

## Notes :

Werner CFSE 1893

 $e^-$  1896

## • Oxidation state

+3

+1

+3

+3

+4

+4

+3

+3

+1

overlap (covalent)

## • Valence Bond theory

CN

Geom

2

linear

L - m - L

3

trigonal planar

L - m - L  
  |  
  |

4

tetrahedral

sq. planar

5

trigonal bipyramidal

sq. pyramidal



## Octahedral

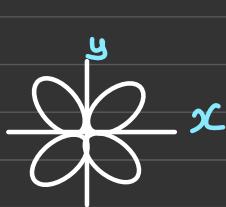
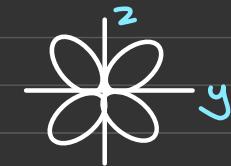
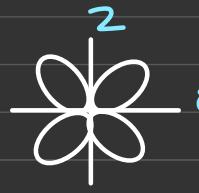
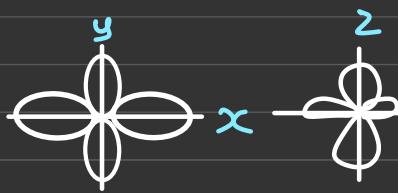
## • CFT

features :-

The two limitations of crystal field theory are it ignores contributions of s and p orbital of the metal and it says nothing about the orbitals of ligands. It has certain number of

- ① The metal centre and ligands are considered as point charges & the interaction b/w metal & ligand is purely electrostatic
- ② The ligand is -ve and metal +ve charge
- ③ No overlapping of atomic orbitals
- ④ for neutral ligands, the -ve end of dipole is oriented towards +ve charged metal centre
- ⑤ e's of metal and ligand have repulsive interaction thus, e's of the metal try to occupy those orbitals which are away from ligand

The five d orbitals :-

 $dxz$  $dyz$  $dxy$  $dz^2$ 

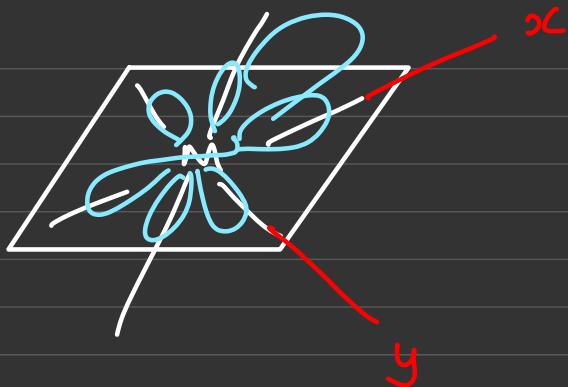
non-axial

axial

CFSE in Octahedral ligand field

Baricentre





- Spectrochem series

The ligands arranged in the ascending order of CFSE ( $\Delta$ ) is called as Spectrochem Series

The series is experimentally obtained by spectroscopy

It is independent of CMA and geometry of complex

It incorporates the effect of  $\sigma$  +  $\pi$  bonding

**Series Order :** halo < 'O' donor < 'N' donor < 'C' donor

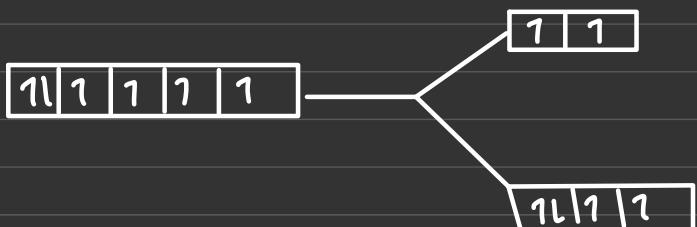
**Series :**  $\frac{I^- < Br^- < Cl^- < F^-}{\text{halo}} < \frac{\text{OH}^- < EtOH < C_2O_4^{2-}}{O}$

$\frac{H_2O < EDTA^{4-} < NH_3 \text{ & Pyridine} < en}{O}$

$\frac{dipyridyl < O\text{-phenanthroline}}{N} < \frac{NO_2^- < CN^-}{C}$

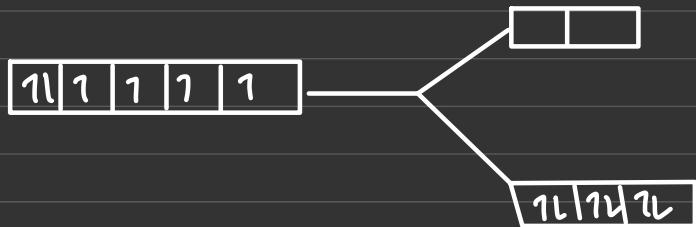
$\frac{Cu}{C}$

- High spin & low spin



WFL (no pairing)  
 $\Delta_o < P$   
 $n = 4$   
paramagnetic  
High spin

eg  $[\text{Co}(\text{NH}_3)_6]^{3+}$



SFL (Pairing)

$$\Delta_0 > P$$

$$n = 0$$

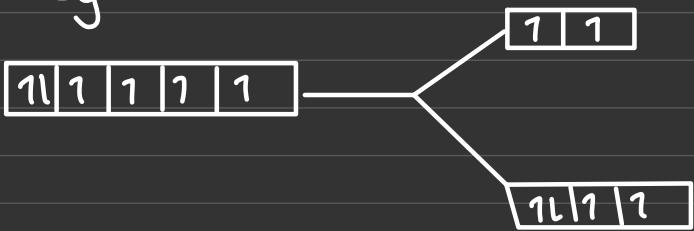
diamagnetic

Low spin

- CFSE (Crystal field stabilization energy)

$$\text{CFSE} = \left[ (-0.4 \times n_{t2g}) + (0.6 \times n_{eg}) \right] \Delta_0 + mP$$

eg



- Spin only magnetic moment ( $M_{sp}$ )

