MAA OMWATI DEGREE COLLEGE

HASSANPUR

NOTES

Session 2021-22

SUBJECT: - Inorganic Chemistry

CLASS:- B.Sc 5th Sem

Syllabus Covered as :- M.D University ,Rohtak

MAA OMWATI DEGREE COLLEGE

HASSANPUR

B. Sc Vth Semester

Paper XVII (Theory) Inorganic Chemistry **Max. Marks: 29**

CH-501 **Time: 3Hrs .**

Note : Examiner will set nine questions and the candidates will be required to attempt five questions in all. Question number one will be compulsory containing five short answer type questions covering the entire syllabus and will be of five marks. Further, examiner will set two questions from each section and the candidates will be required to attempt one question from each section which will be o f s ix marks each

SECTION–A

Metal-ligand Bonding in Transition Metal Complexes

Limitations of valence bond theory, an elementary idea of cr ystal-f ield theory, crystal field split ting in octahedral, tetrahedral and square planar complexes, factors affecting the crystal-f ield parameters.

SECTION–B

Thermodynamic and Kinetic Aspects of Metal Complexe

A brief outline of thermodynamic stability of metal complexes and factors affec ting the s tab ility, substitution reac tions of square planar complexes of Pt(II).

SECTION-C

Magnetic Properties of Transition Metal Complexe

Types of magnetic behaviour, methods of determining magnetic susceptibility, spin-only formula. L-S coupling, correlation of □s and □eff values, orbital contribution to magnetic moments, application of magnetic moment data for 3dmetal complexes.

3

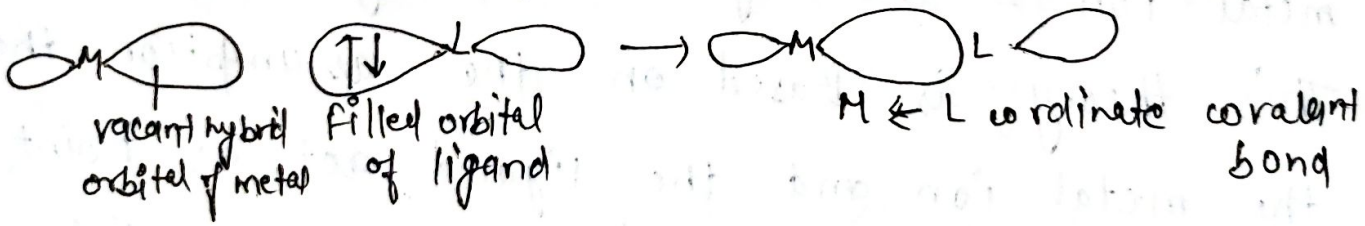
SECTION-D

Electron Spectra of Transition Metal Complexes

Types of electronic transitions, selection rules for d-d transitions, spectroscopic ground states, spectrochemical series. Orgel-energy level diagram for d_1 and d_9 states, discussion of the electronic spectrum of $[Ti(H_2O)_6]^{3+}$ complex ion.

✱ Valance Bond Theory :-

Valence bond theory was dereloped by Linus Pauling and assumes the bonding b/w the metal atoms or ions and the ligand to be purely coralent. It presents a simple description of metal-ligand bonding using hybrid orbitals of the metal & the electron pairs of the ligand. The bonding in metal complexes arise when a filled orbital of the ligand containing a pair electrons overlaps with a vacant hybride orbital on the metal atom or ion forming a coralent sigma bond called coralent bond theory



✱ Limitation of valance bond theory :-

The limitations of valance bond theory are as:-

i) It Provides only Qualitative explanations for complex.

ii) It does not explain the colour & electronic spectrum of complexes.

iii) It does not explain the variation of magnetic moment values with temperature.

iv) It does not take into account the splitting of d- energy levels.

v) It does not predict the stabilities of different str.

☆ Crystal field Theory :- The crystal field theory was dereloped by H-Bethe and V. Bleck. This theory is based on entirely different occumption that the VBT. As We have already learnt that valance bond theory considers the bond b/w metal ion & the ligand as purely covalent. On the other hand CFT consider the bond b/w metal ion & the ligand as purely electrostatics. This theory is Based on the assumption that the metal ion and the ligand act as point charge and the interactions b/w them are purely electrostatics.

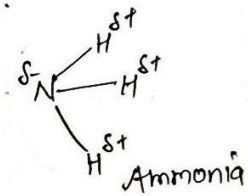
☆ Basis of crystal field Theory :-

1) The transation metal ion is surrounded by the ligand with lone pairs of electrons.

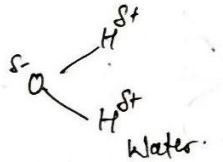
ii) All type of ligand regarded as point charges

2)

i) All type of ligand regarded as point charges the ligand may be either ion or molecules if ligand is neutral molecules then the negative end of the dipole is oriented towards the metal ion.



Ammonia



Water.

iii) The interaction b/w the metal ion and the negative end of anion is purely electrostatic.

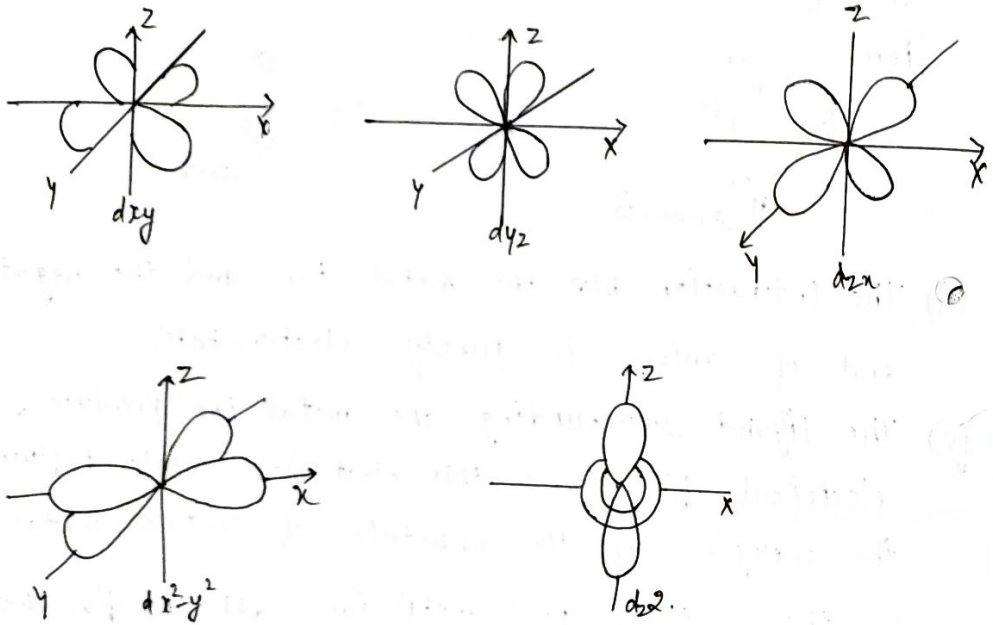
iv) The ligand surrounding the metal ion Produce, electrical field and this electrical field influence the energies of the orbitals of central metal ion.

v) In the case of free metal ion, all the five d-orbitals have the same energy. These orbitals having the same energies are called degenerate orbitals

The conversion of five degenerate d-orbitals of the metal ion into different sets of orbitals having different energies in the presence of electrical field of ligand is called crystal field spliting.

✱ Shapes of d-orbitals :—

There are five — d-orbital These are designated as d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$ & d_{z^2}. The shapes are given below.

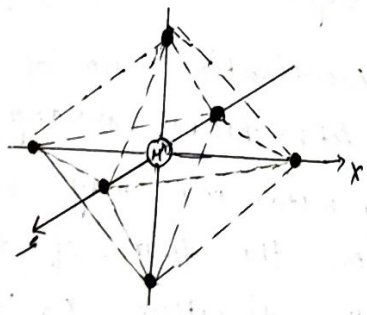


✱ Crystal field splitting in octahedral complexes :—

In an octahedral complex the metal ion is at the centre of octahedron and the ligands are at the six corner as in fig The three axis x, y, z points along the corner of octahedron

Let us supopose that the metal ion M^{n+}, has a single d-e⊖ In the free ion when there

are no ligand the electron can occupy any one of the five d-orbitals because all are of the same energy and are called degenerate orbitals.

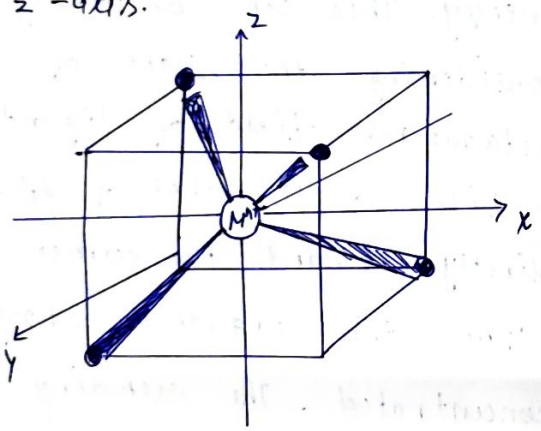


However the octahedral complex MX_6 all the five d-orbitals will not remain of equal energy. This can be easily understood by considering the shapes of these orbitals in the octahedral field of ligand. Two lobe of d_{z^2} orbital & 4 lobe of $d_{x^2-y^2}$ orbital point directly toward the corner of the octahedral where the negative charge of ligand are concentrated. The remaing three orbitals are oriented b/w the axes. In this case of octahedral complexes. the former two orbitals as t_{2g} orbitals.

In octahedral complexes the 5d-orbitals split up into two sets

1) one set consisting of two orbitals of higher energy
2) other set consisting of three orbitals of lower energy.

