

# FACULTY OF ENGINEERING AND TECHNOLOGY

## CYCLE TEST



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DATE \_\_\_\_\_

DEGREE \_\_\_\_\_

NAME P. Panneerelvam

SPECIALISATION \_\_\_\_\_

COURSE \_\_\_\_\_

SEMESTER \_\_\_\_\_

### Crystal field Theory : (1952)

\* This theory was proposed by H. Bethe and Van Vleck, applied this theory to co-ordination compounds. In this theory, ligands are treated as point charge in case of anions and dipoles in case of neutral molecules.

\* (The bonding b/w a central metal ions and its ligands arises from purely electrostatic interaction.) (or)

\* In its simplest treatment CFT does not consider Covalent bonding in complex, but the bonding b/w the metal cation and ligand arises from the electrostatic attraction b/w the nucleus of metal cation and the partial negative charge invariably present on the ligands.

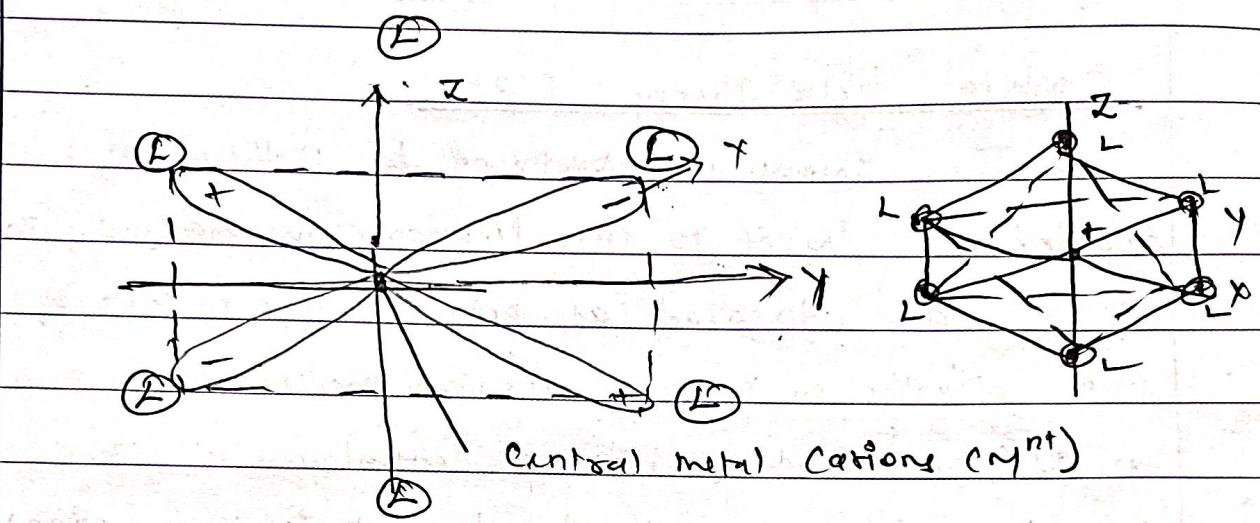
\* The interaction b/w the nuclei of the cation and those of the ligands is entirely repulsive. It is these repulsive force that are responsible for causing the splitting of the 'd' orbitals of the metal cations.

The bonding b/w the metal and ligand are thus purely ionic.

No Additional Sheets will be issued

## Octahedral Complex (oh)

- Octahedral complex co-ordination no: 6
- The central metal ions is at the centre and the ligands occupy the six corners of the oh.



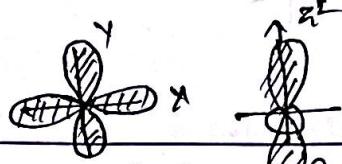
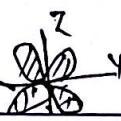
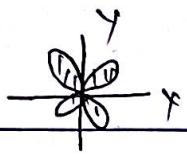
The five 'd' orbitals are classified as

- (i) Three 'd' orbitals i.e.,  $d_{xy}$ ,  $d_{yz}$ , and  $d_{zx}$  are oriented in b/w the axis are called t<sub>2g</sub> orbitals
- (ii) The other two orbitals, i.e.,  $d_{z^2}$  &  $d_{x^2}$  orbitals oriented along the x - y axis are called e<sub>g</sub> orbitals.

Due to approach of ligands, the five d-orbitals split. The splitting of d' orbitals depends on the nature of the crystal field.