$$\sqrt{n(n+1)}$$

$$n = 1 = 1.73$$

$$n = 2 = 2.82$$

$$n = 3 = 3.87$$

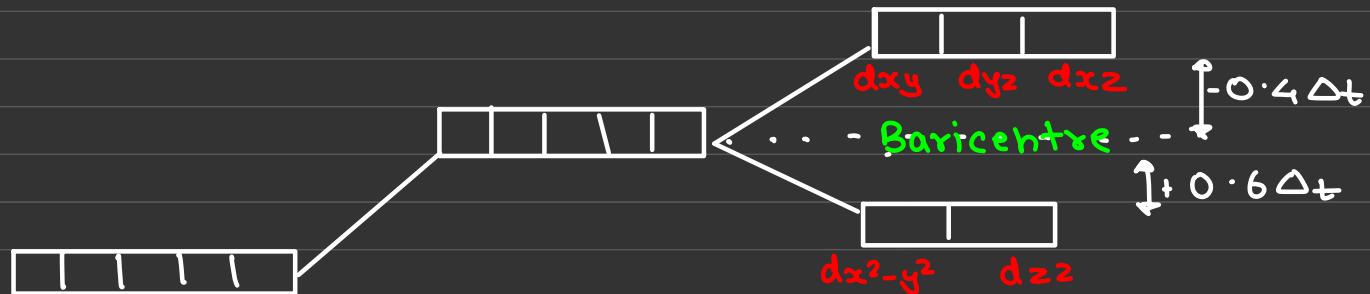
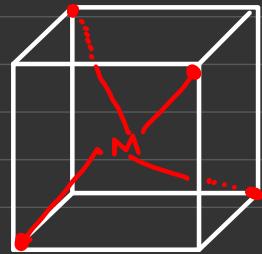
$$n = 4 = 4.89$$

$$n = 5 = 5.91$$

No of e's in d orbital	Arrangement	CFSE	Msp
d <sub>1</sub> WFL SFL	 	$(-0.4 \times 1) \Delta_0$ $\approx -0.4 \Delta_0$	1.73
d <sub>2</sub> WFL SFL	 	$(-0.4 \times 2) \Delta_0$ $\approx -0.8 \Delta_0$	2.87
d <sub>3</sub> WFL SFL	 	$(-0.4 \times 3) \Delta_0$ $-1.2 \Delta_0$	3.89
d <sub>4</sub> WFL SFL	 	$(-0.4 \times 4) \Delta_0$ $+ (0.6 \times 1) \Delta_0$ $\approx -0.6 \Delta_0$	4.89
SFL	 	$(-0.4 \times 4) \Delta_0$ $-1.6 \Delta_0$ $\rightarrow p$	2.82
d <sub>5</sub> WFL	 	$(-0.4 \times 3) \Delta_0$ $+ (0.6 \times 2) \Delta_0$ $= 0$	5.91
SFL	 	$(-0.4 \times 5) \Delta_0$ $-2 \Delta_0$ $+2p$	1.73
d <sub>6</sub> WFL	 	$(-0.4 \times 4) \Delta_0$ $+ (0.6 \times 2) \Delta_0$ $\approx -0.4 \Delta_0$ $+p$	4.89

<p><b>SFL</b></p>	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33.33%;"></td><td style="width: 33.33%;"></td><td style="width: 33.33%;"></td></tr> <tr> <td>1L</td><td>1L</td><td>1L</td></tr> </table>				1L	1L	1L	$(-0.4 \times 6) \Delta_0 \\ = -2.4 \Delta_0 \\ + 3P$	0
1L	1L	1L							
<p><b>d<sub>7</sub> WFL</b></p>	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33.33%; text-align: center;">117</td> <td style="width: 33.33%;"></td> <td style="width: 33.33%;"></td> </tr> <tr> <td>1L</td><td>1L</td><td>7</td> </tr> </table>	117			1L	1L	7	$(-0.4 \times 5) \Delta_0 \\ + (0.6 \times 2) \Delta_0 \\ = -0.8 \Delta_0 \\ + 2P$	3.89
117									
1L	1L	7							
<p><b>SFL</b></p>	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33.33%; text-align: center;">11</td> <td style="width: 33.33%;"></td> <td style="width: 33.33%;"></td> </tr> <tr> <td>1L</td><td>1L</td><td>1L</td> </tr> </table>	11			1L	1L	1L	$(-0.4 \times 6) \Delta_0 \\ + (0.6 \times 1) \Delta_0 \\ = -1.8 \Delta_0 \\ + 3P$	1.73
11									
1L	1L	1L							
<p><b>d<sub>8</sub> WFL SFL</b></p>	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33.33%; text-align: center;">111</td> <td style="width: 33.33%;"></td> <td style="width: 33.33%;"></td> </tr> <tr> <td>1L</td><td>1L</td><td>1L</td> </tr> </table>	111			1L	1L	1L	$(-0.4 \times 6) \Delta_0 \\ + (0.6 \times 2) \Delta_0 \\ = -1.2 \Delta_0 \\ + 3P$	2.42
111									
1L	1L	1L							
<p><b>d<sub>9</sub> WFL SFL</b></p>	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33.33%; text-align: center;">741</td> <td style="width: 33.33%;"></td> <td style="width: 33.33%;"></td> </tr> <tr> <td>1L</td><td>1L</td><td>1L</td> </tr> </table>	741			1L	1L	1L	$(-0.4 \times 6) \Delta_0 \\ + (0.6 \times 3) \Delta_0 \\ = -0.6 \Delta_0 \\ + 4P$	1.73
741									
1L	1L	1L							
<p><b>d<sub>10</sub> WFL SFL</b></p>	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33.33%; text-align: center;">747</td> <td style="width: 33.33%;"></td> <td style="width: 33.33%;"></td> </tr> <tr> <td>1L</td><td>1L</td><td>1L</td> </tr> </table>	747			1L	1L	1L	$(-0.4 \times 6) \Delta_0 \\ + (0.6 \times 4) \Delta_0 \\ = 0 \\ + 5P$	0
747									
1L	1L	1L							

- CFSE (tetrahedral)



$$CFSE = [(-0.6 \times \text{neg}) + (0.4 \times n_{t_{2g}})]\Delta t + p$$

Note  $\Delta t < p$  (always)  
 $\therefore$  only High spin

- Factors affecting CFSE

- ① O.S ↑ , CFSE ↑
- ② no. of d e<sup>-</sup>s ↑ , CFSE ↑ [cos of shielding]
- ③ Pairing energy ↑ , CFSE ↑
- ④ CFSE 3d < 4d < 5d