* Crystal field splitting in Tetrahedral complexes :- The coordination no. of tetrahedral complexes is 4. The tetrahedral arrangement of four ligand surrounding a metal ion may visualized by placing ligand on the four of the right corner of the cube The direction x, y & z point to the centre of the faces of the cube from fig. It is clear that the orbitals d_{xy}, d_{yz}, d_{zx} point b/w x, y & z -axis's.



The presence of tetrahedral field, the degeneracy of 5d-orbitals split up as -

i) The two orbitals $d_{x^2-y^2}$ & d_{z^2} because stable & their energies are lowered these designed as e orbital

ii) The three orbitals d_{xy}, d_{yz} and d_{zx} because unstable & their energies are raised these designed as t_2 orbitals.

4)

crystal field splitting in tetragonal & square planer complexes :- These can easily be understood from the knowing splitting of d- orbitals in octahedral complexes. This is because tetragonal & square planer geometry can be understood by withdrawing two trans ligands from an octahedral complex. This process is called elongation Generally we consider the removal of trans ligand along the z- axis.

As the trans ligands lying along z- axis are completly removed a square planner complex is formed. In the SPC there is further rise in energies of $d_{x^2-y^2}$ & d_{xy} orbital and a further fall in the energies of d_{z^2}, d_{xz} and d_{yz} orbital. It has been observed that the square planner complex the energy of d_{z^2} orbitals falls even below the d_{xy} orbitals The change of an octahedral complex to tetragonal octahedron & finally to square planer arrangement.

It may be remembered that tetragonally distorted str can also be obtained when the two trans ligands are brought closer to the metal ion. This is called flattening of an octahedron. In flattening the octahedron the two trans M-L bonds are shortened while other four M-L bonds become large.

* Factors effecting the crystal field splitting :-

1) Nature of ligand :- The crystal field theory depend upon the nature of ligand. The grater the easy with which the ligands can approach the metal ion. the greater will be the crystal field splitting called cause by it. The ligands which cause only a small degree of crystal field splitting are called weak field ligands. while those which causes a large splitting are called strong field ligand. The spectro-chemical series is an experimentally determined series. It is very difficult to understood.

5)

The variation causes by a no of factors such as

a) small ligand can cause greater crystal field splitting because they can approaches the metal ion closely.

b) The ligand containing easily polarizable electron pair will be drawn more closely to the metal ion.

d) The following pattern of increasing σ donation is observed

halide donors < O donors < N donors < C donors

The effect of crystal field splitting on the ligand attached to Cr(III) is shown below.

complex	Ligand	Donor atom	$\Delta_o (cm^{-1})$
$[CrCl_6]^{3-}$	Cl^-	Cl	13640
$[CrF_6]^{2-}$	F^-	F	15260
$[Cr(H_2O)_6]^{3+}$	H_2O	O	17830
$[Cr(en)_3]^{3+}$	en	N	21680
$[Cr(en)_3]^{3+}$	NH_3	N	21900
$[Cr(CN)_6]^{3-}$	CN^-	C	26280

the spectrochemical series in the increasing order of crystal field splitting is given below.

$I^- < Br^- < SCN^- < Cl^- < NO_3^- < F^- < OH^- < Ox^{2-} < H_2O < EDTA < Py \approx NH_3 < en < dipy < o\text{-}Phen < NO_2^- < CN^- < CO$

from the series it is clear that CO, CN^- and NO_2^- are strong field ligand whereas I^-, Br^- & Cl^- are weak field ligand.

ii) Oxidation state of the metal ion :-

The magnitude of the crystal field splitting depend upon the oxidation state of the transition metal ion. The metal ion with higher oxidation state causes large crystal field splitting than is done by the ion with lower oxidation state

This is clear from the following data in which crystal field splitting energies (Δ_o) for hexaaqua complexes of M^{2+} & M^{3+} ions of the first transition series are given

6)

Metal ion	oxidation state	electronic conf.	Δ_o (cm^{-1})	oxidation state	Electronic conf.	Δ_o (cm^{-1})
V	II	d^3	118000	III	d^2	18000
Cr	II	d^4	13900	III	d^3	17830
Mn	II	d^5	7800	III	d^4	21000
Fe	II	d^6	10400	III	d^5	13700
Co	II	d^7	9300	III	d^6	18600

Similarly, for complexes having other ligand, the Δ_o values in lower oxidation state are similar than Δ_o values in higher oxidation state

complex	oxidation state	Electronic conf.	Δ_o (cm^{-1})
$[Fe(CN)_6]^{4-}$	II	$3d^6$	32,200
$[Fe(CN)_6]^{3-}$	III	$3d^5$	35,000
$[Co(NH_3)_6]^{2+}$	II	$3d^7$	10,200
$[Co(NH_3)_6]^{3+}$	III	$3d^6$	22,870
$[CoF_6]^{3-}$	III	$3d^6$	13,100
$[CoF_6]^{2-}$	IV	$3d^5$	20,300

3) Types of D-orbitals :-

This may be explained on the basis that 4d-orbitals in comparision to 3d-orbitals are bigger in size & extend farther into space. As a result, the 4d-orbitals can interact more strongly

with the ligand & therfore the crystal field spliting is more. similarly 5-d orbitals are bigger than 4d-orbitals and Δ_o for the third transition series is more than that for second transition series. This is evident from the following data.

complex ion	Electronic confi.	$\Delta_o (cm^{-1})$
$[Co(NH_3)_6]^{3+}$	$3d^6$	23000
$[Rh(NH_3)_6]^{3+}$	$4d^6$	34000
$[Ir(NH_3)_6]^{3+}$	$5d^6$	41000

Geometry of the complex :- As mentained earlier, the crystal field splitting energy of tetrahedral complexes (Δ_t) is nearly half the value (Δ_o) for octahedral complexes ($\Delta_t = 4/9\,\Delta_o$)

complex	oxidation state of metal	Geometry	$\Delta (cm^{-1})$
$[Co(NH_3)_4]^{2+}$	II	Tetrahedral	5900
$[Co(NH_3)_6]^{2+}$	II	Octahedral	10,200
VCl_4	IV	Tetrahedral	7,900
$[VCl_6]^{2-}$	IV	octahedral	15,400

1) Thermodynamic stability of complexes :-

In a broad sense the term stability means that the compound exists and under suitable conditions may be stored for a long period of time. The terms stable or unstable are thermodynamic terms which refer to the tendency of species to exist or not

The thermodynamic stability of a complex is the measure of the extent of formation of a complex at equilibrium. The interaction b/w the metal ion & ligand may be regarded as Lewis-acid base reaction. If the interaction is strong the complex formed would be thermodynamically more stable. Therefore the thermodynamic sys stability may be expressed in terms of equi-const for the formation of the complex.

for the reaction

$$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$$

the equi- const K_s is given as

$$K_s = \frac{[Cu(NH_3)_4]^{2+}}{[Cu^{2+}][NH_3]^4}$$

larger the numerical value of K_s the more thermodynamically stable is the complex similar expression can be written for other complexes also and the comparision of the stability const. can be made for various complexes formed under similar condition.

The stability const. for the similar cyanide complex of Cu^{2+},

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

Tetracyanocopper(II)ion

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

is 2.0×10^{27}. This shows that CN^- is a stronger ligand than NH_3 molecules because the stability const. for the cyanide complex is larger in comparision to corresponding ammine complex. similarly in case of Ag^+ complexes

8)

$$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ \quad K_s = 1.6 \times 10^7$$

$$Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2]^- \quad K_s = 5.4 \times 10^{18}$$

Let us compare the stability constant of two nickel complexes-

$$Ni^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+} \quad K_s = 6.1 \times 10^8$$

$$Ni^{2+} + 3en \rightleftharpoons [Ni(en)_3]^{2+} \quad K_s = 4.6 \times 10^{18}$$

The K_s values indicate that bidentate ligand ethylenediamine forms a considerable more stable complex then ammonia.

It may be noted that sometimes, the reciprocal of stable constants, $1/K_s$ called the dissociated constant is also used.

$$[Cu(NH_3)_4]^{2+} \rightleftharpoons Cu^{2+} + 4NH_3$$

The equi. constant K_s may be given by the expression.

$$K_s = \frac{[Cu^{2+}][NH_3]^4}{[Cu(NH_3)_4]^{2+}} = 4.5 \times 10^{21}$$

$$K_{diss} = \frac{1}{K_s} = \frac{1}{4.5 \times 10^{21}} = 2.22 \times 10^{-22}$$

Stability constant of complexes:-

Let us consider the formation of the complex ML_n

$$M + nL \rightleftharpoons ML_n$$

The reaction proceeds by the following steps.

$$M + L \rightleftharpoons ML$$

and the equi-const for this reaction will be

$$K_1 = \frac{[ML]}{[M][L]}$$

Now ML adds to another molecules of ligand L as

$$ML + L \rightleftharpoons ML_2 \text{ and}$$

$$K_2 = \frac{[ML_2]}{[ML][L]}$$

Similarly ML_n formed by following rxn

$$ML_2 + L \rightleftharpoons ML_3 \quad \& \quad K_3 = \frac{[ML_3]}{[ML_2][L]}$$

$$ML_{n-1} + L \rightleftharpoons ML_n \quad \& \quad K_n = \frac{[ML_n]}{[ML_{n-1}][L]}$$

There will be n such equilibrium, where n represent the maximum co-ordination no of the metal ion for the ligand L.

the value of stepwise const decrease in the order

$$K_1 > K_2 > K_3 \dots > K_n$$

example → for the Cu^{2+} & Cd^{2+} complexes with ammonia or cyanide ligand the value of k's are

cation	Ligand	log K_1	log K_2	log K_3	log K_4
Cu^{2+}	NH_3	4.30	3.60	3.10	2.30
Cd^{2+}	NH_3	2.65	2.10	1.44	0.94
Cd^{2+}	CN^-	5.48	5.12	4.63	3.55

another way

$$ex = M + nL \rightleftharpoons ML_n$$

May be expressed as

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

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

$$M + 3L \rightleftharpoons ML_3 \qquad \beta_3 = \frac{[ML_3]}{[M][L]^3}$$

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

β_n is known as n^{th} overall stability const or commulative stability const.

consider for ex the expression for β_3

Let us multiply both numerator and denominator by $[ML]\,[ML_2]$ & then rearrange as

$$\beta_3 = \frac{[ML_3]}{[M]\,[L]^3} \cdot \frac{[ML]\,[ML_2]}{[ML]\,[ML_2]} = \frac{[ML_3]}{[M][L]} \cdot \frac{[ML_2]}{[ML]\,[L]} \cdot \frac{[ML_3]}{[ML_2][L]}$$

$$= K_1 \cdot K_2 \cdot K_3$$

In general

$$\beta_n = \frac{[ML_n]}{[M]\,[L]^n} = \frac{[ML]}{[M][L]} \cdot \frac{[ML_2]}{[ML][L]} \cdots \frac{[ML_n]}{[ML_{n-1}][L]}$$

$$= K_1 \cdot K_2 \cdot K_3 \cdots K_n$$

thus $\beta_n = \prod_{i=1}^{n} K_i$

Therefore

$$\beta_1 = K_1$$

$$\beta_2 = K_1 \cdot K_2$$

$$\beta_3 = K_1 \cdot K_2 \cdot K_3$$

$$\beta_n = K_1 \cdot K_2 \cdot K_3 \cdots \log K_n$$

Thus $\log\beta$ may be used as a measure of stability of the complex.

