

Inorganic Chemistry - II

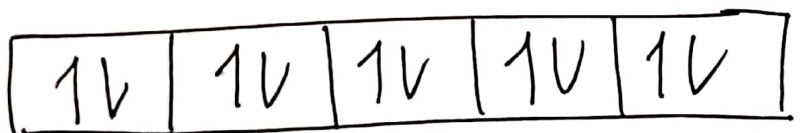
Sem :- 2

Sub code :- MCHO201

Unit - 4 :- Electronic Spectroscopy

★ Concept of Crystal Field Theory (C.F.T)

- ⇒ This theory was proposed by Bethe & Van Vleck.
- This theory was originally applied mainly to ionic crystals.
- This theory is give the idea about colour and magnetic property of complex compounds.
- Structure & position of d orbitals

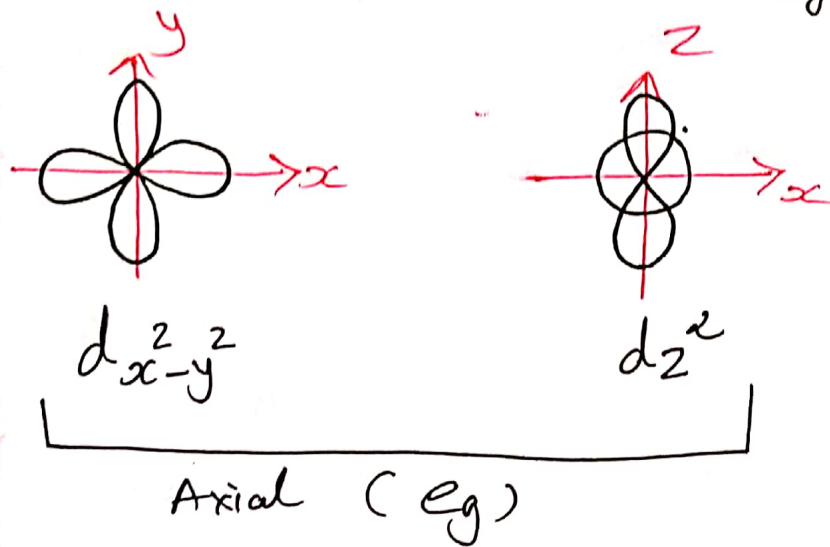
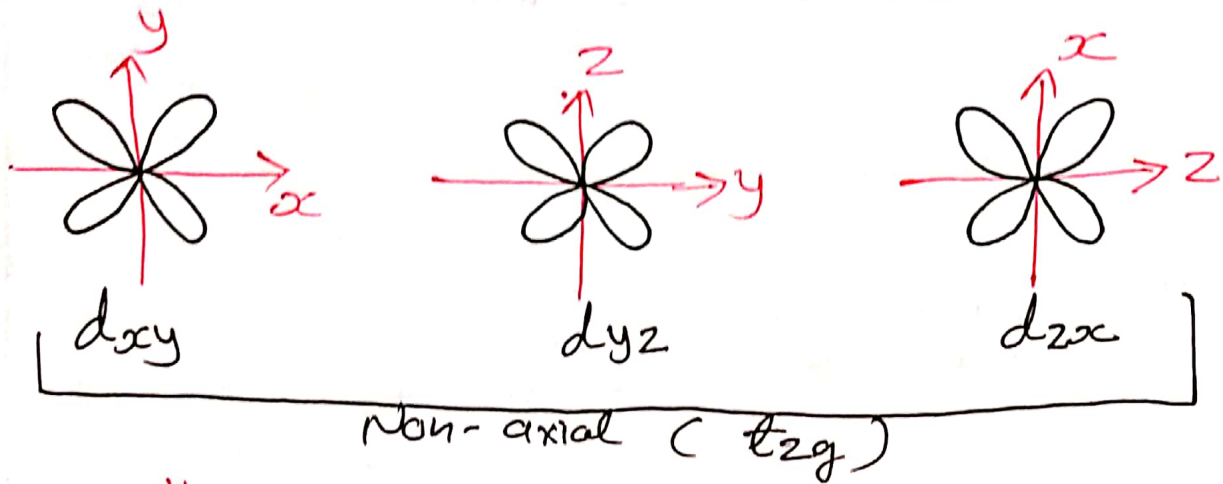


d_{xy} d_{yz} d_{zx} $d_{x^2-y^2}$ d_{z^2}

Non-axial
(t_{2g})

axial
(e_g)

- Shape of d orbitals.



→ Assumption of CFT theory:-

- The central metal cation is surrounded by ligands which contain at least one lone pair of electron.
- The ionic ligands (e.g. F^- , Cl^- , CN^- etc.) are regarded as point charges and the neutral ligand (e.g. CO , NH_3 , H_2O etc.) are regarded as point dipoles or simple dipoles. If the ligand is neutral molecule such as NH_3 , the negative end of the dipole in the molecule is directed towards the central metal cation.

→ There is no interaction between metal orbitals and ligand orbitals i.e. there is no orbital overlap.

→ According to this theory, the bonding between central metal cation and ligand is not covalent bonding but it is regarded as purely electrostatics.

→ So, the bonding in complex may be :

M cation & Negative ligand → Ion-ion attraction

M cation & Neutral ligand → Ion-dipole attraction

→ The d orbitals on the metal, all have the same energy (i.e. degenerate) in the free atom. When a complex is formed, the ligand destroy the degeneracy of these orbitals. i.e. the orbitals now have different energies.

→ In an isolated gaseous metal ion, the five d-orbitals do all have the same energy, and are termed degenerate.

→ If a spherically symmetrical field or negative charge surrounds the metal ion, the d orbitals remain degenerate. However, the energy of orbitals is raised because of repulsion between the field and the electron on metal.

* Ligand Field Theory (LFT)

→ The CFT and Molecular Orbital theory (MOT) ~~was~~ were combined into a more complete theory called LFT.

→ This theory was given by Griffith and Orgel.

→ According to CFT, the splitting of metal d-orbitals is a result solely of electrostatic effects and the bonding between metal and ligand is ionic with no covalent character.

→ The physical measurements such as electron spin resonance (ESR) or electron paramagnetic resonance (EPR), give evidences in favour of covalent bonding in co-ordination complexes.

→ CFT treats ligands as point charge or dipoles and does not take into account the overlap of ligand & metal orbitals.

⇒ L.F.T. for Octahedral Complexes :-

- Molecular orbitals are formed by the linear combinations of metal and ligand atomic orbitals having the same symmetry.