No of e <sup>-</sup> s in d orbital	Arrangement	CFSE	Msp
d <sup>1</sup>	 	$(-0.6 \times 1) \Delta_t$ $- 0.6 \Delta_t$	1.73
d <sup>2</sup>	 	$(-0.6 \times 2) \Delta_t$ $= -1.2 \Delta_t$	2.84
d <sup>3</sup>	 	$(-0.6 \times 3) \Delta_t$ $+ 0.4 \Delta_t$	1.73
d <sup>4</sup>	 	$(-0.6 \times 2) \Delta_t$ $(+0.4 \times 2) \Delta_t$ $= -0.4 \Delta_t$	4.89
d <sup>5</sup>	 		
d <sup>6</sup>	 		
d <sup>7</sup>	 		
d <sup>8</sup>	 		

d<sub>9</sub>

1L	1L	1L
----	----	----

1L	1L
----	----

d<sub>10</sub>

1L	1L	1L
----	----	----

1L	1L
----	----

- Relation b/w  $\Delta_0$  &  $\Delta_t$

$$\Delta_t = \frac{4}{9} \Delta_0 ; \frac{9}{4} \Delta_t \neq \Delta_0$$

also,  $\Delta_0 = 10 D_{0g}$   
L unit.

e.g. Determine CFSE &  $M_{sp}$  of d<sub>6</sub>(Octa) having  
 $\Delta_0 = 25,000 \text{ cm}^{-1}$  &  $P = 15,000 \text{ cm}^{-1}$  in  
 both WFL & SFL

$$\begin{aligned} \text{SOL} \quad \text{WFL} &= -0.4 (25K) + (15K) \text{ cm}^{-1} \\ &\approx -10,000 + 15,000 \\ &= 5000 \text{ cm}^{-1} \end{aligned}$$

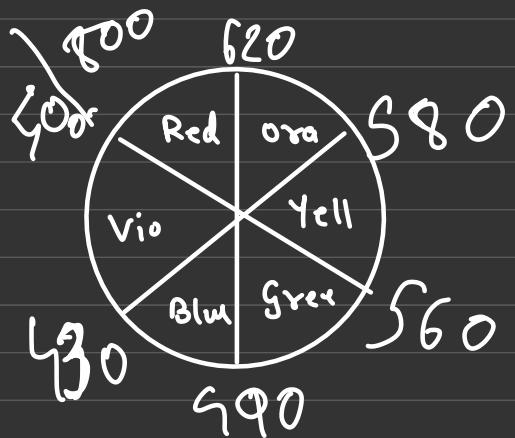
$$\text{SFL} = -2.4 (25000) + 3 (15000)$$

$$= 2.4$$

$$\begin{aligned} &- 60,000 + 2 \\ &= -15,000 \text{ cm}^{-1} \end{aligned}$$

- Optical properties

## ① Color of comp.



The (Octa) complex  $[Ti(H_2O)_6]^{+3}$  has a single d e<sup>-</sup>s to excite this e<sup>-</sup> from ground state t<sub>2g</sub> to eg orbital, this complex absorbs light from 450 - 600 nm, the max<sup>m</sup> absorbance corresponds to Δ<sub>0</sub> and occurs at 499 nm

Calculate the value of Δ<sub>0</sub> in joules and predict the color of the complex

$$E = \frac{hc}{\lambda} = \frac{12400}{\lambda} \text{ A}^{\circ} =$$

The co-ordination comp. with SFL are usually yellow, orange or Red in color, on the other hand with WFL they are often Blue, green or indigo in color.

### \* For SFL

energy gap ↑, splitting energy ↑, λ<sub>abs</sub> ↑

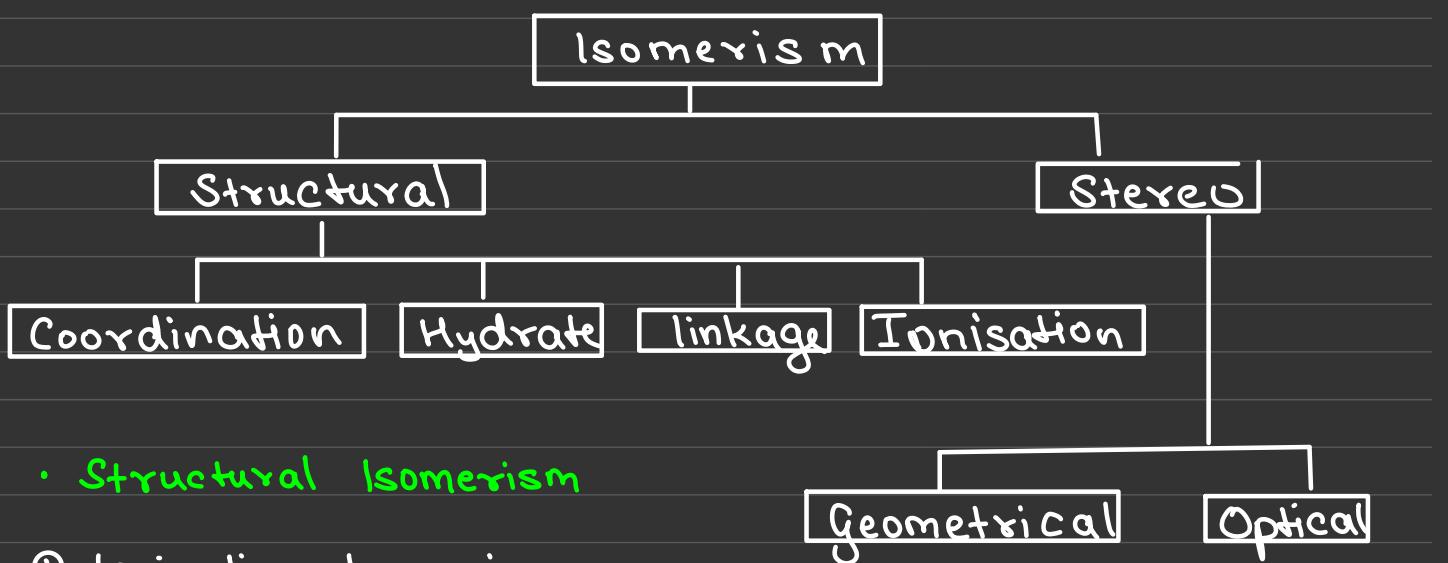
### For WFL

energy gap ↓, splitting energy ↓, λ<sub>abs</sub> ↑

The striking colors exhibited by transition-metal complexes are caused by excitation of an electron from a lower-energy d orbital to a higher-energy d orbital, which is called a **d-d transition** (Figure 3.12.4). For a photon to effect such a transition, its energy must be equal to the difference in energy between the two d orbitals, which depends on the magnitude of Δ<sub>0</sub>.

