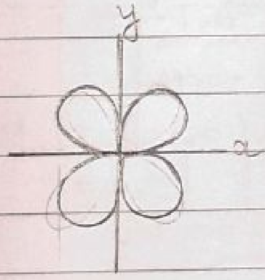
octahedral: on the axis ligand
tetrahedral: b/w axis ligand.

CRYSTAL FIELD THEORY:

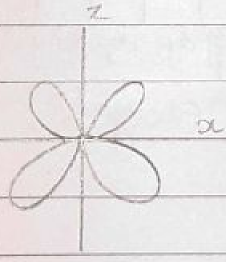
# CRYSTAL FIELD THEORY

# crystal field theory:

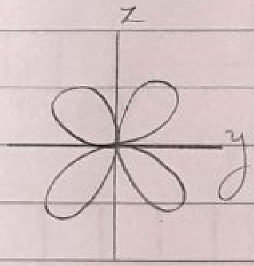
- In crystal field theory, ligands are treated as point charge.
- When ligands approach central metal atom then, they repel each other because of the presence of electron.
- In the electric field of these negative charges, the five d-orbitals of metal atom no longer have exact same energy.
- Extent of splitting of metal d-orbitals depends upon nature and number of ligands. Surrounding it and the charge on the central metal atom.



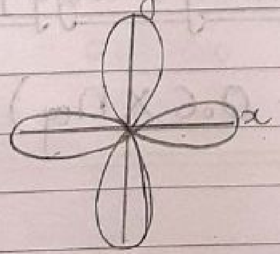
dxy



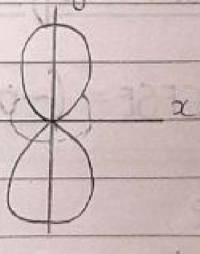
dzx



dyz.