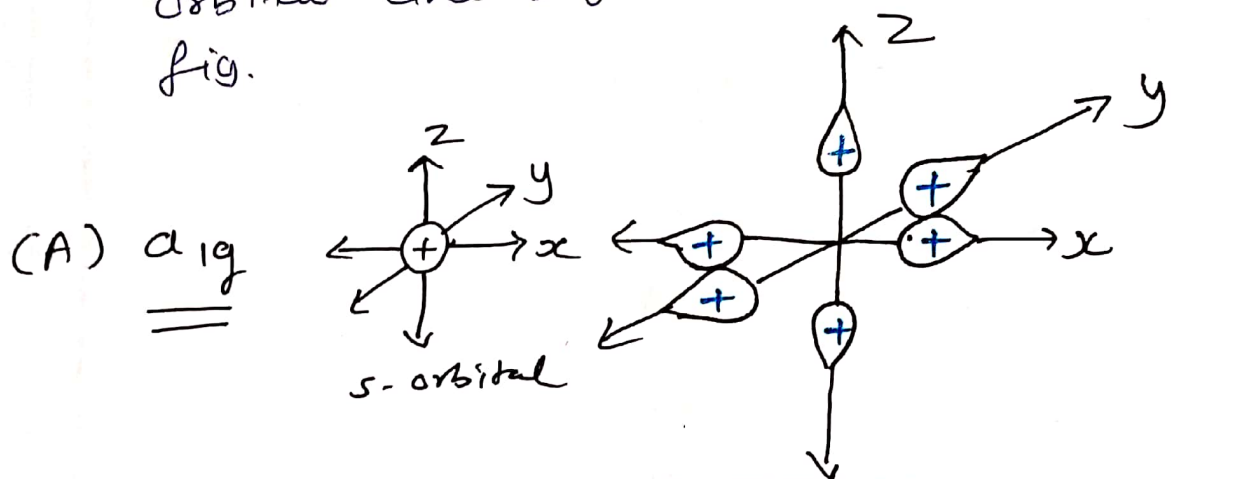
- The linear combination of ligand orbitals of LGO with the metal orbitals occur along the octahedral axes. i.e. ligand orbitals overlap with those metal orbitals which lies on the axes.
- The central metal cation contains ns , np and $(n-1)d$ orbitals. These orbitals are divided by symmetry into four sets.

Metal orbitals	Symmetry	Degeneracy	
s	a_{1g}	1	Bonding
p_x, p_y, p_z	t_{1u}	3	
d_{xy}, d_{yz}, d_{zx}	t_{2g}	3	Non-bonding
$d_{x^2-y^2}, d_{z^2}$	e_g	2	Bonding

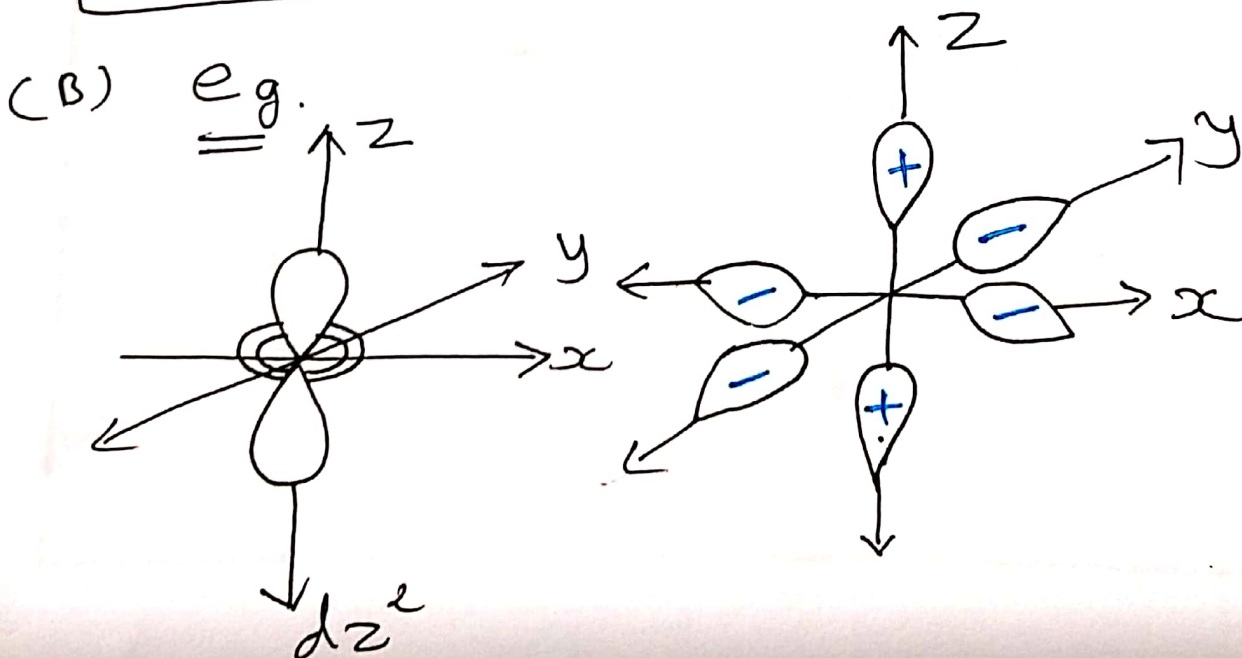
→ In order to formation of σ -bonds within the complex. There must be positive overlap of metal orbitals with the ligand orbitals directed along the bonding axes.

→ The metal and ligand orbitals must also have same sign a_{1g} orbitals is spherical and it overlaps with ligand orbitals on all the axes.

