orbitals superimposed on crystal field splitting diagram. These changes also affect the t_{2g} level. The orbitals having z component i.e. d_{xz} and d_{yz} will move slightly lower in energy while those lying in xy plane (d_{xy}) will move slightly higher in energy. However, these changes do not make any difference in overall energy because they are already singly occupied.

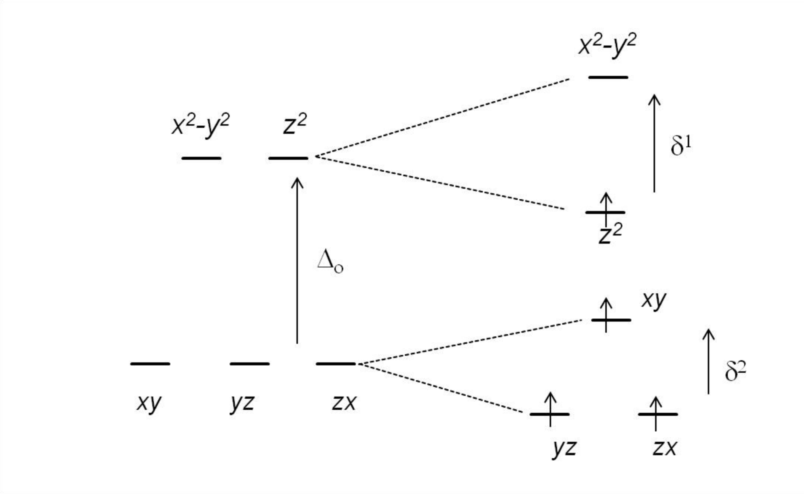


Figure 3.6. Energy levels of d orbitals in tetragonally elongated $[ML_6]^{n+}$ complex.

Now, consider the second situation where we put the fourth electron d_{x2-y2} orbital. Now the ligands along the x, y axes will experience some repulsion and will move out a bit whereas the ligands along the z axis will move in a bit since it is empty so it experiences less repulsion. We again get a slightly distorted octahedral structure but it will look different than the one discussed above (**Figure 3.7**).

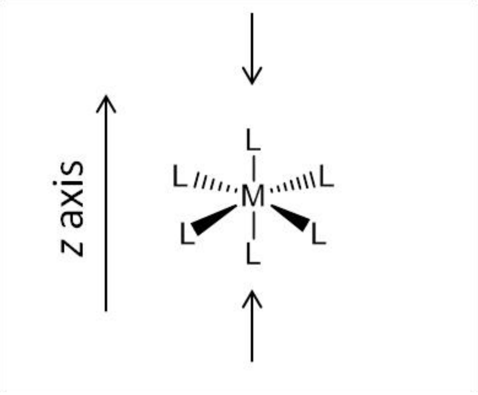


Figure 3.7. Tetragonal compression of $[ML_6]^{n+}$ complex.

We now have two slightly shorter bonds and four slightly elongated bonds. This is called *tetragonal compression* because of the way the octahedron looks now. The energy of the occupied dx^2-y^2 orbital is lowered due to elongation. Here also the t_{2g} levels will split. This time dxz and dyz will move slightly higher in energy and dz^2 will be lowered in energy (**Figure 3.8**). All these distortions discussed above are called Jahn Teller distortions. This theorem given by H. A. Jahn and E. Teller states that a molecule in a degenerate electronic state will undergo geometrical distortion so as to remove degeneracy. The above example which we have discussed for a d4 configuration explains this theorem. Originally, we had a choice to put the fourth electron into dz^2 or dx^2-y^2 orbitals since they were of same energy or they were degenerate. But after putting the electron in either of them the degeneracy is removed that is these two orbitals now had different energies. So, either of those distortions will remove degeneracy.

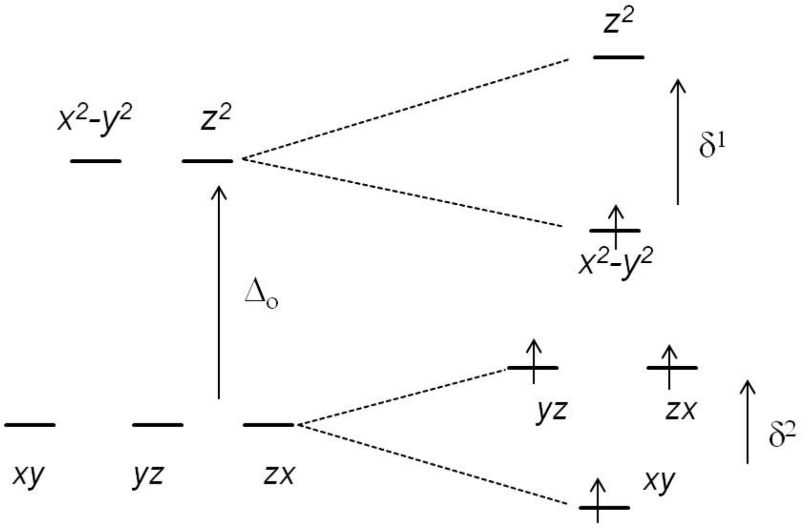


Figure 3.8. Energy levels of d orbitals in tetragonally contracted $[ML_6]^{n+}$ complex.

Coming back to Ti^{3+} having one electron which can go into d_{xy}, d_{yz} or d_{xz} orbitals First let us do the compression and consider that if the electron goes into d_{xy} orbital (*tetragonal compression*) the degeneracy is removed and the energy of d_{xy} orbital is lowered (stabilized) than d_{xz} and d_{yz} orbitals. However, if we do an elongation, we again have a choice weather to put the electron into either d_{yz} or d_{xz} orbital which will both be lower in energy than d_{xy}. In this case we are not removing the degeneracy of the two orbitals just reducing the choice of orbitals from three to two. Hence the condition for Jahn teller distortion of removal of degeneracy is not fulfilled. So, in this case the molecule will undergo compression and not elongation. Note that it is not always possible to tell whether a molecule will undergo elongation or compression such as the previously discussed case of d^4 configuration where we saw that elongation and compression are both successful in removing degeneracy (this happens generally where degeneracy removal involves e_g orbital).

Summarizing we can say that for Jahn Teller distortion to occur the metal ion should have an odd electron. That is a d^3 configuration will not show distortion since all three t_{2g} orbitals are equally filled and have no significant removal of degeneracy which is a prime condition for this distortion. Jahn Teller distortions are bigger if they involve e_g set of orbitals than if they involve t_{2g} set of orbitals. This is simply because e_g set of orbitals point directly at the ligands and hence the repulsions between these electrons and ligand orbitals will be significant. Example: High spin d^4 complex or a d^9 complex.

Table 2. Jahn-Teller distortions for d^1 – d^{10} electronic configurations

Electronic configuration	**Structural implication of JT distortion**
d^1	small compression
d^2	small elongation
d^3	no J-T distortion
d^4 high spin	large distortion, but can't tell which type
d^4 low spin	small compression
d^5 high spin	no J-T distortion
d^5 low spin	small elongation
d^6 high spin	small compression
d^6 low spin	no J-T distortion
d^7 high spin	small elongation
d^7 low spin	large distortion, but can't tell which type
d^8	no J-T distortion
d^9	large distortion, but can't tell which type
d^{10}	no J-T distortion

Returning back to our original query of finding the reason behind the shoulder observed in the UV-Visible absorption band of $[Ti(OH_2)_6]^{3+}$. We can explain its occurrence now by looking at the splitting diagram of *d* orbitals undergoing Jahn Teller distortion. The figure below reveals that the electron instead of having only one choice of transition from t2g to eg orbitals now has two choices. From d_{xy} to dx^2-y^2 or to dz^2 (**Figure 3.9**). This means we will get absorption of light for these two transitions one of which appears as the shoulder on the other. Tetrahedral complexes also undergo Jahn Teller distortion however they more complicated since they distort by changing their bond angles rather than bond lengths.

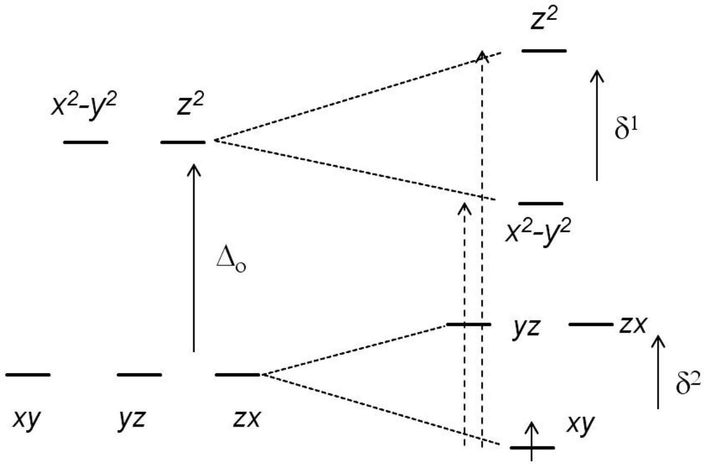


Figure 3.9. Electronic transitions of a $[ML_6]^{n+}$ complex originating due to J-T distortion are shown with vertical dotted arrows.

3.10 THERMODYNAMIC AND RELATED ASPECTS OF CRYSTAL FIELDS:

There are various consequences of crystal field splitting of orbitals and some of them will be discussed in this section.

3.10.1 Hydration Energy

Thermochemical consequence of crystal field splitting can be seen from a hydration energy graph of M^{2+} ions across the first transition metal series. Hydration energy is the enthalpy change for the reaction of a mole of M^{2+} ions with an infinite number of water molecules to give hydrated cations $[M(OH_2)_6]^{2+}$ in solution (**Figure 3.10**). A look at this graph reveals that the value of energy plotted on y axis gets more negative as we move up the axis. This means that as we go from Ca to Zn the reaction is getting more exothermic. This is expected because even if charge on the metal ion remains same the size gets smaller; the charge density increases and interaction with water molecules gets stronger. If there was no crystal field splitting the graph would have followed the dashed line, increasing from Ca (no d electrons) to Zn (Zn^{2+} with d^{10} electronic configuration). A close look at the graph reveals two humps. This is because water is a weak field ligand and so all the hexaquo complexes are high spin complexes. A look at the CFSE table given above will indicate maximum stabilization for d^3 and d^8 configuration and the hydration energy curve also shows a maxima for V^{2+} and Ni^{2+}. Similarly, we expect the point of d^5 configuration to lie close to red dashed line since all five orbitals are singly filled and we have no CFSE and so is observed in hydration energy graph.

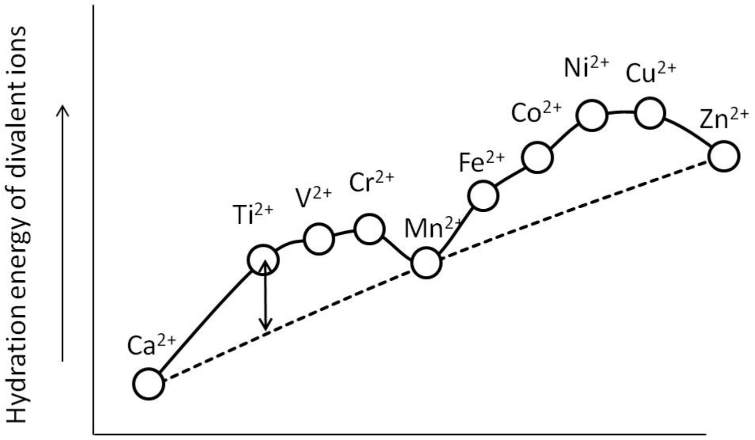


Figure 3.10. Trend of hydration energy of divalent ions

3.11.2 Ionic radii

We can also plot other thermodynamic quantities such as the ionic radii of metal chlorides (**Figure 3.11**). The metal chlorides MCl_2 exist in the solid state as lattices in which the metal ion M^{2+} is octahedrally surrounded by six chloride ions. These complexes are high spin because Cl^- is a weak field ligand. The lattice energy is defined as the enthalpy change required to convert one mole of solid into its constituent gaseous ions.

$$MCl_2\,(s) \rightarrow M^{2+}\,(g) + 2Cl^-\,(g)$$

In this study too a double humped curve is obtained. These solid in most cases are more stable than expected owing to the stability provided by crystal field splitting. Again Ca, Mn and Zn are less stable than expected since they do not possess extra stability (CFSE) gained by crystal field splitting. We can draw a similar graph for ionic radius of M^{2+} ions in these metal chlorides considering that the radius of metal ion in these dichlorides is the shortest distance between M and Cl minus the radius of the chloride ion.

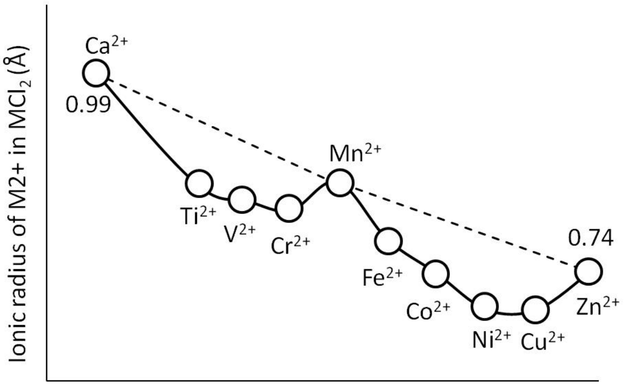


Figure 3.11. Trend of ionic radii of divalent ion in MCl_2 complexes.

In these examples we expect that the ionic radii should decrease steadily across the period as the subsequent electrons are added to *d* orbitals which are not very effective in shielding other electrons from increasing nuclear charge. Surprisingly we get two minima on the graph. When filling the electrons in d orbitals they first go into the t2g orbitals i.e. dxy, dxz and dyz which lie in between the axes so do not interfere with the ligands directly. Thus, the chloride ions do not experience much repulsion and this allows them to move a bit closer to metal center. As a result, the ionic radius M^{2+}appears to shrink a little. For a half filled, high spin d5 metal ion the electrons are spherically distributed so this point lies on the line in the graph. Following same reasoning the graph moves downward when we further fill the t_{2g} orbitals for d^6, d^7 and d^8 configuration and comes back to the dashed line for the fully filled Zn^{2+} where the electrons are spherically distributed.

3.11.3 Lattice Energy

It can be defined as the energy released when one mole of an ionic solid is formed from isolated gaseous ions. It is measured by the Born-Lande equation.

$$E = \frac{N\,A\,Z\,e^2}{4\pi\varepsilon_0 r_0}\left(1-\frac{1}{n}\right)$$

Where N = Avogadro's number
A = Madelung constant (related to the geometry of the crystal)
Z= Charge on the M+ and M¯ ions
ε_0= permittivity of free space
r_0 = distance to the closest ion
n= Born exponent (a number between 5 and 12)

If we look at the difference in the measured and calculated lattice energies of some divalent first row main group and transition metals halides, we find certain discrepancies. These discrepancies for six-coordinate transition metal ions can be explained by CFSE. We would expect a smooth increasing curve of lattice energy for metal ions as ionic radius decreases from left to right but a double humped curve is seen. Ca^{2+} (d0), high spin Mn^{2+}(d^5) and Zn^{2+} (d^{10}) all have zero CFSE and lie almost on the expected line. Ions such as V^{2+} which show high CFSE in with weak field ligands have high lattice energy values and show significant deviation from the calculated lattice energies.

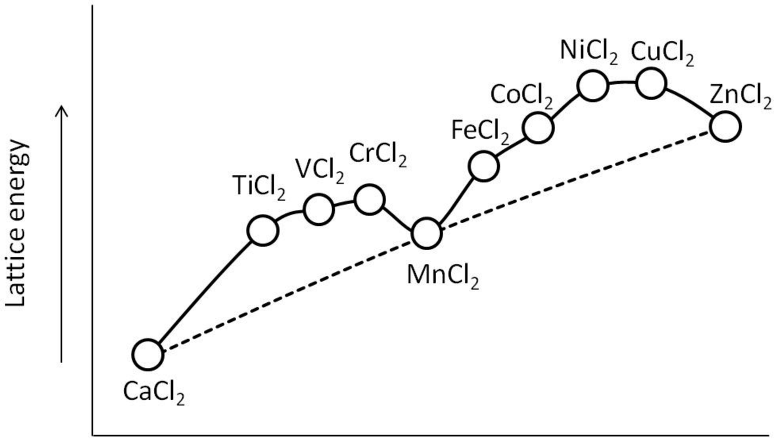


Figure 3.12. Trend of lattice energy of MCl_2 complexes.

3.11.4 Site preference energies/ Site preference of Spinels and reverse Spinels

Spinel is the name given to the mineral $MgAl_2O_4$. They are a class of crystalline solids of the general formula AB_2O_4 or ($A^{II}B^{III}{}_2O_4$) where **A** is a main group (IIA) or transition metal ion in the +2 oxidation state; **B** is main group (IIIA) or transition metal ion in +3 oxidation state. The oxide ions are weak field ligand and provide a cubic closed packed lattice. In one-unit cell of AB_2O_4 there are eight tetrahedral and four octahedral holes.

(a) Normal Spinel: The A^{2+} ions occupy 1/8th of the tetrahedral holes B^{3+} ions occupy half (1/2) of the octahedral holes. *Example*: $MgAl_2O_4$; where Mg^{2+} ions occupy the tetrahedral holes and Al^{3+} ions occupy the octahedral holes.

(b) Inverse Spinel: In inverse spinel the arrangement is altered where divalent ions swap with half of the trivalent ions so that M(II) ions now occupy octahedral sites i.e. $B(AB)O_4$. *Example:* (i) Fe_3O_4 (Magnetite), Fe^{3+} ions in tetrahedral holes whereas octahedral holes have both $Fe^{2+}$and Fe^{3+}ions. (ii) $NiFe_2O_4$: In this case Ni^{+2} is octahedral and half of the Fe^{+3} are tetrahedral.

If A and B both belong to *s* or *p* block elements it always results in normal spinel.

On the basis of CFSE (crystal field stabilization energy) we can answer the question about some transition metal ions preferring inverse spinel structure whereas some other prefer normal spinel structure. *Example*: **1**. Mn_3O_4= $Mn^{II}Mn^{III}{}_2O_4$ (*Normal Spinel*). In this example O^{2-} is a weak field ligand and has Mn^{2+} in d^5 configuration in high spin so CFSE = 0; also, Mn^{3+} ions in d^4 configuration also in high spin state, CFSE = 0.6 Δo. Mn^{2+} ions by exchanging positions with Mn^{3+} in an octahedral hole is not going to gain any extra crystal field stabilization energy. While Mn^{3+} ions by being in the octahedral hole will have CFSE. Therefore, Mn_3O_4 will be *normal spinel.*

Example: **2**. $Fe_3O_4 = Fe^{II}Fe^{III}_2O_4$ (*Inverse Spinel*). In this example the Fe^{2+} ions have d^6 configuration in high spin and CFSE = -0.4 Δo. While, Fe^{3+} ions have d^5 configuration also in high spin having no CFSE (CFSE = 0). Fe^{2+} ions by exchanging position with Fe^{3+} ions in octahedral hole is going to gain extra stabilization from CFSE whereas Fe^{3+} ions in the octahedral hole will not have any CFSE. Thus, Fe_3O_4 will be inverse spinel.

3.11 SUMMARY :

The summary of the present chapter is as,

- This chapter deals with some more aspects of wide field of coordination chemistry and transition metal complexes.
- The progression to various theories covers the aspects which could not be explained by the ones that were proposed earlier. Any theory is acceptable as long as a new theory does not question the salient features of the earlier theories. So far, we have come to know various reasons of *d* orbital splitting such as formation of molecular orbitals (ligand field theory), electrostatic repulsion (crystal field theory) or the choice of the six orbitals for hybridization (valence bond theory).
- Presently, the ligand field theory is able to explain many aspects of the transition metal complexes such as the absorption spectra and magnetic properties. It also explains the effect of ligand on splitting of energy levels. It can successfully explain why a d^3 and low spin d^6 electronic configurations are preferred by octahedral complexes or why a d^8 system will prefer square planar geometry.