10)

For ex.

$[Cu(NH_3)_4]^{2+}$, $\log\beta_4 = \log K_1 + \log K_2 + \log K_3 + \log K_4$

$= 4.30 + 3.60 + 3.10 + 2.30 = 13.30$

$[Cd(NH_3)_4]^{2+}$ $\log\beta_4 = 2.65 + 2.10 + 1.44 + 0.94 = 7.12$

☆ Factors affecting the stability of complexes :-

The stability of complexes depends upon two main factors.

1) Nature of the central metal ion.
2) Nature of the ligand.

- Nature of the central metal ion :-

The stability of a complex depends upon the nature of central metal ion as :-

a) charge on the central metal ion :-

In general the most stable complexes are found with metal ion having high charge density

Where charge density means natural ratio of charge to the radius of the ion. Thus the smaller the size & larger the charge of a metal ion, the more stable are the complexes. A smaller more highly charged ion allows closer approach of the ligand and the greater force of attraction results into stable complex. Thus in general the greater is the charge on the central metal ion, the greater is the stability of the complex. In other word the stability of a complex increase with increase in charge on the central metal ion.

eg. $Fe^{3+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{3-}$

oxidation state of metal ion = +3, $\log \beta = 31$. very stable

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

oxidation state of metal = +2, $\log \beta = 8.3$ Less stable

complex	oxidation state of metal ion	$\log \beta$	stability
$[Fe(CN)_6]^{3-}$	+3	31	very stable
$[Fe(CN)_6]^{4-}$	+2	8.3	Less-stable

b) Size of Metal ion :-

As the size of Metal ion decrease, the stability of complex increases. if we consider the bivalent metal ion, than the stability of their complexes increases with decrease in the ionic radius of the central metal ion as

Ion	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
Ionic radius	91	83	82	78	69	74

Therefore the order of stability is

$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$

- if we include diralant ions of alkaline earth metals such as then complexes of divalant ions increase in the order

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

This order of stability is known as Irving William series.

c) Electronegativity of charge distribution of metal ion :-

The stability of complex ion is also related to the electronic charge distribution of the metal ion. Acc to Ahrland chatt and Davis, Metal ion may be classified into two types.

class 'a' Metals :-

There are fairly electropositive metals & ions include the alkali metals, alkaline earth metals, most of non-transition metal & those transition metal having only a few d valant electrons.

class 'b' Metals :-

There are much less electro-positive metal and include heavy metals such as Rh, Pd, Ag, Ir, Pt, Au, Hg, Pb etc. These have relatively large no of d electrons beyond an inert gas core.

b)

2) Nature of Ligand :-

a) Size of charge of the ligand :-

The electrostatic influence of the size & charge of the ligand are important in determining the stability of a complex. Thus F^- should form more stable complexes than Cl^-, Br^-, I^-,

eg	$Fe F^{2+}$	$\log\beta = 6.0$
	$Fe Cl^{2+}$	$\log\beta = 1.3$

Similarly, large perchlorate ion, ClO_4^- has relatively small tendency to form metal complexes

b) Basic strength :-

The formation of metal ligand bond involves the donation of electron pair from the ligand to the empty orbitals of the central metal ion. The greater the ease of donation of electron pairs

by the ligand, the greater is the stability of the complex formed by it. Greater the basic strength of a ligand the greater will be its tendency to form a metal complex. This means that the ligand which form H^+ firmly should also form stable complexes with metal ion

c) Presence of ring str :-

For multidenate ligand the stability of a complex is also influenced by formation of ring str., ring size, ring strain etc as discussed ahead.

i) chelate effects :-

The complex formed by chleating ligand such as ethylene diamine EDTA .etc more stable then those formed by monodentate ligand such as H_2O or NH_3.

This enhanced stability of complexes containing chelating ligand is called chelate effect

eg -

$$Ni^{2+}(aq) + 6NH_3(aq) \rightleftharpoons [Ni(NH_3)_6]^{2+} \quad \log\beta = 8.61$$

$$Ni^{2+}_{(aq)} + 3en(aq) \rightleftharpoons [Ni(en)_3]^{2+}(aq) \quad \log\beta = 18.28$$

complex	$\log\beta$	stability
$[Ni(NH_3)_6]^{2+}$	8.61	Less stable
$[Ni(en)_3]^{2+}$	18.28	More stable

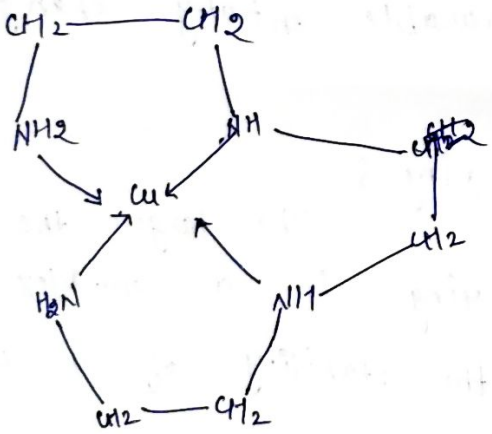
chelating effect can be understood on the basis of favourable entropy change during chelating.

ii) No of chelate ring :-

The larger the number of chelate ring in a complex the greater is the stability of a complex. this is clear from the following given example :-

complex	No of chelate ring	log β
$[Cu(NH_3)_4]^{2+}$	0	12.6
$[Cu(en)_2]^{2+}$	2	20.0
$[Cu(trien)]^{2+}$	3	20.5

When trien is triethylene tetra amine. $H_2N\,CH_2\,CH_2\,NH\,CH_2\,CH_2\,NH\,CH_2\,CH_2\,NH_2$. The chelating behaviour of trien towards Cu^{2+} ion showing three ring is shown below



14)

* Substitution Reaction In square Planer complexes

Metal ion with d^8 electronic configuration usually form four coordination square planer complexes, especially with strong field ligand

These include complexes of Pt(II), Pd(II), Ni(II) Au(III), Rh(I) & Ir(I)

Groups	8	9	10	11
	—	—	Ni(II)	—
	—	Rh(I)	Pd(II)	—
	—	Ir(I)	Pt(II)	Au(III)

- The substitution Reaction involve the replacement or exchange of one ligand by another ligand without any change in either the oxidation state or the coordination number of the central metal atom.

$$[PtCl_4]^{2-} + NH_3 \longrightarrow [Pt(NH_3)Cl_3]^- + Cl^-$$

Similarly

$$[Pt(NH_3)_4]^{2+} + Cl^- \longrightarrow [Pt(NH_3)_2Cl]^+ + NH_3.$$

i) oxidative addition followed by reductive elimination leads to substitution reaction as:-

$$PtMeCl(PMe_2Ph)_2 \xrightarrow{Cl_2} PtMeCl_3(PMePh)_2 \longrightarrow PtCl_2(PMe_2Ph)_2 + MeCl$$

ii) Electrophilic substitution can replace a ligand by another ligand as:-

$$PtMeCl(PMe_2Ph)_2 + HgCl_2 \longrightarrow PtCl_2(PMe_2Ph)_2 + MeHgCl$$

This reaction involves the electrophilic attack of Hg(II) on the Platinum - carbon bond.

iii) Square Planer complexes undergo nucleophilic substitution as:-

$$PtMeCl(PMe_2Ph)_2 + N_3^- \longrightarrow PtMe(N_3)(PMe_2Ph)_2 + Cl^-$$

In this case nucleophile N_3^- replace Cl^- ion.

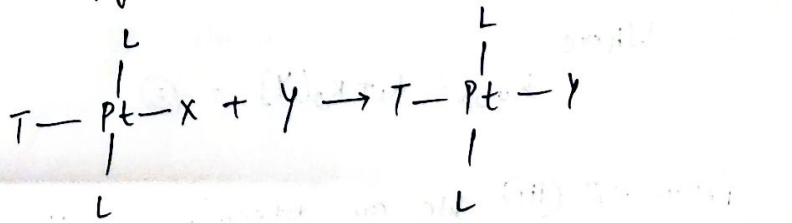
✱ Rate law for Nucleophilic substitution in square Planar complexes :-

consider a general nucleophilic substitution reaction in a square planar complex of Platinum $[PtL_2TX]$ undergoing substitution of ligand X by Y as :-

$$[PtL_2TX] + Y \longrightarrow [PtL_2TY] + X$$

In which Y be entering nucleophilic ligand X is the leaving ligand & T is the ligand trans of X.