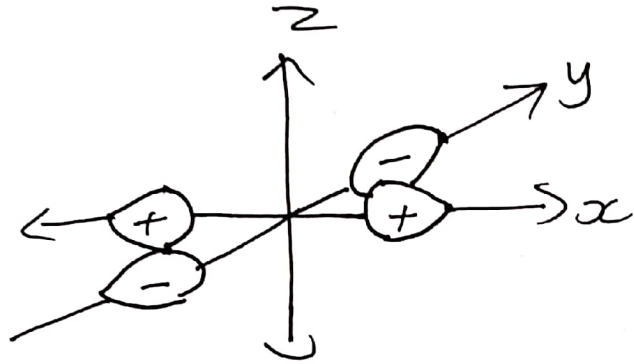
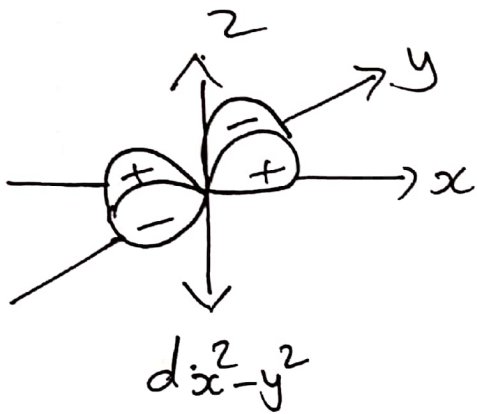
- The t_{1u} & e_g orbitals have lobes which lie on the axes and thus are capable of σ -bond formation.
- The lobes of t_{2g} orbitals lie in between the axes so these orbitals do not overlap with ligand orbitals. Thus t_{2g} orbitals are **non-bonding**.
- The LMO must have the a_{1g} , t_{1u} & e_g symmetry.
- The Bonding interaction between metal orbital and ligand orbital as shown in fig.



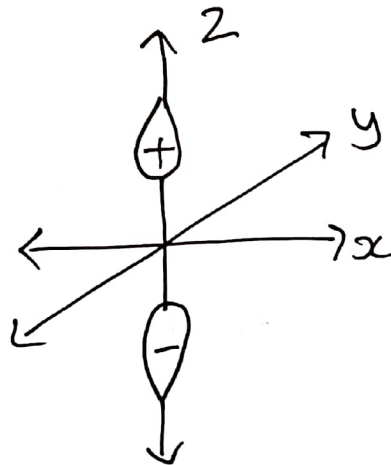
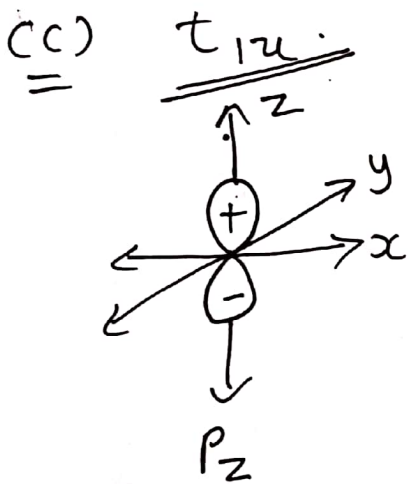
$$E_a = \frac{1}{\sqrt{6}} (\sigma_x + \sigma_{-x} - \sigma_y - \sigma_{-y} - \sigma_z - \sigma_{-z})$$



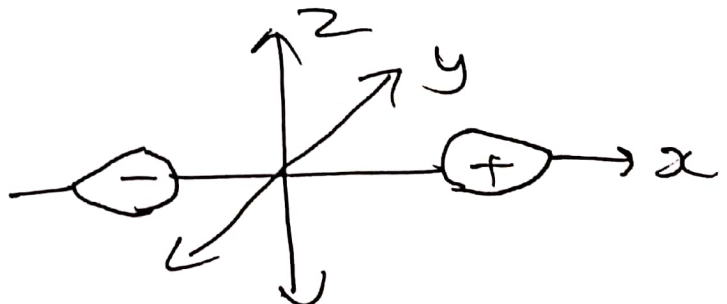
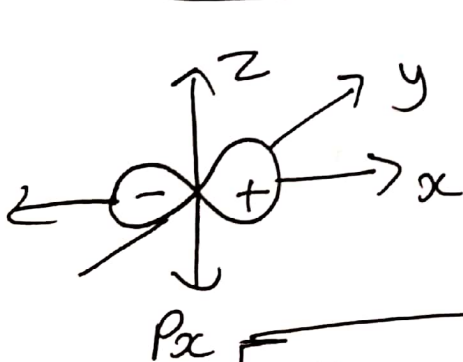
$$E_z = \frac{1}{2\sqrt{3}} [2\sigma_z + 2\sigma_{-z} - \sigma_x - \sigma_{-x} - \sigma_y - \sigma_{-y}]$$



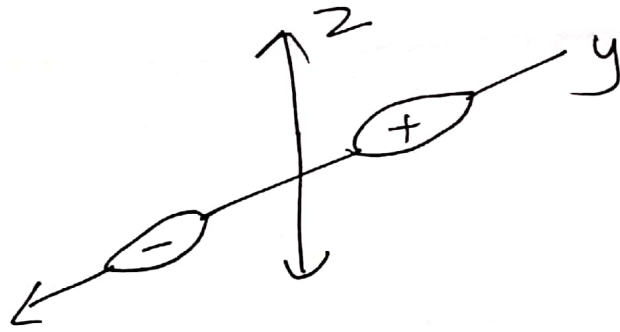
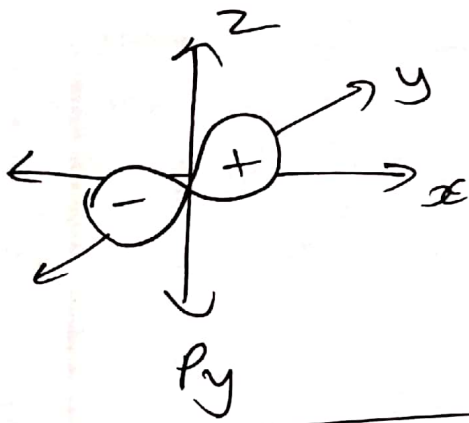
$$E_{x^2 - y^2} = \frac{1}{2} (\sigma_x + \sigma_{-x} - \sigma_y - \sigma_{-y})$$



$$E_z = \frac{1}{\sqrt{2}} (\sigma_z - \sigma_{-z})$$



$$E_x = \frac{1}{\sqrt{2}} (\sigma_x - \sigma_{-x})$$



$$E_y = \frac{1}{\sqrt{2}} (\sigma_y - \sigma_{-y})$$

- Since the six ligands are approaching along the $+x$, $-x$, $+y$, $-y$, $+z$ and $-z$ axes thus the ligand σ -orbitals are represented as σ_x , σ_{-x} , σ_y , σ_{-y} , σ_z and σ_{-z} respectively.
- Since the sign of the wave function for the metal a_{1g} ($4s$) orbital everywhere, the same which is taken to be positive.
- The six ligands can interact equally with this orbitals.
- The linear combination of ligand σ -orbitals which can overlap with the a_{1g} orbital is

$$\Sigma_{a_{1g}} = \frac{1}{\sqrt{6}} (\sigma_x + \sigma_{-x} + \sigma_y + \sigma_{-y} + \sigma_z + \sigma_{-z})$$

$\frac{1}{\sqrt{6}}$ = Normalisation constant.