3.12 SAQs TYPE QUATIONS

A. Multiple choice question

1. Correct electronic configuration of Co^{3+} low spin complex is

a. $t_{2g}^5e_g^1$ b. $t_{2g}^6e_g^0$

c. $t_{2g}^4e_g^2$ d. $t_{2g}^3e_g^3$

2. Which one is most strong field ligand of the following

a. H_2O b. NH_3

c. NO D. Py

3. Correct order of weak field ligand is,

a. $I^- > OH^- > H_2O > CN$ b. $H_2O > OH^- > I^- > CN$

c. $OH^- > I^- > H_2O > CN$ d. $CN > OH^- > H_2O > I^-$

4. Oxidation state of Co in $[Co(NH_3)_6)]^{3+}$

a. +4 b. +3

c. +2 d. +1

5. Crystal field splitting energy (CFSE) of $[Mn(H_2O)_6]^{+2}$ complex is,

a. 0.4Δo b. 0.6Δo

c. 1.2Δo d. 0 Δo

6. Which of the coordination compound are low spin complex

a. $[Co(H_2O)_6]^{+3}$ b. $[Fe(H_2O)_6]^{+3}$

c. $[Mn(H_2O)_6]^{+2}$ d. $[Cr(H_2O)_6]^{+3}$

7. Geometry which have largest crystal field splitting energy,

a. Tetrahedral b. Square planer

c. Octahedral d. All of the above

8. Complex $[Ni(CN)_4]^{-2}$ ion have following type geometry

a. Tetrahedral b. Square planer

c. Octahedral d. Trigonal bipyramidal

9. distorted octahedral natures of Cu^{2+} metal ion can be explained by the effect :

a. Paulling's effect b. John teller effect

c. Crompton effect d. Orgel's effect

10. Factor affecting CFSE is:

a. Nature of metal ion b. Nature of ligand

b. Geometry d. All

11. If the valve of P is greater than 10 D_q then complex will be :

a. Strong field b. Weak field

b. Both d. None

12. Δ_o and Δ_t is related as :

a. $\Delta_t = 4/9\ \Delta_o$ b. $\Delta_o = 4/9\ \Delta_t$

b. $\Delta_t = 2/5\ \Delta_o$ d. $\Delta_t = 3/5\ \Delta_o$

13. Number of lone pair electron in $[Co(NH_3)_6]^{+3}$ is :

a. 3 b. 2

b. 1 d. 0

14. Energy levels in square planar geometry is

a. 5 b. 4

c. 3 d. 2

B. Fill in the bling

(i) Tetrahedral complexes also undergo Jahn Teller distortion however they more complicated since they distort by changing their……… rather than……… .

(ii) Two slightly shorter bonds and four slightly elongated bonds, this is called……

(iii) d-orbital split into two set t_{2g} and e_g. The energy gap between t_{2g} and e_g is called…………

(iv) According to the crystal field theory the bonds between metal and ligand is purely………

(v) In crystal field splitting of tetrahedral complexes the energy of ……is greater than ……..

C. True/False

(i) The colour of [Ti(H2O)6]+3 ion appears purple True/False

(ii) Generally the value of magnetic moment depends upon the number of paired electron True/False

(iii) According to CFT the splitting of the d-orbitals of the metal ion takes place True/False

(iv) Crystal field stabilization energy in octahedral complexes is higher when strong field ligand are present True/False

D. Match the following

i. $[Fe(CN)_6]^{-3}$	a. Inverse spinel
ii. $[FeF_6]^{-3}$	b. Nornal spinel
iii. $NiFe_2O_4$	c. Low spin complex
iv. $MgAl_2O_4$	d. High spin complex

Answer key

A : 1 b 2 c 3 a 4 b 5 d 6 b 7 b 8 b 9 b 10 d 11 b 12 a 13 d 14 a

B : i. bond angles, bond lengths ii. tetragonal compression iii. Crystal field splitting energy iv. Ionic v. t_{2g} , e_g

C : i True ii False iii True iv True

D : i c, ii d, iii a, iv b

3.13 GLOSSARY:

Δo = Crystal field stabilization energy of octahedral

Δt = Crystal field stabilization energy of Tetrahedral

CFSE = Crystal field stabilization energy

CFT = Crystal field theory

LFT = Ligand field theory

3.14 REFERENCES :

1. Banerjea D., (2009), *Coordination Chemistry" (second edition),* Asian Books, 4, 874.
2. House J. E., (2009), *Inorganic Chemistry*, Elsevier,
3. C. E. Housecroft, A. G. Sharpe, (2018), *Inorganic chemistry*, Pearson (Fifth edition), 1256.
4. F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, (1999), *Advanced inorganic chemistry*, Wiley-Interscience (Six Edition), 1376.
5. J. D. Lee, (1999), *Concise inorganic chemistry*, Wiley-Blackwell (Fifth edition), 1072.
6. Atkins; et al. (2010). Shriver and Atkins' Inorganic Chemistry (Fifth ed.). New York: W. H. Freeman and Company. ISBN 978-1-4292-1820-7.
7. Janes R., Moore E. A., (2004), *Metal-ligand bonding*. The Open University, , 23. ISBN 0-85404-979-7
8. Tsuchida R., (1938). *"Absorption Spectra of Co-ordination Compounds. I.*" Bull. Chem. Soc. Jpn. **13** (5): 388–400.

3.15 SUGGESTED READING:

1. Huheey J. E., Keiter E. A., Keiter R. L., (1997), *Inorganic chemistry- Principles of structure and reactivity(Fourth Edition)*, Pearson, 964.
2. Puri B. L., Sharma L. R., Kalia K. C., (2020), *Principles of Inorganic Chmistry, (33rd Edition)*, Vishal Publishing.
3. Miessler G. L. , Fischer P. J., Tarr D. A., (2014) *Inorganic Chemistry(5th edition),* 696.
4. Miessler, G. L., Tarr, D. A., (2011). *Inorganic Chemistry* (4th ed.). Prentice Hall, 395–396. ISBN 978-0-13-612866-3.

3.16 TERMINAL QUESTIONS :

Q.1 Discuss the various limitations of the crystal field theory.

Q.2 What is Delocalized-Molecular Orbital Theory and how did it address limitations of the CFT.

Q.3 Discuss the Jahn-Teller distortion in Cu^{2+} complexes.

Q.4 What is Crystal Field Stabilization Energy? Give calculation of CFSE for high spin and low spin d^5 metal ion in spherical ligand environment.

Q.5 Discuss MO diagram for an octahedral complex

Q.6 Discuss site preference energy in case of spinels and reverse spinels.

UNIT FOURTH

ELECTRONIC SPECTRA OF TRANSITION METAL COMPLEXES

Structure of unit

Unit-Fourth

ELECTRONIC SPECTRA OF TRANSITION METAL COMPLEXES

4.1 INTRODUCTION

Transition metal compounds display a wide variety of colours. A compound is coloured if it absorbs part of the visible light. When a sample absorbs visible light, the colour observed by us is the sum of the remaining colours that are reflected or transmitted by the sample and strikes our eyes. The colour of these compounds is due to the electronic transitions generated by the incident light, causing absorption at certain wavelengths which depend on the structure and bonding in the molecule. Based on Crystal Field Theory (CFT), Ultraviolet (UV)–Visible spectroscopy is used to evaluate the absorption properties of the transition metal complexes.

The electronic transitions in the transition metal compounds can be categorized into three classes: charge transfer, d–d transition and f–f transitions. Charge transfer bands occur when the excited electrons move either from a metal orbital to a ligand orbital (metal–to–ligand charge transfer – MLCT) or from a ligand orbital to a metal orbital (ligand–to–metal charge transfer – LMCT). MLCT transitions are more common than LMCT. d–d transitions occur when the excited electron moves from one d orbital to another d orbital of the metal and f-f transition occur when the excited electron moves from f orbital to f orbital of the same metal centre . The d-d or f-f transitions can further be classified as spin–allowed transition where the spin quantum number in the ground and excited states are the same while in the spin–forbidden transition, the spin state changes during the excitation.

4.2 OBJECTIVES

In this unit, our concern will be with the electronic spectra of transition metal complexes, mainly those of the first transition series. The energy required for the promotion of an electron from one orbital to another, the excitation of a molecule from its ground state to an electronic excited state, corresponds to absorption of light in the near-infrared, visible or ultraviolet regions of the spectrum. By going through this unit, you will be able to understand:

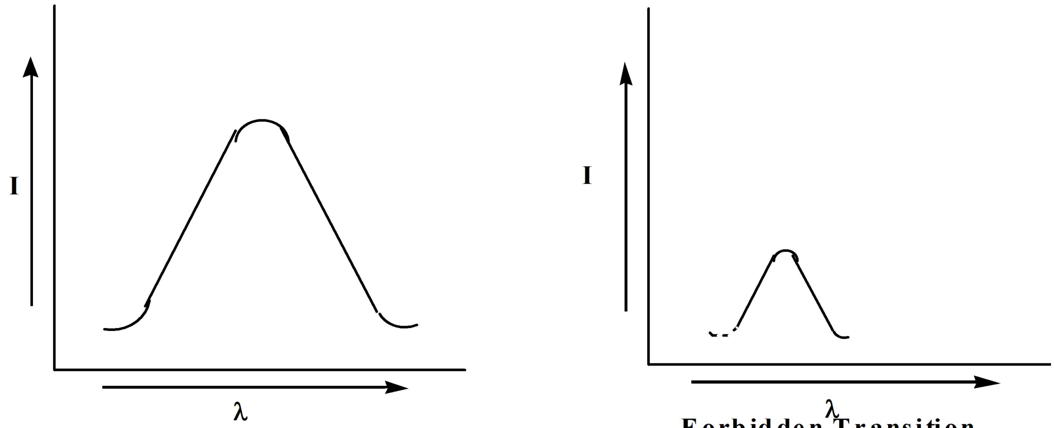
- Electronic transitions
- Selection rules for electronic transitions
- Term symbol
- Spectrochemical series
- Orgel diagrams

4.3. TYPES OF ELECTRONIC TRANSITIONS

When the Electromagnetic Radiation (EMR) is passed from the sample of the transition metal complexes, the transition of electron can occur by the absorption of certain EMR to give the electronic spectra.

Electronic transitions can be classified into two different types, which are given below (Figure 4.1):

1. **Allowed transitions:** The types of electronic transition which can generate the high intense spectra are known as allowed transitions.
2. **Forbidden transitions:** The types of electronic transition which can generate the low intense spectra are known as forbidden transitions.



Allowed Transition **Forbidden Transition**

Fig. 4.1 Types of d-d transition

4.4. SELECTION RULE FOR d-d TRANSITION

To define the allowed or forbidden nature of electronic transitions, 2 different selection rules can be used which are given below:

4.4.1 Spin selection rule

According to the spin selection rule, all the electronic transitions in the transition metal complexes which does not involve the change in the spin multiplicity are called as spin allowed transitions while on the other hand all the electronic transitions which can involve the change in the spin multiplicity are known as spin forbidden transitions. Therefore,

$$\Delta S = 0 \text{ (Allowed transition)}$$

$$\Delta S \# 0 \text{ (Forbidden transition)}$$

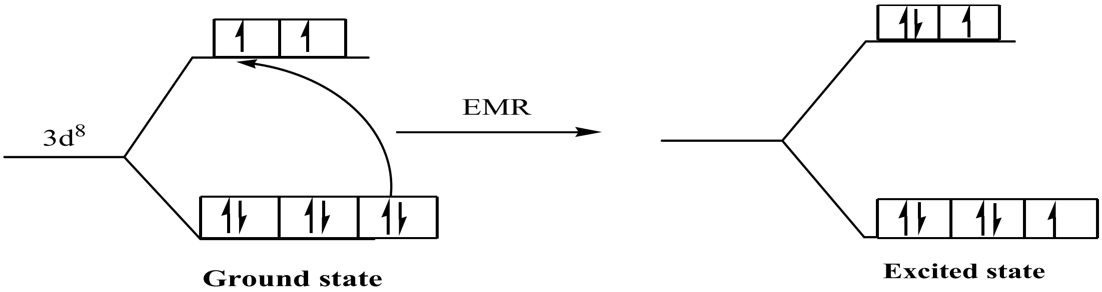
Example:

(i) $[Ni(H_2O)_6]^{+2}$ ion.

$Ni - 3d^8, 4s^2$

$Ni^{+2} - 3d^8, 4s^0$

According to CFT:



Spin multiplicity

$$\underbrace{\begin{matrix}\text{Ground state} & \quad & \text{Excited state} \\ n + 1 = 3 & \quad & (n + 1) = 3\end{matrix}}_{\Delta S = 0}$$

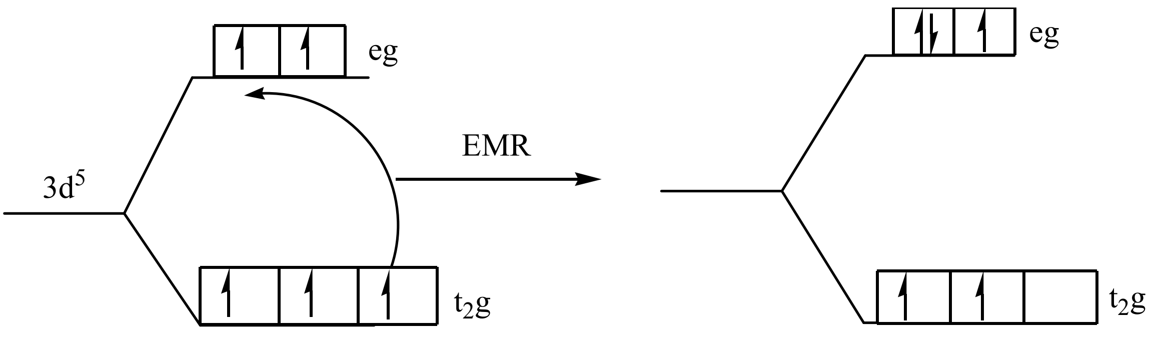
Allowed transition

(ii) $[Mn(H_2O)_6]^{+2}$ ion.

$Mn \; - \; 3d^5, 4s^2$

$Mn^{+2} \; - \; 4s^5, 4s^0$

According to CFT:



Ground state **Excited state**

Spin multiplicity

$$\underbrace{\begin{matrix}\text{Ground state} \\ n+1 = 6\end{matrix} \qquad\qquad \begin{matrix}\text{Excited state} \\ (n+1) = 4\end{matrix}}_{\Delta S \,\#\, 0}$$

Forbidden transition

4.4.2. Laporte selection rule

According to the this rule, all the electronic transitions which occur from G (g) to U (u) (gerade to ungerade) or u to g orbitals, are known as Laporte allowed or symmetry allowed transitions while all the electronic transitions, which occur from g to g or u to u orbitals are known as Laporte forbidden transition or symmetry forbidden transition.

$$\left.\begin{matrix} G \longrightarrow U \\ U \longrightarrow G \end{matrix}\right\} \text{Allowed} \qquad \left.\begin{matrix} G \longrightarrow G \\ U \longrightarrow U \end{matrix}\right\} \text{Forbidden}$$

According to this selection rule all the d-d transition phenomena in the transition metal complexes bung forbidden.

Therefore, according to the Laporte selection rule, all the electronic transitions in which there does not occur any change in the orbital quantum no (l) value are known as Laporte forbidden transition while all the electronic transitions which involve certain change in the orbital quantum number are known as Laporte allowed transition.

$\Delta l = 0$ (Laporte forbidden transitions)

$\Delta l \# 0$ (Laporte allowed transitions)

Thus, according to this selection rule, it is observed that all the d-d transitions (g-g transitions) are Laporte forbidden. There are certain relaxations in Laoprte selection rule due to the possibility of certain extent of d-p mixing.

4.5. TERM SYMBOL AND SPECTROSCOPIC GROUND STATE TERM

In quantum mechanics, the term symbol is the energy level of a single or multi-electron atom which is deduced from total angular momentam quantum number including orbital quantum number and spin quantum number. The atomic term symbols can be calculated from L-S coupling (Russell-Saunders coupling or Spin-Orbit coupling) and the ground state term symbol is predicted by Hund's rules.

Russell- Saunder coupling (Spin orbital or L-S coupling)

Russell and Saunder have proposed a coupling scheme i. e. Russell- Saunder coupling to calculate the term symbol for the various electronic configurations, which involve the following qauantum numbers:

(1) Total orbital momentum quantum number or L term

Vector summation of the l values of the differfent electrons present in a particular configuration is known as total orbital angular momentum quantum number (L term) for the configuration.

Different symbols for the different L value can be written as:

L	=	0	1	2	3	4	5	6	7
Symbol	=	S	P	D	F	G	H	I	J

(2) Total spin momentum quantum number or S term

Vector summation of spin angular momentum quantum number of all electrons present in any configuration (s values) is known as total spin angular momentum quantum number or S term.

$$S = \frac{n}{2}$$

Where n is the number of unpaired electrons

(3) Total angular quantum number or J term

Vector summation of L and S terms for a particular electronic configuration is known as total angular quantum number or J term which arises due to L-S coupling. The values of J are

$$J = L - S, L-S-1, L-S-2 \text{ ...... upto } L + S$$

For less than half filled configuration

$$J = L - S$$

For a configuration which is more than half filled

$$J = L + S$$

(4) Spin multiplicity or M term

Total number of the possible spin orientations of the unpaired electrons in a particular configuration is known as spin multiplicity or M term.

$$M = n + 1$$

$$= 2S+1$$

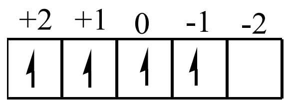
Where n = number of unpaired electrons

According to the above four different terms, term symbol for a particular configuration can be written as

$$^{M}L_{J}$$

For example for d^4 configuration

d^4 =



$$L = 2\ (D)$$

$$S = \frac{n}{2} = \frac{4}{2} = 2$$

For an electronic configuration less than half filled

$$J = L - S = 0$$

$$M = 4 + 1 = 5$$

So, the term symbol for d^4 configuration is $^{M}L_{J}$ = $\mathbf{^{5}D_{0}}$

Term symbol for the various d^n configuration, P^n configuration, S^n configuration can also easily determined:-

Hund's rule for ground state term

The calculation of term symbol for the ground state of an atom is relatively easy to using Hund's rules. Ground state term symbol corresponds to a state with maximum S and L values. Each electronic configuration except fully filled has large number of possible arrangements which are known as microstates which can be calculated as follow:

$$\text{Number of microstates} = \frac{n!}{r!\,(n-r)!}$$

Where n is maximum capacity (maximum number of electrons that can be accommodated in the orbital) of the particular configuration and r is number of electron in the configuration.

Out of the various possible electronic arrangements, one of the arrangement i.e. ground state electronic arrangement can be calculated with the help of different rule proposed by the Hund, which are given below:

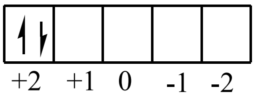
Rule 1: According to the Hund's rule, out of the various electronic arrangements, the arrangement having the maximum value of spin multiplicity will be the ground state electronic arrangement.

Rule 2: If more than one electronic arrangement has the same value of spin multiplicity, than the electronic arrangement with higher L value will be the ground state electronic arrangement.

Rule 3: Among various the ground state electronic arrangements with different J values, if the electronic configuration is less than half filled, than the ground state term will be withleast J value while if the configuration is more than half filled, than the ground state term will be the term with maximum J value.