The energy diff b/w t<sub>2g</sub> and e<sub>g</sub> level is denoted by  $\Delta_o$  and is called crystal field splitting energy.

(Non axial orbitals)

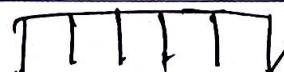


is -  $t_{2g}$  and  $e_g$  are present in  $x^2-y^2$  field &  $z^2$  field respectively.

The lobes are present in between  $x^2-y^2$  and  $z^2$  field e.g.  $t_{2g}$  &  $e_g$ .

in axis (i.e)  $\perp$  to the  $x, y, z$  axis i.e.,  $t_{2g}$  &  $e_g$

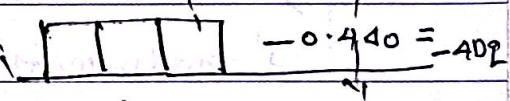
distortion parameter,  $\Delta$  of octahedral  $pd_3 + 0.640 = +6Dq$



10 Dq (or)

$\Delta_0$

$t_{2g}$  and  $e_g$  are present in  $x^2-y^2$  field (hypothetical)



$-0.440 = -4Dq$

$t_{2g} \perp e_g$

Free metal degeneracy of  $t_{2g}$  and  $e_g$  is removed due to distortion parameter  $\Delta$  (i.e.,  $pd_3 + 0.640 = +6Dq$ )

### Crystal Field Stabilisation Energy (CFSE)

According to the CFT, Under the influence of ligands approaching towards the central metal ion during the formation of octahedral complex,

The  $d^5$  orbital of the central metal ions are split in to two sets viz.  $t_{2g}$  (lower energy sets) and  $e_g$  (higher energy sets).

The energy gap b/w these two sets is lowered by is equal to  $10 Dq$  (or)  $\Delta_0$

- The energy of  $t_{2g}$  set is lowered by  $2\delta_s - \Delta_0$   
 $\approx (-0.44\text{eV})$  or  $4\text{Dq}$ , while that of  $e_g$  set is raised by  $3\delta_s + \Delta_0$  ( $= 0.64\text{eV}$ )  
 or  $6\text{Dq}$  relative to the energy of hypothetical degenerate ' $d'$  orbitals.
- Thus the  $e^-$  occupying  $t_{2g}$  orbitals loses the energy of  $2\delta_s$  by  $-0.44\text{eV}$  ( $= -4\text{Dq}$ ), while the going into  $e_g$  orbitals increases its energy by  $+0.64\text{eV}$  ( $= +6\text{Dq}$ )
- $-$  and  $+$  signs indicate decrease and increase of the energy of ' $d'$  orbitals caused by the splitting under the influence of six ligands.

Now consider a  $d^5$  ion with  $p\pi^-$  in  $t_{2g}$  and  $q\pi^-$  in  $e_g$  orbitals. Quite Obviously,

$$\left. \begin{array}{l} \text{Gain in energy due to } \\ q\pi^- \text{ in } e_g \text{ orbitals} \\ (\text{in terms of } \Delta_0) \end{array} \right\} = +0.64\Delta_0$$

(4)

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and loss in energy due to

$\psi$  in  $t_{2g}$  in terms of  $A_0$

Thus

net change in energy for  $d^{pq}$  ion

(in terms of  $A_0$ )

$$= [-0.4P + 0.6q]A_0$$

This change in energy in terms of  $Dq$  will be given by utilising the relation

$$A_0 = 10Dq \text{ Thus}$$

$$\text{change in energy (in terms of } Dq) = [-0.4P + 0.6q] \times 10Dq$$

$$= [-4P + 6q] Dq$$

The change in energy is called crystal field stabilisation energy (CFSE), since it stabilises all orbitals by lowering their energy which result from their splitting into  $t_{2g}$  &  $e_g$  orbitals.

Ex! for a  $d^0$  ion with  $t_{2g}^6 e_g^4$  configuration, the net change in energy ( $P = 6 - 9 = 4$ )

$$= [-0.4 \times 6 + 0.6 \times 4] A_0 = 0$$

For  $d^5$  (high spin) ion with  $t_{2g}^3, e_g^2$  configuration,

The net change in energy ( $P=3, q=2$ )

$$= [-0.4 \times 3 + 0.6 \times 2] A_0 = 0$$

If  $P$  = mean pairing energy which is the energy required to pair two  $\bar{e}$  against  $\bar{e}-\bar{e}$  repulsion

In the same orbitals and  $m$  = No. of unpaired  $\bar{e}$ ,

Then CFSE for  $d^{p+q}$  ion in terms of  $A_0$ )

$$= [-0.4P + 0.6q] A_0 + mq$$

Ex:  $d^3$  ion having distribution of three  $\bar{e}$ .