→ Since one lobe of $4p_x$ orbital has positive sign and other has negative sign. Thus the linear combination of ligand σ -orbitals that can overlap with $4p_x$ orbital is

$$\Sigma_x = \frac{1}{\sqrt{2}} (\sigma_x - \sigma_{-x})$$

→ Similarly for $4p_y$ & $4p_z$ orbitals, the linear combination of ligand σ -orbitals that can overlap with $4p_y$ & $4p_z$ orbitals is

$$\Sigma_y = \frac{1}{\sqrt{2}} (\sigma_y - \sigma_{-y}) ;$$

$$\Sigma_z = \frac{1}{\sqrt{2}} (\sigma_z - \sigma_{-z})$$

→ The ligand σ -orbitals (LGOs) that can interact with $d_{x^2-y^2}$ orbital of metal will have components only along the x & y axes.

$$\Sigma_{x^2-y^2} = \frac{1}{2} (\sigma_x + \sigma_{-x} - \sigma_y - \sigma_{-y})$$

→ The ligand σ -orbitals (as LGO) that matches d_{z^2} metal orbitals is,

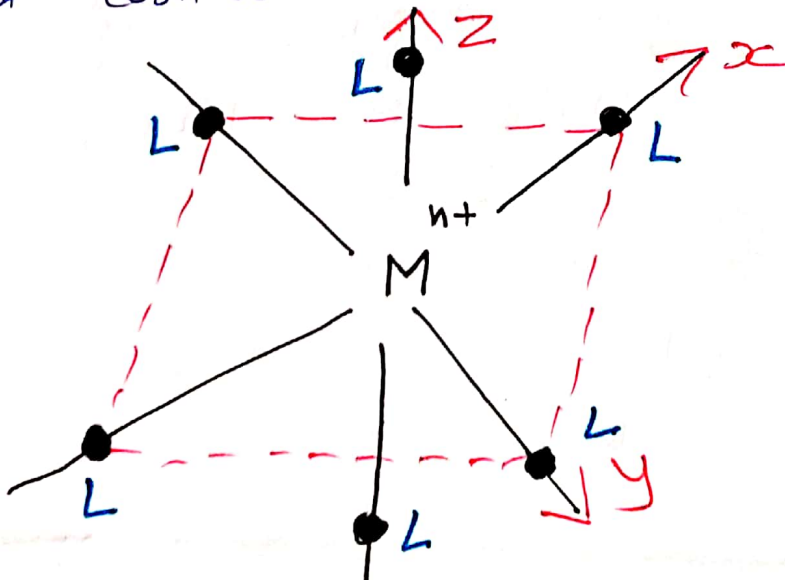
$$\Sigma_{z^2} = \frac{1}{2\sqrt{3}} (2\sigma_z + 2\sigma_{-z} - \sigma_x - \sigma_{-x} - \sigma_y - \sigma_{-y})$$

→ Since the LGO have no symmetry of t_{2g} , the t_{2g} orbitals will not participate in σ -bond formation and hence t_{2g} orbitals are non-bonding where there is no possibility of π -bonding.

→ If the LGO have appropriate symmetry, the t_{2g} orbitals can participate in π -bonding. In this case t_{2g} orbitals are represented by $\pi_{xy} = \pi_{yz} = \pi_{zx}$.

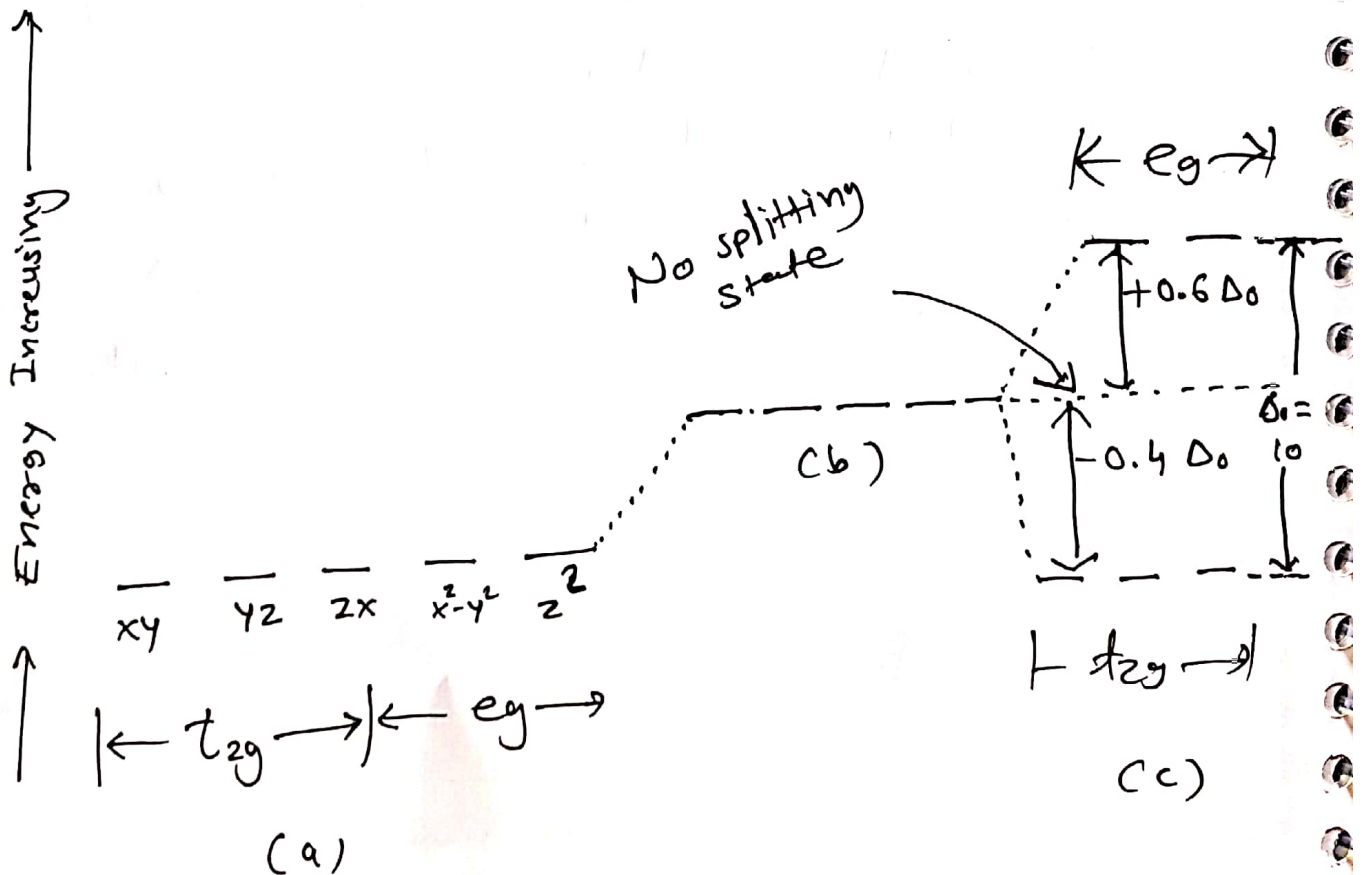
(*) Splitting of d-orbitals in Octahedral Complexes ∴