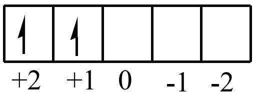
Example: Evaluation of ground state term symbol for d^2 configuration.

d^2 -



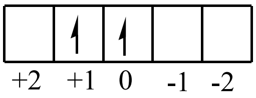
L = 4 (G)
S = 0
J = 4
M = 1

d^2 -



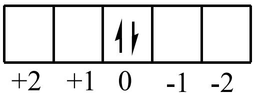
L = 3(F)
S = 1
J = 2,3,4
M = 3

d^2 -



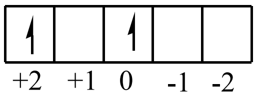
L = 1 (P)
S = 1
J = 0,1,2
M = 3

d^2 -



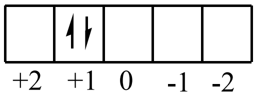
L = 0 (S)
S = 0
J = 0
M = 1

d^2 -



L = 2 (D)
S = 1
J = 1,2,3
M = 3

d^2 -



L = 2 (D)
S = 0
J = 2
M = 1

According to the Hund's rule, second arrangement will be the actual ground state electronic arrangement for d^2 configuration. Thus, the term symbol for d^2 configuration will be $^3F_2$.

4.6 SPECTROSCOPIC GROUND STATE TERM

The Spectra of transition metal complexes is not as simple as it appears from just the splitting of d-orbitals with electron gets promoted from the lower energy orbital se to a higher energy orbital set. Generally, energy levels of a transition metal atoms or ion with a particular electronic configuration are described not only by the electronic configuration itself but also by different types of electronic transitions such as spin-spin, orbital-orbital or spin –orbital which can be categorized by some special symbols, called as term symbol. The ground state term determined by the Hund's rule. Before the determination of spectroscopic ground state we have to know about the term symbol and its determination this is described above.

4.7. SPECTROCHEMICAL SERIES

Order of ligands arranged according to the strength of ligand and arrangement of metal ions on the basis of oxidation number, group and its identity is called as spectrochemical series. According to crystal field theory, ligands can change the difference in energy between the two sets of d orbitals (Δ_o) called the ligand-field splitting parameter for ligands or the crystal-field splitting parameter, which can be the cause of differences in color of similar type of metal-ligand complexes.

The spectrochemical series was first given in 1938 and was based on the results of absorption spectra of cobalt complexes. Spectrochemical series of the ligands from smaller value of Δ_o to larger value of Δ_o is given below.

$O_2^{2-} < I^- < Br^- < S^{2-} < SCN^- < Cl^- < N^{3-} < F^- < NCO^- < OH^- < C_2O_4^{2-} \approx H_2O < NCS^- < CH_3CN <$ py (pyridine) $< NH_3 <$ en (ethylenediamine) $<$ bipy (2,2'-bipyridine) $<$ phen (1,10-phenanthroline) $< NO_2^- < PPh_3 < CN^- \approx CO$

Ligands present on the left end of this spectrochemical series are generally known as weaker ligands and cannot cause pairing of electrons within 3d level and thus, form outer

orbital octahedral complexes and are called as high spin ligands. While, ligands present at the right end of the series are stronger ligands which can form inner orbital octahedral complexes after forcible pairing of electrons within 3d level and hence, are called as low spin ligands.
The strong ligands in the spectrochemical series are also called as л-acceptor ligands while weak ligands are known as σ-donor ligands.

4.8 ORGEL AND TANABE-SUGANO DIAGRAMS FOR TRANSITION METAL COMPLEXES (d^1-d^9 STATES)

It is clear that electronic transitions are always accompanied by vibrational as well as rotational changes which results in a considerable broadening of the bond in the UV- Visible spectra of transition metal complexes too. The nature of these transitions is quite complexes to understand the requires some basic knowledge of Quantum mechanics and chemical applications of group theory.
Splitting of Russel Saunders states in octahedral and tetrahedral crystal field:
To know about the nature of electronic transitions in transition metal complexes, we need to know how the splitting of electronic energy levels and spectroscopic term occurs in s,p,d and f orbitals. The following points may be notated.

1. An s- orbital is spherically symmetrical and is not affected by an octahedral field. Hence no splitting takes place in this case.
2. The p- orbitals are directional in nature but they have same type of orientation. These are affected by an octahedral field but no equal extent. Therefore, there energy levels remain equal and no splitting occurs.
3. The 5-d orbitals are splitting by an octahedral field in to two levels t_2g (dxy, dyz, dzx) and e_g (dx^2-y^2, dz^2) having different energies. The difference between these two levels is 10 Dq (Δ_o). The t_2g levels is triply degenerated and is 4Dq below the non- generated levels while eg level is doubly degenerate and is 6 Dq above the non- generated levels. For d^1 configuration the splitting is given figure:

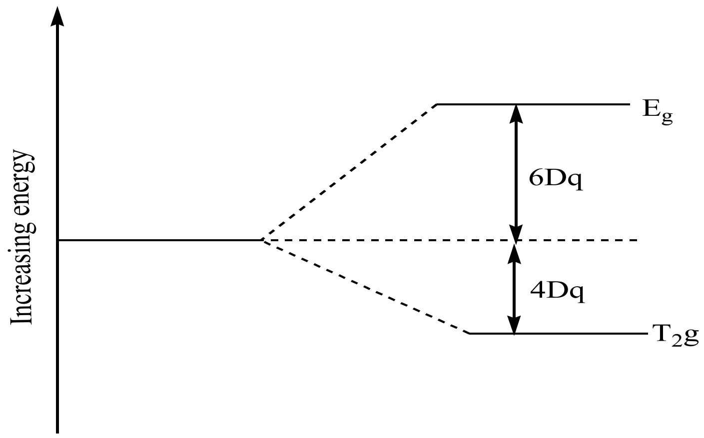


Fig. 4.2 Splitting of the d-orbital

4. In case of f- orbital, there are seven f- orbitals and these splitted by an octahedral field in to three levels. For an f^1 arrangement, the ground state is a ^3F state and is split in to a triply degenerate T_1g state which is $6D_q$ below the center, a triply degenerate T_2g level which is $2D_q$ above the center and a single A_2g state which is $12D_q$ above the center shown given figure:

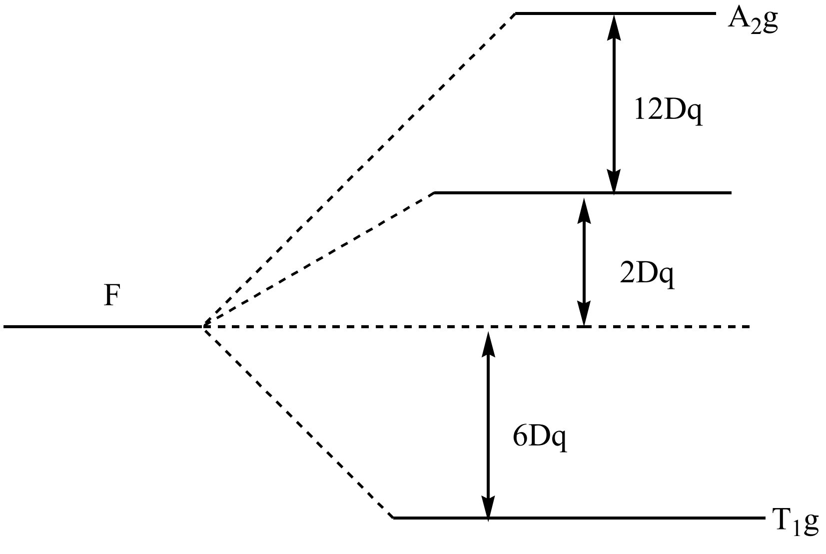


Fig.4.3 Splitting of the f-orbital

According to above discussion, we can summaries that in an octahedral field, Orgel energy level diagram for d^1 and d^9 state,

S and P states do not split

D state split in to two states, E_q and T_2g

F state split in to three states, A_2g, T_2g and T_1g

These states split by the external field are called Mulliken symbol.

It may be noted that common Mulliken symbols are used in the octahedral and tetrahedral field these are distinguished by introducing the symmetry symbol 'g' in octahedral field.

Correlation of Spectroscopic terms in to Mulliken symbol

Spectroscopic Term	Mulliken symbol	
	Octahedral field	Tetrahedral field
S	A_1g	A_1
P	T_1g	T_1
D	$E_g + T_2g$	$E + T_2$
F	$A_2g + T_1g + T_2g$	$A_2 + T_1 + T_2$
G	$A_1g + Eg + T_1g + T_2g$	$A_1 + E + T_1 + T_2$

The A, E and T represented, doubly and triply degenerate state, respectively. The presence of 'g' in symmetry designation of the octahedral field is for the grade or Centro symmetric environment.

Terms correlation in the tetrahedral and octahedral field:

The quantitative description of different energy term for d^n and d^{10-n} configuration from free ion to strong crystal field configuration ignoring inter electronic repulsion can be given as:

1. The total number of energy levels remains the same under the influence of weak and strong field.
2. The one to one correspondence of different energy levels in a strong crystal field may get stabilized or destabilized in comparison to the weak field case.
3. Energy levels of the same symmetry never cross each other and each level has a contribution in its energy from all other energy states of the symmetry.
4. Term correlation for d^1, d^9, d^2 and d^8 configuration are shown completely while for d^3, d^4, d^5, d^6, d^7 are shown partially by taking only lower energy levels.
5. According to the hole formation, the number of microstates and hence all free ion terms for d^n and d^{10-n} configuration are same. Now, as the magnitude for the crystal field experienced by the negative electrons, but is of opposite sign, therefore, the splitting pattern for d^n and d^{10-n} configuration are opposite in each other.
6. The splitting pattern of d^n tetrahedral is just the opposite of what is for d^n octahedral. However no 'g' or 'U' is used in the tetrahedral case because there is no center of symmetry.

The correlation diagrams (with corresponding microstates shown below each level) for different electronic configuration in transition metal complexes with four coordinated tetrahedral and six coordinated octahedral symmetry are given below.

Orgel diagrams are the correlation diagrams that represent the relative energies of electronic terms in transition metal complexes. These diagrams are firstly drown by Leslie Orgel. Orgel diagrams are drawn for only weak field complexes (i.e. high spin). These are the diagrams drawn between Δ_o. These diagrams are qualitative and no energy calculations can be carried out from these diagrams. In Orgel diagrams, only symmetry states with the highest spin *multiplicity* are used instead of all possible terms. With the help of Orgel diagrams, we can deduce the number of spin allowed transitions. In these diagrams, the gtound state term (atomic term) (P, D, or F) is located at the center of the diagram in the absence of ligand field while in presence of ligand field, the atomic term splits into molecular Mulliken terms. On the basis of the above discussion, Orgel diagram for the various d^n configuration of transition metal complexes, are discussed in this section.

A. Orgel diagram for d^9 octahedral complexes

Orgel diagram of octahedral complexes with d^9 configuration can be drawn in the three different steps which are given below (Figure 4.2):

Step I:

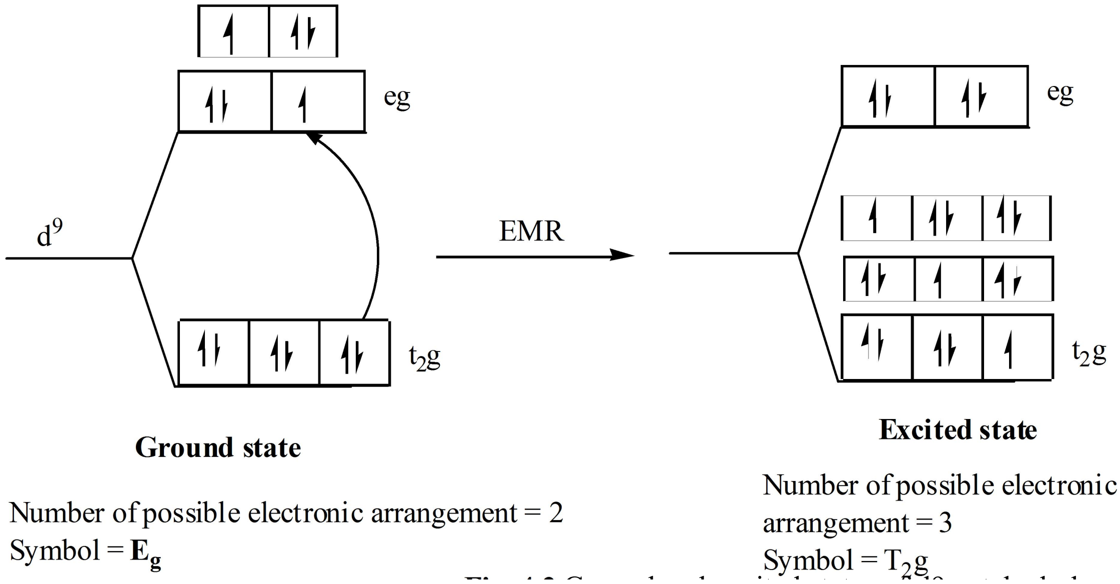
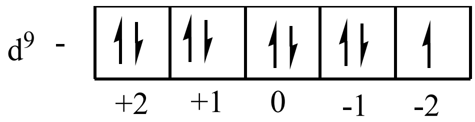


Fig. 4.4 Ground and excited states of d9 octahedral complexes

Step II:



L = 2 (D)
S = 1/2
J = 5/2
M = 2

So, the term symbol for d^9 configuration = $\mathbf{^2D_{5/2}}$

Step III: Formation of Orgel diagram (Figure 4.3).

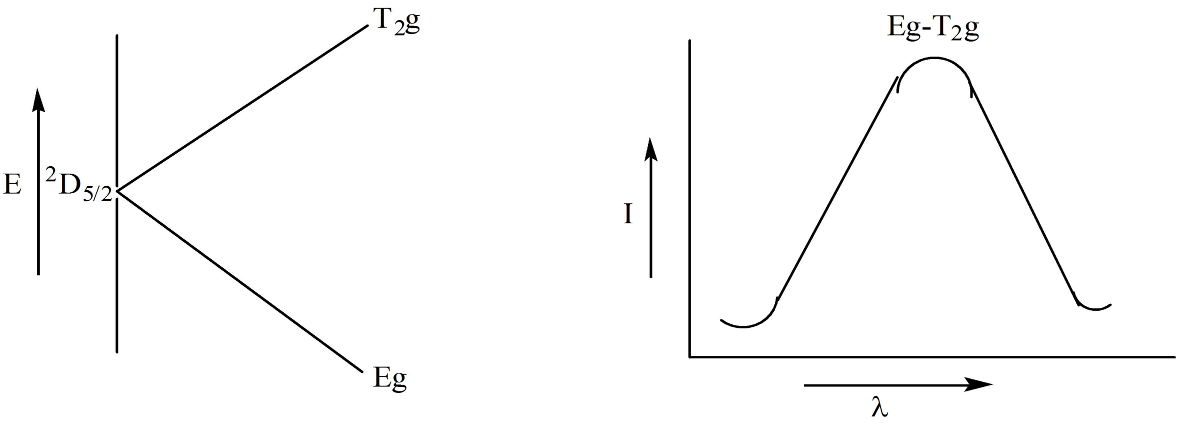
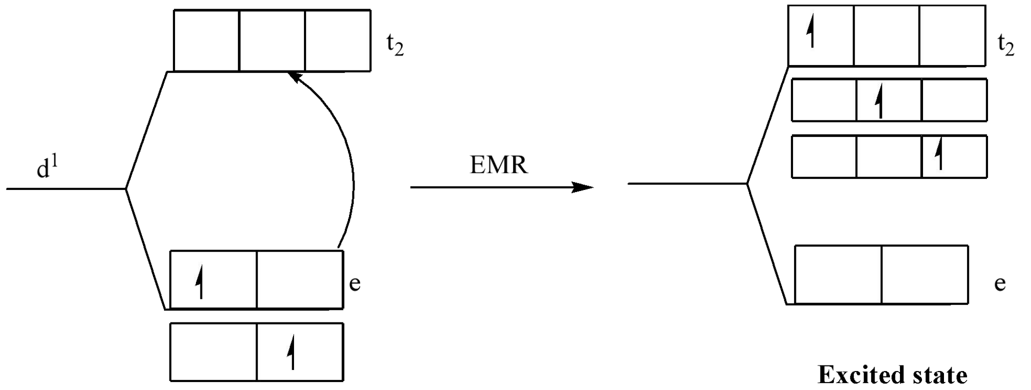


Fig. 4.5 Orgel diagram and absorption spectra of d9 octahedral complexes

B. Orgel diagram for the d^1 tetrahedral complexes: Orgel diagram for the d^1 configuration of tetrahedral complexe can be explained in the three different steps, is are givenin Figure 4.6 and Figure 4.7.

Step I:



Ground state

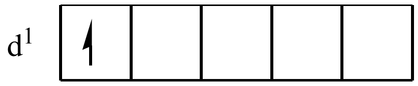
Number of possible electronic arrangement = 2
Symbol = **E**

Excited state

Number of possible electronic arrangement = 3
Symbol = $\mathbf{T_2}$

Fig. 4.6 Ground and excited state of d1 tetrahedral complexes

Step II:



L = 2(D)
S = 1/2
J = 3/2
M = 2

So, the term symbol for d^1 configuration = $\mathbf{^2D_{3/2}}$

Step III:

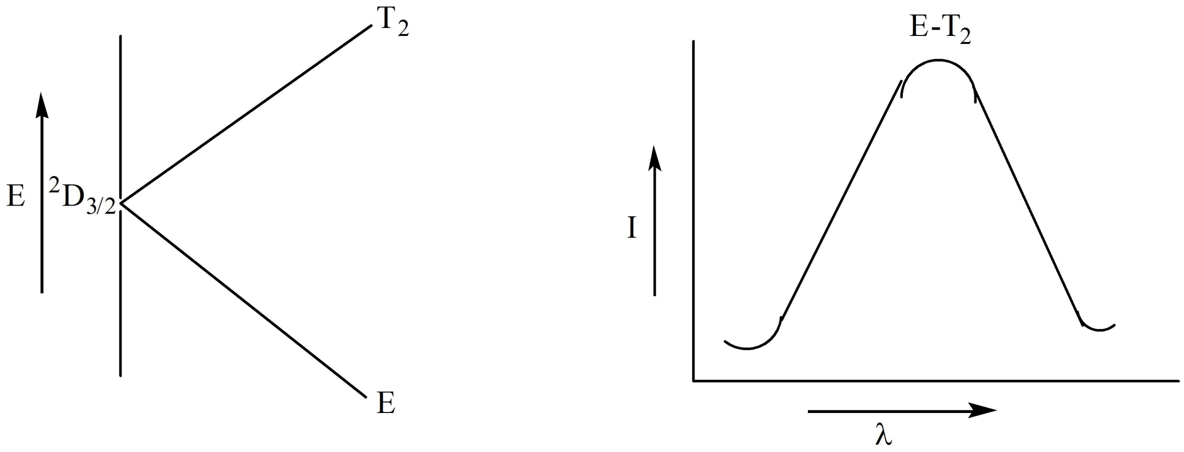


Fig. 4.7 Orgel diagram and absorption spectra of d1 tetrahedral complexes

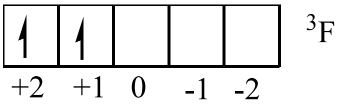
Thus, from the above, it can be concluded that d^n tetrahedral complexes and d^{10-n} octahedral complexes have same spectra while d^n tetrahedral complexes and d^{10-n} tetrahedral complexes or d^n octahedral complexes and d^{10-n} octahedral complexes have opposite spectra.

C. Orgel diagram for d^2 octahedral complexes

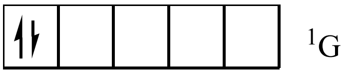
In the electronic spectra of d^2 configuration with octahedral ligand field, such as $[V(H_2O)_6]^{+3}$, it two peaks in the range of 1700cm^{-1} and 2100 cm^{-1} are obtained which indicates that the d^2 configuration with octahedral field ligands can exhibit two types of the electronic transitions.