$dx^2-y^2$



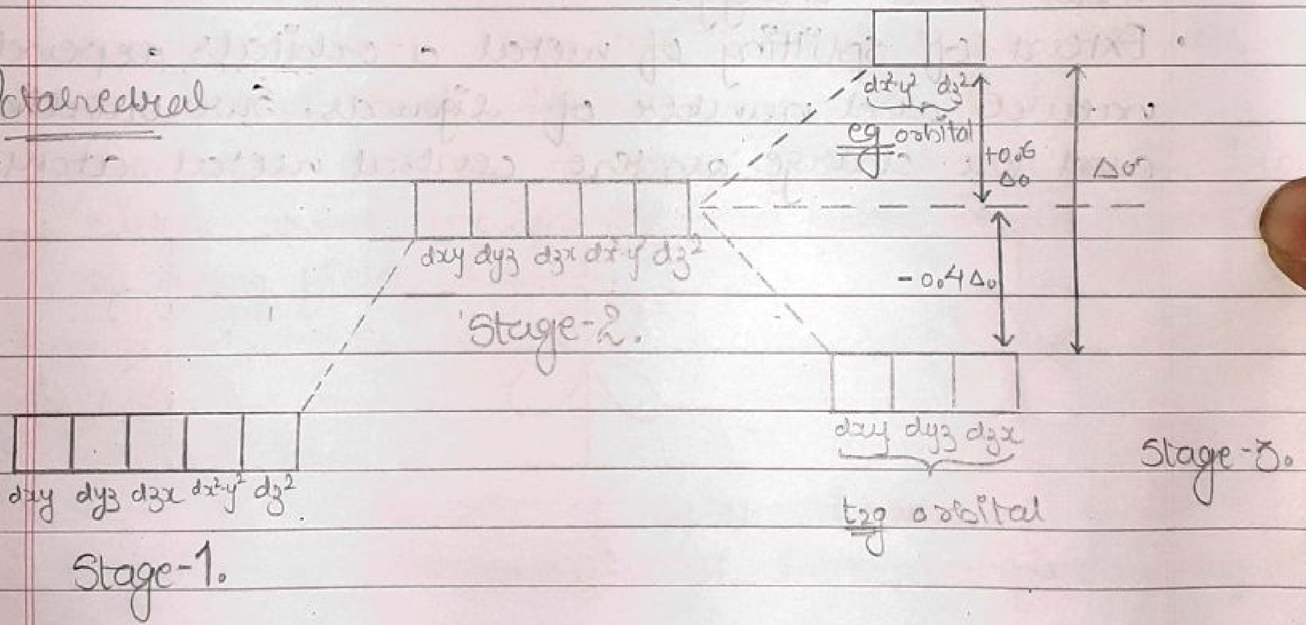
$dz^2$

## * CF Splitting in octahedral co-ordination complex:

- In case of octahedral co-ordination complex, ligands (point charge) approach 'd-orbital' on the axis.

- In octahedral complex, the five degenerate orbitals splits up to two sets. One set consists of two orbitals known as Eg orbitals ($d_{x^2-y^2}$ and $d_{z^2}$) of higher energy and the another set consist of three orbitals known as $t_{2g}$ orbitals ($d_{xy}$, $d_{yz}$, $d_{zx}$).

Octahedral :



⟹ **Calculation of CFSE [CF splitting Energy]:**

$$\boxed{CFSE = (-0.4 \times n_{t_{2g}} + 0.6 \times n_{eg})\Delta_0}$$

where,

$n_{t_{2g}}$ = no. of electrons in $t_{2g}$ orbital.
$n_{eg}$ = no. of electrons in eg orbital.
$\Delta_0$ = CFSE for octahedral complex.

## ⟹ calculation of NSE (Net Splitting Energy):

$$\Longrightarrow \boxed{NSE = (-0.4 \times n_{t_{2g}} + 0.6 \times n_{eg})\,\Delta_o + x_p}$$

where,

$x_p$ = pairing energy

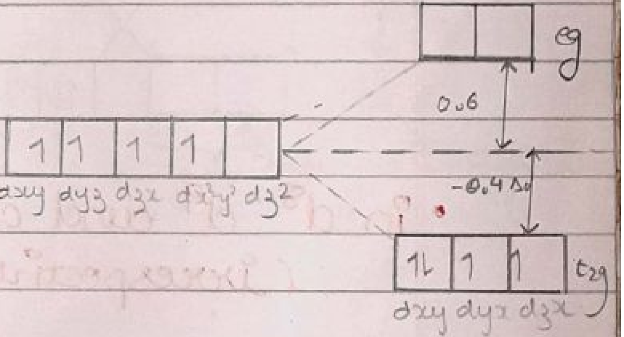
$x$ = no. of paired electrons.

**Q:01.** Find out the electronic configuration, CFSE and NSE for $d^4$ (coordin. no = 06.) in the presence of strong field ligand and weak field ligand.

→ **CASE:01.** if complex is low spin complex then electronic configuration is: $t_{2g}^4\ eg^0$