The substitution proceed with retention of the configuration at the metal as



The kinetic of the reaction were studies by making the conc. of Y to be very large

as compare to the conc. of the complex so that the conc. of Y. i.e [Y] be assumed to be const.

$$\text{rate} = -\frac{d[PtL_2TX]}{dt}$$

$$= k_1[PtL_2TX] + k_2[PtL_2TX][Y] \quad -(1)$$

Where $[PtL_2TX]$ = conc. of the complex

$[Y]$ = conc. of the incoming ligand

The above expression may be rearranged to give.

$$\text{rate} = [k_1 + k_2 Y][PtL_2TX]$$

$$= k_{obs}[PtL_2TX] \quad -(2)$$

Where

$$k_{obs} = k_1 + k_2[Y] \quad -(3)$$

from eqn (iii) We can determine both k_1 & k_2 by carrying out the reaction at various conc of Y. This gives a plot of k_{obs} verse [Y], which is a straight line & We get k_1 as

intercept and k_2 as slope, The plots of rate const as a function of nucleophilic conc (Y) for the rxn of trans $[Pt(Py)_2Cl_2]$ With various nucleophiles in methanol at 30°c.

1) Associative rxn :- In this type of rxn the rate determine step is the formation of intermediate with an increased coordination number. This means that Pt-Y bond is first formed before Pt-X begins to break.

2) Dissociative Reaction :- In this type of rxn the rate determine step is the formation of the intermediate in which one ligand is lost.

3) Interchange associative :- In this type of rxn the Pt-bor begins to break before Pt-Y bond is fully formed but bond making is

more significant than bond making breaking.

4) Interchange dissociative :- In this type of rxn the Pt-Y bond begins to form before the Pt-X bond is fully broken but bond breaking is more significant than bond making.

It has been observed that the value of both k_1 and k_2 were non zero which indicate the PtL_2TX complex reacts in two diff. path way.

Thus the two term rate law may be expressed as :-

$$\text{rate} = k'[PtL_2TX][S] + k_2[PtL_2TX][Y] \quad -(4)$$

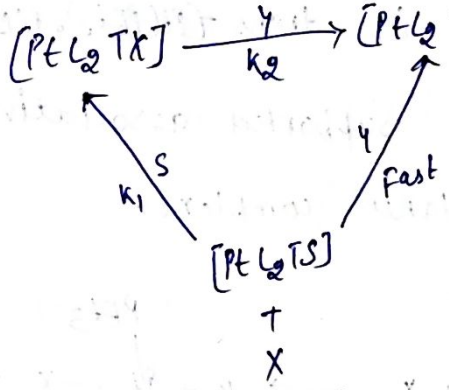
however since solvent is present in large excess, it conc., [S] remains practically const so that

$$k'[S] = k_1$$

(17)

Therefore the eqn iv) simplifies to eq^n (1)

The associative pathways may be summarized as



As mentioned above,

$$[PtL_2TX] \xrightarrow{-X} [PtL_2T] \xrightarrow{+Y} [PtL_2TY]$$

The coordinate complex.

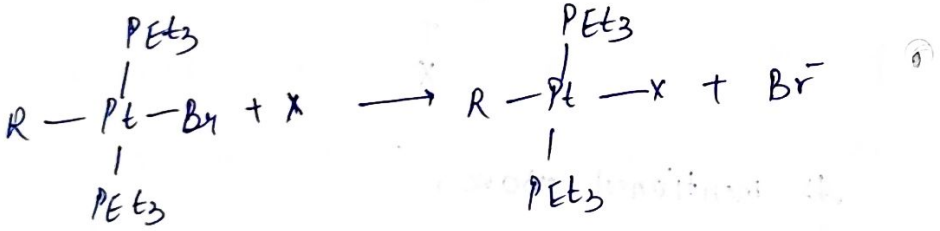
- The following evidences has supported the associative mechanism:-

i) It is observed that the rxn take place faster in more nucleophilic solvent suggisting the solvent attack plays an important role.

ii) The dissociative rxn should be accn. by

by the Presence of sterically demanding ligands

iii) The thermodynamics studies for the substitution of pro mide in trans-$[Pt(PEt_3)_2RCBr]$ by iodide or thiourea supported associative mechanism in square planer complexes



★ Trans Effect :-

In 1926, Cherny ear introduce the concept of trans effect in Platinum complexes.

The ability of an attached gp to direct sub. into a position trans itself is called trans effect such a g/p has marked effect on the rate of reaction.

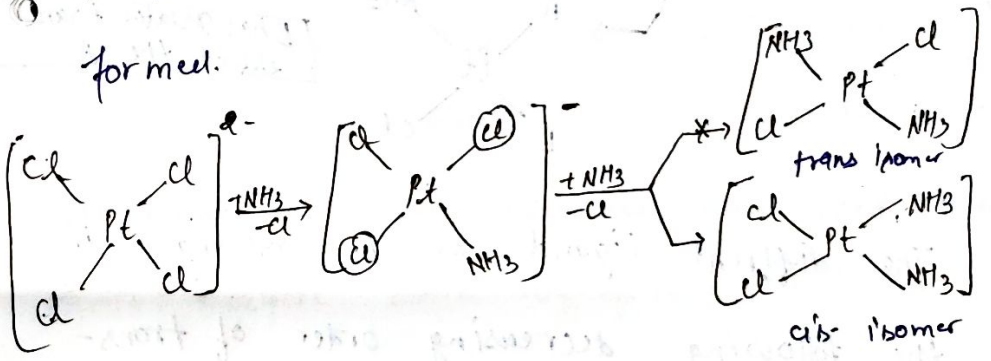
18)

Let us illustrate this by considering the preparation of two geometric isomers of $[PtCl_2(NH_3)_2]$ complex.

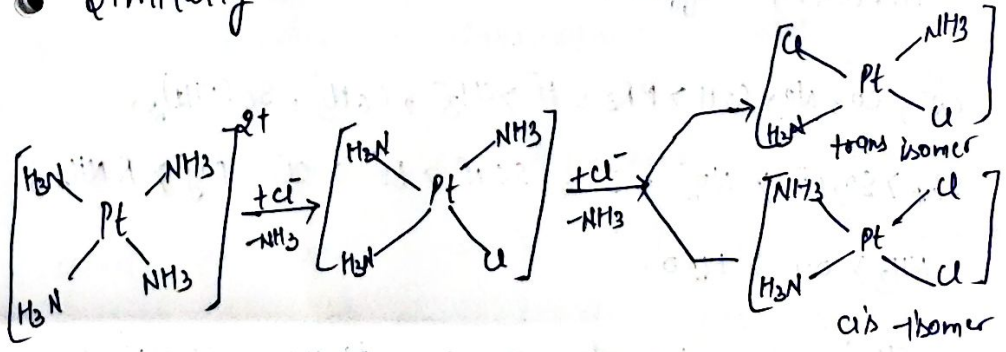
i) replacement of Cl^- in $[PtCl_4]^{2-}$ by NH_3

ii) replacement of NH_3 in $[Pt(NH_3)_4]^{2+}$ by Cl^-

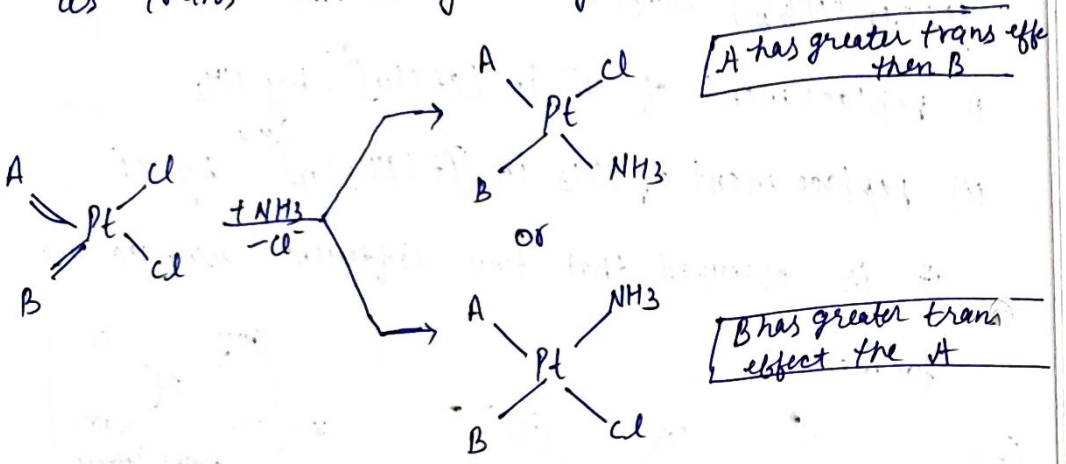
- It is observed that two different isomers are formed.



- Similarly



The labilization of ligand trans to other ligand which can then be regards as trans directing ligand.



The diffrent ligand can be arrangeed in the following decreasing order of trans-directing effect.

$CN^-, CO, NO, C_2H > PR_3, H^- > CH_3^-, C_6H_5^-, SC(NH_2)_2, SR_2 > SO_3H^- > NO_2^-, I^-, SCN^- > Br^- > Cl^- > Py > RNH_2 > NH_3 > OH^- > H_2O$.

This is also known as trans directing series.

Section - B
Chapter - 3

* Magnetic Properties of transition metals :-

There are mainly two types of magnetic behaviour shown by substance.

i) Diamagnetism or diamagnetic substance :-

The sub. having paired electrons are repelled by magnetic field. These are called diamagnatic substance. Since all elements except hydrogen have filled electron shells, therfore some diamagnetism will be shown by substance.

ii) Paramagnetism or Paramagnetic substance :-

The sub. Which are attracted by the magnetic field are called paramagnetic substance. The paramagnetism is caused by the presence of unpair electrons. Larger the no. of unpaired electrons, in a sub. greater is the paramagnetic character.