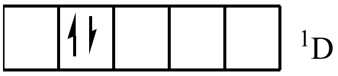
According to Orgel, d^2 configuration has ground term symbol ^3F and various exited state term symbols like ^1S, ^1D, ^1G and ^3P. Out of these, only ^3P term (both having same multiplicity) symbol is used during the electronic transition because the electronic transitions from ground state to this excited state are allowed while the electron transitions from ground state to other excited states such as ^1S, ^1G and ^1D are spin forbidden. The Orgel diagram corresponding to this allowed transition for the d^2 configuration with octahedral field ligand can be given below.

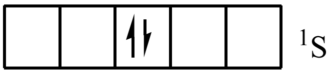
Ground state electronic arrangement for d^2 octahedral complexes is as follows:

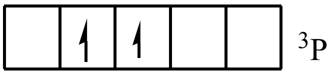


Exited state electronic arrangement for d^2 octahedral complexes is as follows:









Thus, according to the above discussion, the Orgel energy level diagram and spectra for d^2 configuration with octahedral field ligand can be represented as shown in Figure 4.8.

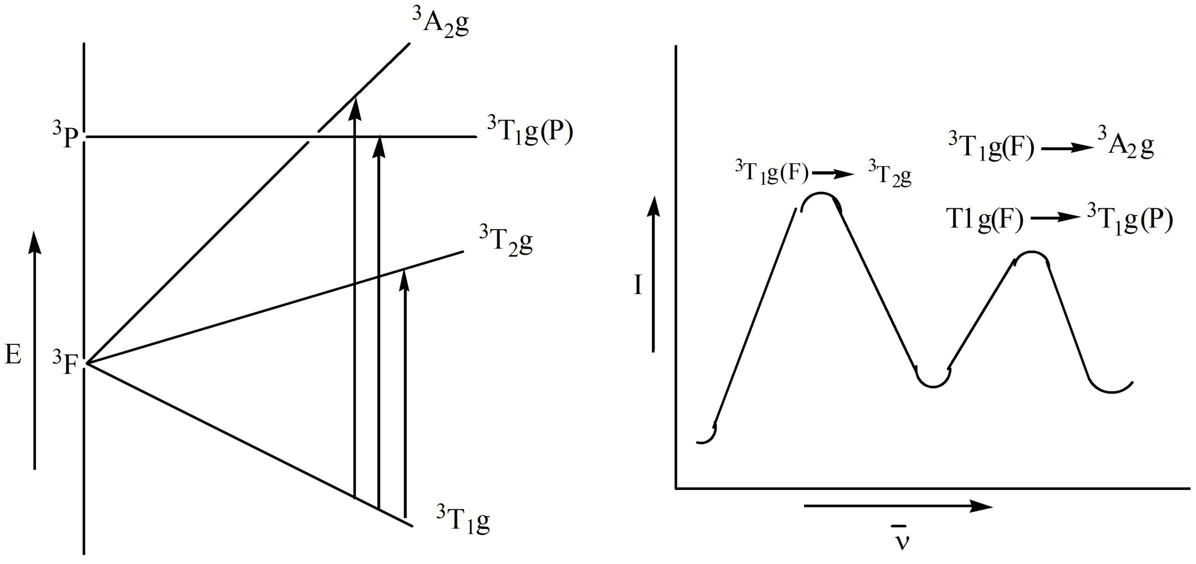


Fig 4.8 Orgel diagram and absorption spectra of d2 octahedral complexes

D. Orgel energy level diagram for d^8 octahedral complexes

The spectra of octahedral complexes with d^8 configurationcontains different peaks which indicates that octahedral complexes like $[Ni(H_2O)_6]^{+2}$, have different types of the transitions (Figure 4.9).

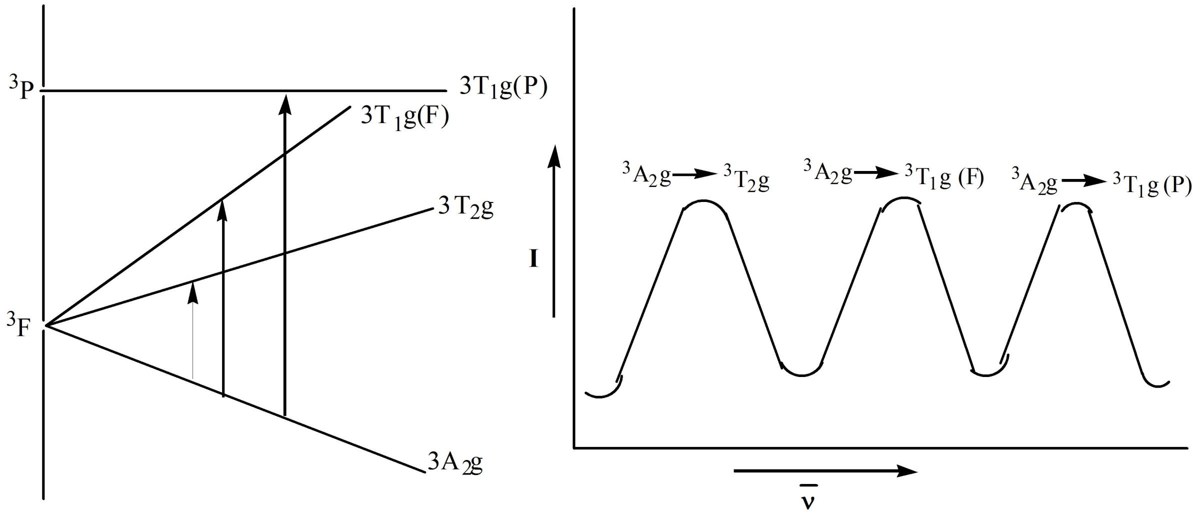


Fig. 4.9 Orgel diagram and absorption spectra of d2 octahedral complexes

4.9 CALCULATIONS OF RACAH PARAMETERS

When an atom has more than one electron there will be some electrostatic repulsion between those electrons. The amount of repulsion varies from atom to atom, depending upon the number and spin of the electrons and the orbitals they occupy. The total repulsion can be expressed in terms of three parameters *A*, *B* and *C* which are known as the **Racah parameters** after Giulio Racah, who first described them.

The parameters are actually determined from spectral data. The energy of each term originating from a given electronic configuration may be expressed as the linear combination of three Racah parameters A, B and C. For example, energy (E) for different terms arising from the d^2 configuration are

$^1S = A + 14B + 7C$

$^1G = A + 4B + 2C$

$^1D = A - 3B + 2C$

$^3P = A + 1B$

$^3F = A - 8B$

The differences in energy between states are given by B and C only; for states with same spin multiplicity, the difference is given by B only. Here, separation between ^3F and ^3P is equal to 15B. This is also hold to V^{2+} (d^3) for which

Separation between ^4F and ^4P terms = 15B

Separation between ^4F and ^2G terms = 4B + 3C

Since complex formation reduces interelectron repulsion, the values of B and C in complexes are much lower than the free ion values. Usually, the former are 70% of the respective free ion values in the first transition series. Ion if the first transition series have a C/B ratio of about 4, with B lying around 1000 cm^{-1}

4.10 CHARGE TRANSFER TRANSITION

In inorganic compounds, most of the charge-transfer complexes involve electron transfer between metal atoms and ligands. The charge-transfer bands of transition metal complexes result from shift of charge density between molecular orbitals (MO) that are predominantly metal like nature and those that are predominantly ligand like nature. If the transfer occurs from the MO with ligand character to the MO with metal-like character, the complex is called a ligand-to-metal charge-transfer (LMCT) complex and the transfer is LMCT. If the electronic charge shifts from the MO with metal character to the MO with ligand character, the complex is called a metal-to-ligand charge-transfer (MLCT) complex. Thus, oxidation of the metal center occurs as a result of MLCT, whereas a LMCT results in the reduction of the metal center.

Depending on the direction of charge transfer, these are classified as either ligand-to-metal (LM) or metal-to-ligand (ML) charge transfer

(a) Ligand-to-metal charge transfer (LMCT)

LMCT complexes arise from the transfer of electrons from MO having ligand character to those having metal character. This type of transfer occurs when complexes have ligands with relatively high-energy lone pairs and if the metal has low-lying empty orbitals. In such complexes, metals have higher uncommon oxidation states or less number of d-electrons (even d^0). These conditions suggest that the acceptor metal level is available which is of low energy.

Consider a d^6 octahedral complex, such as $IrBr_6^{3-}$, whose t_{2g} orbitals are filled. As a result, an intense absorption peak is observed around 250 nm corresponding to a transition from ligand like σ MO to the empty e_g MO of metal like character. However, in case of $IrBr_6^{2-}$, a d^5 complex, two absorption peaks, one near 600 nm and another near 270 nm, are observed. This is because two transitions are possible, one to t_{2g} (that can now accommodate one more electron) and another to e_g. The 600 nm band corresponds to transition of electron from ligand orbital to the t_{2g} MO of metal and the 270 nm band correspond to transfer of electron from ligand MO to the e_g MO of the metal.

Charge transfer bands may also arise from transfer of electrons from nonbonding orbitals of the ligand to the e_g MO of metal.

Examples:

MnO_4^-: The permanganate ion with tetrahedral geometry is intensely purple coloured due to strong absorption involving charge transfer from MO of filled oxygen p orbitals to empty MO of manganese (VII).

CdS: The yellow color of cadmium sulphide is due to the transition of electrons from Cd^{2+} (5s) ← S^{2-} (π).

HgS: It is red due to Hg^{2+} (6s) ← S^{2-} (π) electronic transition.

(b) Metal-to-ligand charge transfer

Metal-to-ligand charge-transfer (MLCT) complexes arise as a result of transfer of electrons from MO with metal-like character to those with ligand-like character. These transitions are most common in complexes with ligands having low-lying π* orbitals, especially aromatic ligands. For these transitions to occur, metal should have low oxidation state with sufficient number of electrons and should be relatively high in energy.

Examples:

i. **Tris (2, 2'-bipyridyl) ruthenium (II):** This is a orange-colour complex due to MLCT.

ii. $W(CO)_4(phen)$

iii. $Fe(CO)_3(bipy)$

4.11 RUSSELL-SAUNDERS (R-S) COUPLING

The ways in which the angular momentum associated with the orbital and spin motions in many electron atoms can be combined together are many and varied. In spite of this seeming complexity, the results are frequently readily determined for simple atom systems and are used to characterize the electronic states of atoms.

The interactions that can occur are of three types:

1. spin-spin coupling (S)
2. orbit-orbit coupling (L)
3. orbit-orbit coupling (L)

There are two principal coupling schemes used:

1. Russell-Saunders (or L - S) coupling
2. j - j coupling.

In the Russell Saunders scheme it is assumed that:

Spin-spin coupling > orbit-orbit coupling > spin-orbit coupling.

This is found to give a good approximation for first row transition series where J coupling can generally be ignored, however for elements with atomic number greater than thirty, spin-orbit coupling becomes more significant and the j-j coupling scheme is used.

1. Spin-Spin coupling:

S–is the resultant spin quantum number for a system of electrons. The overall spin S arises from adding the individual ms together and is as a result of coupling of spin quantum numbers for the separate electrons.

The total spin is normally reported as the value of 2S + 1, which is called the multiplicity of the term:

S =	0	½	1	3/2	2	5/2
2S + 1	1	2	3	4	5	6
	singlet	doublet	triplet	quartet	quintet	sextet

2. Orbit-Orbit coupling:

L–is the total orbital angular momentum quantum number defines the energy state for a system of electrons. These states or term letters are represented as follows:

By analogy with the notation s, p, d ... for orbitals with l = 0, 1, 2, ..., the total orbital angular momentum of an atomic term is denoted by the equivalent upper case letter:

Total Orbital Momentum:

L	0	1	2	3	4
	S	P	D	F	G

3. Spin-Orbit coupling

Coupling occurs between the resultant spin and orbital moment of an electron which gives rise to J the total angular momentum quantum number. Multiplicity occurs when several levels are close together and is given by the formula (2S+1). The multiplicity is written as a left superscript representing the value of L and the entire label of a term is called a term symbol.

The Russell Saunders term symbol is then written as: (2S+1)L.

1. R-S coupling for d^1 configuration:

S= +½, hence (2S+1) = 2; L=2 and the ground term is written as ^2D (doublet dee). For an s^1p^1 configuration:

S= both +½, hence (2S+1) = 3; or paired hence (2S+1) = 1; L= 0 + 1 = 1 and the terms arising from this are ^3P (triplet pee) or ^1P (singlet pee).

2. R-S coupling for d^2 configuration:

For two d-electrons, L may have values 4,3,2,1 and 0 corresponding to G, F,D, P and S terms respectively. S may be either 0 or ± 1. Corresponding (2S + 1) values are 1 and 3. Now we may apply Hund's rules to select the lowest energy or ground term:

4.12. SUMMARY

The present unit may be summarized as follow:

- Electronic spectra of transition metal complexes help us to understand the structure and bonding in these complexes. A very special characteristic of transition metal complexes is that they exhibit colours of varying intensity of the visible region.
- It has been established that colour of the complex compounds is because of d-d transition. The electrons excite from lower energy set of d orbital to high energy set of d orbitals.
- Energy from the visible range is absorbed by the transition metal complexes and the energy of complementary colour is transmitted. It is the transmitted radiation that from the colour of the substance.

4.13 SAQs TYPE QUESTIONS

A. Multiple choice question

1. Which metal complex ion is expected to be subject to a Jahn-Teller distortion?

   a. $[Cr(H_2O)_6]^{+3}$ b. $[Cr(NH_3)_6]^{+2}$

   c. $[Cr(CN)_6]^{-3}$ d. $[Cr(bpy)_3]$

2. A d^1 electron configuration corresponds to which of the following terms?

a. ^2D b. ^1D

c. ^2P d. ^3P

3. How many microstates are possible for a d^2 configuration, including both weak and strong field limits?

a. 15 c. 45

c. 10 d. 90

4. The'd-d' transitions in an octahedral $[NiX_6]^{2+}$ complexes are:

a. Laporte forbidden but spin allowed b. Laporte forbidden and spin forbidden

c. Laporte allowed and spin allowed d. Laporte allowed but spin forbidden

5. Why does the absorption spectrum of aqueous $[Ti(OH_2)_6]^{3+}$ exhibit a broad band with a shoulder?

a. The ground state of $[Ti(H_2O)_6]^{3+}$ is Jahn-Teller distorted

b. The excited state of $[Ti(H_2O)_6]^{3+}$ undergoes a Jahn-Teller distortion

c. $[Ti(H_2O)_6]^{3+}$ is a d^2 ion and therefore there are two absorptions

d. $[Ti(H_2O)_6]^{3+}$ is partly reduced to $[Ti(H_2O)_6]^{2+}$ in aqueous solution and two absorptions which are close in energy are observed, one for each species

6. Ground state term for d^2 configuration is:

a. ^3F b. ^3P c. ^1G d. ^1S

7. For Laporte forbidden transitions,

a. $\Delta l = 0$ b. $\Delta S = 0$ c. $\Delta l = -1$ d. $\Delta l = \pm 1$

8. Mullikin symbol for spectroscopic term P in octahedral field is:

a. A_{1g} b. T_{1g} c. T_{2g} d. E_g

9. The ground state for $2p^3$ is:

a. $^4S_3$ b. $^3P_4$ c. $^4S_{3/2}$ d. $^2P_1$

10. The ground state term for p^6 is same for

a. d^{10} b. d^6 c. p^3 d. d^5

B. Fill in the bling

i. The types of electronic transition which can generate the high intense spectra are known as……………….

ii. The calculation of term symbol for the ground state of an atom is relatively easy to using……………..

iii. Order of ligands arranged according to the …………….and arrangement of metal ions on the basis of oxidation number, group and its identity is called as…………… .

iv. Orgal diagram use for the only …………ligand

C. True and false

i. If spin multipicity reamin same then spin selection rule allowed. True/false

ii. Colour of complex depend on spin selection rule as well as lepart rule. True/false

iii. Arrengment of ligand in increasing order of their splitting power is known as spectrochemical series. True/False

iv. D state split in to only one states True/False

D. Match the following

a. Spin allowed	i. MnO_4^-
b. Leporte allowed	ii. $[Ni(H_2O)_6]^{+2}$
c. LMCT	iii. $Fe(CO)_3(bipy)$
d. MLCT	iv. $[NiCl_4]^{-2}$

Answer key

A. 1 a **2** a **3** b **4** c **5** b **6** a **7** a **8** b **9** c **10** a

B. i. allowed transitions, ii. Hund rule, iii. Strength of ligand, spectrochemical series iv. Weak field

C. i. True ii. True iii. True iv. False

D. a ii b iv c i d iii

4.14 GLOSSARY :

T_2g = triply degenerate state

Eg = Doubly degenerate state

Ag = Non-degenerate state

Mo = molecular orbital

LMCT = ligand to metal charge transfer

MLCT = Metal to ligand charge transfer

4.15 REFERENCES :

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1. J. Ferguson, (1979). *Spectroscopy of 3d Complexes*, Prog. Inorg. Chem. 12, 158.

2. S.F.A. Kettle, Physical Inorganic Chemistry.
3. Zumdahl, Steven S. Chemical Principles Fifth Edition. Boston: Houghton Mifflin Company, 2005. Pages 550-551 and 957-964.
4. D. F. Shriver and P. W. Atkins. (2001). *Inorganic Chemistry*, 3rd ed. Oxford University Press.
5. James E. Huheey, Ellen A. Keiter and Richard L. Keiter. (1993). *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed. Harper Collins College Publishers.
6. C. E. Housecroft,and A. G. Sharpe. (2008). *Inorganic Chemistry*, 3rd ed. Prentice Hall..
7. P. J. Atkins and D. F. Shriver. (1999). *Inorganic Chemistry*, 3rd ed. W.H. Freeman and Co., New York.
8. Donald A. Tarr and Gary L. Miessler. (1991). *Inorganic Chemistry,* 2nd ed. Prentice Hall.
9. R. L. Madan. *Chemistry for Degree Students. B. Sc. III*. S. Chand and Company PVT. LTD.

4.16 SUGGESTED READDING :

1. Banerjea D., (2009), *Coordination Chemistry" (second edition),* Asian Books, 4, 874.
2. House J. E., (2009), *Inorganic Chemistry*, Elsevier,
3. C. E. Housecroft, A. G. Sharpe, (2018), *Inorganic chemistry*, Pearson (Fifth edition), 1256.
9. F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, (1999), *Advanced inorganic chemistry*, Wiley-Interscience (Six Edition), 1376.
10. J. D. Lee, (1999), *Concise inorganic chemistry*, Wiley-Blackwell (Fifth edition), 1072.
11. Atkins; et al. (2010). Shriver and Atkins' Inorganic Chemistry (Fifth ed.). New York: W. H. Freeman and Company. ISBN 978-1-4292-1820-7.
12. Janes R., Moore E. A., (2004), *Metal-ligand bonding*. The Open University, , 23. ISBN 0-85404-979-7
13. Tsuchida R., (1938). "*Absorption Spectra of Co-ordination Compounds. I.*" Bull. Chem. Soc. Jpn. **13** (5): 388–400.