→ In an ~~octahedron~~ Octahedral complex, the central metal cation is at the centre of the octahedron and the ligands are at the six corners of the octahedron as shown in fig. The axes x , y & z point to three adjacent corners of the octahedron.



- Now. Suppose the ligands on each of the three axes are allowed to approach towards the central metal cation (M^{n+}) from both the ends of the axes.
- In this process the electrons in d-orbitals of the central metal cation are repelled by negative point of point charge or by negative end of the dipole at the ligands.
- The repulsion will raise the energy of all the five d orbitals.
- If all the ligands are symmetrically positioned, (ligands are at equal distance from each of the orbitals), the energy of each of five d-orbitals will raise by the same amount. (i.e. all the d-orbitals will still degenerate), but now they will have higher energy than before (free metal cation).
- This is only a hypothetical situation and all this energy state is called barycentre or centre of gravity.
- It is obvious that not all of the d-orbitals will be affected to the same extent.
- The lobes of the e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}) point along the axes x, y and z.
- The lobes of the t_{2g} orbitals (d_{xy} , d_{yz} , d_{zx}) point in between the axes.

- The d-orbitals lying along the axes ($d_{x^2-y^2}$ & d_{z^2}) will be more strongly repelled than the orbitals with lobes directed between the axes (d_{xy} , d_{yz} , & d_{zx}).
- Thus the energy of e_g orbitals ($d_{x^2-y^2}$ & d_{z^2}) will increase much more than the t_{2g} orbitals (d_{xy} , d_{yz} , & d_{zx}).
- Under the influence of an octahedral ligand field, the d-orbitals are, thus split into two sets with e_g orbitals at higher energy than t_{2g} orbitals.



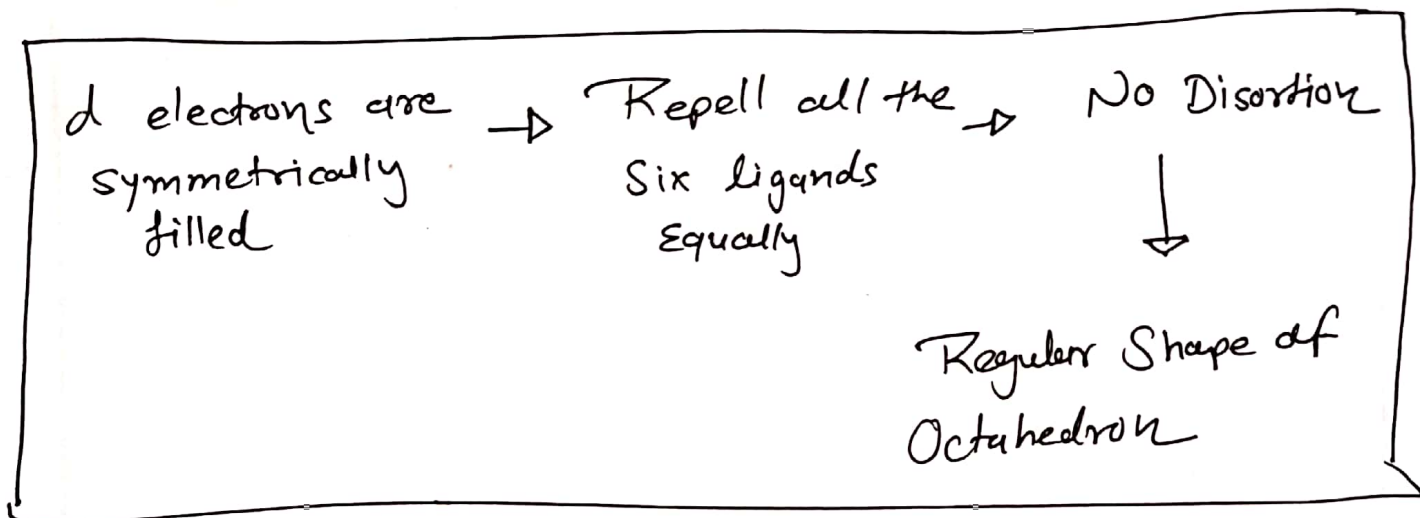
- Greater is the repulsion, greater will be the increase in energy.
- Thus under the influence of octahedral ligand field, the d-orbitals split into two sets of different energies.
- The energy difference between t_{2g} & e_g sets is denoted by Δ_0 or Dq . Where 0 in Δ_0 standing for octahedral. Δ_0 or Dq is called crystal field splitting energy.
- The energy of e_g orbitals is $0.6 \Delta_0 (= 6 Dq)$ higher than the hypothetical energy state and energy of the t_{2g} orbital is $0.4 \Delta_0 (= 4 Dq)$ lower than the hypothetical energy state.
- We can say that the t_{2g} orbitals are stabilized by amount $-0.4 \Delta_0$, while the e_g orbitals are destabilized by $0.6 \Delta_0$ with respect to the average energy state.

* Tetragonal distortion of Octahedral Complexes [Jahn Teller Distortion]

- It is a geometric distortion of non-linear molecule system which reduces its symmetry & energy typically. observed in octahedral complexes.
- Any non-linear molecular system in degenerate electronic state will be unstable and will undergo some sort of distortion to lower its symmetry and remove degeneracy.
- The shape of transition metal complexes is determined by the tendency of electron pairs to occupy position as far away from each other as possible.
- The shape of transition metal complexes are affected by whether the d orbitals are symmetrically or asymmetrically filled.
- Repulsion by six ligands in an octahedral metal split the d orbital on central metal into e_g & t_{2g} level.