①

$d^3$  ion. w.r.t the distribution of three  $\bar{e}$ .

Three  $d-\bar{e}$  in  $t_{2g}$  &  $e_g$  levels in both the field

(i.e. strong & weak) is  $t_{2g}^3$  &  $e_g^0$  and

$m=0$ , Thus  $p=3, q=0$  &  $m=0$  and hence

CFSE for born field

$$(strong \& weak) = [-0.4 \times 3 + 0.6 \times 0] A_0 + 0 + P$$

High spin & low spin

$$= 1.2 A_0 = -1.2 Dq$$

⑥

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②  $d^4$  ion (a) weak field ligand (high spin complex)

$$d^4 = t_{2g}^3 eg' \text{ Thus } p=3, q=1 \text{ and } m=0 \text{ and hence}$$

CFSE =

$$\begin{aligned} \text{for weak field} &= [ -0.4 \times 3 + 0.6 \times 1 ] \Delta_0 + 0 \times p \\ &= -0.6 \Delta_0 = -6 \Delta_0 \end{aligned}$$

(b) for strong field (low spin complex)

$d^4 = t_{2g}^4 eg'$ , Thus  $p=4, q=0$  and  $m=1$  and hence CFSE for

$$\begin{aligned} \text{Strong field } \} &= [ -0.4 \times 4 + 0.6 \times 0 ] \Delta_0 + 1 \times p \\ &= -1.6 \Delta_0 + p = -16 \Delta_0 + p \end{aligned}$$

③  $d^7$  ion (a) For weak field (high spin complex)

$$(a) d^7 = t_{2g}^6 eg', \text{ Thus } p=6, q=1 \text{ and } m=0$$

$p=5, q=2$  and  $m=2$  and hence

$$\begin{aligned} \text{CFSE for weak field} &= [ -0.4 \times 5 + 0.6 \times 2 ] \Delta_0 \times 2P \\ &= -0.8 \Delta_0 + 2P \\ &= -8 \Delta_0 + 2P \end{aligned}$$

(b) for strong field (low spin complex)

$$d^7 = t_{2g}^5 eg'. \text{ Thus } p=6, q=1 \text{ and } m=3 \text{ and hence}$$

$$\begin{aligned} \text{CFSE for strong } \} &= [ -0.4 \times 6 + 0.6 \times 1 ] \Delta_0 + 3P \\ &= -1.8 \Delta_0 + 3P = -18 \Delta_0 + 3P \end{aligned}$$

Table 1 CFSE values (in the units of  $\Delta_0$  and  $\Delta_g$ ) for  $d^0$  to  $d^{10}$  Configuration of metal ions in (high spin) weak field and (low spin (strong field) octahedral complexes.  $m$  = total no. of paired  $e$  in  $t_{2g}$  deg orbitals;  $P$  = Mean pairing energy