4.17 TERMINAL QUESTIONS

1. Why metal complexes are having colors?
2. If the transition is between one set of d-orbital to another set of d-orbital, only one color should be there for a complex. However, different colors are seen for different complexes. Why?
3. Why d-d transitions are weak as compared to CT transitions?
4. Calculate the term symbol for d^9 octahedral complex.
5. Differentiate between LS coupling and JJ coupling.
6. Why do tetrahedral complexes of an element give much more intense d-d spectra than its octahedral complexes?
7. Discuss the electronic spectra of $[Co(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$ complexes.
8. What are spin multiplicity forbidden and Laporte forbidden transitions?
9. What are selection rules for electronic spectra?
10. Discuss the spectral features of Mn(II) in octahedral complexes of weak ligand fields.
11. Write briefly about L-S coupling.
12. Discuss the absorption spectra for Co(II) octahedral and Co (II) tetrahedral complexes.
13. Calculate the ground state terms with spin multiplicity for the following octahedral ions: Vi^{3+}, Ni^{2+}, Cu^{2+}
14. Discuss the Orgel diagram and absorption spectra for a d^8 ion.
15. Determine the ground state term symbol of anion with d^1 configuration.
16. Draw the energy level diagram for d^2 configuartion in tetrahedral and octahedral fields showing three possible transitions.
17. How does Hund's rule help to arrange the different spectroscopic terms in order of their increasing energies? How does it help to find the terms in ground state?
18. Discuss Russel-Saunders states for d^2 configurations.
19. Discuss the special features of electronic spectra of $[Ni(H_20)_6]^{2+}$ ion.
20. Discuss special features of electronic spectra of Cr(III) octahedral and Mn(II) octahedral complex ions.
21. Arrange the different spectroscopic terms of titanium with the help of Hund's rules.
22. State and explain the Laporte selection rule.
23. What are the two important limitations of Orgel diagrams?
24. Draw combined Orgel diagram for d^1 and d^9 octahedral complexes.
25. What are Orgel diagrams? What information is conveyed by these diagrams?
26. Give a detailed account of the selection rules of electronic spectra.

27. State and explain Hunds rule for assigning ground state spectroscopic term with suitable examples.
28. Why do tetrahedral complexes give much more intense d-d transition than octahedral complexes?
29. Calculate the term symbol for ground state of Cr.

UNIT : FIFTH

MAGNETIC PROPERTIES OF TRANSITION METAL COMPLEXES

Structure of unit :

Unit-Fifth

MAGNETIC PROPERTIES OF TRANSITION METAL COMPLEXES

5.2 INTRODUCTION:

The magnetic property of coordination compounds is an important parameter in reference to understand their physical behaviour. These properties of any compound can be determined from the electronic configuration and size of the atoms of that compound. The magnetism generated by the electronic spin and the number of unpaired electrons present in the compound. In this chapter the magnetic properties of transition metal complexes is discussed in detail.

The study of magnetic properties of coordination compounds has contributed a lot to understand the chemistry of transition metal complexes, the stereochemistry of the central metal ion and the nature of the metal ligand bonding. Therefore, the study of origin of the magnetic behaviour exhibited by the transition metal complex becomes an important parameter in coordination chemistry.

It is well known that any moving charged particle produces a magnetic field. Accordingly, the moving electron (in orbit) as well as nuclei of atom is also capable of producing magnetic field. However, the magnetic field generated by nuclei is about 10^4 times weaker than the magnetic field generated by a moving electron. Therefore, the magnetic phenomenon associated with moving electrons has been studied extensively till the discovery of the phenomenon of nuclear magnetic resonance (NMR). The NMR has now become an extremely useful tool for studying the nature of inorganic as well as organic compounds. This chapter is mainly focused on the study of magnetic behaviour that is generated only by the moving electrons.

Before discussing about the magnetic behaviour of coordination compounds let us first define the various terms which are being frequently used during explanation of magnetic properties of such compounds.

Pole strength of magnet: The strength of a magnet may be expressed in terms of unit pole. A unit pole may be defined as a pole that repels or attracts another unit pole placed 1 cm apart with a force of 1 Dyne. Thus the unit intensity of magnetic field exists at the place where the unit pole experiences a force of 1 Dyne.

Lines of force: If a magnetic pole is placed at any point in a magnetic field, it will experience a force in the direction of the magnetic field and it would move freely and follow the path under the action of this induced force. The direction of moving pole at every point is the direction of the field. Such a path is known as a line of force. A field of unit intensity is taken to give unit lines of force per square centimetre. If a pole of strength m is placed inside a sphere of radius one centimetre, then the surface area of the sphere is 4π and a total of 4πm lines of force will emerge from the pole. Thus, the number of line of force at per square centimetre of surface will be given by

$$\frac{4\pi m}{4\pi} = m\ (which\ is\ the\ pole\ strength)$$

Magnetic field strength or intensity: Magnetic field strength or intensity at any point in a magnetic field can be defined as the force experienced by a unit pole placed at that point. This force is also known as the strength of magnetic field. The mathematical relation for magnetic field strength is shown as:

$$F = \frac{m}{r^2}$$

The unit of magnetic intensity or field is oersted.

1 oersted = 1 dyne/unit pole

Thus, if a unit pole placed at any point in the magnetic field experiences a force of *H* dynes, the strength of the magnetic field will be *H* oersted. A smaller unit of filed strength is gamma (γ).

$$10^{-5} \text{ oersted} = \gamma$$

If a pole of strength m is placed at the point in the field, the forced experienced is given by

$$F = mH \text{ dynes}$$

Intensity of magnetization: The intensity of magnetization induced in a body by an applied field is expressed in terms of the pole strength induced per unit area of the body.

$$I = \frac{Magnetic\ moment}{Volume}$$

For example if a magnetic dipole having length l and pole area A, and its pole strength is m. Then the intensity of magnetization can be given as

$$I = \frac{Magnetic\ moment}{Volume} = \frac{m \times l}{A \times l}$$

$$I = \frac{m}{A}$$

Thus, the intensity of magnetization can be defined as the magnetic moment per unit volume. Its unit is *Ampere/meter* (or A/m). It should be noted that the intensity of magnetization is differ than intensity of magnetic field. The intensity of magnetic field defined as the forces that the poles of a magnet experiences in a magnetic field, whereas, the intensity of magnetisation explains the change in the magnetic moment of a magnet per unit volume.

Magnetic induction: When a specimen of a magnetic material is placed in a magnetic field. Magnetism is induced in the specimen. This phenomenon is known as magnetic induction. The end of the specimen from which the lines of force enter becomes the South Pole, and the end from which the lines of force leave the specimen is become the North Pole. Magnetic induction is also defined as the total number of lines of force crossing per unit area around the located point in the specimen placed in the magnetic field. It is also known as magnetic flux density. The flux density is directly proportional to magnetic field. When a sample is subjected to a magnetic field of strength H (*i.e.* H lines of force per unit area) then the total lines of force coming out of the sample will be given by the sum of H and the induced magnetization. Since I is the pole strength induced per unit area, thus magnetic induction can be represented as

$$B = H = 4\pi I$$

Magnetic permeability: Magnetic permeability (P) is defined as the ratio of the magnetic flux density at any point in the specimen to the strength of magnetic field applied. If B is the magnetic flux density and H is the strength of the magnetic field applied then permeability can be shown as

$$P = \frac{B}{H}$$

$$P = 1 + \frac{4\pi I}{H}$$

Magnetic susceptibility: The magnetic susceptibility is a measure of how much a material will become magnetized in an applied magnetic field. It is the ratio of the magnetization of the specimen of the material and the strength of the Magnetic field applied. Thus the magnetic susceptibility can be shown as

$$\chi = \frac{I}{H}$$

Since I, is the magnetic moment per unit volume, thus χ would be expressed as per unit volume. That is why χ also known as volume magnetic susceptibility and is represented as χ_v

Thus

$$\chi_v = \frac{I}{H}$$

Similarly, the gram magnetic susceptibility χ_g is the susceptibility per gram of the material. Thus

$$\chi_g = \frac{\chi_v}{d}$$

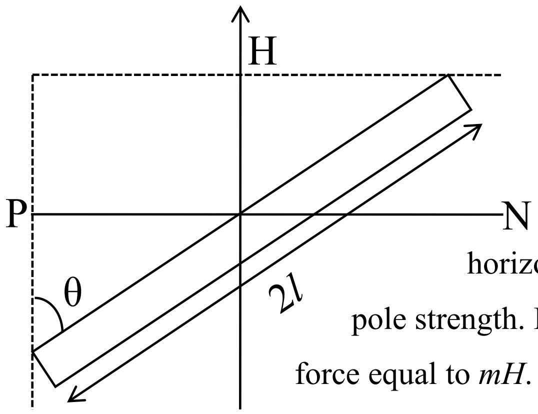
Where, *d* is the density of the material.

Likewise, molar susceptibility χ_m is the susceptibility per mole of the substance. Thus

$$\chi_m = \chi_g \times m$$

In subsequent discussion on magnetic susceptibility the symbols like χ_A, χ_B *and* χ for magnetic susceptibility of atoms, bonds and molecules per moles, respectively.

Magnetic moment (μ): The magnetic moment is the most convenient property for the discussion of mangetochemistry. If a magnet is suspended freely under the influence of earth magnetic field, the North Pole of magnet will point towards the north and South Pole of the magnet will point towards the south.



Suppose, *H* is the horizontal component of earth field and *m* is the pole strength. Each pole of the magnet will experience a force equal to *mH*. Since two poles are opposite in nature, they will form a couple such that moment of the couple can be given as

Moment of the couple = Force x distance

$$= mH \times PN$$

From figure; PN = $2l\sin\theta$

$$= mH \times 2l\sin\theta$$

$$= m \times 2l \times H\sin\theta$$

If H =1 oersted and θ = 90°,

Then, $H.\sin 90° = 1$

$$\text{Moment of the couple} = m \times 2l \times 1$$

$$\text{Moment of the couple} = m \times 2l$$

$$\text{Moment of the couple} = \mu$$

Where, m.2l gives the magnetic moment (μ) of the sample. Experimentally, it is the susceptibility of the sample that is determined. The susceptibility is then converted into magnetic moment with the help of Curie equation. The susceptibility is additive in property, while square of the moment is additive in nature.

Thus, magnetic moment may be defined as the moment of the couple when a magnet is suspended freely in a field of 1 oersted such that it makes an angle of 90° with the field direction. The unit of magnetic moment is Bohr magnetron (BM).

$$1\text{BM} = 5564\, gauss.cm.mole^{-1}$$

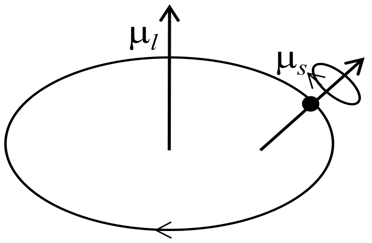
5.2 OBJECTIVES:

At the end of this unit learner would be able to

- Learn about the various terms used to explain the magnetic properties of transition metal complexes.
- Know how the magnetism originate in coordination compounds
- Know how the orbital magnetic moment ($_l$) and Spin magnetic moment ($_s$) originates in the coordination compounds
- Learn different kinds of magnetic behaviors of the transition metal ions.
- Know how to determine the magnetic susceptibility of substances by using different methods
- Know about the quenching and contribution of orbital magnetic moment
- Learn about the magnetic properties of coordination complexes on the basis of crystal field theory
- Learn to identify the transition metal ions having the magnetic moment higher than spin only magnetic moment $_s$.
- Know about the derivation of Van Vleck equation to evaluate the magnetic susceptibility of multi electron system
- Know about the spin cross over and anomalous magnetic moment
- Learn the various applications of magnetic moment data to study the compounds of 3d metal complexes.

5.3 ORIGIN OF MAGNETISM:

The origin of magnetism in an atom is due to the motion of its negatively charged electrons. Since an electron involves two types of motions one is orbital motion and other is the spin motion, thus both the motions of a moving electron generate corresponding magnetic moments. Therefore, the overall magnetic moment of an atom is the resultant of the magnetic moment generated by the orbital motion of electrons (*i.e.* orbital magnetic moment, μ_l) and the magnetic moment is generated by the spin motion of electron (*i.e.* spin magnetic moment, μ_s). The generation of orbital magnetic moment and spin magnetic moment is shown as



5.3.1 Orbital Magnetic Moment (μ_l):

Let us consider an electron of charge *e* and mass *m* is moving in a circular orbit. The motion of electron in a circular orbit is similar to the flow of electric current in a circular wire. The electron motion, therefore, generates a magnetic field in a direction perpendicular to the plane of orbit. If the angular velocity of ω (omega), then the number of revolutions made by the electron in one second are

$$number\ of\ revolutions\ per\ second = \frac{\omega}{2\pi} \ldots\ldots\ldots\ldots(1)$$

Therefore, current can be calculated as

$$i = \frac{charge\ \times number\ of\ revolutions\ per\ second}{velocity\ of\ light}$$

$$i = \frac{e\ \times \omega}{c\ \times 2\pi} \ldots\ldots\ldots\ldots(2)$$

The moment of the magnetic field so generated can be calculated by the product of electric current and the surface area of the orbit. Thus the orbital magnetic moment is given as

$$\mu_l = current\ \times surface\ area\ of\ the\ orbit$$

$$\mu_l = \frac{e\ \times \omega}{c\ \times 2\pi}\ \times \pi r^2 \ldots\ldots\ldots\ldots(3)$$

$$\mu_l = \frac{e\ \omega r^2}{2c}\ \ldots\ldots\ldots\ldots(4)$$

Where r is the radius of orbit, c is the velocity of light.

As it is known that an electron moving in an orbit generates orbital angular momentum (*l*) which is perpendicular to the plane of orbit and is given as

$$(l) = \sqrt{l(l+1)} \times \frac{h}{2\pi} \text{............}(5)$$

Where, h is plank's constant and *l* is the angular momentum quantum number. It must be noted that (*l*), the orbital angular momentum and *l*, the angular momentum quantum number are entirely different quantities.

Since, the orbital angular momentum of a particle having mass *m* moving with angular velocity ω (omega) in a circle of radius *r* can be calculated as

$$orbital\ angular\ momentum = m\omega r^2 \text{............}(6)$$

Hence, from equation 5 and 6 we have

$$(l) = m\omega r^2 = \sqrt{l(l+1)} \times \frac{h}{2\pi} \text{............}(7)$$

or

$$\omega r^2 = \sqrt{l(l+1)} \times \frac{h}{2\pi m} \text{............}(8)$$

From equation 4 and 8 we have

$$\mu_l = \frac{e}{2c}\sqrt{l(l+1)} \times \frac{h}{2\pi m} \text{............}(9)$$

Or

$$\mu_l = \sqrt{l(l+1)}\ \frac{eh}{4\pi mc} \text{............}(10)$$

$$\mu_l = \sqrt{l(l+1)}\ B.M. \text{............}(10)$$

Where, $\frac{eh}{4\pi mc}$ = 1 B.M.

Thus orbital magnetic moment μ_l is measured in units of Bohr Magnetron (BM). Thus for an electron moving in an orbit around the nucleus, μ_l in units of B.M. and (*l*) in units of $\frac{h}{2\pi}$ have the same magnitude, viz., $\sqrt{l(l+1)}$. Both μ_l and (*l*) are vector quantities. These are collinear but in opposite directions and are perpendicular to the plane of orbit.

5.3.2 Spin Magnetic Moment (μ_s):

In 1926, while explaining certain spectral phenomenon, Uhlenback and Goudsmit observed that a moving electron possesses angular momentum in excess of orbital magnetic momentum. They justify the excess angular momentum to the spinning of the electron around its own axis. The negatively charged electrons during their spin motion also produce magnetic field whose moment is directed along the spin axis. It was also observed that the ratio of spin magnetic moment μ_s to the spin angular momentum (s) is twice the ratio of μ_l to (l) in their respective units of B.M. and $\frac{h}{2\pi}$. Since the ratio of μ_l to (l) in their respective units is 1, the ratio of μ_s to (s) should be 2. The ratio of spin magnetic moment to spin angular momentum is called *Lande splitting factor*, *g*. Thus

$$\text{Spin magnetic momentum} = \text{Spin angular momentum} \times \frac{e}{mc} \text{........}(1)$$

$$\mu_s = \sqrt{s(s+1)}\,\frac{eh}{2\pi mc} \text{...........}(2)$$

$$\mu_s = 2\sqrt{s(s+1)}\,\frac{eh}{4\pi mc} \text{...........}(3)$$

$$\mu_s = 2\sqrt{s(s+1)}\,BM \text{...........}(4)$$

The spin angular momentum of the electron is equal to $\sqrt{s(s+1)}\,\frac{h}{2\pi}$, where s is the spin angular momentum quantum number. It must be noted again that *s* and (*s*) represent different quantities. The *s* represents the spin angular momentum quantum number and (*s*) represents the spin angular momentum.

The orbital equation and spin equation are often written as

$$\mu_l = \mathrm{g}\sqrt{l(l+1)}\,B.M \qquad (\mathrm{g} = 1)$$

and

$$\mu_s = \mathrm{g}\sqrt{s(s+1)}\,B.M \qquad (\mathrm{g} = 2)$$

g is called the gyromagnetic ratio i.e., the ratio of magnetic moment to corresponding angular momentum.

When an external magnetic field is applied, both μ_l and μ_s will interact with the applied magnetic field. They will tend to align themselves with the applied magnetic field, like a small bar magnet, and reinforce the applied magnetic field. In a multielectron atom the spin magnetic moments of individual electron will interact with one another to give resultant orbital spin magnetic moment. Thus for calculating the resultant spin magnetic moment (μ_S) we shall use the resultant angular moment quantum number *S*. Similarly, the resultant angular quantum number (*L*) is used for calculating resultant orbital magnetic moment, (μ_L).

The overall magnetic moment μ for a multielectron system will be a resultant of μ_S and μ_L provided (*L*) and (*S*) vectors do not couple or mix with each other. If (*L*) and (*S*) get coupled, then μ of the system will be calculated from the resultant angular momentum quantum number J.

$$\mu_{eff} = \sqrt{4s(s+1) + L(L+1)}\ B.M$$

5.4 TYPES OF MAGNETIC BEHAVIOURS:

The different kinds of magnetic behaviours observed in magnetic materials are as:

1. Diamagnetism
2. Paramagnetism
3. Ferromagnetism
4. Antiferromagnetism

(1) Diamagnetism: When a substance is placed in a magnetic field, if the substance is repelled away from the magnetic field, it is called the diamagnetic substances. Diamagnetism is produced due to the presence of paired electrons and also with the increase in atomic number, the diamagnetic behaviour increases. Examples of diamagnetic substances are Bi, Sb, Au, H_2O, quartz, Zn, Ag, N_2, H_2 etc. Diamagnetic substances show the following properties:

1. Diamagnetic substances are repelled by the magnetic field. It is presence of paired electrons as the magnetic field produced by one electron is opposed by neutralized by the magnetic field produced by the second electron because each of them has equal and opposite magnetic moment. Therefore diamagnetic substances have zero resultant magnetic moment; as a result they experience the repulsion in magnetic field.

2. Diamagnetic substances when placed in a magnetic field they align themselves at right angle to the applied magnetic field. However, in a non uniform magnetic field, they accumulate towards the lowest part of the applied magnetic field.

3. Diamagnetic substances have permeability less than one.

4. The value of magnetic susceptibility of diamagnetic substance is very small and negative (about -1×10^{-6}).

5. The diamagnetic susceptibility is independent of applied magnetic field and the temperature as well.

6. A diamagnetic liquid placed in a U-tube shows a depression in applied magnetic field.

7. The intensity of induced magnetization is less in diamagnetic substances than the applied magnetic field in vacuum.

The diamagnetic susceptibility is expressed as:

$$\chi_A = \frac{N_A\, e^2}{6mc^2} \sum_{i=1}^{i=n} \overline{r_1^2} \;.........(1)$$

Where χ_A = Atomic diamagnetic susceptibility

N_A = Avogadro number

e = charge of the electron

m = mass of the electron

$\overline{r_1^2}$ = mean square radius

$$\chi_A = -2.83 \times 10^{10} \sum_{i=1}^{i=n} \overline{r_1^2} \;.........(2)$$

(2) Paramagnetism: Paramagnetic substances are those which on placing in a magnetic field are attracted towards the magnetic field. Paramagnetism of a substance is produced due to the presence of unpaired electrons and with the increase in number of unpaired electrons the Paramagnetism also increases. Examples of paramagnetic substances are mainly the transition elements like Pt, Cr, Mn etc., and free radicals such as trimethylphenyl radical etc. The properties of paramagnetic substances are as:

1 Paramagnetic substances have small attraction towards the magnetic field as each unpaired electron produces magnetic moment and the magnetic field produced by these unpaired electrons are not mutually can celled. Therefore, these substances have some permanent and definite value of resultant magnetic moment (which is combination of spin and orbital magnetic moment). This resultant magnetic moment overcomes the small magnetic field induced by the applied magnetic field with the result that the paramagnetic substances feel attraction in an applied magnetic field.