$CFSE = (-0.4 \times 4) + 0$

$= \underline{-1.6}\ \Delta_o$



$NSE = (-1.6)\,\Delta_o + 1P$

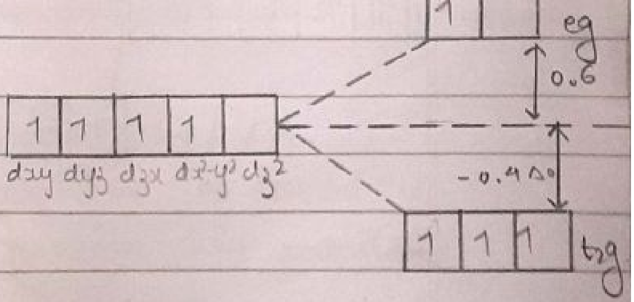
$=$

**CASE:02.** if complex is high spin complex then electronic configuration is: $t_{2g}^3\ eg^1$

$CFSE = (-0.4 \times 3 + 0.6 \times 1)\,\Delta_o$

$= (-1.2 + 0.6)\Delta_o$

$= \underline{-0.6\ \Delta_o}.$



$NSE = (-0.6)\Delta_o + 0P$

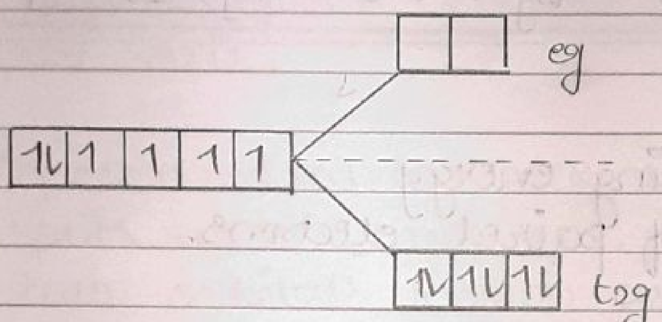
$= \underline{-0.6\ \Delta_o}.$

- if $\Delta_o >$ Pairing energy (P) → low spin complex (Hybri: $d^2sp^3$)
- if $\Delta_o <$ Pairing energy (P) → high spin complex (Hybri: $sp^3d^2$)

low spin → નીચેના ભરવા પેલા.
high → nichena 3 પછી ઉપરના 2 પછી ફરીનીચે.

$d^6$ Q:2 Find CFSE, MSE and electronic config. for $K_4[Fe(CN)_6]$:

→ $d^6$ → as CN is strong ligand. ∴, low spin complex



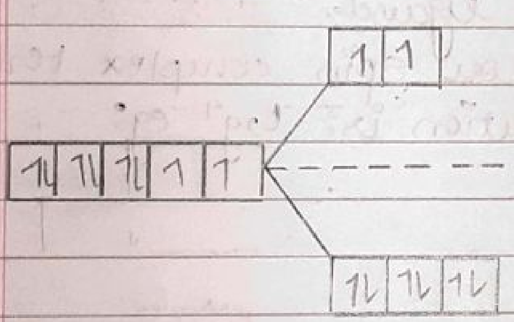
$CFSE = (-0.4 \times 6 + 0.6 \times 0)\Delta_0$
$= -2.4\Delta_0$.

$MSE = -2.4\Delta_0 + 3P$.

$E.C = t_{2g}^6 \; eg^0$

Q:3 Find CFSE for $d^8$.

→



if low spin or at highspin
$e.c = t_{2g}^6 \; eg^2$.

$0.4 \times 6 \quad 0.6 \times 2$

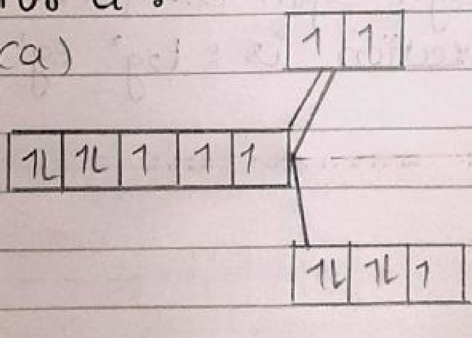
$CFSE = (-2.4 + 1.2)\Delta_0$
$= -1.2\Delta_0$

$MSE = -1.2\Delta_0 + 3P$.

- in $d^8$, $d^9$ and $d^{10}$ E.C will always be $sp^3d^2$. (irrespective of high / low spin complex).

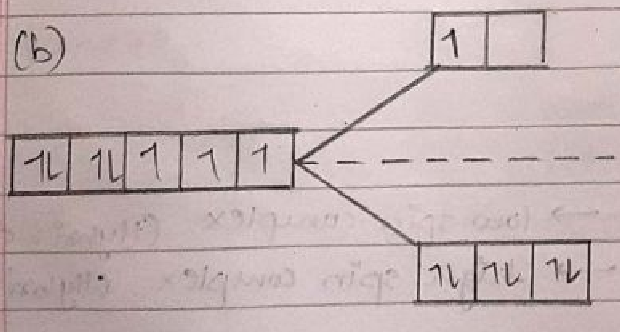
Q:4 For $d^7$.