→ There are three conditions for Distortion

• Condition: I :- No Distortion Condition



d orbital configuration

① d^3



e_g



t_{2g}

② d^5



e_g

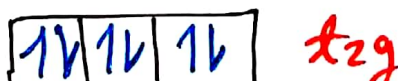


t_{2g}

③ d^6



e_g



t_{2g}

All are symmetrically filled d orbitals
i.e. there is no distortion

[15]

④ d^8



e_g



t_{2g}

Symmetrically filled-d orbitals. No distortion

⑤ d^{10}



e_g



t_{2g}

● Condition:- II : For Slight distortion

[When t_{2g} orbitals are asymmetrically filled]

① d^1



e_g



t_{2g}

② d^2



e_g



t_{2g}

③ d^4



e_g

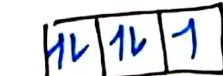


t_{2g}

④ d^5



e_g

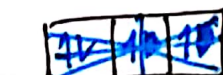


t_{2g}

⑤ d^6



e_g



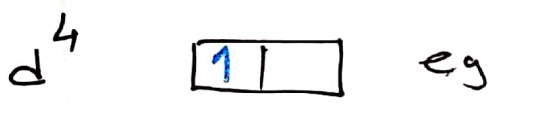
t_{2g}



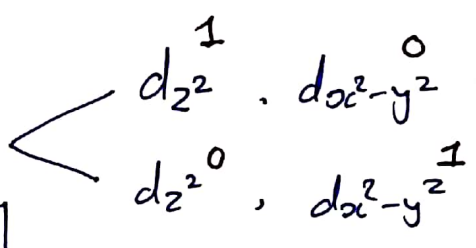
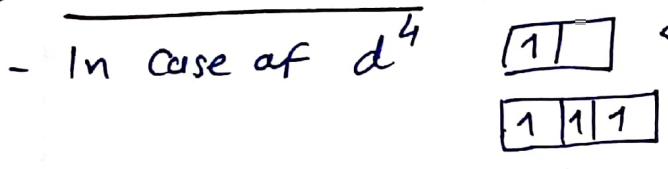
[16]

Condition III for strong distortion

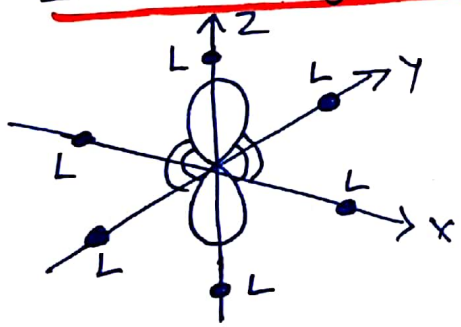
[eg orbitals are asymmetrically filled]



→ Cause of distortion:



- One electron in d_{z^2} orbital → more repulsion on ligand along the z-axis → Bond along the z-axis elongated → Tetragonal distortion.



Spectrochemical Series:-

* "It is the order of splitting power of ligands to split the metal d orbitals:"

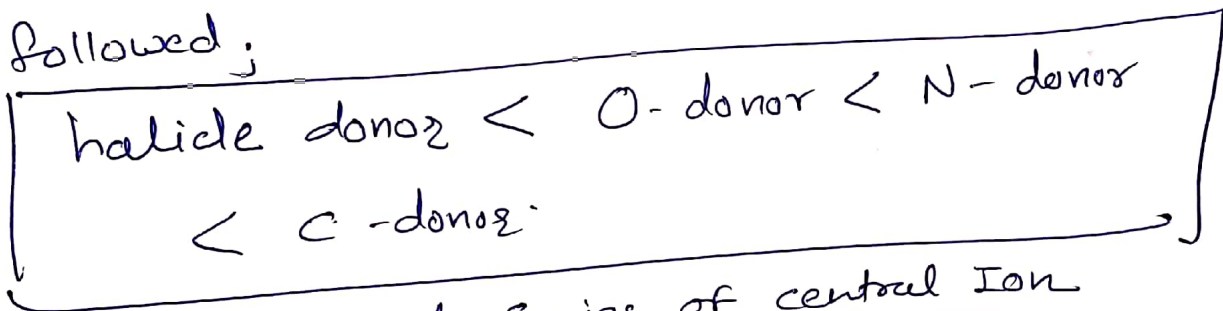
- $I^- < Br^- < S^{2-} < SCN^- < Cl^- < N_3^- < F^- < Urea < OH^- < ethanal < OX < O^{2-} < H_2O < EDTA < NCS^- < NO_2^- < CH_3^- < C_6H_5^- < CN^- < CO$.

→ The spectrochemical series is an experimentally determined series. It is difficult to explain the order as it incorporates both the effect of σ & π bonding.

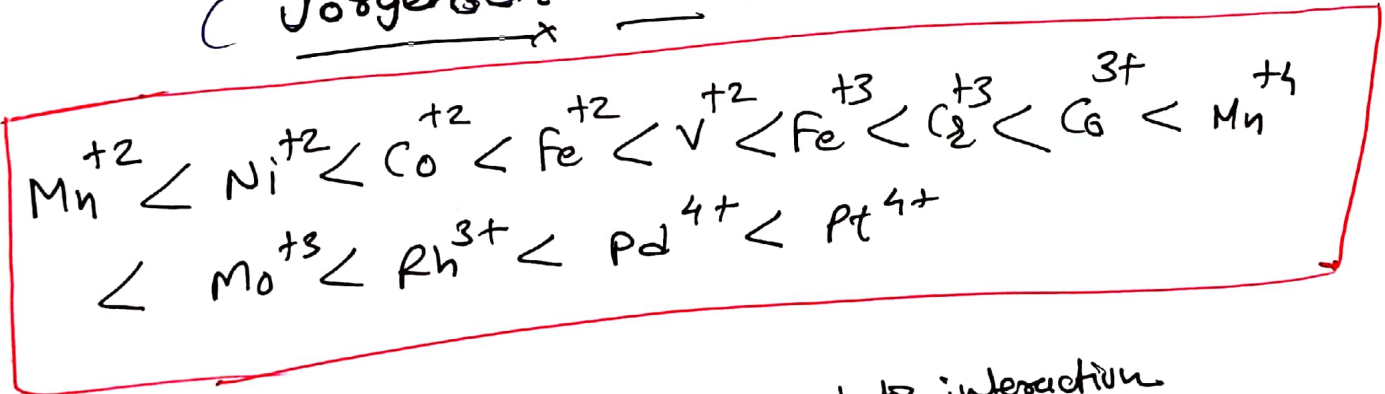
→ The halides are in the order expected from electrostatic effects.