The magnetic Moment due to spin of the electron on its axis is called spin magnetic moment

Orbital Magnetic moment :-

The magnetic moment due to motion of the electron around the the nuclear is called orbital magnetic moment.

The magnetic Moment of sub. are generally expressed in terms of units called Bohr magneton.

$$\mu_s = \frac{e\hbar}{4\pi mc}$$

$$1\ B.M = \frac{e\hbar}{4\pi mc} \quad \text{①}$$

The spin magnetic moment, μ_s of a single electron is given as

$$\mu_s = g\sqrt{s(s+1)} \quad \text{②}$$

s = spin quantum no, g = gyp gyromagnetic ratio

Let $s = \frac{1}{2}$, $g = 2$ the spin magnetic moment for one $e^{\ominus}$

$$\mu_s = 2\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)} = \sqrt{3} = 1.732\ B.M$$

for atom & ion having more than one unpair $e^{\ominus}$ the overall spin moment is given by

$$\mu_s = g\sqrt{s(s+1)}$$

$s = \frac{1}{2}$, Cr^{3+} has four unpair $e^{\ominus}$

so that $s = 4 \times \frac{1}{2} = 2$

& Mn^{2+} have five unpair electrons $s = 5 \times \frac{1}{2} = \frac{5}{2}$

Since the value of g is taken as 2.0 the spin magnetic momentum may also be written as

$$\mu_s = \sqrt{4s(s+1)}$$

for one unpair $e^{\ominus}$

$s = \frac{1}{2}$ so that

$$\mu_s = \sqrt{4 \times \frac{1}{2}\left(\frac{1}{2}+1\right)} = \sqrt{3} = 1.732 \text{ B.M}$$

Similarly for two $e^{\ominus}$

$$S = \left(\frac{1}{2} + \frac{1}{2}\right) = 1$$

so that

$$\mu_s = \sqrt{4 \times 1(1+1)} = 2\sqrt{2} = 2 \times 1.414 = 2.828 \text{ B.M}$$

for three unpaired $e^{\ominus}$

$S = 3/2$ so that

$$\mu_s = \sqrt{4 \times \frac{3}{2}\left(\frac{3}{2}+1\right)} = 3.87 \text{ B.M}$$

The spin magnetic moment can also be calculate from the relation

$$\mu_s = \sqrt{n(n+2)} \text{ B.M}$$

Where n is the no of unpair electron.

eg → for one unpaireel $e^{\ominus}$

$$\mu_s = \sqrt{1(1+2)} = \sqrt{3} = 1.732 \text{ B.M}$$

for two unpair $e^{\ominus}$

$$\mu_s = \sqrt{2(2+2)} = 2\sqrt{2} = 2 \times 1.414 = 2.828 \text{ B.M}$$

The total magnetic moment which is dependent of both the spin & orbital magnetic moment is given by

$$\mu_{s+l} = \sqrt{4S(S+1) + L(L+1)}$$

★ Measurement of Magnetic Properties :-

The magnetic properties (moment) are not measured directly. However the parameter which is actualy measured is magnetic susceptibility from which it is possible to measure magnetic moment

The magnetic susceptibility is a measure of the capacity of a sub. to take up magnetism an applied magnetic field. If substance is placed in a magnetic field of strength H. Then magnetic induction and magnetic flux density B within it, is given by

$$B = H + 4\pi I$$

Where I is called Intensity of magnetisation the ratio B/H called Magnetic Permeability of the substance can be given as :-

$$\frac{B}{H} = 1 + 4\pi\frac{I}{H}$$

or $$\frac{B}{H} = 1 + 4\pi K$$

Where $\frac{I}{H}$ is K & is called magnetic suspectibility per unit volume. or simply as volume susceptibility (B/H) , in vacuum B/H = 1 so that

$$1 = 1 + 4\pi k \quad \text{or} \quad K = 0$$

It may be noted that since we deal with masses of solids rather than their volumes, We generally define the terms specific or mass susceptibility, χ or molar susceptibility χ_m as

$$\text{Mass Susceptibility} = \chi = \frac{K}{\rho}$$

Where ρ is the density

$$\text{Molar susceptibility}, \chi_m = \frac{K \cdot M}{\rho}$$

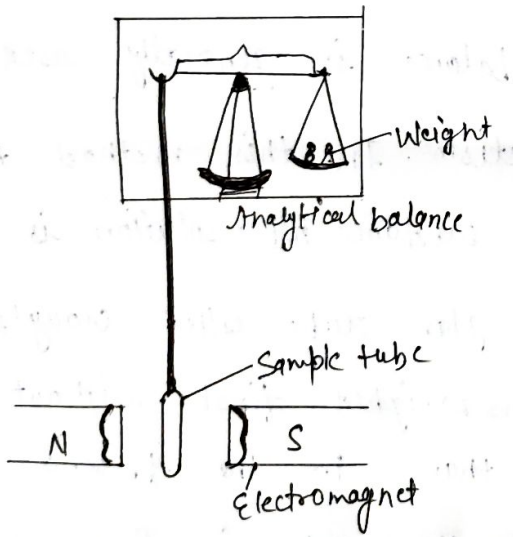
Where M is the molecular weight of the compound

★ Experimental Measurement of magnetic moment

i) Gouy's Method :-

A simple device known as Gouy's balance is generally used to measure paramagnetism. In this method the finely powdered substance or solution is taken in a pyrex glass tube called Gouy's tube. The substance is weighed first without magnetic field & than in the presence of magnetic field if the sub. is Paramagnetic. It will weigh more in the presence of magnetic field than in its absence. The increase in weight is the measure of Para magnetism of the sub

larger the no of unpair electron in a sub. greater is the increase in its weight in a magnetic field. A diagrammatic sketch of Gouy's balance is show in fig: the suspectibility can be easily cal. from the difference from the difference in weight of the sample when the magnet is off and when it is on.



Calculation of Magnetic Moment :- The Gouy Produce a very simple method for measuring magnetic susceptibility.

23)

The sample in the form of a cylinder is suspended in a non-homogeneous magnetic field & the force exerted on the sample is determine by weighing. The force acting on the sample is

$$F = \frac{1}{2} A K H^2 \quad (1)$$

In the above eqn if sample is surround the air then the eqn become

$$F = \frac{1}{2} A H^2 (K - K') \quad (2)$$

eqn (2) become

$$F = \frac{1}{2} A H^2 (K - K') + \delta$$

for a sample of const length & cross-sectional area the factor AH^2 is const.

$$10^6 \chi = \frac{\alpha + \beta F'}{\omega}$$

$\chi = 1644 \times 10^{-6}$ at 20°C.

Advantage of Gouy's method :—

1) The apparatus is simply & easy to assemble
2) It is easy to handle & use

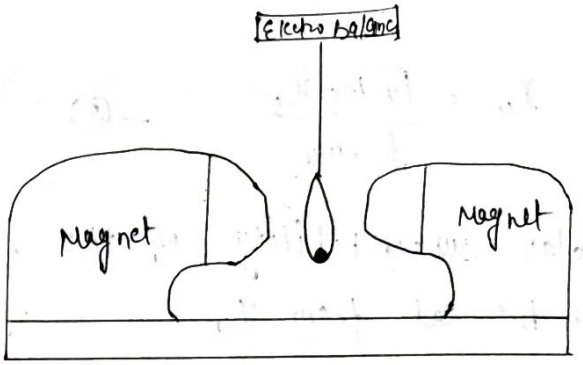
3) Since the amount of sample taken in the Gouy's tube is quite large, the force are large therefore, even a chemical balance can measure the changes in mass.

Disadvantages of this method :-

1) It is required large amount of sample
2) It requires perfect uniform packing of the substance in the Gouy's tube.

* Faraday's method :-

The faraday's method gives the specific susceptibility directly it use a very small amount of sample that is suspended in an inhomogeneous field such that $H_0(\delta H/\delta x)$ is const over the entire volume of the sample. sample set up are given in fig.



The sample is suspended b/w magnet poles that have been carefully shaped so that the value of $H_0(\delta H/\delta x)$ is const over the region occupied by the sample.

The sample will exprience a force (f) along δx due to gradient as

$$f = m\chi H_0 \left(\frac{\delta H}{\delta x}\right) \quad \text{(1)}$$

Now if the same magnetic field and gradient are used for both the standard (s) unknown (u) is not necessary to know the precise values of other quantities Hence

$$\frac{f_s}{m_s \chi_s} = \frac{f_u}{m_u \chi_u}$$

$$\chi_u = \frac{f_u m_s \chi_s}{f_s \cdot m_u} \quad -(2)$$

The molar susceptibility of the sample χ_m can be cal from χ_u

Advantages of faraday's Balance :-

1) This method requires very small quantity of the substance for measurement and the sample need not be homogeneous. In this method generally several milligrams of sub is sufficient for measurements.

★ Relation ship b/w magnetic susceptibility & magnetic moment :-

The magnetic susceptibility is related to magnetic moment μ as :-

$$\chi_M \text{ corr} = \frac{N_0 \mu^2}{3kT}$$

Rearranging the above eqn.

$$\mu^2 = \frac{3k}{N_0} \cdot \chi_M^{corr} \cdot T$$

$$\mu = \sqrt{\frac{3k}{N_0}} \cdot \sqrt{\chi_m^{corr} \cdot T}$$

$$= \text{const} \sqrt{\chi_m^{corr} \cdot T}$$

where const, $\sqrt{\frac{3k}{N_0}}$ comes out to be 2.828

Thus magnetic moment can be cal. from the magnetic susceptibility using the relation.

$$\mu = 2.828 \sqrt{\chi_m^{corr} \cdot T} \text{ B.M}$$

★ Orbital contribution to Magnetic Moment :-

The unpaired electron in a first transition series transil are present in the 3d orbitals. A transition metal ion has five 3d orbitals which are degenerate. An electron will possess angular momentum along a given axis if it is possible to transform its orbital by rotation

around this axis into another orbital which is equivalent to its in shape, size and energy.