→ (a)



at high spin.
$E.C = t_{2g}^5 \; eg^2$
$CFSE = (-0.4 \times 5 + 0.6 \times 2)\Delta_0$
$= -0.8\Delta_0$
$MSE = -0.8\Delta_0 + 2P$

(b)

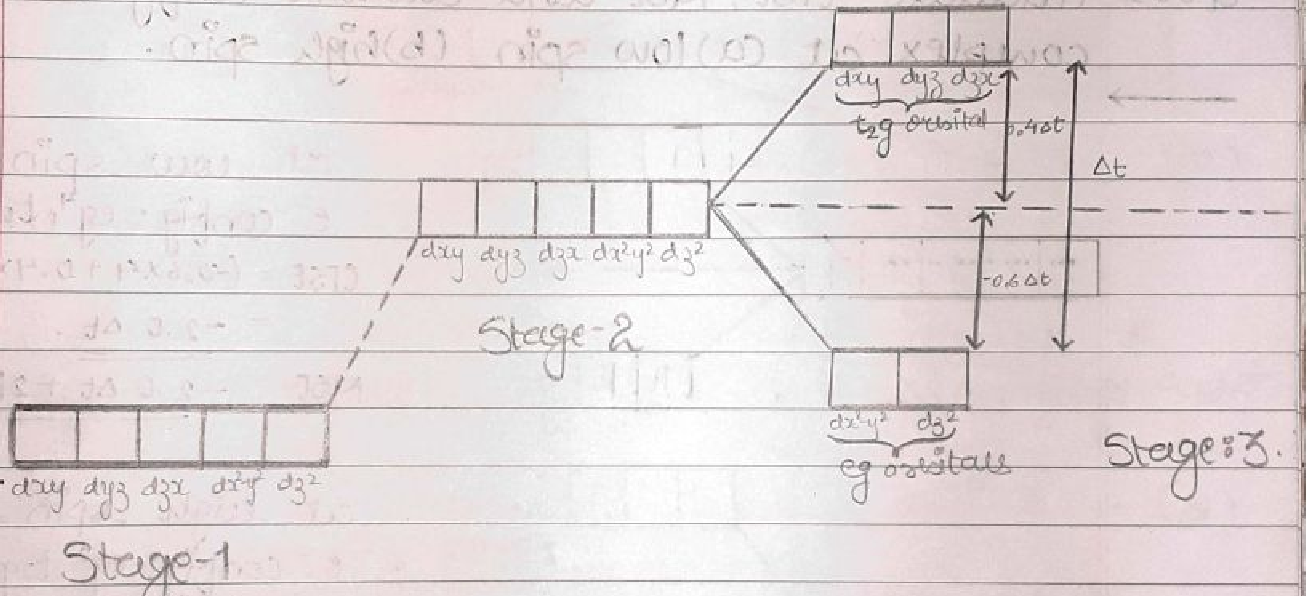


at low spin.
$E.C = t_{2g}^6 \; eg^1$
$CFSE = (-0.4 \times 6 + 0.6 \times 1)\Delta_0$
$= -1.8\Delta_0$
$MSE = -1.8\Delta_0 + 3P$

## * CF Splitting in tetrahedral co-ordination complex:

- In case of tetrahedral coordination complex, 4 (four) ligands approaches in between the axis of 'd-orbitals'.

- In that case, $t_{2g}$ orbitals face more repulsion in compare to eg orbitals. Hence, energy of $t_{2g}$ orbitals is more than eg orbitals.



⟹ calculation of CFSE in complex:

$$\boxed{CFSE = (-0.6 \times n_{eg} + 0.4 \times n_{t_{2g}})\,\Delta t}$$

where,

$\Delta t$ = CFSE of tetrahedral complex.
$n_{eg}$ = no. of electrons in eg orbital.
$n_{t_{2g}}$ = no. of electrons in $t_{2g}$ orbital.