→ In other cases we must consider covalent bonding to explain the order.

→ A pattern of increasing σ donation is followed;

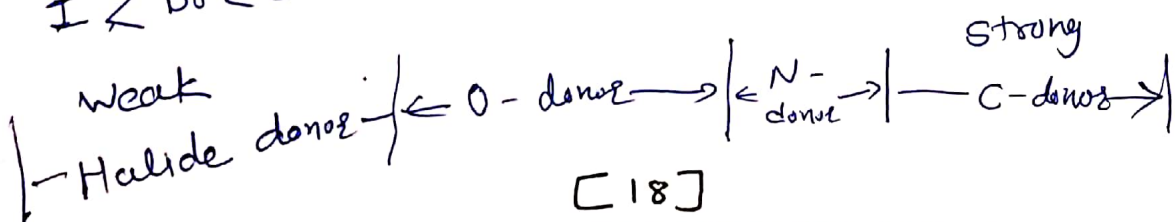
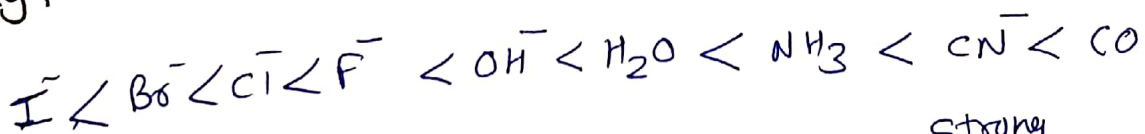


→ Spectrochemical Series of central Ion
(Jorgensen Series)



∴ weak field ligand : low electrostatic interaction

High field ligand : High electrostatic interaction



* The Nephelauxetic Series:-

- Racah parameters are empirical integers and are denoted by 'B' & 'C'.
- This parameter are used to determined the energy gap between two spectroscopic terms which arises due to electron-electron repulsion.
- In case of complexes, the value of Racah parameter (B) are found to be lower than that in the case of free metal cation.
- In the case of complexes, there is delocalization of electrons from metal cation to the ligands, Thus there is decrease in electron density on metal cation. Hence, electron-electron repulsion decreases. & the value of Racah parameter also decreases.
- The reduction in the value of Racah parameter (B) due to delocalization of electrons towards the ligands is called "Nephelauxetic Series".
- The nephelauxetic effect indicate that there is some covalent character behaviour of metal cation and ligand.

Nephelauxetic effect = Evidence for covalent character in complexes.

B' for complex $<$ B for free metal cation

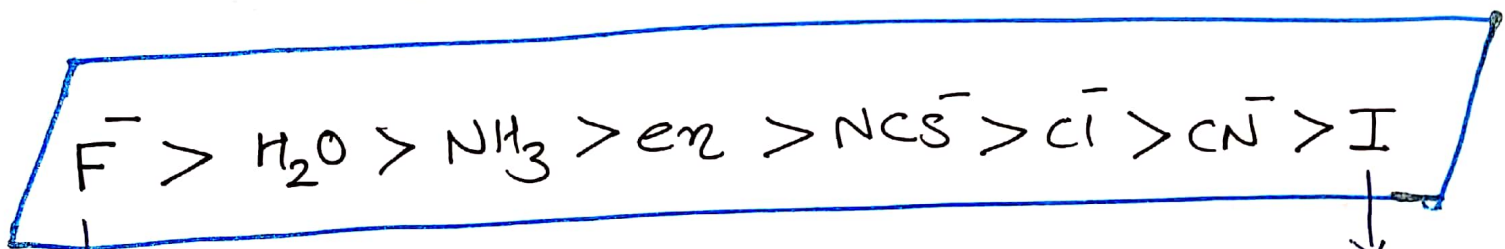
$$\therefore \text{Nephelauxetic parameter } (\beta) = \frac{B' \text{ complex}}{B \text{ metal cation}}$$

$$\therefore \beta = \frac{B'}{B} < 1$$

→ Lower the value of β , higher will be the covalent character.

→ Nephelauxetic Series:-

Nephelauxetic effect (increase)



Ionic character

Covalent character increase

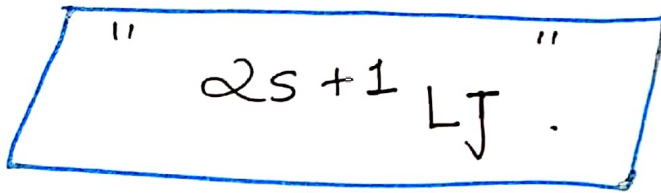
Covalent character

Nephelauxetic parameter (β)

∴ Electronic Repulsion ↓ β complex ↓ Nephelauxetic effect ↑

* Electronic state & term Symbol :-

→ The term symbol is represented as



→ Total Spin Angular Momentum (S)

→ Every electron in atom can be considered to be spinning about an axis as well as motion in orbit about the nucleus. Its spin motion is designated by the spin quantum number 's' which can have a value of $+\frac{1}{2}, 0, -\frac{1}{2}$.

→ Total Orbital Angular Momentum (L)

→ An electron moving in its orbital about a nucleus possesses orbital angular momentum, It is denoted as "L".

L →	0	1	2	3	4	5	6
	↓	↓	↓	↓	↓	↓	↓	
	S	P	D	F	G	H	I
	"Term Symbol."							

→ Total Angular Momentum "J"

→ It is the sum of orbital angular momentum and spin angular momentum.

$$\boxed{J = L + S}$$

→ j value can be calculated by L-S coupling.

$|L + S|$ → More than Half field

$|L - S|$ → Less than Half field.

→ " $2S + 1$ " is known as spin multiplicity.

Example 1: Oxygen (Find out the term symbol.)

Electronic Configuration $1s^2 \underline{2s^2 2p^4}$

— We need to calculate the valance shell electron. i.e. 6.

Magnetic quantum No.