\* Cu(I) complex such as CuI tend to be colorless whereas Cu(II) is bright because, Cu(I)  $3d^10 \rightarrow$  no unpaired e<sup>-</sup>s  
 Cu(II)  $3d^9 \rightarrow$  paired e<sup>-</sup>s  
 ∴ colorless  
 ∵ color

## • Isomerism



### • Structural Isomerism

#### ① Ionisation Isomerism



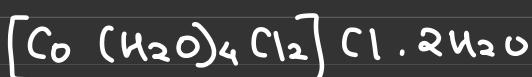
#### ② Hydrate isomerism



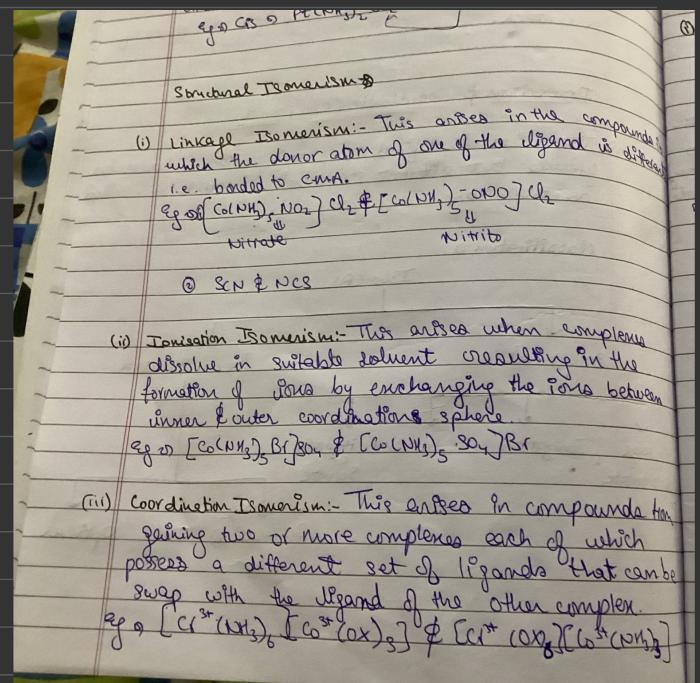
violet



red



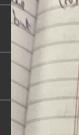
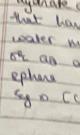
dark green



### ③ Linkage isomerism (only in ambidentate ligands)



(A) hydrate or solvate isomers: It refers to the isomers that have same composition but differ in whether water molecule is directly linked to CN or N ligand or as a potential counter molecule outside the sphere.  
e.g.  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}] \text{Cl}_2 \cdot \text{H}_2\text{O}$

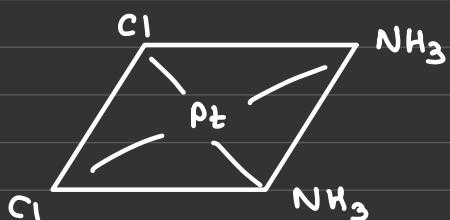
Stereoisomerism  
 1) general: e.g.  $\text{H}_2\text{O}$  attached to one face.  
 2) symmetrical