## ⟹ Calculation of NSE in complex:

$$NSE = (-0.6 \times n_{eg} + 0.4 \times n_{t2g})\Delta t + xp$$

where,

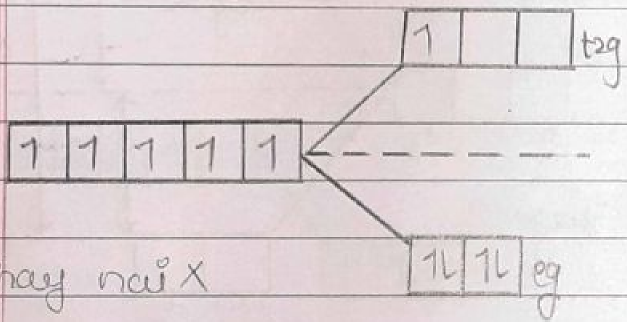
x = no. of paired electrons.

xp = pairing energy.

Q:05 Calculate CFSE, NSE and electronic configuration $d^5$ complex at (a) low spin (b) high spin.

⟶

(a)



at low spin.

$e^-$ config: $eg^4\ t2g^1$

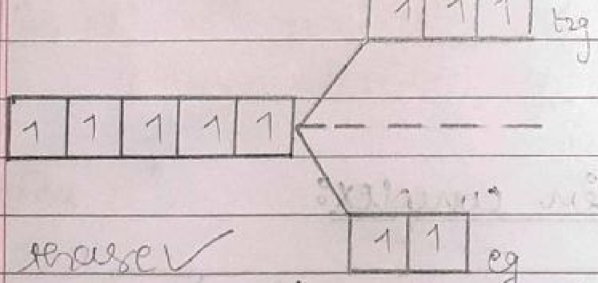
$CFSE = (-0.6 \times 4 + 0.4 \times 1)\Delta t$

$= \underline{-2.0\ \Delta t}$.

$NSE = \underline{-2.0\ \Delta t + 2P}$

$sp^3$ thay nai X

(b)



at high spin.

$e^-$ config: $eg^2\ t2g^3$

$CFSE = (-0.6 \times 2 + 0.4 \times 3)\Delta t$

$= \underline{0\Delta t}$

$NSE = \underline{0\Delta t + 0P}$

$sp^3$ thase ✓

## ⟹ CFSE in Square Planer complex:

- in this case, all the ligands approaches on the axis. except z-axis.