In general, for generating orbital momentum, the following condition should be satisfied

i) the orbitals should be degenerate.

ii) The orbital should be similar in shape and size so that they should be transformable into one another by rotation about some axis

iii) the orbitals should not contain electrons of identical spin.

In another words for orbital contribution to magnetic moments there must be two or more degenerate orbitals which can be inter converted by rotation about a

suitable axis and these orbitals must be unequally occupied. If the orbital degeneracy is lost by chemical bonding or crystal field effects, the orbital contribution to the total magnetic momentum is partially or completly quenched.

Let us consider a free mental ion in which all the d orbitals are degenerate. An electron in $d_{x^2-y^2}$ orbital will contribute to orbital angular momentum equally equal to 2 units of $h/2\pi$ along z-axis because a rotation of $d_{x^2-y^2}$ orbital by 45° around the z-axis will transform it into equivalent d_{xy} orbital. d_{x^2} orbital cannot be transformed into any other equivalent orbital by rotation around z-axis & therefore, it has zero orbital angular momentum along z-axis

Quenching of orbital Angular momentum in octahedral complexes :-

As already learnt, in octahedral field of ligand, the five d orbitals split into two sets, t_{2g} and e_g. Therefore, the equivalent $d_{x^2-y^2}$ and d_{xy} orbitals vanish and consequently, their orbitals contribution get quenched. However, there will be some contribution of orbital angular momentum along z-direction because d_{xz} and d_{yz} orbitals are still equivalent in energy in octahedral field. Therefore, an electron in d_{xz} or d_{yz} orbital will contribute an orbital angular moment along z-axis in octahedral complexes. for ex→ the d_{xz} orbital can not be transformed by rotation into equivalant d_{yz} orbital because this already has an electron. Thus the orbital magnetic moment will have zero value.

Orbital contribution in octahedral complexes

No of electrons d^n	High spin octahedral		Low spin octahedral	
	Electronic conf.	orbital contribution	Electronic conf.	orbital contribution
d^1	t_{2g}^1	Excepted	t_{2g}^1	Excepted
d^2	t_{2g}^2	excepted	t_{2g}^2	Excepted
d^3	t_{2g}^3	Not expected	t_{2g}^3	Not expected
d^4	$t_{2g}^3 e_g^1$	Not expected	t_{2g}^4	Expected
d^5	$t_{2g}^3 e_g^2$	Not expected	t_{2g}^5	Expected
d^6	$t_{2g}^4 e_g^2$	Expected	t_{2g}^6	Not expected
d^7	$t_{2g}^5 \cdot e_g^2$	Expected	$t_{2g}^6 e_g^1$	Not expected
d^8	$t_{2g}^6 e_g^2$	Not expected	$t_{2g}^6 e_g^2$	Not expected
d^9	$t_{2g}^6 e_g^3$	Not expected	$t_{2g}^6 e_g^3$	Not expected

★ Orbital contribution in Tetrahedral complexes

In the case of tetrahedral, the five d-orbitals split into two sets t_2 and e orbitals. The energies of t_2 orbitals are higher than the energies of e orbitals. Thus in tetrahedral complex

the mental ions having the following conf. will not have orbital contribution.

$d^1(e^1)$, $d^2(e^2)$, $d^5(e^2t_2^3)$, $d^6(e^3t_2^3)$ & $d^7(e^4t_2^3)$

on the other hand, the tetrahedral complexes having the following conf. will have orbital contribution.

$d^3(e^2t_2^1)$, $d^4(e^2t_2^2)$, $d^8(e^4t_2^4)$ & $d^9(e^4t_2^5)$

Orbital contribution in tetrahedral complexes.

n d^n	Electronic configuration	orbital contribution
d^1	e^1	Not expected
d^2	e^2	Not expected
d^3	$e^2t_2^1$	expected
d^4	$e^2t_{2_3}$	expected
d^5	$e^2t_{2_3}$	Not expected
d^6	$e^3t_{2_3}$	Not expected
d^7	$e^4t_{2_4}$	Not expected
d^8	$e^4t_{2_5}$	expected
d^9	e^4t_2	expected

There may be contribution from spin orbital coupling. In these case, the magnetic moments can be cal. by using the following eqn

$$\mu_{eff} = \mu_0 \left(1 - \alpha \frac{\lambda}{\Delta}\right)$$

Orbital contribution in complexes of Lower symmetry :-

The probability contribution is less if the symmetry of a complex is lower. It can be seen that orbital contribution is possible in the complexes having following configuration of metal ion.

Square Planar and square Pyramidal :- d^2 & d^4

Trigonal bipyramidal :- d^1, d^3, d^4 & d^5

Dodecahedral :- d^7 & d^9.

Chapter - 4

✱ Term symbols and coupling scheme :-

In our earlier studies we have learnt that the complete description of the electrons in an atom can be obtained in terms of four Quantan number. These four quantam no. are:-

Principal Quantam number (n) :-

It determines the main energy level or shell in which the electron is present. It can have whole no. of values as:-

$$n = 1, 2, 3, 4 \text{ ---}$$

ii) Angular Quantam no :-

It is related to the angular momentum of the electron. In multielectron atom, the energy besides depending upon n, also depends on l. corresponding to each value of n. there are n possible values of l as:-

$$l = 0, 1, 2, 3 \text{ --- } (n-1)$$

the various values of l are designated as s, p, d, f --

value of l	0	1	2	3	4	--
Designation	s	p	d	f	g	---

iii) Magnetic Quantam number (m) :-

It refers to the different orientation of the orbitals in space for a given value of l, m can have (2l+1) value as $m = -l, -(l-1) \text{ --- } 0 \text{ --- } +(l-1), +l$

iv) Spin quantam number :-

This describes the spin orientation of the electron. Since the electron can spin in two ways. clockwise and anticlockwise, s can have only two values $+1/2$ or $-1/2$. The values may be express by

arrow pointing up (↑) & down (↓) respectively. It determines the spin angular momentum.

The distribution of electrons in different level in an atom is known as electronic configuration. The filling of orbitals is governed by three rules:-

1) Aufbau Principle :-

Electron generally occupy orbitals of lowest energy. This means that the electron enter the orbitals of lowest energy first & subsequent electron are fed in increasing order of energy (1s, 2s, 2p, 3s, 4s, 3d ---)

2) Pauli's exclusive Principle :-

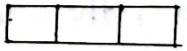
No two electrons in an atom can have the same values for the four quantum numbers.

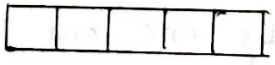
Hund's rule :-

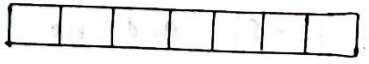
When several orbitals of the same energy are available, the electrons tend to remain unpaired as for as possible. i.e the electrons tends to retain parallel spin as much as possible.

The electronic conf. of the outer shell is generally represented by a box diagram. In this the boxes represent orbitals and electron are indicated by arrows for example the s-orbital indicated by one single box, all orbitals are indicated as following:-

one s-orbital 

three p-orbital 

five d-orbital 

seven f-orbital 

★ L-S or Russell saunders coupling :-

This is applicable to system in which spin orbital interaction are relatively small. In this scheme the individual orbital angular momenta of a electron couple to give a resultant angular momentum represented by the quantam number, L for the state. In individual electron spin momenta also couple to give a resultant spin momentum described by the quantam number S. The L and S values determine the total angular momentum, J which can take quantized positive values ranging from $|L-S|$ to $|L+S|$

In this method, the consecutive values are seperated by one and $|\ |$ indicates the absolute value of $|L-S|$ and no regard is paid to the sign. so that J is also ≥ 0.

$$J = |L+S|, |L+S-1| \text{ --- } |L-S|$$

Rules to determine the terms symbol acc to L-S coupling scheme :-

There are following rules are given below

A. Determining total spin angular momentum (ss coupling

For a single electron, spin quantam no $m_s = 1/2$.

When two or more electrons are present in a subshell, then their magnetic field couple to produce resultant spin quantum number S. The resultant spin quantam no. is given as

$$S = (s_1 + s_2), (s_1 + s_2 - 1) \text{ --- } |s_1 - s_2|$$

Where the modulus sign $(|\ |)$ indicate the positive value. for ex for a subshell having two electrons (p^2 or d^2)

$$S = 1/2 + 1/2 \ , \ 1/2 + 1/2 - 1$$

$$S = 1 \ , \ 0$$

The spin multiplicity is given by the relation $2S+1$ and is written in the upper left hand

corner of the symbol for the state.
Depending upon the spin multiplicity.
We call singlet state, triplet state and so on.

unpaired electron	S	(2S+1)	Name of state
0	0	1	singlet
1	1/2	2	Doublet
2	1	3	Triplet
3	1/2	4	Quartet
4	2	5	Quintet

B) Determination of resultant orbital angular momentum (jj coupling) :-

When two electrons, with angular quantum number l_1 and l_2 interact, the resultant quantum no. L are given by the relation ship:

$$L = (l_1 + l_2), (l_2 + l_2 - 1), (l_1 + l_2 - 2) \cdots |l_1 - l_2|$$

|| sign indicate positive value.

for example :-

for a p- subshell having two electrons $l_1 = 1$ and $l_2 = 1$ so that

$$L = (1+1), (1+1-1), \cdots (1-1)$$
$$= 2, 1, 0$$
$$= D, P, S$$

therefore, p^2 $e^\ominus$ will be represented by three energy states S, P and D corresponding to L = 0, 1 and (2 respectively)

Similarly, for d^2 conf.