### ④ Co-ordination isomerism

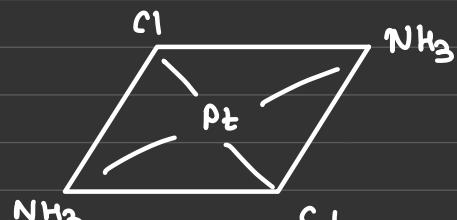


#### • Geometrical Isomerism

##### ① $[\text{MA}_2\text{B}_2]$

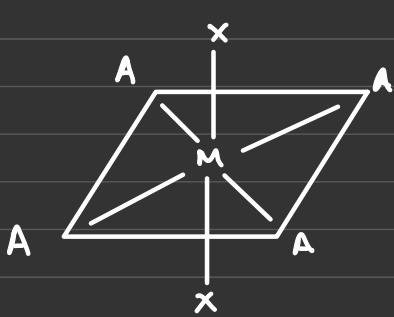


Cis - platin

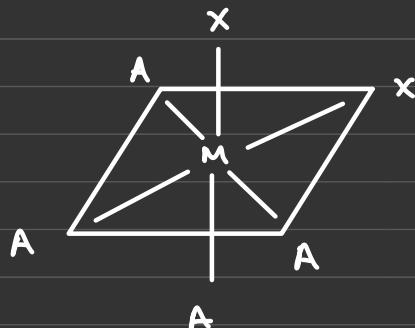


trans - platin

##### ② $[\text{MA}_4\text{X}_2]$

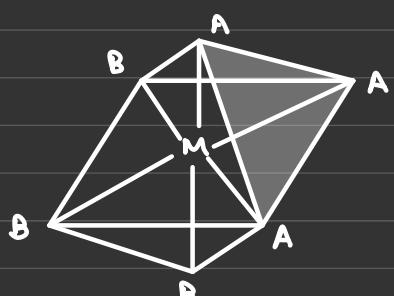


trans

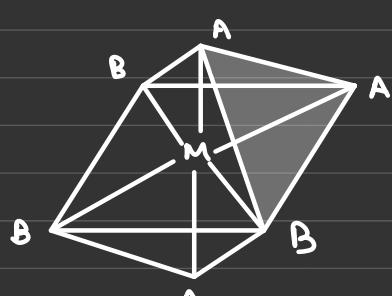


cis

##### ③ $[\text{MA}_3\text{B}_3]$

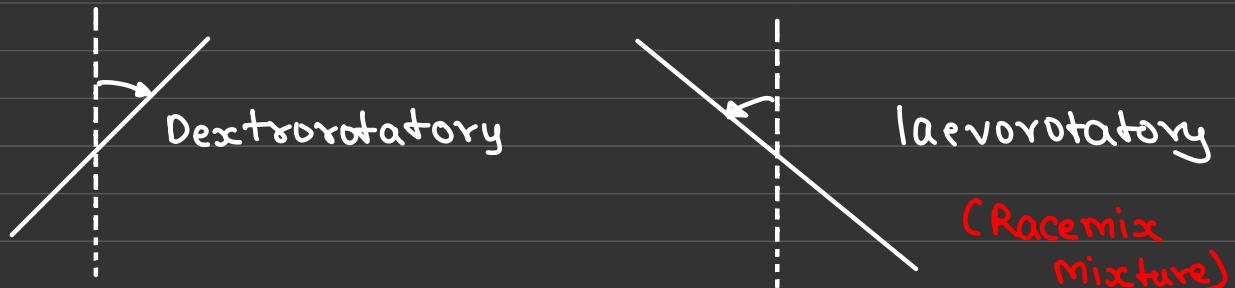
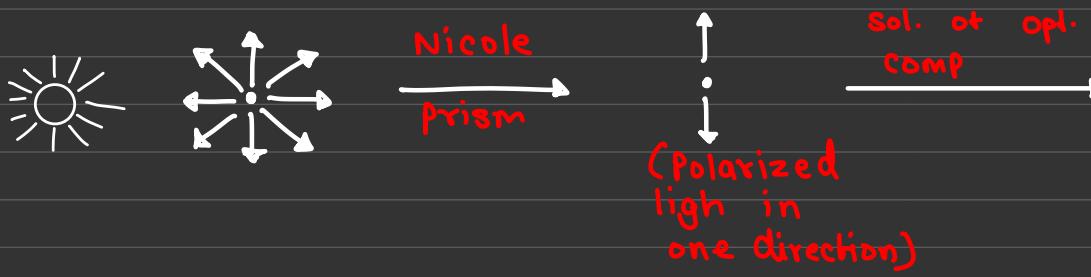


Facial



Mixed

## • Optical Isomerism



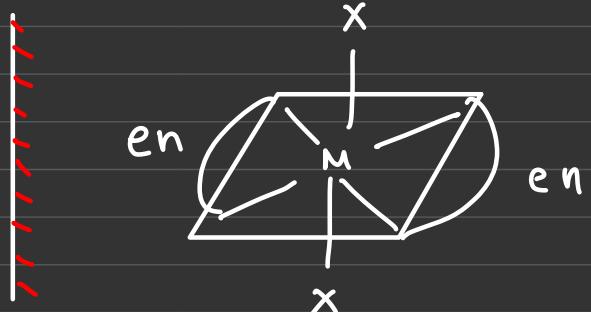
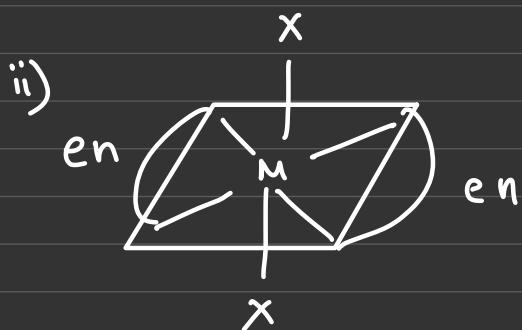
**Criteria for optical :-**

- Non - superimposable mirror img
- No plane of symmetry

eg:- i)

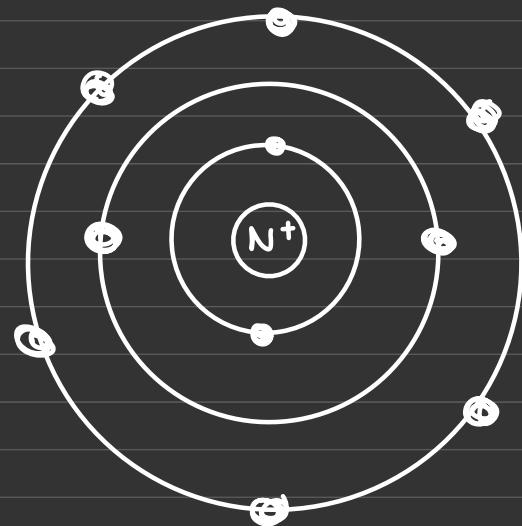


(Optical active) [ follows both criteria ]



optically inactive

## • Effective Nuclear Charge ( $Z_{\text{eff}}$ )



$$Z_{\text{eff}} = Z - \sigma$$

atomic no

Screening / Shielding const.

## • Factors affecting splitting

① Nature of ligand (Spectrochem Series)

② Oxidation state of metal

OS ↑, size ↓, Interact with ↑, splitting ↑  
ligand

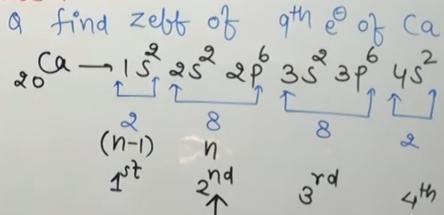
## • Slater's Rule

### Calculation of $Z_{\text{eff}}$

#### Slater's Rule #

- Case ① If  $e^-$  in question resides in s or p subshell
- All  $e^-$ 's present in shells higher than in question contribute zero to  $\sigma$
  - All  $e^-$ 's present in same shell contribute 0.35 to  $\sigma$
  - All  $e^-$ 's present in  $(n-1)$  shell contribute 0.85 to  $\sigma$
  - All  $e^-$ 's present in deep shells contribute 1 to  $\sigma$