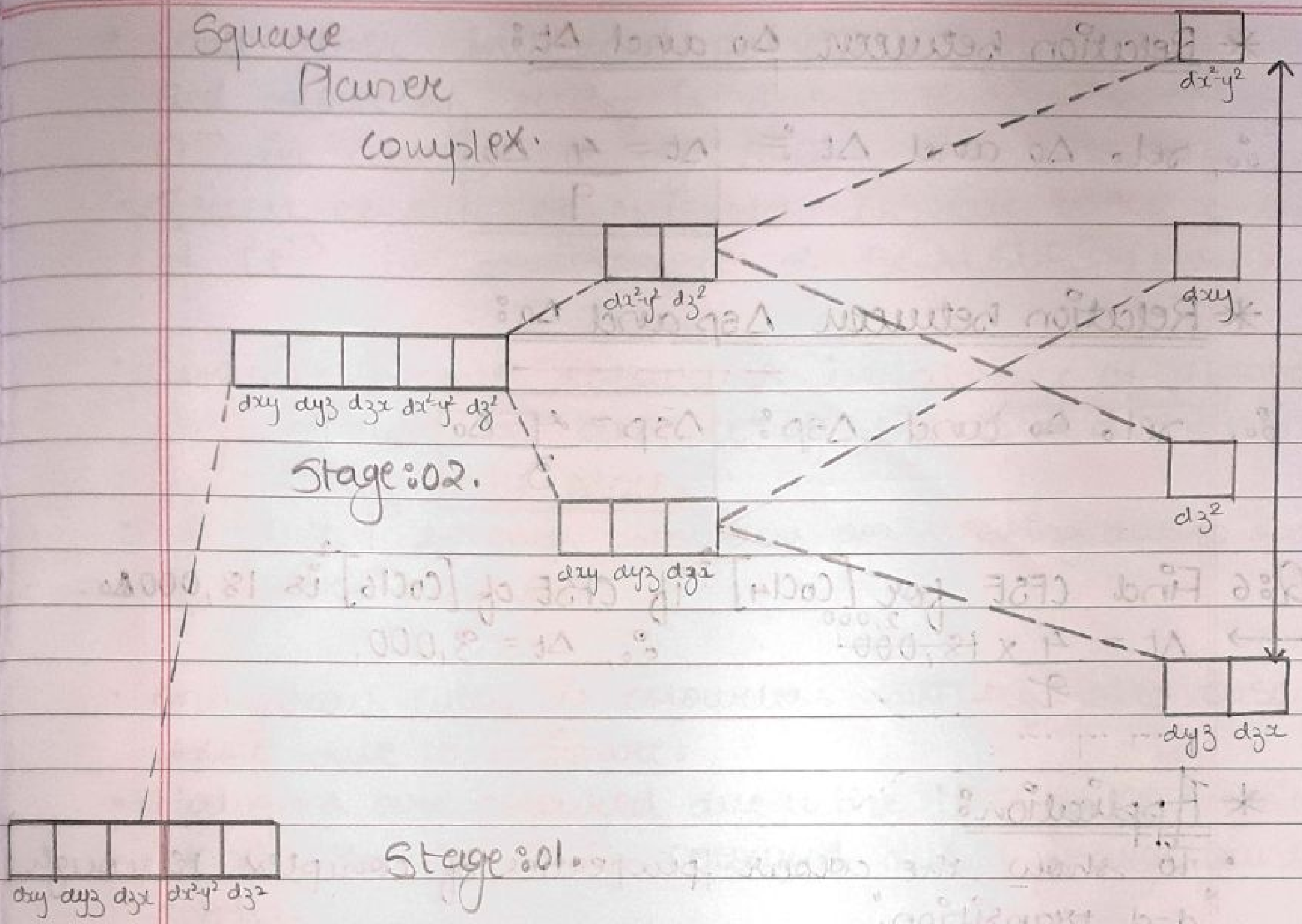
board imp

✱ NOTE:

- SPECTROCHEMICAL SERIES:

→ series representing relative strength of ligands.

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < edta^{4-} < NH_3 < en < CN^- < CO$



## * Factors affecting CFSE:

1.) Strength of ligand:

→ CFSE is more in strong field ligand in compare to weak field ligand.

2.) Oxidation state of central metal ion/atom:

→ CFSE is more is the oxidation state of central metal is ↑.

3.) Transition state of d-block elements:

→ 5d > 4d > 3d (increasing order of transition state).

4.) Geometry of co-ordination compound:

→ $\Delta_{sp} > \Delta_o > \Delta_t$ (Sq. planer > octahedral > tetrahedral)

## * Relation between $\Delta o$ and $\Delta t$:

∴, rel. $\Delta o$ and $\Delta t$ ÷ $\boxed{\Delta t = \frac{4}{9} \Delta o}$

## * Relation between $\Delta sp$ and $\Delta o$:

∴, rel. $\Delta o$ and $\Delta sp$ ÷ $\boxed{\Delta sp = \frac{4}{3} \Delta o}$

Q:6 Find CFSE for $[CoCl_4]^{-2}$ if CFSE of $[CoCl_6]^{-2}$ is 18,000 $\Delta o$.

$\longrightarrow \Delta t = \frac{4}{9} \times \overset{2,000}{\cancel{18,000}}$ ∴, $\Delta t = 8,000$.

## * Application:

- To show the colour properties of complex through "d-d transition."
- $d^0$ & $d^{10}$ configuration complexes are colourless while complexes with configuration from $d^1$ to $d^9$ are coloured.
- calculate magnitude of paramagnetism
- To predict the geometry of the compound if its inner orbital complex or outer orbital complex

## * Limitation:

- CFT do not account upon covalent bonding b/w metals which was explained by advanced theory of Ligand Field Theory
- considers electrostatic interaction only, ignoring other factors i.e. overlapping of orbitals.

(High spin)
Q. CFSE ગણો • (a) $[Mn(H_2O)_6]^{+3}$ (b) $[Co(H_2O)_6]^{+2}$ (a) $[Co(H_2O)_6]^{+3}$ ~~(d)~~ $[Fe(H_2O)_6]^{+3}$

- <u>Some other important points:</u>
- Red colour of ruby is due to the presence of $Cr^{+3}$ in atmosphere of $Al_2O_3$.
- Green colour of emerald is due to the presence of $Cr^{+3}$ in atmosphere of $Be_3Al_2Si_6O_{18}$ (beryl).