$d$	$P+Q$	$t_{2g} + e_g$ Configuration in weak field	$m$	$CFSE = [-0.4P + 0.69] \Delta_0 + mP$ $= [-4P + 6.7\Delta_g + mP]$	$t_{2g}^P + e_g^2$ Configuration in strong field (low spin)	$m$	$CFSE = [-0.4P + 0.69] \Delta_0 + mP$ $= [-4P + 6.9] \Delta_g + mP$
$d^0$		$t_{2g}^0 e_g^0$	0	0	$t_{2g}^0 e_g^0$	0	0
$d^1$		$t_{2g}^1 e_g^0$	0	$-0.4\Delta_0 (-4\Delta_g)$	$t_{2g}^1 e_g^0$	0	$-0.4\Delta_0 (-4\Delta_g)$
$d^2$		$t_{2g}^2 e_g^0$	0	$-0.8\Delta_0 (-8\Delta_g)$	$t_{2g}^2 e_g^0$	0	$-0.8\Delta_0 (-8\Delta_g)$
$d^3$		$t_{2g}^3 e_g^0$	0	$+1.2\Delta_0 (+12\Delta_g)$	$t_{2g}^3 e_g^0$	0	$+1.2\Delta_0 (+12\Delta_g)$
$d^4$		$t_{2g}^3 e_g^1$	0	$-0.6\Delta_0 (-6\Delta_g)$	$t_{2g}^4 e_g^0$	1	$-1.6\Delta_0 (0s - 16\Delta_g) + P$
$d^5$		$t_{2g}^3 e_g^2$	0	$0.0\Delta_0 (0.0\Delta_g)$	$t_{2g}^5 e_g^0$	2	$2.0\Delta_0 (0s - 20\Delta_g) + 2P$
$d^6$		$t_{2g}^4 e_g^2$	1	$-0.4\Delta_0 (0s - 4\Delta_g) + P$	$t_{2g}^6 e_g^0$	3	$-2.4\Delta_0 (0s - 24\Delta_g) + 3P$
$d^7$		$t_{2g}^5 e_g^2$	2	$-0.8\Delta_0 (0s - 8\Delta_g) + 2P$	$t_{2g}^6 e_g^1$	3	$-1.8\Delta_0 (0s - 18\Delta_g) + 3P$
$d^8$		$t_{2g}^6 e_g^2$	3	$-1.2\Delta_0 (0s - 12\Delta_g) + 3P$	$t_{2g}^6 e_g^2$	3	$-1.2\Delta_0 (0s - 12\Delta_g) + 3P$
$d^9$		$t_{2g}^6 e_g^3$	4	$-0.6\Delta_0 (0s - 6\Delta_g) + 4P$	$t_{2g}^7 e_g^3$	4	$0.6\Delta_0 (0s - 6\Delta_g) + 4P$
$d^{10}$		$t_{2g}^7 e_g^4$	5	$0.0\Delta_0 (0.0\Delta_g) + 5P$	$t_{2g}^7 e_g^4$	5	$0.0\Delta_0 (0s - 0.0\Delta_g) + 5P$

⑩

## Application of CFT

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(i) Colour of Transition metal complex: <sup>one</sup> of the major success of the CFT is that it can provide an explanation for the observed colours of transition metal complex.

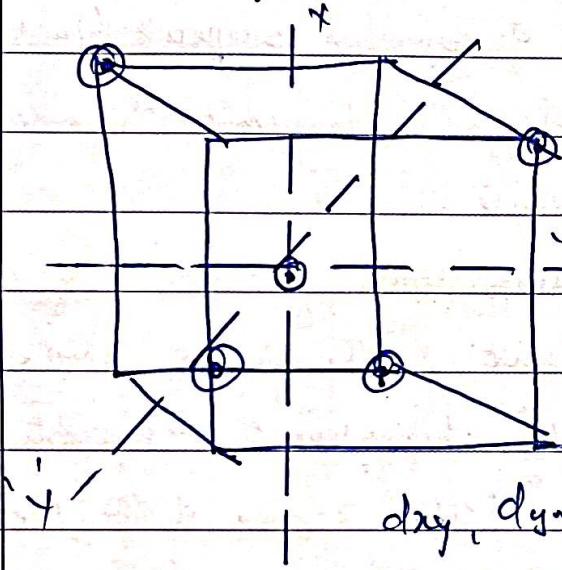
When white light allowed to fall on a complex, <sup>in</sup> the following things may occurs:

- (i) The complex may absorb the whole of the white light. In this case, the complex appears black.
- (ii) The complex may reflect (or transmit) the whole light. In this case it appears white.
- (iii) The complex may absorb some of it and may reflect (or transmit) the remaining light. In this case the complex has some colour, i.e., it is coloured. The absorption of light by the coloured complex takes place in the visible region of the spectrum which extend from  $4000\text{ A}^\circ$  to  $7000\text{ A}^\circ$  in wavelength. The colour of absorbed light is different from that of the transmitted light.

The colour of the transmitted light is called the complementary colour of that of the absorbed light and is, in fact, the colour of the complex.

## Crystal Field Splitting in Tetrahedral Complex

The co-ordination number for tetrahedral complex is 4. The tetrahedral arrangement of four ligands surrounding a metal ion may be visualized by placing ligands at the alternate corners of a cube as shown in fig.