### Periodic Table



$$\sigma = 2 \times 0.85 + 7 \times 0.35 + 8 \times 0 + 2 \times 0$$

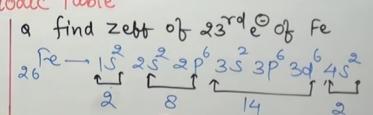
$$Z_{\text{eff}} = 20 - \sigma =$$

### Calculation of $Z_{\text{eff}}$

#### Slater's Rule #

- Case ② If  $e^-$  in question resides in d or f subshell
- All  $e^-$ 's present in shells higher than in question contribute zero to  $\sigma$
  - All  $e^-$ 's present in same shell contribute 0.35 to  $\sigma$
  - All  $e^-$ 's present in  $(n-1)$  & lower shell contribute 1 to  $\sigma$

### Periodic Table



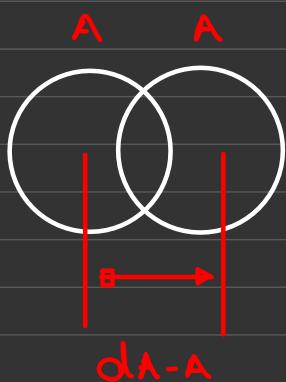
$$\begin{aligned} \sigma &= 10 \times 1 \\ \sigma &= 13 \times 0.35 + 2 \times 0 \\ Z_{\text{eff}} &= 26 - \sigma \end{aligned}$$

## • Atomic radius

We cannot calc. atomic rad. coz of :-

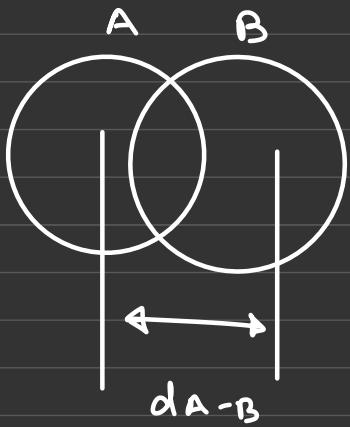
- i) The position is not fixed (wave nature)
- ii) The atom is not isolated i.e. always bonded

## Covalent rad.



$$r_A = \frac{d_{A-A}}{2}$$

## Ionic rad.



Two cases

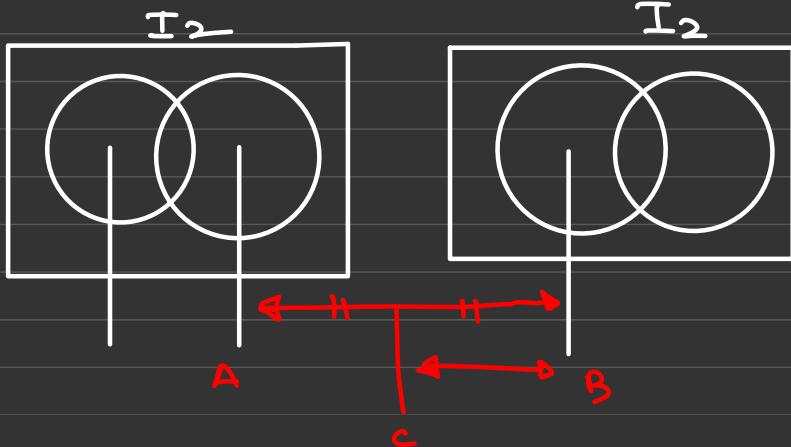
$$\text{i) } \Delta \chi = \text{low}$$

$$d_{A-B} = r_A + r_B$$

$$\text{ii) } \Delta \chi = \text{high (HCl)}$$

$$d_{A-B} = r_A + r_B - 0.09(\chi_A - \chi_B)$$

## Vanderwaal's rad.



$A-B$  = Vand. intermol. dist.

$C-D$  = Vand. rad.

## Ionic rad.

$L \rightarrow R$   $\downarrow$

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

$T \rightarrow B$   $\uparrow$

$$M^- < M^{-2} < M^{-3}$$

### • Ionisation energy

↳ eng. req. to remove outermost e's from isolated gaseous atom to convert into catio~

### • Factors

① Atomic size  $\uparrow$ , IE  $\downarrow$

②  $Z_{\text{eff}} \uparrow$  IE  $\uparrow$

③ Half & fully

④ Quantum No (Shell)

⑤ Elec. conf.

$d^5 < p^3 < d^{10} < p^6$  (Stability)

eg 2<sup>nd</sup> period

expected  $Li < Be < B < C < N < O < F < Ne$

actual  $Li < B < Be < C < O < N < F < Ne$

## • Electron Affinity

Amt. of energy released when an  $e^-$  is added to isolated gas atom to convert to anion

Q.J) i)  $Ca^{+2}$  has smaller ionic rad. frm  $K^+$

ii) On going frm C  $\rightarrow$  N values of  $e^-$  affinity  $\downarrow$  instead of  $\uparrow$

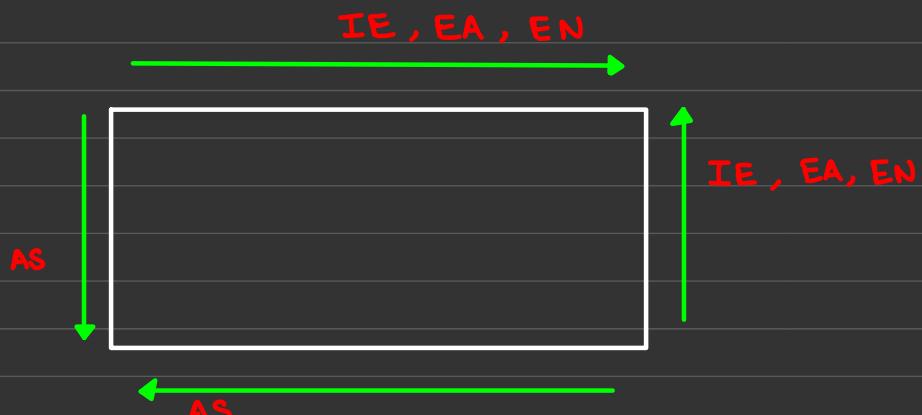
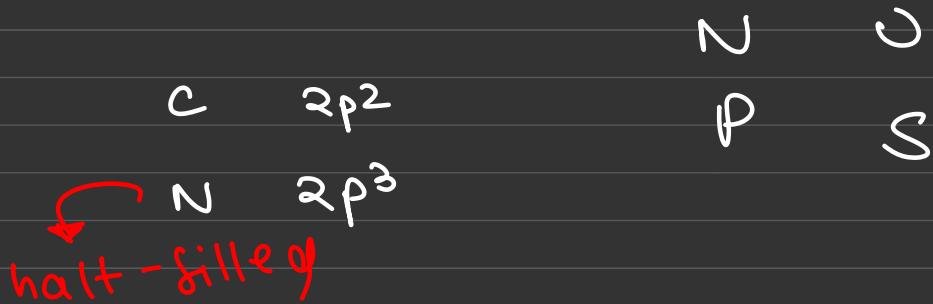
iii) Arrange the following in inc. order of atomic radii