- Complex becomes colourless in absence of ligand field because in absence of ligand d-d transition would not take place.
- $[Ti(H_2O)_6]^{3+}$ becomes colourless on heating due to removal of water molecules.

- Anhydrous $CuSO_4$ is colourless but hydrated $CuSO_4$ is blue due to moisture.
- Halogens are coloured due to the HOMO-LUMO transition.
- $KMnO_4$, $K_2Cr_2O_7$, $CrO_2Cl_2$, coloured due to charge transfer spectra.

કોઈ ૧ પણ assymetrical હશે તો JT લાગશે જ.

imp

## * Jahn Teller Effect:

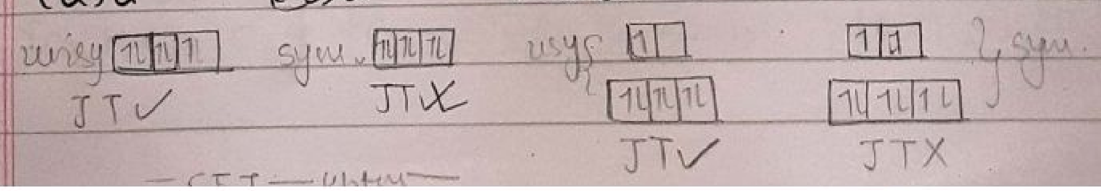
- applicable only when t2g and eg orbitals are asymmetrical.
- it isn't applicable over t2g and eg with symmetrical orbitals i.e.

$$\left.\begin{matrix} t_{2g}^0 & t_{2g}^3 & t_{2g}^6 \\ e_g^0 & e_g^2 & e_g^4 \end{matrix}\right\} \text{Symmetrical Orbitals}$$

- Applicable over: $\left.\begin{matrix} t_{2g}^1 & t_{2g}^2 & t_{2g}^4 & t_{2g}^5 \\ & e_g^1 & e_g^3 & \end{matrix}\right\}$ Asymmetrical orbitals.

Q:7 On which compound of the following the 'JTE' is not applicable
(a) $d^5$ (b) $d^6$ (c) $d^7$ (d) $d^8$

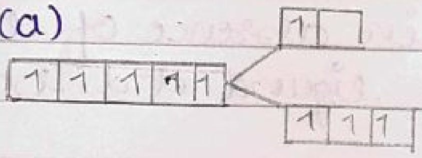
Strong field ligand
low spin

→


— CFT — [illegible]

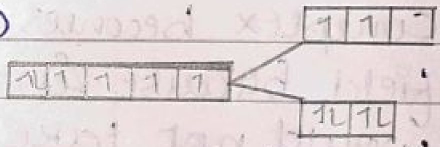
Q:8 Find magenetism ($\mu$) in:
(a) $d^4$ (high spin) (octahedral)
(b) $d^6$ (low spin) (tetrahedral)
(c) $d^6$ (high spin) (octahedral)
(d) $d^5$ (low spin) (octahedral).

(a)



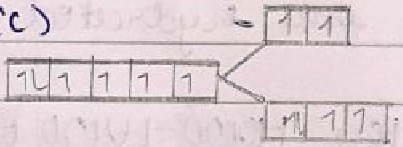
paramagnetic ∴, $\mu = \underline{\underline{4.85}}$

(b)



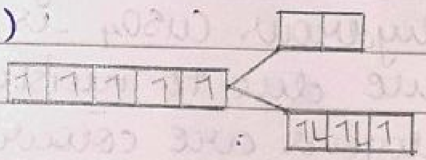
paramagnetic ∴, $\mu = \underline{\underline{2.85}}$

(c)



paramagnetic ∴, $\mu = \underline{\underline{4.85}}$

(d)



paramagnetic ∴, $\mu = \underline{\underline{1.85}}$