$l_1 = 2$, $l_2 = 2$

$$L = (2+2), (2+2-1), 2+2+2, 2+2-3, 2-2$$
$$4 \quad 3 \quad 2 \quad 1 \quad 0$$
$$G \quad F \quad D \quad P \quad S$$

Thus, d^2 configuration is represented by five energy states S, P, D, f and G corresponding to L = 0, 1, 2, 3, 4 respectively

c) Spin orbital of L-S coupling :-

In an atom the magnetic effects of the resultant angular momentum L and the resultant spin moment S coupling together to give new quantum number J called the total angular quantum number. The J values can be obtained by the vectorial combination of L and S and the coupling scheme is called L-S coupling.

The J can acquire all acquire all quantized positive values ranging from $|L-S|$ to $|L+S|$ as

$$J = (L+S), (L+S-1), (L+S-2) \text{ --- } |L+S|$$

The J value are seperated by 1. The modulus sign indicate the absolute value of $|L-S|$ so that $J \geq 0$

Let us illustrate these values by taking the example of p^2 and d^2 configuration.

p^2 - configuration :-

For both p - electrons $L_1 = 1$, $L_2 = 1$

$$L = (1+1), (1+1-1), (1+1-2)$$
$$2 \qquad 1 \qquad 0$$
$$D \qquad P \qquad S$$

The energy states are S, P and D

For two electrons

$$S = (+1/2 + 1/2), (+1/2 + 1/2 - 1)$$
$$1 \qquad 0$$

The spin multiplicity $(2S+1)$ is:-

For $S = 1$, spin multiplicity = 3 (triple)

$S = 0$, spin multiplicity = 1 (singlet)

Therefore we have six states

^3S, ^3P, ^3D, ^1S, ^1P and ^1D

Let us cal. J values

a) When $L = 2$, 1 and 0 and $S = 1$

i) When $L = 2$, $S = 1$ i.e ^3D state

$$J = (2+1), (2+1-1), (2+1-2)$$
$$3 \qquad 2 \qquad 1$$

complete spectroscopic term symbols are

$^3D_3$, $^3D_2$ and $^3D_1$

ii) Where L = 1 and S = 1 i.e ^3P state

$J = (1+1)\ ,\ (1+1-1)\ ,\ (1+1-2)$

$\quad\quad 2 \quad\quad\quad 1 \quad\quad\quad 0$

complete spectroscopic terms are

$^3P_2$, $^3P_1$ and $^3P_0$

iii) When L = 0 and S = 1 i.e ^3S state

$J = 1+0$

$\quad = 1$

complete spectroscopic terms is

$^3S_1$

b) When L = 2, 1 and 0 and S = 0

i) When L = 2 and S = 0 i.e ^1D state

$J = 2+0$

$\quad\quad 2$

complete spectroscopic term

$^1D_2$.

ii) When L = 1 and S = 0 i.e ^1P state

$J = 1+0$

$\quad = 1$

complete spectroscopic term is

$^1P_1$

iii) When L = 0 and S = 0 i.e ^1S state

$J = 0$

complete spectroscopic term is

$^1S_0$

Thus, the total term symbols for P^2 conf are :—

$^3D_3$, $^3D_2$, $^3D_1$, $^3P_2$, $^3P_1$, $^3P_0$, $^3S_1$, $^1D_2$, $^1P_1$ & $^1S_0$

Each of these value corresponds to an electronic arrangement. These values gives very useful information.

★ Determination of spectroscopic Ground state term :—

All the terms derived from the given electronic configuration of an atom do not possess the same energy. The different terms can be arranged in order of energy and the ground state term is identified on the

bases of Hund's rules. The rules for determining the order of energy for different terms are:-

1) The terms are arranged depending upon their spin stability decreases as the value of S decreases. This means that the most stable states has maximum unpaired electrons because this gives the minimum electrostatic repulsion. This is in accordance with Hund's rule.

2) For a given value of S, the state with the highest value of L is the most stable state. This means that if two or more terms have the same value of S, the state with ligand highest value of L will have lowest energy.

3) For a given value of S and L, the terms with smallest J values is more stable.

If the subshell is less than half filled and the term with maximum J values is most stable if the subshell is more than half filled.

Thus ground state

Less than half filled = Smallest J values

More than half filled = Maximum J values

Let us apply these rules to the terms derived for p^2 and d^2 configurations

i) p^2 configuration :-

The term for ground state of p^2 configuration are ^3P, ^1D and ^1S.

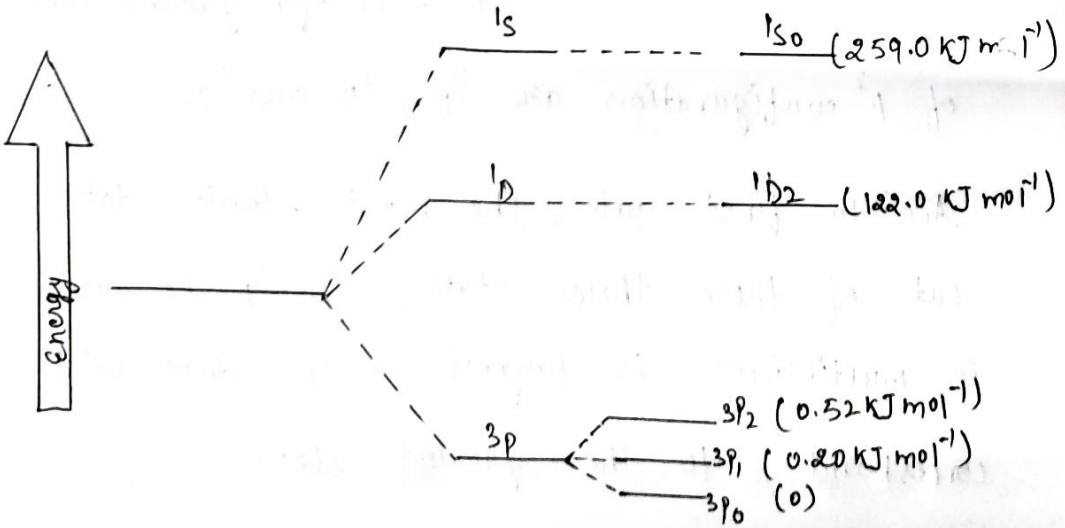
Acc to first rule, the most stable state out of these three states is ^3P because it multiplicity is largest so ^3P state will correspond to the ground state.

Acc to second rule, the ^1D state corresponds to $L=2$ and is more stable than ^1S state where $L=0$ because both have same multiplicity.

Now the triplet P state has three terms $^3P_2$, $^3P_1$ and $^3P_0$. Acc to third rule $^3P_0$ is the lowest energy term & these term may be arranged as

$$^3P_0 < ^3P_1 < ^3P_2$$

The diff terms of carbon are arranged in the increasing order of energy



ii) D^2 configuration :-

The term for ground state of d^2 conf. are ^1S, ^3P, ^1D, ^3F and ^1G

According to first rule, the stable state corresponds to highest multiplicity. In this case both ^3P and ^3F have multiplicity 3. Applying second rule, ^3F term will be stable because it has higher value of L. So energies of these two states are :-

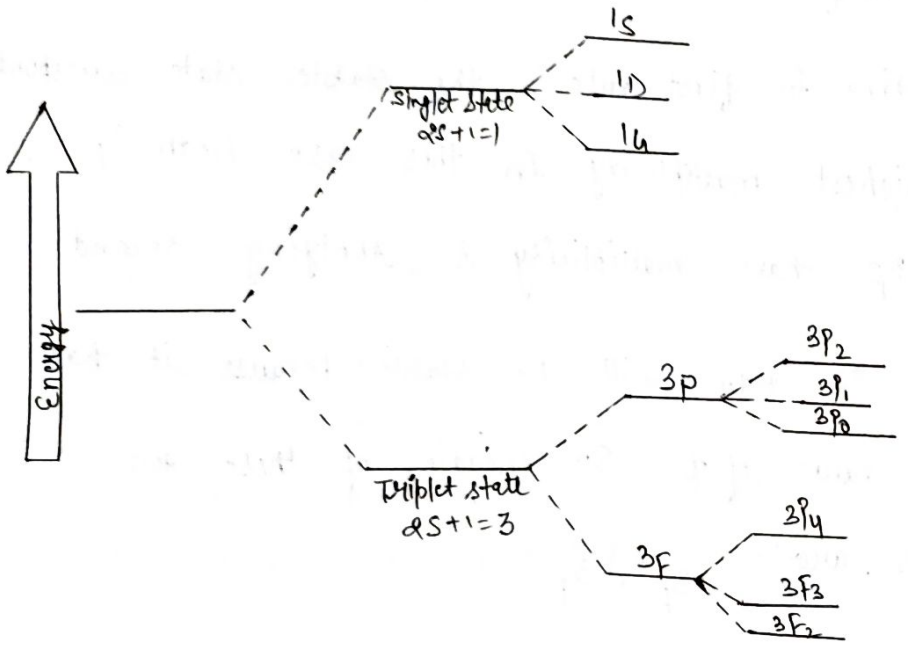
$$^3F < ^3P.$$

The remaining three states have same spin multiplicity = 1. These can be arranged according to L values as

$$^1G < ^1D < ^1S.$$

The splitting of terms in ground state of d^2 conf shown in fig. It may be noted that the two triplet states ^3F and ^3P can

further split and arranged according to the rule 3 as shown.



splitting of terms in d^2 conf.

ground state term for d^1 to d^{10} conf.

configuration	ground state term	Example
d^1	^2D	Ti^{3+}
d^2	^3F	V^{3+}
d^3	^4F	Cr^{3+}
d^4	^5D	Cr^{2+}
d^5	^6S	Mn^{2+}
d^6	^5D	Fe^{2+}
d^7	^4F	Co^{2+}
d^8	^3D	Ni^{2+}
d^9	^2D	Cu^{2+}
d^{10}	^1S	Cu^{+}

☆ Spectro chemical series :-

The analysis of spectra of a large no of complexes with different ligand and with different metal ions having provided considerable data on ligand field splitting energy Δ. It has been observed that if the ligand of ML_6 complexes are arranged in the increasing order of Δ_o for each metal ion. the order is generally independant of the metal ion. This arrangements of the ligand in increasing order of ligand field splitting energy (Δ) is called spectrochemical series. spectro chemical series in decreasing order of ligand field splitting is given below.