N      S      P      O

(Explain)

i)  $Ca^{+2} < K^+$  ( $Z_{eff} \uparrow$  rad  $\downarrow$ )

ii)

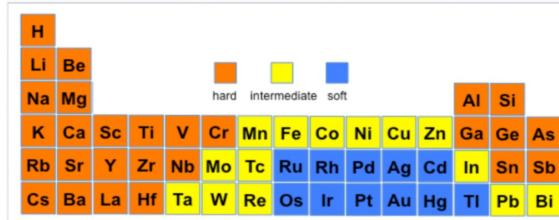


## • Hard-Soft Acid basic principle (HSAB)



Hard acid	Soft - acid
① Smaller size	① Larger in size
② High O.S	② zero / low O.S
③ Charge/rad. +	③ Charge/rad. ↑
④ Non-polarizable ↳ fajan's rule	④ Polarizable
⑤ Prefer to bind with hard base	⑤ Prefer to bind with soft base
⑥ light metals	⑥ heavy metals
⑦ No d e <sup>-</sup> s	⑦ have d e <sup>-</sup> s

Hard-soft trends for acids



(A) Acids -

so soft or hard  
if asked?

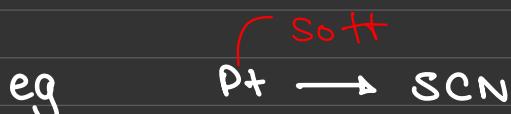
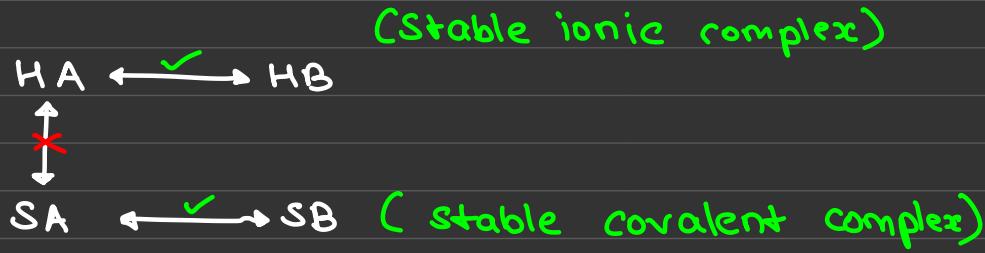
Hard	Borderline	Soft
$\text{H}^+$ , $\text{Li}^+$ , $\text{Na}^+$ , $\text{K}^+$	$\text{Fe}^{2+}$ , $\text{Co}^{2+}$ , $\text{Ni}^{2+}$	$\text{Cu}^+$ , $\text{Ag}^+$ , $\text{Au}^+$ , $\text{TI}^+$
$\text{Be}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Ca}^{2+}$	$\text{Cu}^{2+}$ , $\text{Zn}^{2+}$ , $\text{Pb}^{2+}$	$\text{Hg}^+$ , $\text{Pd}^{2+}$ , $\text{Cd}^{2+}$
$\text{Cr}^{2+}$ , $\text{Cr}^{3+}$ , $\text{Al}^{3+}$	$\text{SO}_4^{2-}$ , $\text{BBr}_3$	$\text{Pt}^{2+}$ , $\text{Hg}^{2+}$ , $\text{BH}_3$ , $\text{Br}_2$
$\text{SO}_3^{2-}$ , $\text{BF}_3$ , $\text{BCl}_3$		$\text{Br}^-$
$\text{HX}$ (H-bonding)		$\text{M}^0$ (metal atoms) and bulk metals

Hard Base	Soft - base
① Smaller in size	① Larger in size
② High EN	② Low EN
③ Non - P	
④ Prefer to bind with Hard acid	
⑤ All ligands containing $F^-$ , $OH^-$ or N cont. ligands	⑤ $Br^-$ , $F^-$ , C donating ligands

Hard-soft trends for bases						
hard			intermediate			soft
C	N	O	F			
P	S		Cl			
As	Se		Br			
Sb	Te		I			

(B) Bases :

Hard	Borderline	Soft
$F^-$ , $OH^-$ , $H_2O$ , $NH_3$	$NO_2^-$ , $SO_3^-$ , $Br^-$	$H^-$ , $R^-$ , $CN^-$ , $CO$ , $I^-$
$CO_3^{2-}$ , $NO_3^-$ , $O^{2-}$	$N_3^-$ , $N_2$ , $C_6H_5N$	$SCN^-$ , $R_3P$ , $C_6H_6$
$SO_4^{2-}$ , $PO_4^{3-}$ , $ClO_4^-$ , $(Cl^-)$	$SCN^-$	$R_2S$



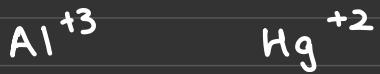
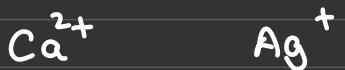
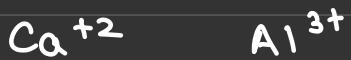
hard

• Exception :-

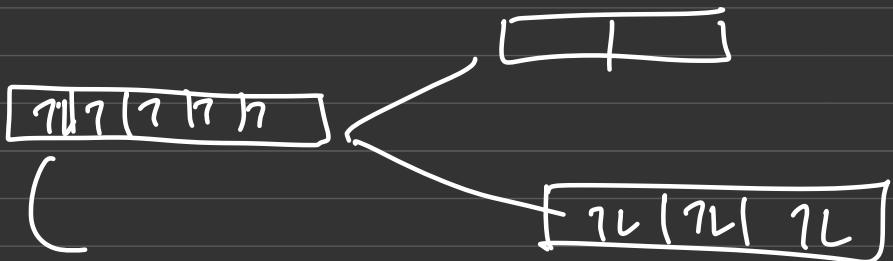


② Be  $\rightarrow$  HB so ionic comp but still covalent comp.