It can be seen shown that

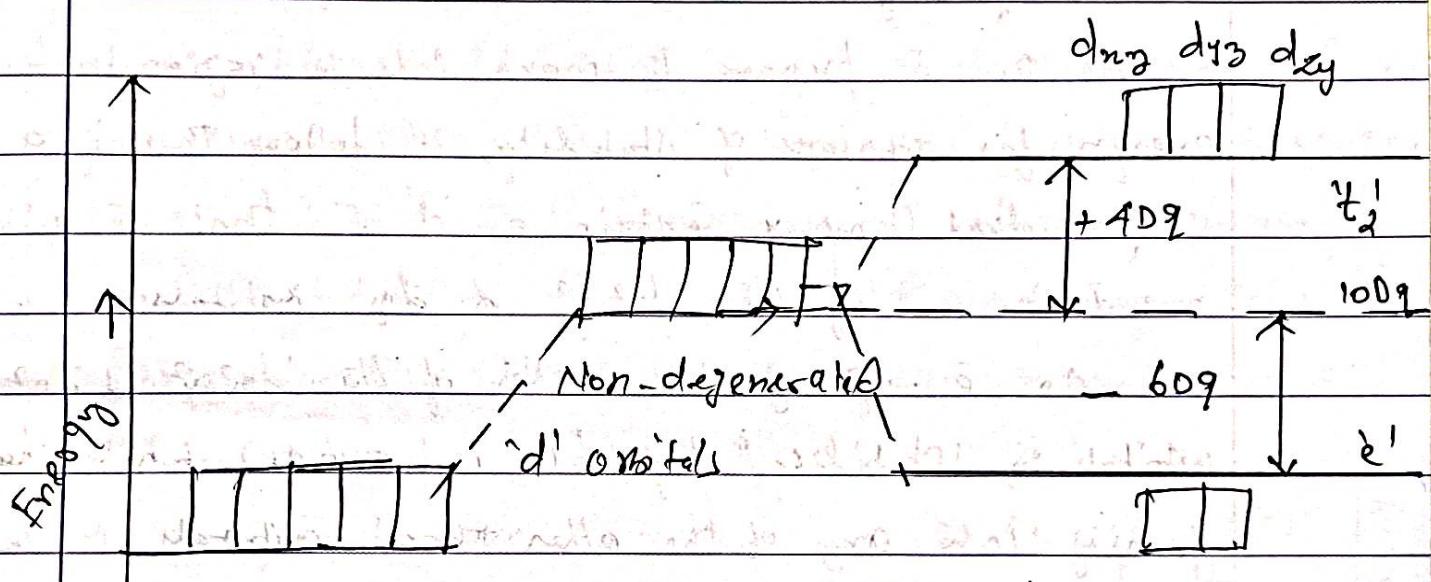
in a tetrahedral structure, none of the 'd' orbitals points exactly towards ligands.

The three 'd' orbitals  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$  are pointing close to the direction, in which ligands are approaching while two orbitals,  $d_{x^2-y^2}$  &  $d_{z^2}$  are lying b/w the ligands.

As a result of this, The energy of the former three orbitals increases to the energy of the latter two orbitals because the  $\epsilon^-$  in the former orbitals would not be repelled by ligand  $\epsilon^-$  more strongly than  $\epsilon^-$  in the latter orbitals. Thus the 'd' orbitals are again split into two groups but in a reverse order.

[Dr. P. Panneerselvam]

The three orbitals  $d_{xy}$ ,  $d_{yz}$  &  $d_{zx}$  designated as ' $t_2$ ' orbitals, now have higher energy than the two orbitals  $d_{x^2-y^2}$  &  $d_{z^2}$  designated as ' $e'$  orbitals.



For metal degeneracy of all five orbitals

(Isolated central atom)

The crystal field splitting ( $\Delta_e$  the energy difference between the two sets of orbitals), in this case denoted by  $\Delta_t$ , the subscript 't' indicating tetrahedral Complex.

$\Delta_t$  is less than  $\Delta_o$ , observed in the case of octahedral Complex. It has been estimated that  $\Delta_t \approx -\frac{4}{9} \Delta_o$ , the minus sign denotes that the order of splitting

In tetrahedral complex is reverse that of in octahedral Complex. The smaller value of  $\Delta_t$  is compared to  $\Delta_o$  is partially due to lesser number of ligand in the tetrahedral field.

Since the  $\sigma$  prefer to move into a region in lower energy for reasons of stability, it follows that if a tetrahedral Complex contain a  $d^1 \sigma$ , that  $\sigma$  will reside in one of the  $d_{x^2-y^2}$  &  $d_{z^2}$  orbitals.