$I^- < Br^- < Cl^- < SCN^- < F^- < OH^- <$ acetate $< ox^{2-} < H_2O < NCS^- <$ glycine $<$ Py $\simeq NH_3 <$ en $<$ dipy $\approx$ o-Phen $< NO_2^- < CN^- < CO$

Ligands are commonly classified by their donor and acceptor capability. The ligand like ammonia are σ donors only, with no orbitals of appropriate symmetry for π bonding. The ligand field splitting depends on the degree of overlap. Ethylamine has a strong effect than ammonia among these ligands generating a large Δ.

The halide ions ligand field strength are in the order

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

Which is the order of proton basicity of these ligands

When ligands have vacant π^* or d-orbitals, there is possibility of π-back bonding & the ligands are π-acceptor. This interaction of bonding scheme increase.

The ligands which can do this effectively are CN^-, CO etc. In keeping with σ-donor strength we can arrange the ligands in terms of their donor atoms as:-

halogen < oxygen < nitrogen < carbon.

The metal ion also influence the magnitude of Δ_o through the overlap and energy match criteria.

The following metal ion spectrochemical series is observed.

$$Mn^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < V^{2+} < Fe^{3+} < Cr^{3+} < V^{3+} < Co^{3+} < Mn^{4+} < Mo^{3+} <$$

$$Ru^{3+} < Pd^{4} < Ir^{3+} < Re^{4+} < Pt^{4+}$$

This trend is keeping with increase in Δ with increase in the formal charge on the ion. The crystal field splitting is influenced by the oxidation state of metal ion greater is the crystal field splitting Δ_o increase with increase in metal charge.

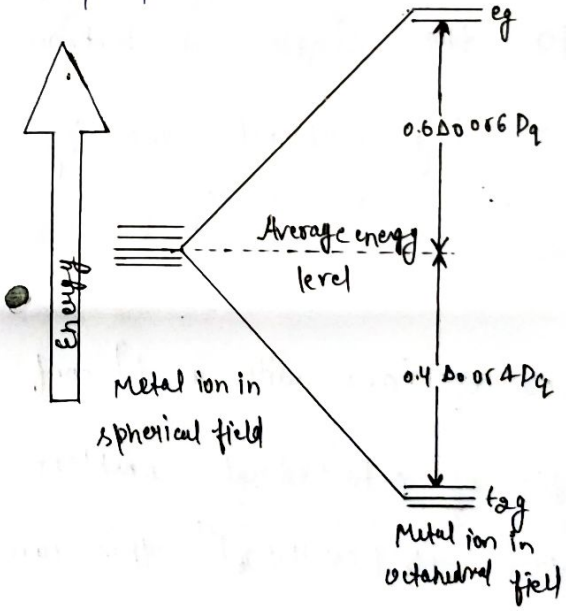
★ Orgel energy level diagrams :—

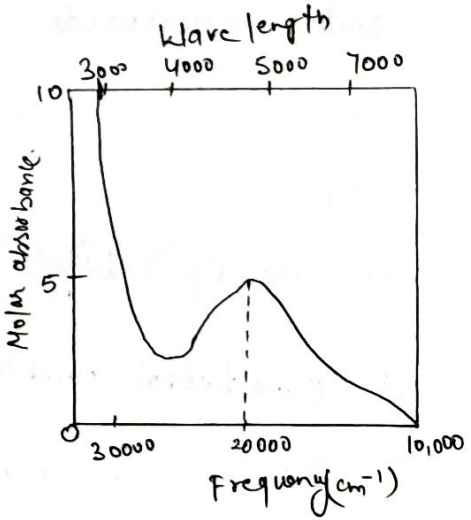
1) Spectra of d^1 and d^9 ions

a) Octahedral complexes of metal ion with d^1 configuration :—

In a free gaseous metal ion, the five d-orbitals are degenerate & therefore, no electronic transition is possible. Hence there will be no spectra for d^1 conf. However, when this ion is in complex form the electrostatics field of the ligand splits the d-orbitals into two gp. t_{2g} and e_g as already discussed. The simplest ex of a d^1 complex is Ti in octahedral complexes such as $[Ti(H_2O_6)]^{3+}$ or $[TiCl_6]^{3-}$. The splitting is shown as in fig. In a ground state the single electron occupies the lower t_{2g} level and only one transition from $t_{2g} \rightarrow e_g$ is possible consequently the absorption spectrum of $[Ti(H_2O)_6]^{3+}$

shows only one band with a peak at 20300 cm^{-1} as shown in fig. The energy corresponding to this wavelength corresponds to green and yellow light which are absorbed from the white light while the blue & red portions of light are emitted. Therefore, Ti soln of complex $[Ti(H_2O)_6]^{3+}$ looks purple.





The intensity of the absorption band is very weak ($\epsilon = 5-10$). This is because of the reason

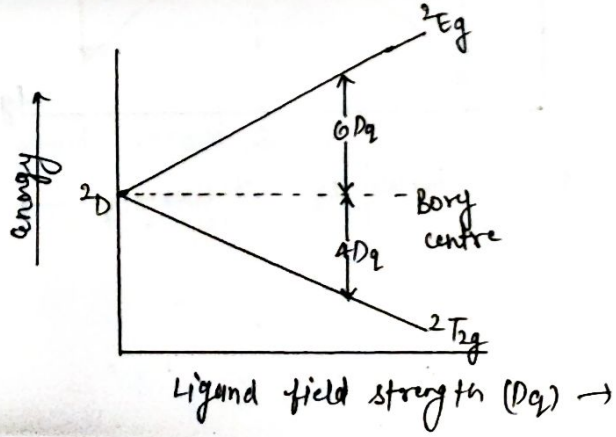
that the transition and therefore, the frequency of maximum absorption vary in the spectra of these complexes.

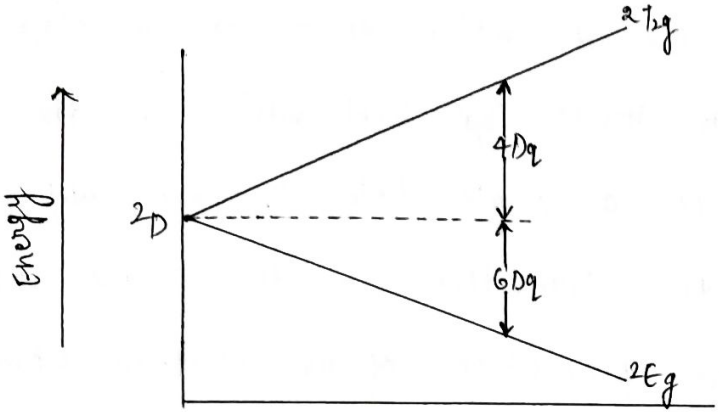
The effect of an octahedral ligand on d^1 ion as shown on the left. Under the influence of a ligand field, this split into two steps which are describe by Mulliken symbols ^2E_g and $^2T_{2g}$. The lower T_{2g} state corresponds to the single d-electron occupying one of the T_{2g} orbitals and ^2E_g state corresponds to the electro occupying one of the E_g orbitals.

b) Octahedral complexes of ions with a d^9 conf.

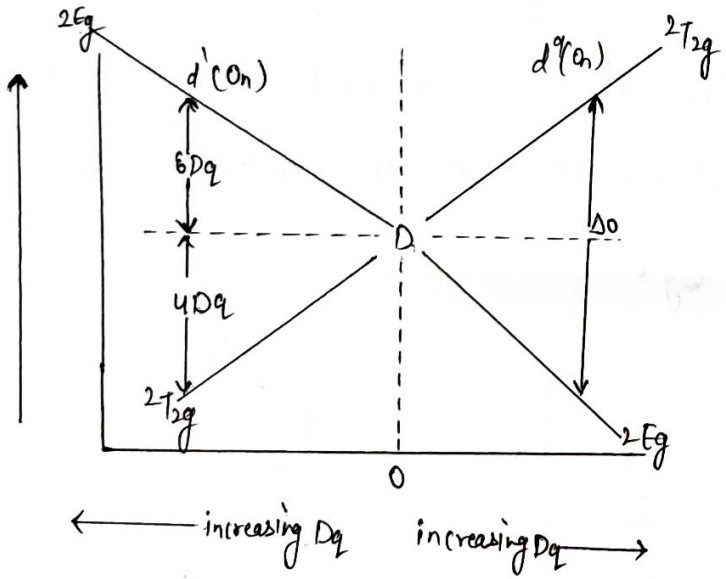
The common example of octahedral complexes with d^9 electronic conf. is $[Cu(H_2O)_6]^{2+}$. This can be explained in a similar way to the Ti^{3+} octahedral complexes with a d^1 arrangement.

In the d^1 complex there is a single $e^{\ominus}$ in the lower T_{2g} level while in the d^9 complex there is a single hole in the upper E_g level. Thus, the transition in the d^1 case corresponds to the promotion of an electron from the T_{2g} to E_g level. Thus the transition in the d^1 case corresponds to the promotion of an electron from the T_{2g} to E_g level. Whereas the transition in the d^9 case corresponds to the promotion of an electron as the transfer of a hole form E_g to T_{2g}.





The energy level diagram for d^1 & d^9 in octahedral field (O_h) are shown below



Limitation of Orgel Energy level Diagrams:-

Orgel energy level diagrams are useful for interpreting spectra of transition metal complexes. However these have two important limitations:-

1) The orgel energy level diagram consider only the energy levels obtained by splitting the energy terms when the metal ion is subjected to weak octahedral field or tetrahedral field. In other words, orgel energy level diagram consider only weak field cases.

2) The orgel energy level diagrams consider spin allowed transition in which the ground and excited states are of same multiplicities, In other words in orgel diagrams, excited