Q.] Which pair form sulphides



$d^6$  Octa ( $SFL$ )



+ 3 p-p

## Chem Imp Points

- Note :-

① When splitting energy asked, we need to find  $\Delta_0$

Where, 
$$\Delta_0 = E = \frac{hc}{\lambda}$$

② CFSE = Crystal field Stabilization energy

Where CFSE = [ ]  $\Delta_0 + P$

③ Also in hc, don't use  $12400 / 1240$ , just directly substitute:-

$$h = 6.63 \times 10^{-34}$$

$$c = 3 \times 10^8 \text{ m/s}$$

- To calculate  $\sigma$

Case - 1 (normal s/p)

$$(n+1) = 0$$

$$n = 0.35$$

$$(n-1) = 0.85$$

$$(n-2)(n-...) = 1$$

Case - 2 (in d/f orbital)

$$(n+1) = 0$$

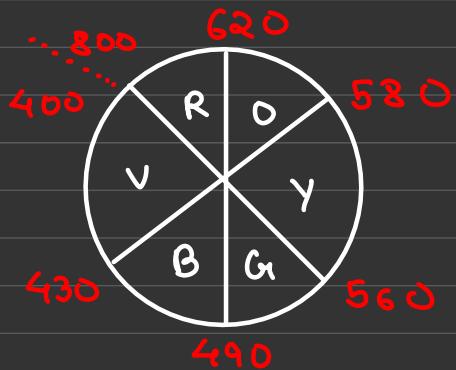
$$n = 0.35$$

$$(n-1)(n-...) = 1$$

Case - 3 (ls orbital)

$$n = 0.30$$

- Color Wheel



In Question  $\lambda_{abs}$  will be given, its complementary is  $\lambda_{ref}$

- Factors affecting CFSE

- ① O.S  $\uparrow$ , CFSE  $\uparrow$
- ② no. of d e<sup>-</sup>s  $\uparrow$ , CFSE  $\downarrow$  [cos of shielding]
- ③ Pairing energy  $\uparrow$ , CFSE  $\downarrow$
- ④ CFSE       $3d < 4d < 5d$

- Spin only magnetic moment ( $M_{sp}$ )

$$\sqrt{n(n+2)}$$

$$\begin{aligned}
 n = 1 &= 1.73 \\
 n = 2 &= 2.89 \\
 n = 3 &= 3.73 \\
 n = 4 &= 4.89 \\
 n = 5 &= 5.91
 \end{aligned}$$

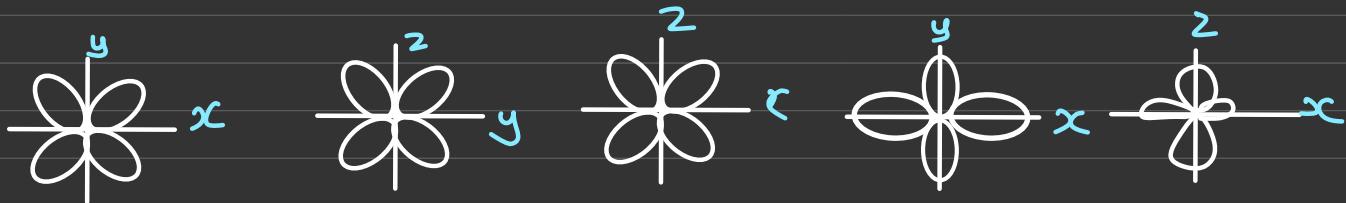
- $$CFSE = \left[ (-0.4 \times n_{t2g}) + (0.6 \times n_{eg}) \right] \Delta_o + mP$$

- Type of ligand

① Halogen /  $S^{2-}$  / Oxygen donating = WFL

② Nitrogen / Carbon donating = SFL

- Orbitals

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

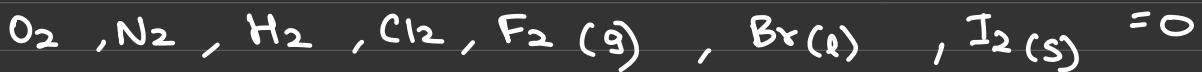
— non- axial —  $\rightarrow$   $\leftarrow$  axial —————

- Optical Iso

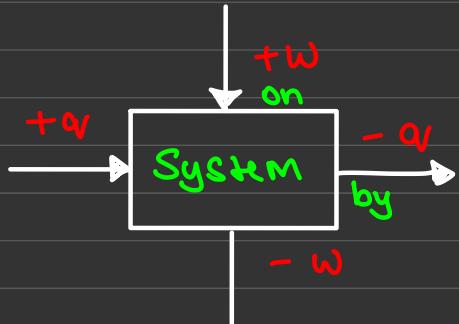
Plane of symmetry : Optically inactive [No optical iso]

## Unit - 2

- **Enthalpy**



- **First law**



- **Entropy**

$$\Delta S > 0 \quad [\text{spont}]$$

$$\Delta S < 0 \quad [\text{non-spont}]$$

$$\Delta S_{\text{sys}} + \Delta S_{\text{surv}} > 0$$

$$\Delta S_{\text{adia}} = 0 \quad (\text{No Heat exchange})$$

$$\Delta S_{\text{irreversible}} > 0$$

$$\Delta S_{\text{reversible}} = 0$$

- **Electro**