2 The paramagnetic substances align themselves in the direction of applied magnetic field.

3 These substances allow more lines of magnetic force to pass through them; therefore, the permeability of paramagnetic substances is slightly more than one.

4 The magnetic susceptibility of paramagnetic substance is relatively high and positive is lies in between 1 to 100 x 10^{-6}.

5 Paramagnetic susceptibility is independent of the applied field however; it shows inverse relation with temperature.

6 A paramagnetic liquid placed in a U-tube shows a depression in applied magnetic field.

7 The intensity of magnetization is greater in paramagnetic substances than that produced in a vacuum by the same magnetic field.

The paramagnetic susceptibility can be expressed as:

$$\chi_M = \chi_P + \chi_{TIP} + \chi_{dia} \text{.........}(1)$$

Where χ_M = molar paramagnetic susceptibility

χ_P = normal paramagnetic susceptibility

χ_{TIP} = temperature independent magnetic susceptubility

χ_{dia} = diamagnetic susceptibility which is sum of $(\chi_{Atom} + \chi_{Bond})$

Since, the value of χ_{TIP} is generally not known hence the corrected molar magnetic susceptibility can be written as:

$$\chi_M^{CORR} = \chi_P + \chi_{dia} \text{.........}(2)$$

The normal paramagnetic susceptibility can be given as

$$\chi_P = \frac{N_A \, \mu^2}{3kT} \text{ ....}(3)$$

Where N_A = Avogadro number

μ = magnetic moment

k = Boltzmann constant (1.38 x 10^{-16} erg/deg)

T = absolute temperature

Thus equation (3) becomes (the corrected molar susceptibility is termed as effective magnetic moment)

$$\chi_M^{CORR} = \frac{N_A \, \mu_{eff}^2}{3kT} \text{ ....}(4)$$

$$\mu_{eff} = \sqrt{\frac{3kT\chi_M^{CORR}}{N_A}} \text{.........}(5)$$

$$\mu_{eff} = 2{,}84\sqrt{\chi_M^{CORR} \times T} \; B.M. \text{.........}(6)$$

(3) Ferromagnetism: Ferromagnetic substances are the magnetically concentrated substances in which the individual magnetic centers are close enough to initiate magnetic interaction between neighbouring magnetic centers. When paramagnetic centers are kept close enough strong magnetic interaction takes place between these neighbouring paramagnetic centres it result an enhancement in their magnetic moment. Such substances are called the *Ferromagnetic* substances and this property is called the *Ferromagnetism*.

Examples of these substances are Fe, Co, Ni, alloys of Fe, Co and Ni, magnetite (Fe_3O_4) etc. In these substances, infinite effective fields are formed which are known as domains. The neighbouring spins in these domains aligned parallel, and the number of atoms in each domain ranges from 10^{17} to 10^{21}. The Properties of Ferromagnetic substances are as follow:

1) These substances exhibit greater force of attraction in a magnetic field.
2) The permeability of ferromagnetic substances is of the order of 10^3.
3) The susceptibility of these substances is positive and its value is very high, *i.e.* about 1×10^2.
4) The Ferromagnetism is a magnetic field dependent property.
5) Ferromagnetic substances start losing their magnetic property on heating.
6) Because of random arrangement of domains, the effective magnetic moment of such substances is zero in absence of magnetic field. However, in presence of magnetic field, they align in parallel direction.
7) All the domains present in the ferromagnetic substances are aligner parallel to the applied magnetic field at certain field strength.
8) Above the optimum filed strength the susceptibility does not rise with the applied filed, thus the extent of parallel alignment of domains increases with the applied field strength.

If we neglect the contribution of orbital magnetic moment and assume that only the spin magnetic moment contributes towards μ_{eff} of a magnetically concentrated substance, then ΔE, the energy of spin interaction of paramagnetic ions in such a substance is given by

$$\Delta E = 2J(S)_i\,(S)_k$$

Where $(S)_i$ *and* $(S)_k$ are the total electron spin of *i*th and *k*th metal ion substance. *J* is known as the exchange coupling constant (it should not to be confused with spin-orbital coupling constant). *J* is a measure of the strength of interaction between the total electron spins of the metal ions. For ferromagnetic substances the *J* is positive and hence the total spins of all the paramagnetic ions in the magnetically concentrated substance in ground state get aligned parallel.

(4) Antiferromagnetism: The magnetically concentrated substances in which the secondary magnetic interaction between neighbouring paramagnetic centers takes place with the reduction in magnetic moment are known as antiferromagnetic substances. In antiferromagnetic substances, the neighbouring spins or domains are opposed to each other. In antiferromagnetic substances the induced magnetism increases with temperature up to a critical point *i.e.* antiferromagnetic Curie temperature. Beyond, this temperature the antiferromagnetic substances behave like normal paramagnetic substances. Above the antiferromagnetic Curie temperature the magnetic susceptibility of such substances decreases with increase in temperature, however, below antiferromagnetic Curie temperature the magnetic susceptibility of such substances decreases. The magnetic susceptibility of such substances may depend on magnetic field strength. Examples of such substances are titanium sesquioxide, MnO_2, FeO, copper acetate, oxovanadium (iv) etc.

The magnetic susceptibility of antiferromagnetic substances is positive but its numerical value is very small and it is of order of 0.1×10^{-6} cgs unit. Likewise ferromagnetic substances, the spin interaction energy can be given as

$$\Delta E = 2J(S)_i\,(S)_k$$

For antiferromagnetic substances the *J* value is negative, so the total electron spin tends toi get paired and magnetic susceptibility is very low.

5.5 DETERMINATION OF MAGNETIC SUSCEPTIBILITY:

There are several methods given for the determination of magnetic susceptibility of a substance. Two important methods anong them are discussed below.

1. The Guoy's Method: This is the simplest method for the determination of magnetic susceptibility of a substance (specially the transition metal complexes). It is proposed by a French physicist named Louis George Guoy in 1889. He obtained a mathematical relation revealing that the force is actually proportional to volume susceptibility (K) of the substance or that the material in a uniform external magnetic field. With his mathematical derivation Guoy suggested that the balance measurements taken for a tube containing material suspended in a magnetic field could evaluate the expression for volume susceptibility. The schematic diagram of Guoy's balance is shown figure below. According to principle of this method, on placing a compound in a magnetic field, its mass gets changed. The measurement of change in the weight of the compound under investigation in a magnetic field is the key observation of Guoy's method.

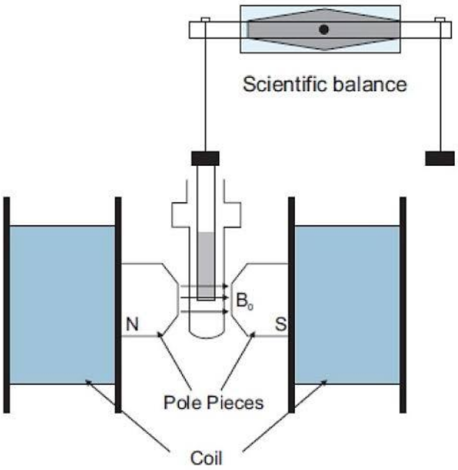


Figure 5.1 Schematic diagram for Guoy's Balance

In Guoy's balance, at one end of the microbalance a silver wire is joined through which tube of the sample is suspended. The sample tube is cylindrical glass tube with flat bottom. The sample is taken either as a uniformly packed solid or as a solution in a glass tube suspended from the balance. The sample tube is suspended from one arm of sensitive balance such that its lower end is in strong magnetic field while its upper end experiences almost zero magnetic field. The pole pieces of the magnet are usually cylindrical so that the magnetic field is symmetrical about the axis of the magnate. The magnetic field strength is strongest at the center where the bottom of sample column is placed. The magnetic field falls off rapidly in radial direction so that it is very small at the top of the sample column. Under these conditions, there is an apparent change in weight of the sample when the magnetic field is turned on. The change in weight of the substance is related to the magnetic susceptibility of the magnetic substance.

The magnitude of force acting on the compound can be measured which is related to the magnetic susceptibility. If the field gradient over the small volume of compound *dV* is *dH/dl,* and if the sample *dV* experience a force *dF* under the applied field, then the force *dF* is given as

$$dF = K.H.dV.\frac{dH}{dl} \text{............}(1)$$

Where H = magnetic field strength

K = volume susceptibility

dV = small volume of compound

dH/dl = magnetic field gradient

if the cross section area of sample is *A* and *dl* is the small height of sample compound, then

$$dV = A\,.\,dl \text{...........}(2)$$

$$dF = K.H.A\,.\,dl.\frac{dH}{dl}\text{...........}(3)$$

$$dF = K.H.A\,.\,dH\text{...........}(4)$$

Since, the compound moves in a non-homogeneous magnetic field (maximum at center and minimum at top of the sample column) the total force experienced by the compound when it moves from outside the magnetic field ($H = 0 = H_0$) to the center of the field (H) can be obtained by integrating the equation 4 between H and H_0.

$$\int dF = \int_{H_0}^{H} K.H.A\,.\,dH \text{ ....}(5)$$

$$F = K.A\,.\frac{1}{2}(H^2 - H_0^2)\text{...........}(6)$$

Since, volume susceptibility K can be defined as

$$K = \chi_g\,.\,\rho \text{ ....}(7)$$

Thus

$$F = \chi_g.\,\rho\,.\,A\,.\frac{1}{2}(H^2 - H_0^2)\text{...........}(8)$$

or

$$F = \chi_g.\,\frac{m}{V}\,.\,A\,.\frac{1}{2}(H^2 - H_0^2)\text{...........}(9)$$

$$F = \chi_g.\,\frac{m}{A\,.\,l}\,.\,A\,.\frac{1}{2}(H^2 - H_0^2)\text{...........}(10)$$

$$F = \chi_g.\,\frac{m}{l}\,.\frac{1}{2}(H^2 - H_0^2)\text{...........}(11)$$

Where m = mass of the sample; and l= length of the sample

When H_0 is negligible then equation (11) becomes

$$F = \chi_g.\,\frac{m}{2l}\,.\,H^2\text{...........}(12)$$

Applying the Buoyancy correction on equation (12) we have

$$F = (\chi_g - \chi_g^0)\frac{m}{2l}\,.\,H^2\text{...........}(13)$$

Where χ_g^0 = the magnetic susceptibility of air, which is a very small quantity.

The force F exerted by the magnetic field on the entire sample is equal to the difference in the weights of the sample when magnetic field is switched off and switched on. Let us say it is Δw. Thus equation (12) will become as

$$\Delta w = \chi_g.\,\frac{m}{2l}\,.\,H^2\text{...........}(14)$$

or

$$\chi_g = \Delta w . \frac{2l}{m \, . H^2} \text{ ....(15)}$$

The sample tube is first weighed without applied magnetic field and then with the applied magnetic field is on, thus the difference in the weights of the sample tube is calculated. The sample tube is then filed up to the mark with a standard compound (which may be paramagnetic and diamagnetic) whose susceptibility is known accurately. Then it is weighed without applied magnetic field and then with the applied magnetic field is on, thus the difference in the weights of the standard is calculated.

The sample tube is then cleaned and the weight of the empty tube is also taken without the same applied magnetic field and then with the same applied magnetic field is on, thus the difference in the weights of the standard is measured. The sample tube is filled up to the mark with a sample compound whose susceptibility is to be determined. Then it is weighed without applied magnetic field and then with the applied magnetic field is on, thus the difference in the weights of the standard is calculated. The magnetic susceptibility of given sample can be calculated by using given form of the Guoy's equation.

$$\chi_g = (\chi_g)_s \times \frac{w_s}{\Delta w_s} \times \frac{\Delta w_c}{w_c} \text{ ....(16)}$$

Where χ_g = susceptibility of the sample (unknown)

$(\chi_g)_s$ = susceptibility of the standard

w_s = weight of the standard compound

Δw_s = change in weight of the standard compound in magnetic field

w_c = weight of the sample compound

Δw_c = change in weight of the sample compound in magnetic field

Sources of error: Following are the basic reasons that might cause error in the measurement of susceptibility of a sample correctly.

1) Loose packing of the sample leads to error in the volume of the sample.
2) There may be balance error during the measurement of the change of the weight of sample, especially when the sample has low magnetic susceptibility value, where change in weight is very small.
3) Lateral oscillations of the sample may cause error in weighing. Therefore the apparatus must be kept in an oscillation free environment.

2. Quincke's Method: In 1885 Quincke developed this method for determine magnetic susceptibility of diamagnetic or paramagnetic substances in the form of a liquid or an aqueous solution. In this method, the applied force is determined by hydrostatic pressure. This method is based on the theory that 'when the external force is applied at the surface of fluid the surface gets changed and the change in the surface of liquid/fluid is directly proportional to the applied filed'. When a column of liquid magnetic sample is placed in a magnetic field *H*, it causes a change in the surface of the magnetic sample due to which the hydrostatic pressure is also changed. The change in hydrostatic pressure of liquid/fluid can be measured by the difference of fluid/liquid surface without and with the applied magnetic field is on.

In this method, a U-tube (glass) consisting of a capillary tube is taken. The upper end of capillary tube is placed in strong magnetic field. A scale used for the measurement of the difference in fluid surface height (Δh) with and without the magnetic field. The sample compound is filled in the sample tube and in the absence of magnetic field; the reading of fluid surface is measured. Now sample compound fluid surface is measured with and without magnetic field. The difference in sample compound fluid surface (Δh_c) with and without the magnetic field is then calculated. Now, similar procedure is repeated by standard compound and difference in standard fluid surface (Δh_s) is measured with and without the magnetic field.

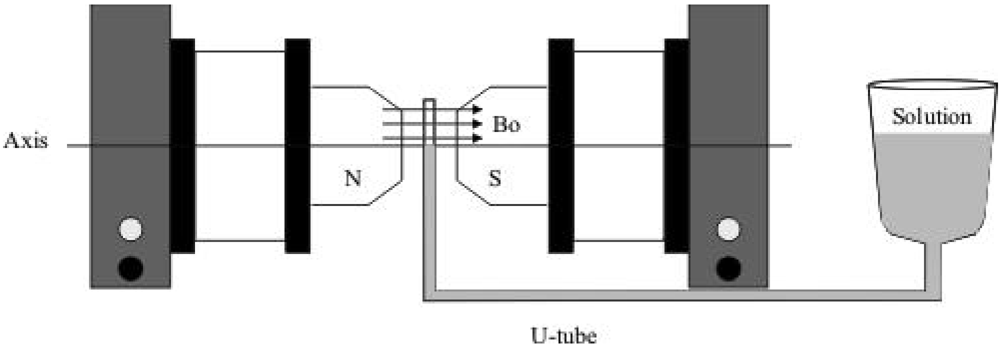


Figure 5.2 Quincke's apparatus

The hydrostatic pressure of liquid can be represented as

$$P = \rho . g . \Delta h \text{............}(1)$$

Where; ρ = density of liquid

g = gravitational force

Δh = change in height of liquid surface

Since force is directly related to hydrostatic pressure (P) and area of cross section (A) given as

$$F = P \, . A \text{...........(2)}$$

$$F = \rho . g . \Delta h \, . A \text{ ....(3)}$$

Since

$$F = \frac{1}{2} . K \, . A \, . H^2 \text{ ....(4)}$$

or

$$\rho . g . \Delta h \, . A = \frac{1}{2} . K \, . A \, . H^2 \text{ ....(5)}$$

$$K = \frac{2\rho . g . \Delta h}{H^2} \text{ ....(6)}$$

Since $K = \chi_g \, . \rho$ or $\chi_g = \frac{K}{\rho}$ thus equation (6) can be written as

$$\frac{K}{\rho} = \frac{2 . g . \Delta h}{H^2} \text{ ....(7)}$$

or

$$\chi_g = \frac{2 . g . \Delta h}{H^2} \text{ ....(8)}$$

This method can be made simpler, by taking a standard compound. If the magnetic field strength is not known then the change in the heights (Δh) is determined for the standard and the sample compound. The magnetic susceptibility $(\chi_g)_s$ is known accurately for standard and magnetic susceptibility $(\chi_g)_s$ of sample compound can be calculated as

$$\frac{(\chi_g)_s}{\chi_g} = \frac{\Delta h_c}{\Delta h_s} \text{ ....(9)}$$

Where: χ_g = susceptibility of the sample (unknown)

$(\chi_g)_s$ = susceptibility of the standard

Δh_c = change in height of the sample compound in magnetic field

Δh_s = change in weight of the standard compound in magnetic field

5.6 THE QUENCHING OF ORBITAL MAGNETIC MOMENT:

The explanation offered by Valence Bond theory for the magnetic moment of transition metal complexes is purely qualitative.

There are different mathematical expressions derived for the calculation of μ_{eff} of substance depending upon the particular situations. These expressions are given as

$$\mu_{eff} = \sqrt{4s(s+1) + L(L+1)}\; B.M \ldots\ldots\ldots (a)$$

When the *J* energy levels of the ground state are very close to one another, so that all of those *J* values are almost equally populated at room temperature;

$$\mu_{eff} = \mathrm{g}\sqrt{J(J+1)}\; B.M \ldots\ldots\ldots (b)$$

When the *J* energy levels of the ground state are well separated from one another so that the energy gaps between adjacent *J* levels of the ground state >*kT*;

and

$$\mu_{eff} = \sqrt{4s(s+1)}\; B.M \ldots\ldots\ldots (c)$$

When, the orbital angular momentum is almost completely quenched so that its contribution to μ_{eff} is practically zero.

When the μ_{eff} values were calculated for transition metal ion complexes of 3d transition series using these expressions are given in Table 2.1. The experimental values are also given for the sake of comparison.

Table 5.1: μ_{eff} values calculated for high spin octahedral complexes using different expression and determined experimentally

Ions	**μ_{eff} calculated using**			**μ_{eff} experi-mentally**
	$\mu_{eff} = \sqrt{4s(s+1) + L(L+1)}$	$\mu_{eff} = \mathrm{g}\sqrt{J(J+1)}$	$\mu_{eff} = \sqrt{4s(s+1)}$	
Ti^{+3} (d^1)	3.00	1.55	1.73	1.7-1.8
Ti^{+2}, V^{+3} (d^2)	4.47	1.65	2.85	2.7-2.9
V^{+2}, Cr^{+3} (d^3)	5.20	0.70	3.87	3.7-3.9
Cr^{+2}. Mn^{+3} (d^4)	5.48	0	4.90	4.8-4.9
Mn^{+2}, Fe^{+3} (d^5)	5.92	5.92	5.93	5.7-6.0
Fe^{+2}, Co^{+3} (d^6)	5.48	6.71	4.90	5.0-5.6
Co^{+2} (d^7)	5.20	6.63	3.87	4.3-5.2
Ni^{+2} (d^8)	4.47	5.59	2.87	2.9-3.5
Cu^{+2} (d^9)	3.00	3.55	1.73	1.8-2.1

It can be seen from above table that the values of μ_{eff} calculated by using all three expression differ considerably from the values determined experimentally. The values closest to the experimental values are those calculated by suing the relation $\mu_{eff} = \sqrt{4s(s+1)}\ B.M$ involving only the spin of the electrons. This indicates that the orbital angular momentum makes negligible contribution to μ_{eff} in the case of the complexes of 3d transition series. The valence bond theory could not explain the precise mechanism for the quenching of orbital angular momentum. VBT only suggested that the orbital angular momentum of electrons in the complexed metal ion may be partly or completely destroyed or quenched due to the surrounding of the metal ion by the ligands. The orbital motion of the *d* electrons of the metal ion will be severely disturbed by the electrons of the ligands. This could not provide any quantitative idea like the extent of quenching of orbital angular momentum etc.