An  $\sigma$  going into either of the  $d_{x^2-y^2}$  &  $d_{z^2}$  orbital is stabilised by  $6Dq$  (or  $0.6\Delta_t$ ) while that going into any of the other three orbitals is destabilised by  $4Dq$  (or  $0.4\Delta_t$ ).

The CFSE for tetrahedral Complex having diff electronic Configuration can also be calculated by the following same procedure as for octahedral Complex.

$$\text{For ex: } d^1 \text{ CFSE} = 0 - (-6Dq) = 6Dq$$

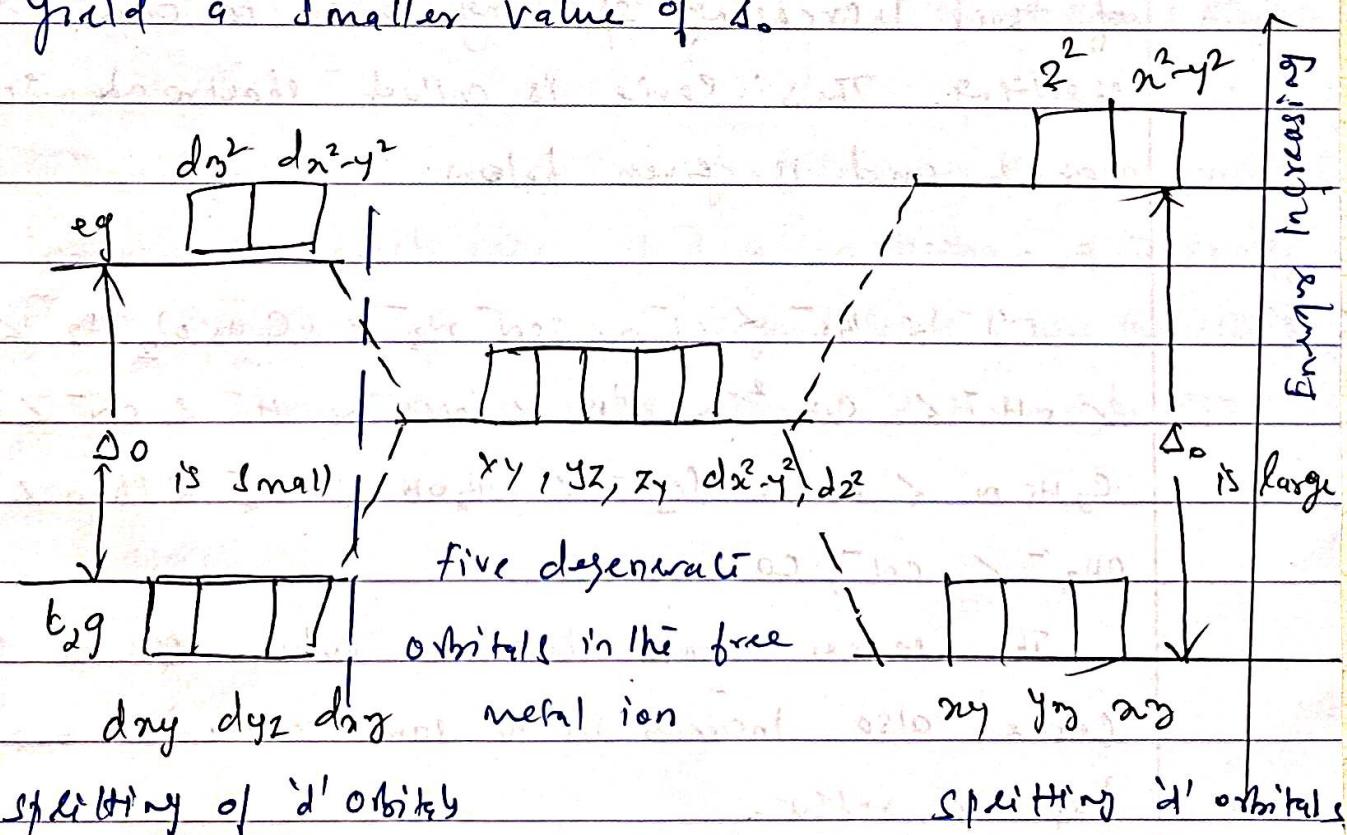
$$d^2 \text{ CFSE} = 0 - (-12Dq) = 12Dq$$

## Spectrochemical Series:

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### C Strong(er) and weak(er) ligands

The magnitude of  $\Delta_0$  varies from stronger or weaker ligands. Stronger ligands are those which exert a stronger field on the central metal ion and hence higher splitting power while the weaker ligands are those which have a weaker field on the central metal cation and consequently relatively lower splitting power. Thus strong ligand ( $\text{en}^-$ ,  $\text{CN}^-$ ) give larger value of  $\Delta_0$  and weak ligand ( $\text{Cl}^-$ ,  $\text{F}^-$ ) yield a smaller value of  $\Delta_0$ .