→ $\begin{array}{|c|} \hline +1/2 \quad -1/2 \\ \hline 1 \\ \hline \end{array}$
 $2s^2$

$$\begin{array}{|c|c|c|} \hline +1/2 & -1/2 & +1/2 \\ \hline 1 & 1 & 1 \\ \hline \end{array}$$

 $2p^4$

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

$$\boxed{S = 1}$$

[22]

$$\begin{aligned} \therefore \text{Spin multiplicity} &= 2s + 1 \\ &= 2(1) + 1 \\ &= 2 + 1 \end{aligned}$$

$$\boxed{2s + 1 = 3.}$$

→ Calculation of "L":

$$\begin{array}{c} \boxed{1L} \\ 0 \end{array} \quad \begin{array}{c} \boxed{1L \quad 1 \quad 1} \\ +1 \quad 0 \quad -1 \end{array}$$

$$\begin{aligned} \therefore L &= [2 \times (0)] + [2 \times (+1)] + [1 \times (0)] + [1 \times (-1)] \\ &= 0 + 2 + 0 - 1 \\ &= 2 - 1 \end{aligned}$$

$$\boxed{L = 1 \Rightarrow P}$$

$$\begin{array}{cccccc} \therefore L \Rightarrow & 0 & \boxed{1} & 2 & 3 & 4 & 5 \\ & S & \boxed{P} & D & F & G & H \end{array}$$

→ Calculation of J value:-

$$\begin{aligned} \therefore J &= |L + S| \\ &= |1 + 1| \\ &= |2| \end{aligned}$$

$$\boxed{J = 2}$$

→ Therefore, term symbol = ${}^{2s+1}L_J = {}^3P_2$

[23]

→ If we ignore the value of J, then it is called term.

→ If we calculate the value of J, then it is called Level.

∴ For Oxygen, the Level is 3P_2 & term is 3P .

Example 1- 2

→ The ground state term for a free ion with d^1 configuration.

2	1	0	-1	-2
1				

$$\therefore S = \frac{1}{2}$$

$$\therefore L = 2 \times 1 = 2 \quad \therefore L \rightarrow D.$$

$$\therefore J = |L - S| = \left| 2 - \frac{1}{2} \right| = \left| \frac{3}{2} \right|$$

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

$$\therefore \text{Term symbol} = {}^{2S+1}L_J = {}^2D_{3/2}$$

* Microstates :-

→ The electronic configuration of an atom, ion or molecule is an incomplete description of the arrangement of electrons in atoms.

→ In the configuration p^2 , for instance, the two electrons might occupy orbitals with different orientation of their orbital angular momenta.

→ The different ways in which the electrons can occupy the orbitals specified in the configuration are called "microstates" of the configuration.

→ Calculation of number of Microstates :-

$$\therefore \text{No. of microstates} = \frac{N!}{x!(N-x)!}$$

∴ where $N = 2(2l+1) =$ Twice the no. of orbitals.

$x =$ Number of electrons.

Example :- p^2 - $p_x, p_y, p_z = 3$ orbitals

$$N = 6, \quad x = 2$$

$$\therefore \text{No. of Microstates} = \frac{6!}{2!(6-2)!} = \frac{6 \times 5 \times 4 \times 3 \times 2 \times 1}{2 \times 1 \times 4 \times 3 \times 2 \times 1} = 15$$

[25]

★ Term Symbol for Closed Subshell

Configuration :- (s^2, p^6, d^{10})

→ If a subshell is completely filled, such as $s^2, p^6, \text{ or } d^{10}$ configuration, both L and S are zero. This closed shell always gives $1S_0$ term symbol.

→ Calculation of Ground state Term & Ground state term symbol.

Steps :-

- 1) Write the electronic configuration
- 2) Determine the spin multiplicity $(2S+1)$
- 3) Determine the maximum possible value M_L . $(= \sum m_l) \sum m_l$.
- 4) Select maximum value of J for more than half filled subshell and minimum J value for less than half filled shell.
" [26]

⇒ For s^2 configuration:-

→ Electronic Configuration:- 1s

→ $S = +\frac{1}{2} - \frac{1}{2} = 0$

∴ $2S + 1 = 2(0) + 1 = 1$

∴ $L = 0 \Rightarrow \boxed{L \Rightarrow S}$

→ ∴ $J = |L + S| \dots |L - S| = 0$

∴ Term Symbol = $^{2S+1}L_J = {}^1S_0$

⇒ For p^6 configuration:-

	+1	0	-1
-	↑↓	↑↓	↑↓
	$+\frac{1}{2} - \frac{1}{2}$	$+\frac{1}{2} - \frac{1}{2}$	$+\frac{1}{2} - \frac{1}{2}$

- $S = +\frac{1}{2} - \frac{1}{2} + \frac{1}{2} - \frac{1}{2} + \frac{1}{2} - \frac{1}{2} = 0$

- $2S + 1 = 2(0) + 1 = 1$

- $L = +1 + 0 - 1 = 0 \Rightarrow \boxed{L \Rightarrow S}$

- $J = |L + S| \dots |L - S| = 0$

- Term Symbol = $^{2S+1}L_J = {}^1S_0$

\Rightarrow For d^{10} configuration :-

+2	+1	0	-1	-2
$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$

- $S = 0$ (\because No unpaired electron)
- $2S + 1 = 2(0) + 1 = 1$
- $L = 0 \Rightarrow \boxed{L \Rightarrow S}$
- $J = 0$
- Term symbol :- ${}^{2S+1}L_J = {}^1S_0$

(*) Problems :- (Self calculation)

Calculate the term symbol for following configurations :- $s^1, p^1, p^2, p^3, d^1, d^2, d^3, d^4, d^5$ etc. -

⊛ Derivation of term for p^2, d^2 configuration.

⇒ For p^2 configuration

+1	0	-1
1	1	
$+1/2$	$+1/2$	

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

$$\therefore 2S+1 = 2(1)+1 = 3$$

$$\therefore L = (+1) + (0) = +1$$

$$\therefore \boxed{L \Rightarrow P}$$

$$\begin{aligned} \rightarrow J &= |L \pm S| \quad (\text{Less than half filled}) \\ &= |1 - 1| \\ &= 0 \end{aligned}$$

$$\therefore \text{Ground state term} = {}^{2S+1}L = {}^3P$$

$$\therefore \text{Ground state term symbol} = {}^{2S+1}L_J = {}^3P_0$$

→ For d^2 configuration :-

+2	+1	0	-1	-2
1	1			

$+1/2$ $+1/2$

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

$$2S+1 = 2(1)+1 = 3$$

$$\rightarrow L = 2+1 = 3 \quad \therefore \boxed{L = D \quad D}$$

$$\rightarrow J = |L-S| \quad (\text{Less than half filled subshell})$$

$$= |3-1|$$

$$\boxed{J = 2}$$

$$\rightarrow \text{Ground state term} = {}^{2S+1}L = {}^3D$$

$$\rightarrow \text{Ground state term symbol} = {}^{2S+1}L_J = {}^3D_2$$