This theory also fails to explain why in some cases the observed magnetic moment μ_{eff} values are higher and in other cases lower than the spin only magnetic moment ($\mu_{s.o}$). Similarly, the valence bond theory also could not explain satisfactorily why μ_{eff} values of tetrahedral complexes of metal ion are different from the μ_{eff} of octahedral complexes of the same metal ion containing the same number of unpaired electrons. For example, the μ_{eff} values for tetrahedral complexes of Co(II) containing tree unpaired electrons range between 4.4-4.8BM, whereas, for octahedral outer orbital complexes of Co(II) also containing three unpaired electrons range from 4.8-5.2 BM. Similarly, the μ_{eff} for tetrahedral complexes of Ni(II) containing two unpaired electrons rages between 3.2-4.0 BM, whereas, μ_{eff}_for octahedral complexes of Ni(II), also containing two unpaired electrons, ranges between 2.9-3.3 BM. Valence bond theory also states that the formation of inner orbital complexes of metal ions with d^7, d^8 and d^9 configurations requires promotion of electrons to higher orbital which is sometimes energetically unfavourable.

These dissimilarities in μ_{eff} values are explained with more justified manner by Crystal field theory. According to the crystal field theory, in the presence of ligands, the degeneracy of *d*-orbitals of metal ion is removed, due to which the motion of orbital is very much hindered so that the quenching of orbital magnetic moment takes place. For the ions such as Mn^{+2}, Fe^{+3} etc., the value of $L = 0$ indicating that there is no contribution of orbital magnetic moment to the μ_{eff} value. Thus the μ_{eff} of such complexes may be calculated as:

$$\mu_{eff} = \sqrt{4s(s+1)}\ B.M$$

$$\mu_{eff} = \sqrt{n(n+2)}\ B.M$$

Where n = number of unpaired electrons.

5.7 THE CONTRIBUTION OF ORBITAL MAGNETIC MOMENT:

Since in heavier elements the *j*– *j* coupling becomes important therefore the spin orbit coupling constant for those elements is very high; hence, the spin only formula of magnetic moment is not good for the calculation of μ_{eff} values of second and third transition series elements. Therefore, determination of the contribution of orbital magnetic moment becomes important to study the μ_{eff} of a transition metal complex. In order to this, these 3*d* electrons must fulfil the given conditions.

- The orbitals should be degenerated.
- The orbitals should be of similar shape and size. These orbitals should be transformable by rotation about some axis. In a free atom or ion, the d_{xy} and $d_{x^2-y^2}$ orbitals are related by rotation through 45° and d_{xz} and d_{yz} orbitals by 90° about the *z*-axis. Thus an electron in any of these orbitals has angular orbital momentum. A d_{z^2} electron has no angular momentum about *z*-axis.
- The orbital must not contain electrons of same spin.

The crystal field theory suggested that in the presence of ligands, splitting of degenerate d-orbitals takes place. For example, in octahedral and tetrahedral complexes, the five d-orbitals split into two set of orbitals of different energies. Thus the moment of orbitals is restricted due to the energy gap between two energy sets of orbitals. Although the d_{z^2} and $d_{x^2-y^2}$ orbitals are degenerate orbitals in octahedral ligand field but their shapes cannot be transformable into one another by rotation. Thus as per the second condition mentioned above, the e_g set in octahedral (or tetrahedral) geometry cannot produce any orbital moment. Hence these orbitals are known as non-magnetic doublet (non-magnetic in the sense of orbital moment only). However, d_{xy}, d_{xz} and d_{yz} orbitals in t_{2g} set fulfil the first two conditions discussed above. For example, the d_{xz} and d_{yz} orbitals can be transformed by into one another by rotation of 90° about the *z*-axis. Thus it is the condition third, that will decide the orbital contribution of t_{2g} set. The d^1 and d^2 complexes in octahedral geometry fulfil the all three conditions mentioned above; whereas, d^3 complexes in octahedral geometry do not fulfil the third condition. Thus d^1 and d^2 will have the orbital moment contribution in resultant μ_{eff} value of complexes, whereas the d^3 will not have any orbital moment contribution in resultant μ_{eff} value. The d_{xy} and $d_{x^2-y^2}$ orbitals are now separated by Δ (the CFSE) and a d_{z^2} electron has no orbital angular momentum and the orbital contribution of d_{xy} and $d_{x^2-y^2}$ orbitals contribution is now completely quenched or suppressed by the ligand field.

Thus μ_{eff} for metal ions with the following configurations in their octahedral complexes will have no contribution from orbital magnetic moment:

Spin free or High spin

t_{2g}^3 (ground state $^4A_{2g}$), $t_{2g}^3e_g^1$ (ground state ^5E_g), $t_{2g}^3e_g^2$ (ground state $^6A_{1g}$),

$t_{2g}^6e_g^2$ (ground state $^3A_{2g}$), $t_{2g}^6e_g^3$ (ground state ^2E_g)

Spin paired or Low spin

t_{2g}^6 (ground state $^1A_{1g}$), $t_{2g}^6e_g^1$ (ground state ^2E_g)

However, μ_{eff} for metal ions with the following configurations in their octahedral complexes will have non-zero contribution from orbital angular moment:

t_{2g}^1 (ground state $^2T_{2g}$), t_{2g}^2 (ground state $^3T_{1g}$) (low spin),

t_{2g}^4 (ground state $^4T_{1g}$). t_{2g}^5 (ground state $^2T_{2g}$)

This is because of the fact that all these configurations have electronic arrangements which contain electron in d_{xz} and/or d_{yz} orbital and which generate non-uniform distribution of electronic charge around the nucleus. Thus from above discussion it is clear that all configuration of metal ions in octahedral complexes, which have no orbital angular momentum along the direction of the applied field and hence have no orbital magnetic moment contribution to μ_{eff} value, have either A or E ground state. Similarly, all configurations which have some orbital angular momentum retained, and hence make some orbital magnetic moment contribution to overall μ_{eff} value, have T ground state.

Similar conclusion can be drawn for metal ions in tetrahedral ligand environment. For example, μ_{eff} value from metal ions having configurations e_g^1, $e_g^3t_{2g}^3$ (ground state E) and e_g^2, $e_g^4t_{2g}^3$ (ground state A_2) in their tetrahedral complexes have no contribution from orbital angular momentum and fro metal ions having configurations $e_g^4t_{2g}^2$, $e_g^4t_{2g}^5$ (ground state T_2) and $e_g^2t_{2g}^1$, $e_g^4t_{2g}^4$ (ground state T_1) will have non-zero contribution from orbital angular momentum.

From above discussion it can be generalize that the orbital angular momentum is completely quenched when the metal ion in complexes has A or E as the ground state and is partially quenched when the metal ion in its complexes has T as the ground state.

Although, in most of the ions with A or E ground state, the experimentally observed μ_{eff} value is very close to μ_{so} value and is temperature independent, yet some ions show a slight variation from it. This variation is because the low lying excited T state of the same spin multiplicity as the ground state mixes up due to spin orbit coupling with A or E ground state, as a result of which the excited T state will have some character of A or E ground state and A or E ground state will have some character of excited T state. Due to which the μ_{eff} value is different from μ_{so} value. The contribution of orbital angular momentum to overall μ_{eff} value in such cases depends upon the extent of mixing of ground state and the excited state and is therefore inversely proportional to Δ (the crystal field energy difference between excited state and ground state). Thus the following equation has been suggested for μ_{eff} value.

$$\mu_{eff} = \mu_{so}\left(1 - \frac{\alpha\lambda}{\Delta}\right) \ldots\ldots\ldots.(A)$$

Where α is a constant and it depends upon the spectroscopic ground state term and number of *d*-electrons; λ is the spin orbit coupling parameter which is positive for d^n configuration with n < 5 and negative for d^n configuration with n > 5. The equation (A) represents the correlation in μ_{eff} and μ_{so}.

For E ground state α = 2; the above equation (A) become as

$$\mu_{eff} = \mu_{so}\left(1 - \frac{2\lambda}{10\mathrm{D_q}}\right) \ldots\ldots\ldots.(B)$$

For A ground state α = 4; the above equation (A) become as

$$\mu_{eff} = \mu_{so}\left(1 - \frac{4\lambda}{10\mathrm{D_q}}\right) \ldots\ldots\ldots.(C)$$

Above equation (A) connects the magnetic moment value and crystal field splitting energy of a complex quantitatively. From these equations it is evident that greater the value of CFSE, smaller is the mixing effect and hence less is the orbital contribution. The strong donor ligands have high CFSE value hence they will reduce the orbital contribution.

5.8 THE VAN VLECK EQUATION:

In Van Vleck equation, the change in energies of molecules is considered when external magnetic field is applied. When magnetic field is applied, the magnetic dipoles present in the paramagnetic substances align themselves along the direction of applied magnetic field.

A multielectron system possesses several *J* levels. The *J* levels of a particular term form a multiplet and a particular *J* level of the multiplet is called component of that multiplet. In an applied magnetic field *H*, the *J* levels split in to (2*J*+1) levels. This splitting is known as first order Zeeman effect. Second order Zeeman effect arises due to the mixing of the wave functions of a particular level with those of its neighbouring level and thus some characters of the excited state are introduced into the ground state. In Van Vleck equation both these effects are included.

5.8.1 Derivation of van vleck equation:

In the derivation of Van Vleck equation two assumptions are made

1. The susceptibility does not depend on applied magnetic field.
2. The energy of the n^{th} level of atom or ion can be given as

$$W_n = W_n^0 + W_n^1(H) + W_n^2(H) + \ldots\ldots\ldots.$$

Where W_n^0 = Energy of the nth level in absence of applied field (*H*)

W_n^1 = First order Zeeman effect

W_n^2= Second order Zeeman Effect

On applying external magnetic field the energy of the magnetic dipole will be $-\mu H$ given by the product of projection of the magnetic moments in the direction of field and field strength. On differentiating $-\mu H$ we have

$$\frac{\partial \omega}{\partial H} = -\bar{\mu} \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where $\bar{\mu}$ = projection of μ along *H*

Considering the n^{th} level, we have

$$\bar{\mu}_n = W_n^1 - 2W_n^2(H) \ldots\ldots\ldots\ldots\ldots (2)$$

Assuming that there are several states like n, each state is having its characteristics $\bar{\mu}$ value. An average value $\bar{\mu}$ can be taken, thus

Susceptibility

$$\chi_M = \frac{N.\bar{\mu}}{H} \ldots\ldots\ldots\ldots (3)$$

and

$$\bar{\mu} = \frac{\sum n_n . \bar{\mu}_n}{N} \ldots\ldots\ldots\ldots (4)$$

Populations of these levels are given by Boltzmann's law

$$n_n = n_0\, e^{\left(\frac{-W_n}{kT}\right)} \text{...........}(5)$$

Where n_n = number of molecules in the n^{th} level

n_0 = number of molecules in the ground level

Since

$$e^{\left(\frac{-W_n}{kT}\right)} = e^{\left(\frac{-W_n^0 - W_n^{(1)}(H) - W_n^{(2)}(H)^2}{kT}\right)} \text{............}\ (6)$$

$$= e^{\left(\frac{-W_n^0}{kT}\right)} e^{\left(\frac{W_n^{(1)}(H) - W_n^{(2)}(H)^2}{kT}\right)} \text{..............}(7)$$

The energy difference between the successive levels is gβ*JH*. The product gβ*H* is only ~1 cm-^{1} at *H* = 10000 gauss so that gβ*H* is quite small compared to *kT* ~200cm^{-1} at 25°C. Thus the second order Zeeman susceptibility will be further less.

When the value of *x* is small, $e^x = (1-x)$

Thus

$$e^{\left(\frac{-W_n}{kT}\right)} = e^{\left(\frac{-W_n^0}{kT}\right)} \left[1 - H.\frac{W_n^{(1)}}{kT}\right]\left(\frac{1 - H^2 W_n^{(2)}}{kT}\right) \text{..............}(8)$$

Since, susceptibility is independent of applied field, thus

$$\bar{\mu} = \frac{n_0 .\ \sum_n \mu_n e^{\left(\frac{-W_n}{kT}\right)}}{n_0 .\ \sum_n e^{\left(\frac{-W_n}{kT}\right)}} \text{...........}(9)$$

Substituting the value of $e^{\left(\frac{-W_n}{kT}\right)}$ from equation (8) to equation (9) and solving the resultant equation we will have

$$\mu_n = \frac{H \sum_n \left(\frac{W_n^{(1)2}}{kT} - 2W_n^{(2)}\right) e^{\left(\frac{-W_n^0}{kT}\right)}}{e^{\left(\frac{-W_n^0}{kT}\right)}} \text{..............}(10)$$

Substituting the value of equation (10) in to equation (3) the susceptibility χ_M will be as

$$\chi_M = \frac{N \sum_n \left(\frac{W_n^{(1)2}}{kT} - 2W_n^{(2)}\right) e^{\left(\frac{-W_n^0}{kT}\right)}}{e^{\left(\frac{-W_n^0}{kT}\right)}} \text{..............}(11)$$

Equation (11) is known as the Van Vleck equation.

Case I: When *L* and *S* vectors interacts strongly, then it may consider that the second order Zeeman effect $W_n^{(2)}$ equal to zero, also in absence of external applied field the nth level $W_n^{(0)}$ can be taken as zero.

Thus

$e^{\left(\frac{-W_n^0}{kT}\right)} = 1$, each *J* level has (2*J*+1) of M_J levels.

Applying above conditions the equation (11) become as

$$\chi_M = \frac{N\sum_n \left(\frac{W_n^{(1)2}}{kT}\right) e^{\left(\frac{-W_n^0}{kT}\right)}}{\sum_n e^{\left(\frac{-W_n^0}{kT}\right)}} \ldots\ldots\ldots\ldots\ldots(12)$$

or

$$\chi_M = \frac{N\sum_{M_J=-J}^{J} \frac{M_J^2 g_J \beta^2}{kT}}{(2J+1)} \ldots\ldots\ldots\ldots\ldots(13)$$

or

$$\chi_M = \frac{N\frac{g_J\beta^2}{kT}}{(2J+1)} \sum_{M_J=-J}^{J} M_J^2 \ldots\ldots\ldots\ldots\ldots(14)$$

Solving equation (14) we have

$$\chi_M = \frac{N\beta^2}{3kT}\, g_J\, J(J+1) \ldots\ldots\ldots\ldots\ldots(15)$$

Equation (15) is a correlation between Van Vleck equation and large band width.

Case II: Taking the second order Zeeman effect $W_n^{(2)}$ equal to zero, the Van Vleck equation (11) can be represented as equation (12)

$$\chi_M = \frac{N\sum_n \left(\frac{W_n^{(1)2}}{kT}\right) e^{\left(\frac{-W_n^0}{kT}\right)}}{\sum_n e^{\left(\frac{-W_n^0}{kT}\right)}} \ldots\ldots\ldots\ldots\ldots(12)$$

Above equation can be broken in to two position to show the first and second order Zeeman effects.

First order Zeeman effect

$$\chi_M = \frac{N\sum_n\left(\frac{W_n^{(1)2}}{kT}\right)}{(2J+1)} \ldots\ldots\ldots\ldots\ldots(13)$$

The second order Zeeman effect

$$\chi_M = \frac{-2N\sum_n\left(W_n^{(2)}\right)e^{\left(\frac{-W_n^0}{kT}\right)}}{e^{\left(\frac{-W_n^0}{kT}\right)}} \ldots\ldots\ldots\ldots\ldots(14)$$

Since $W_n^0 = 0$, then

$$\chi_M = \frac{-2N\sum_n\left(W_n^{(2)}\right)}{(2J+1)} \ldots\ldots\ldots\ldots\ldots(15)$$

Since

$$\chi_M = N\alpha = \frac{-2N\sum_n\left(W_n^{(2)}\right)}{(2J+1)} \ldots\ldots\ldots\ldots\ldots(16)$$

$$\alpha = \frac{-2\sum_n\left(W_n^{(2)}\right)}{(2J+1)} \ldots\ldots\ldots\ldots\ldots(17)$$

Equations (13) and (17) are the correlation in Van Vleck equation and small multiplet band width. The first order Zeeman susceptibility equation (13) contain the term *kT*, shows its temperature dependence. The first order Zeeman susceptibility is inversely proportional to the temperature T. Whereas, the second order Zeeman susceptibility does not carry the term *kT* and thus it is independent of temperature. Thus it is also called temperature independent Paramagnetism (Van Vleck Paramagnetism of residual Paramagnetism).

5.9 SPIN CROSS OVER:

In octahedral geometry for d^4, d^5, d^6 and d^7configurations, the high spin complexes and low spin complexes have the same energy when CFSE (Δ) = Pairing energy (P). If we have a coordination complex where the CFSE is critically close to the P value, then the energy difference between the high spin and low spin states of the complex will be in the range of thermal energy, *kT*. In such complexes, equilibrium between the two spin states will give anomalous magnetic moment value. Change in the temperature will lead to a change in the population of two spin states. If the ground state of the complex is low spin, with the rise in the temperature the energy of the system will increase, which will favour the $low\ spin\ \rightleftharpoons high\ spin$ change. For a given metal ion in a given oxidation state that value of $\Delta = P$ is known as the critical 10*Dq* or cross over region. When Δ exceeds P, the low spin form becomes the ground state, while when Δ is less than P, the high spin state is the low energy state. For a given metal ion in a given valance state, P is a constant quantity while Δ varies from complex to complex. Since, the pairing energy (P) changes somewhat irregularly among the elements of first transition series. However, with increase in the principal quantum number the pairing energy decreases for the elements of second and third transition series. Since the value of P are substantially decreases and the Δ are substantially increases from the first transition series to the second and third transition series, because the spin pairing is favoured in the second and third transition series.

The cross over region is very sensitive to several factors. The following are the factors on which the cross over situation depends.

1. **Inter electronic repulsion:** Decrease in inter-electronic repulsion results the decrease in pairing energy (P), It will lead to the cross over region is found at a lower Δ value.
2. **Effect of substitution on ligands:** The substitution on ligand structure is responsible for the change in the Δ value.
3. **Effect of Pressure:** The low-spin form of a complex has a shorter metal-ligand bond length than its high spin form. As a result, increase in pressure is likely to shift the high spin – low spin equilibrium in favour of lower molecular volume *i.e.* towards the low spin form.

5.10 ANOMALOUS MAGNETIC MOMENT:

Anomalous magnetic moment may arise in magnetically concentrated systems. In magnetically concentrated systems magnetic exchange coupling takes place between neighbouring paramagnetic metal ion center. The magnetic exchange coupling between neighbouring paramagnetic metal ions affects the magnetic properties of the complexes and sometimes overlooks the ligand field effects. When the paramagnetic centers are close enough for direct or indirect orbital overlap, the exchange interaction occurs between the spin of the neighbouring paramagnetic ions. Almost all paramagnetic ions are involved in exchange coupling to a certain extent and the interaction is dominant only at very low temperatures. If the exchange interaction is greater than the thermal energy, *kT*, cooperative phenomenon of ferromagnetism or anti ferromagnetism is obtained. These couplings may lead to either elevation or lowering of magnetic moment compare to that of expected on monomer or no coupling basis. Enhancement in magnetic moment is the characteristic of ferromagnetic substances and the lowering in magnetic moment is the characteristics of antiferromagnetic substances.