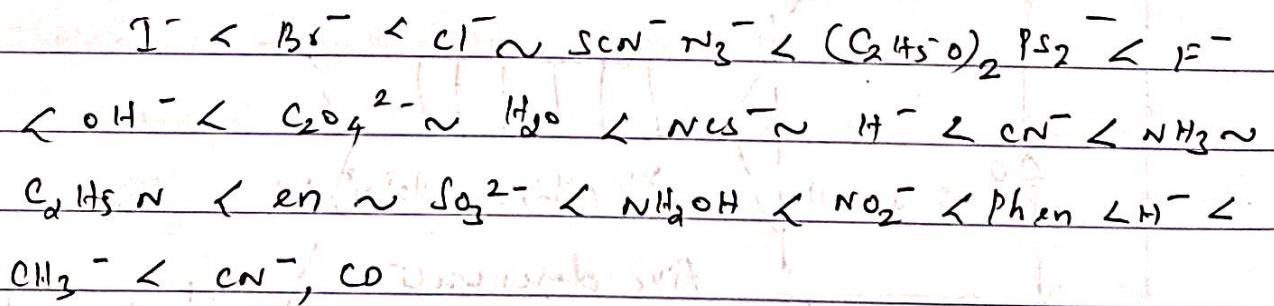
splitting of 'd' orbitals  
in presence of weak  
ligands ( $\text{Cl}^-$ )

CFT for octahedral  
complex.

splitting 'd' orbitals  
in presence of stronger  
ligands ( $\text{CN}^-$ )

The fig shows that not only  $\Delta_o$ , which represents the energy diff b/w the  $t_{2g}$  and  $e_g$  sets of orbitals, is smaller in the weak field complex than in the strong field ligand, but also that both the  $t_{2g}$  and  $e_g$  level of the weaker field are correspondingly closer to the level of the degenerate five d orbitals of the free isolated metal ion than are those, respectively, of the stronger field.

The common ligands can be arranged in the order of their increasing splitting power to cause d' orbitals splitting. This series is called spectrochemical series and is given below.



The series shows that the value of  $\Delta_o$  in the series also increases in the same order, i.e., from left to right.

## Limitation of CFT

(Dr. P. Panneerselvam)

- (i) CFT consider only the metal ion 'd' orbitals and gives no consideration at all to other metal orbitals such as  $s^-$ ,  $p_x^-$ ,  $p_y^-$  and  $p_z^-$  orbitals and the ligand  $\pi$  orbitals. Therefore, to explain all the properties of the complex depend on the  $\pi$ -ligand orbitals will be outside the scope of the CFT. CFT does not consider the formation of Ti-bonding in complex.
- (ii) CFT is unable to account satisfactorily for the relative strength of ligands, e.g., It gives no explanation as to why  $H_2O$  appears in the spectrochemical series as a strong ligand than  $OH^-$ .
- (iii) According to the CFT, the bond between the metal and ligands are purely ionic. It gives no account of the partly covalent nature of the metal-ligand bonds. Thus the effects directly depend on Covalency cannot be explained by CFT.

Crystal field stabilisation energies (CFSE) in terms of  $A_0$  and  $Dq$  for  $d^0$  to  $d^{10}$  configuration of metal ions in high spin and low spin tetrahedral complex

No. of d electron	$d^0$	$d^1$	$d^2$	$d^3$	$d^4$	$d^5$	$d^6$	$d^7$	$d^8$	$d^9$	$d^{10}$
High spin (weak field)	0.40 0.09	0.27 2.67	0.54 5.34	0.36 3.56	0.18 1.78	0 0	0.27 2.67	0.54 5.34	0.36 3.56	0.18 1.76	0 0
Low spin (strong field)	0.20	0.27	0.54	0.81	1.08	0.90	0.72	0.54	0.36	0.18	0

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