5.11 APPLICATIONS OF MAGNETIC MOMENT DATA FOR 3d METAL COMPLEXES:

The applicability of magnetic moment data to the study of compounds, reactions find its uses in all branches of chemistry (inorganic, organic, physical and biochemistry). For the first transition series metal ions the equation

$$\mu_{eff} = \sqrt{4s(s+1) + L(L+1)} \text{ B.M.}$$

is generally used to calculate the value of μ_{eff} as the coupling of *L* and *S* vector is weak and thus these vectors can maintains their individuality. For the metal ions such as Mn^{+2} and Fe^{+3}, $L = 0$ that means there is no contribution of orbital magnetic moment to μ_{eff}. For those ions, for which $L = 0$, the magnetic moment can be calculated as

$$\mu_{eff} = \sqrt{4s(s+1)} \text{ B.M.}$$

or

$$\mu_{eff} = \sqrt{n(n+2)} \text{ B.M.}$$

In these cases the μ_{eff} contains only the contribution made by spin magnetic moment resulting from the spin motion of the electrons and is called spin only magnetic moment and thus can be given by

$$\mu_{so} = \sqrt{4s(s+1)} \text{ B.M.}$$

or

$$\mu_{so} = \sqrt{n(n+2)} \text{ B.M.}$$

In the first transition series, magnetic properties originate from the 3*d*-orbitals. These 3*d*-orbitals are generally disturbed by the ligands and the solvents molecules and thus the orbital magnetic moments are significantly suppressed or quenched and the spin moments accounts for their magnetic behaviour.

Similar to ions with $L = 0$ such as Mn^{+2} and Fe^{+3}, the spin only formula is useful for other ions for calculating their magnetic moments. The values of magnetic moments for the ions containing unpaired electrons n = 1,2,3,4 and 5 are; 1.73, 2.83, 3.87, 4.90 and 5.92 B.M., respectively. However, cobalt (II) and nickel (II) often given magnetic moments considerably higher than those expected from the above equation for μ_{so} (Table 2,1 summarises the magnetic moment values calculated from different equations). This variation is due to the spin orbit coupling as there is some mixing of ground state with excited state. Spin-orbit coupling generally resists the quenching of orbital momentum by coupling it with the spin angular momentum which is not directly influenced by the ligand field. Thus the mixing of higher energy states has the effect of modifying μ_{so} , the value calculated on spin only formula according to the equation given

$$\mu_{eff} = \mu_{so}\left(1 - \frac{\alpha\lambda}{\Delta}\right)$$

Where α is a constant and it depends upon the spectroscopic ground state term and number of *d*-electrons; λ is the spin orbit coupling parameter, Δ separation between the ground state energy level and the excited state.

From the knowledge of magnetic moment values, it is possible to derive some information which is given below:

1. The valence state of metal:

Table 2.2 summarizes the values of μ_{so} and μ_{eff} of first transition series metals in low spin octahedral complexes. The valence state of the metal in complexes can be found out as shown by the following examples:

(i) If the magnetic moment value of an octahedral complex of cobalt is 1.73BM as for $Hg_2[Co(CNS)_6]$. The ligand (CNS) is a strong field ligand it result the spin paired complex (inner orbital octahedral complex) thus it would be concluded that in the given complex the cobalt has two unpaired electrons it would only possible when the cobalt is in the bivalent state Co^{+2} (d^7).

(ii) If an octahedral complex of iron is found to possess a magnetic moment value of 2.2 B.M. as in $[Fe(diph)_3(ClO_4)_3]$, The ligands are strong field ligand it result the spin paired complex (inner orbital octahedral complex) thus it would suggest that there are 3 unpaired electrons present in central metal ion of complex thus it may be concluded that the iron is in the trivalent state, Fe^{+3} (d^5) in given complex.

(iii) Similarly, in the complex $K_3[Cr(CNS)_6]$ the magnetic value of 3.72 BM suggest that the metal ion in complex has 3 unpaired electrons hence it would be in trivalent state Cr^{+3} (d^3) in given complex.

Table 2.2: values of μ_{so} and μ_{eff} of first transition series metals in low spin octahedral complexes

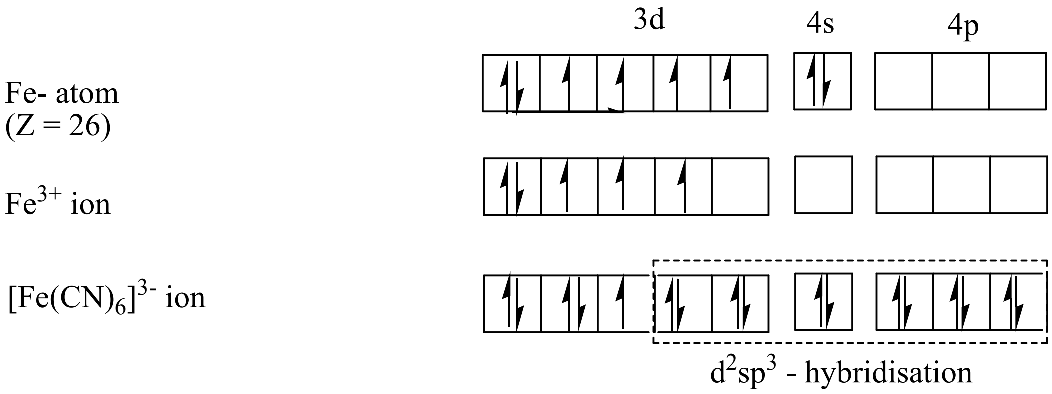
Ions	**n_1 (unpaired electrons in ground state)**	**n_2 (unpaired electrons in the influence if ligand)**	**μ_{so}**	**μ_{eff} experi-mentally**
V^{+2}, Cr^{+3} (d^3)	3	3	4.1	3.70 – 3.90
Cr^{+2}. Mn^{+3} (d^4)	4	2	2.93	2.73 – 2.85
Mn^{+2}, Fe^{+3} (d^5)	5	1	2.2	1.73 – 1.85
Fe^{+2}, Co^{+3} (d^6)	4	0	0	0
Co^{+2} (d^7)	3	1	4.5	1.73 – 1.85

(iv) The magnetic moment value of the ion $[Fe(CN)_6]^{-3}$ is 1.8 BM The ligand (CN^-) is a strong field ligand it result the spin paired complex (inner orbital octahedral complex) thus indicating the presence of one unpaired electron hence the iron would be in the trivalent state, Fe^{+3} (d^5) in given complex.

(v) The magnetic moment value of $[Fe(F)_6]^{-3}$ is 5.9 B.M., where the ligand (F^-) is a weak field ligand it result the spin free complex (outer orbital octahedral complex) thus indicating the metal ion present in complex have 5 unpaired electrons, it may be concluded that the iron is in the trivalent state, Fe^{+3} (d^5) in given complex.

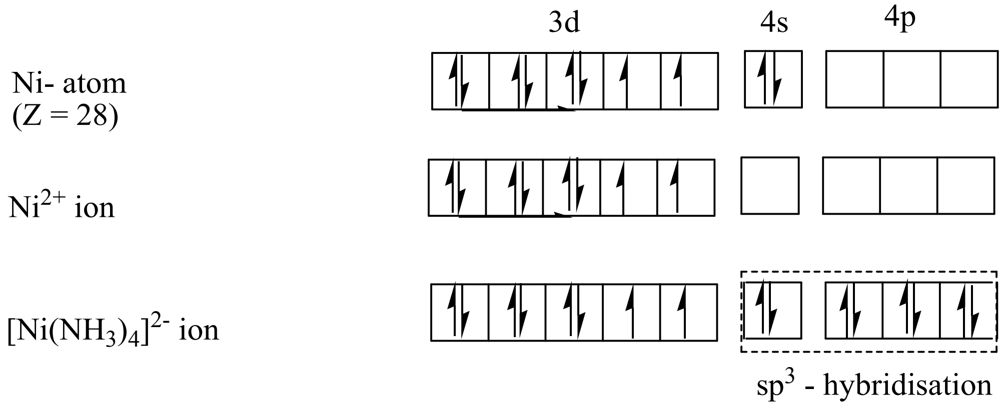
2. Nature of Bonding in complexes: It has been observed that for low spin octahedral complexes the value of experimental magnetic moment μ_{eff} is less than that of μ_{so} value calculated from the spin only formula for the free metal ion. This fact can be used to know whether the given complex is a high spin or a low spin octahedral complex. Thus when the μ_{eff} is less than that of μ_{so} value then the complex is low spin complex otherwise it would a high spin complex. Table 2.2 comprises the above facts quantitatively.

3. Geometry of the complexes: If the magnetic moment value of a complex is known, it is possible to predict the geometry of the complex. Consider an example of complex potassium ferricyanide, the magnetic moment value of the complex is observed as 1.8 B.M. indicates that the metal ion (iron) has one unpaired electron. The iron is in trivalent state *i.e.* Fe^{+3} (d^5) in given complex. Since, six CN^- ligands donate 12 electrons (6 pairs) to coordinate with Fe^{+3} metal ion. These 12 electrons need 6 vacant orbitals to distribute themselves to form 6 covalent bonds. These 6 orbitals either may be from 4s, 4p and 4d or from 3d, 4s and 4p orbitals. If the 6 CN^- ligands form covalent bond with Fe^{+3} ion using 4s, 4p and 4d orbitals then there must be 5 unpaired electrons, which result the magnetic moment value about 5.92 B.M. The experimental value of magnetic moment was observed 1.8 BM, which indicates that the 6 CN^- ligands form covalent bond with Fe^{+3} ion using 3d, 4s and 4p orbitals. The CN^- ligand is a strong field ligand which causes the spin pairing of the d^5 electrons as $t_{2g}^5 e_g^0$. Hence the complex formation takes place via inner orbital thus known as inner orbital octahedral complex with d^2sp^3 hybridization.



Formation of $[Fe(CN)_6]^{3-}$ ion by d^2sp^3 - hybridisation

Similarly, in tetraammine nickel sulphate $[Ni(NH_3)_4]SO_4$, the magnetic moment was observed 2.8 BM experimentally. This indicates that the complex has two unpaired electrons in metal ion, and the Ni is in +2 oxidation state.



Formation of $[Ni(NH_3)_4]^{2-}$ complex by sp^3- hybridisation

The four NH_3 ligands may acquire 4s and 4p orbitals to form 4 covalent bonds with four NH_3 ligands; on the other hand these may acquire 3d, 4s and 4p orbitals to form 4 covalent bonds with four NH_3 ligands. The latter case needs the pairing of d electron to make the inner *d*-

orbital free for bonding, and this result the complex with no unpaired electron (diamagnetic complex). The magnetic moment value suggested that the complex formation takes place via 4s and 4p orbitals to form 4 covalent bonds with four NH_3 ligands.

5.12 SUMMARY:

The present unit may be summarized as follow

- Different kinds of terminologies that are being used during the study of magnetic properties of any substance, such as pole strength, line of forces, intensity of magnetic field, magnetic permeability, magnetic susceptibility etc.
- It has been discussed in the present unit how magnetism originates in substances.
- Determination of orbital magnetic moment (μ_l) and spin magnetic moment (μ_s) is also elaborated in the present unit.
- The various types of magnetic behaviours such as Diamagnetism, Paramagnetism, Ferromagnetism, Antiferromagnetism etc. is also explained in the present unit.
- Different methods for determination of magnetic susceptibility (*i.e.* Guoy’s method, Quincke method) have also been discussed in detail.
- The magnetic behavior of the coordination complexes can be easily explained based on the crystal field theory. Strong field ligands having very high splitting energy lead to the formation of the low spin complexes, however, weak field ligands having low splitting energy lead to the formation of the high spin complexes.
- The magnetic moment of the most of transition metal ions are very close to spin only magnetic moment μ_S means completely neglecting the orbital motions which is known as quenching of orbital magnetic moment.
- In some transition metal ions spin-orbit coupling takes place and contributes to the overall magnetic moment. For spin-orbit coupling to occur, following three conditions must be satisfied: (1.) There must be a half-filled or empty orbital similar in energy, (2.) There must be a half-filled or empty orbital similar in shape and symmetry, (3.) The nearby symmetry related orbital must not contain an electron with the same spin as the first electron.

- The loss of degeneracy of the d orbitals affects the unrestricted motion of electrons about the nucleus. The degeneracy of the d orbitals is lost to a greater extent. In such a complex, the magnetic moment μ_{eff} is close to μ_S.
- At the end the applications of magnetic moment data for determination of various properties of 3d metal complexes is elaborated.

5.13 SAQs TYPE QUESTIONS :

A. Multiple choice questions

1) Ratio of *I*/*H* is known as

a) Permeability b) Susceptibility

c) Induction d) none the above

2) For diamagnetic substances

a) $P < 1$ b) $P > 1$

c) $P = 1$ d) none the above

3) For paramagnetic substances

a) $P >1$ b) $P < 1$

c) $P = 1$ d) none the above

4) Susceptibility of diamagnetic substance is

a) Positive b) negative

c) Both (a) and (b) d) none the above

5) Susceptibility of paramagnetic substance is

a) Positive b) negative

c) Both (a) and (b) d) none the above

6) For ferromagnetic substances, the value of θ is

a) Positive b) negative

c) Both (a) and (b) d) none the above

7) For d^4 low spin complex the value of λ will be

a) Positive b) negative

c) Both (a) and (b) d) none the above

8) The range of anomalous magnetic moment value for Ni(II) high spin complex in octahedral field is

a) 3.0 - 3.3 b) 3.0 – 3.45

c) 3.45 – 4.0 d) 4.0 and above

9) The ground state of Ni(II) in octahedral field carry

a) Orbital contribution b) No orbital contribution

c) Both (a) and (b) d) none the above

10) For tetrahedral vanadium (IV), value of μ_{eff} is expected to be

a) $\mu_{eff} < \mu_{so}$ b) $\mu_{eff} > \mu_{so}$

c) $\mu_{eff} = \mu_{so}$ d) Both (a) and (b)

11) The magnetic moment value (μ_{eff}) of Ni(II) octahedral complex is expected to be

a) $\mu_{eff} < \mu_{so}$ b) $\mu_{eff} > \mu_{so}$

c) $\mu_{eff} = \mu_{so}$ d) Both (a) and (b)

12) For octahedral copper (II) complex the value of λ will be

a) Positive b) negative

c) Both (a) and (b) d) none the above

13) The value of Δ depends upon

a) nature of ligand b) oxidation state of metal ion

c) principal quantum number d) all the above

14) μ_{eff} for 3*d* electrons are equal to

a) μ_{so} b) μ_L

c) μ_J d) none the above

15) Fe_3O_4 is a

a) Ferromagnetic b) Antiferromagnetic

c) paramagnetic d) diamagnetic

16) Which of the following is paramagnetic

a) Dimond b) Oxygen

c) NaCl d) Iron

17) Zinc is a

a) Ferromagnetic b) Antiferromagnetic

c) paramagnetic d) diamagnetic

18) The magnetic moment value of 2.2 BM of complex $[Fe(diph)_3(ClO_4)_3]$ indicate that bonding is

a) Spin free b) Spin paired

c) Both (a) and (b) d) none the above

19) The diamagnetic nature of four coordinated complex of Ni(II) complexes have geometry

a) Square planar b) Tetrahedral

c) Octahedral d) Square pyramidal

20) The magnetic susceptibility of paramagnetic substances is

a) Independent of temperature b) Increase with increase in temperature

c) Decrease with increase in temperature d) None the above

B. Fill in the bling

i. Paramagnetic substances are those which on placing in a………..are attracted towards the magnetic field.

ii. The magnetic susceptibility is a measure of how much a material will become……………in an applied magnetic field.

iii. When the paramagnetic centers are close enough for direct or indirect orbital overlap, the exchange interaction occurs between the spin of the ……………………… ions.

iv. The valence bond theory could not explain the……………. for the quenching of orbital angular momentum.

C. True/ False

i. Diamagnetic substance have more then one unpaired electrons. True/False

ii.If any substance have no unpaired electron such type substance is called paramagnetic. True/False

iii. Gouy's method used to determination of magnetic susceptibility. True/False

iv. Whenever theoretical value not match with experimental value of magnetic moment this due to orbital contribution and temperature-independent paramagnetism. True/False

D. Match the following

Compound	**Magnetic moments**
a. $[Fe(CN)_6]^{-2}$	i. 3.9
b. $[CoF_6]^{-3}$	ii. 5.9
c. $[Mn(H_2O)_6]^{+2}$	iii. 4.9
d. $[Cr(NH_3)_6]^{+3}$	iv. 0

Answer Keys

A. 1(b) 2 (a) 3 (a) 4 (b) 5(a) 6 (a) 7 (b) 8 (a) 9 (a) 10 (a) 11 (b) 12 (b) 13 (d) 14 (a) 15 (a) 16 (b) 17 (d) 18 (b) 19 (a) 20 (b)

B. i. Magnetic field, ii. Magnetized, iii. Neighouring paramegnetic, iv Precise Mechanism

C. i. False ii. False iii. True iv. True

D. a iv b iii c ii d i

5.14 GLOSSARY :

CFSE = Crystal field stabilization energy

NMR = Nuclear magnetic resonance

VBT = Valence bond theory

BM = Bohr Magneton

5.15 REFERENCES :

1. Huheey J. E., Keiter E. A., Keiter R. L., (1997), *Inorganic chemistry- Principles of structure and reactivity(Fourth Edition)*, Pearson, 964.
2. Puri B. L. Sharma L. R. Kalia K. C.,(2020), *Principles of Inorganic Chmistry, (33rd Edition)*, Vishal Publishing.
3. Miessler G. L. , Fischer P. J., Tarr D. A., (2014) *Inorganic Chemistry(5th edition),* 696.
4. Banerjea D., (2009), *Coordination Chemistry" (second edition),* Asian Books, 4, 874.
5. House J. E., (2009), *Inorganic Chemistry*, Elsevier,

5.16 SUGGESTED READING :

1. C. E. Housecroft, A. G. Sharpe, (2018), *Inorganic chemistry*, Pearson (Fifth edition), 1256.
2. F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, (1999), *Advanced inorganic chemistry*, Wiley-Interscience (Six Edition), 1376.
3. J. D. Lee, (1999), *Concise inorganic chemistry*, Wiley-Blackwell (Fifth edition), 1072.
4. Janes R., Moore E. A., (2004), *Metal-ligand bonding*. The Open University, , 23. ISBN 0- 85404-979-7
5. Tsuchida R., (1938). *"Absorption Spectra of Co-ordination Compounds. I.*" Bull. Chem. Soc. Jpn. 13 (5): 388–400.

5.17 TERMINAL QUESTIONS :

(I) Short answer questions

1. Why some compounds shows paramagnetic behaviour while some show diamagnetic behaviour. Explain.
2. Write a note on diamagnetism.
3. Describe the Guoy's method for the determination of magnetic susceptibility of complexes.
4. How the magnetic data is useful to the elucidation of nature of binding in complexes.
5. Explain the use of magnetic data in the elucidation of geometry of complexes.
6. Explain why, the ferromagnetic substances are more magnetic than the paramagnetic substances.
7. Discuss the types of magnetic behaviours.
8. Define spin orbit coupling in complexes.
9. Explain magnetic properties of first transition series elements.
10. What do you understand by the quenching of orbital moments? Explain.
11. Write the requirements for orbital contribution to the magnetic moments.
12. How will you determine the oxidation state of the metal ion in complex using magnetic moment data? Explain with example.
13. Why spin only formula is used to calculate the magnetic moment of first transition series elements.
14. Describe the Quincke's method for determination of magnetic moments.
15. Explain the cause of Paramagnetism in reference of the different motions of electron.

(II) Long answer questions

1. Explain the types of magnetic materials,
2. Discuss the origin of magnetism in a material.
3. Explain the different methods for determination of magnetic susceptibility.
4. Discuss the contribution of orbital magnetic moment.
5. What is orbital quenching? Give the various requirements for orbital contribution.
6. Explain the various applications of magnetic moment data in respect of first transition series elements.