CRYSTAL FIELD THEORY

This theory advanced by Bethe and Van Vleck was originally applied mainly to ionic crystals and is therefore called crystal field theory (CFT).

It is mainly concerned with the interaction of d orbital of central metal with the surrounding ligands that produce crystal field effects.

Salient features:

1. A complex is considered to be a combination of central metal ion surrounded by various ligands.

2. The interaction between the metal ion and ligand is purely electrostatic (ionic).

3. It does not consider any orbital overlap.

4. The ligands are either negatively charged ions e.g., F^- and CN^- or neutral molecules e.g. H_2O and NH_3. The ligands approach the central metal ions with negative poles closest to the metal ions. Neutral molecules are polarised by the positive charge of the cation.

5. The interaction between the electrons of the metal ion and those of the ligand is purely repulsive. It is the repulsive forces that are responsible for causing the splitting of the d-orbital of the metal into two groups t_{2g} and e_g. This effect is known as crystal field splitting.

6. The number of ligands and their arrangement around the central ions will determine the crystal field.

7. Different crystal fields will have different effect on the relative energies of the five d-orbitals.

Spectrochemical Series:

* The ligands which split the d-orbitals of the central metal cation into t_{2g} and e_g sets of orbitals to a greater extent are called stronger ligands.

* Thus stronger ligands (eg CN^-, co etc) give larger value of Δ_0.

* The weaker ligands (eg. I^-, Br^- etc) yield a smaller value of Δ_0.

* If the ligands like I^-, Br^-, Cl^- etc are arranged in the increasing order of their power to split the d-orbitals of the central cation into t_{2g} and e_g sets of orbitals, we get the series namely,

$$I^- < Br^- < Cl^- \sim SCN^- < F^- < OH^- < C_2O_4^{2-} \sim H_2O < NH_3 < en < NO_2^- < CN^- <$$
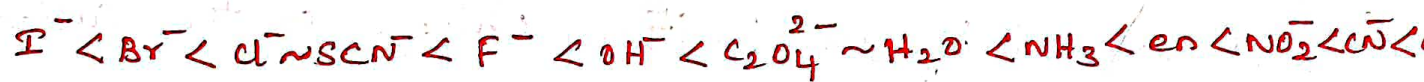
which is called Spectrochemical series.

* The octahedral complexes containing weaker ligands attached with the central cation are called weak field or low field complexes. (or) high spin complexes.

* while those containing stronger ligands are called <u>strong field</u> or <u>high field complexes</u> or <u>low spin complexes</u>.

* In case of <u>weak field</u> complexes $\Delta_0 < P$ while in case of <u>strong field</u> complexes $\Delta_0 > P$ where Δ_0 = <u>energy difference between t_{2g} and e_g sets</u> and P = <u>average pairing energy</u> which is the energy required to pair <u>two electrons in the same orbital</u>.

Crystal field splitting of d-orbitals:

The outcome of crystal field theory is that degeneracy of the d-orbitals of the central metal ion is when the ligands approach it consequently the d-orbitals split into two groups. To understand this we recollect the shapes of d-orbitals. They are as follows.

dxy

dxz

dyz

dx²-y²

dz²
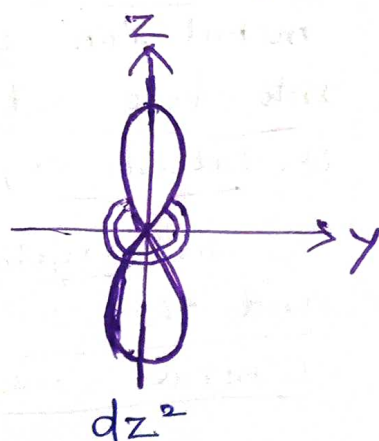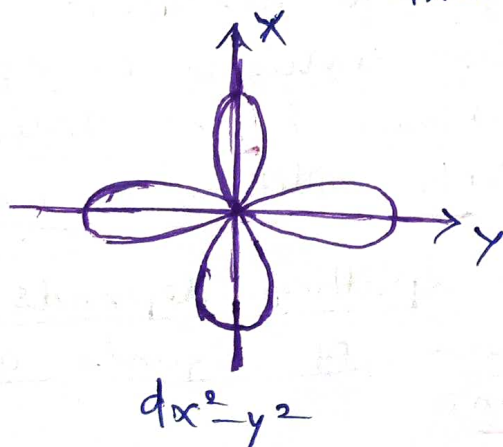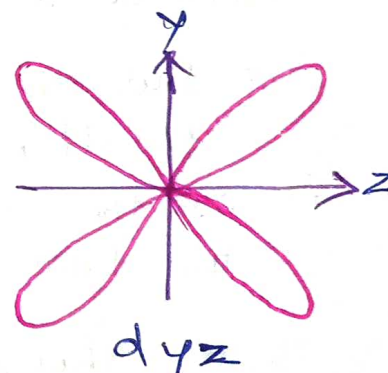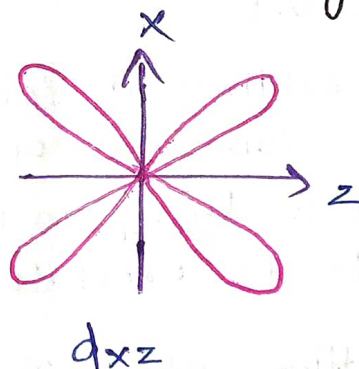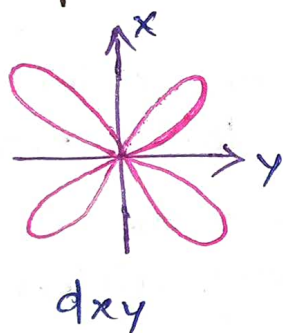
* In a free metal ion all the five d-orbit
are degenerate ie have the same energy.

d_{xy}, d_{yz},

* Orbitals lie between xy, yz, zx axes respectively. They ar
known as t_{2g} set of orbitals.

* $d_{x^2-y^2}$, d_{z^2} orbitals are oriented along the
X-axis and y-axis. They are called as eg set of orbi

* On the approach of the ligands, the electrons in the
d-orbitals of the central ion are repelled by the lone
pairs of the ligands.

* As a result, an energy of the entire system will be
raised.

* If the electric field arising from the ligands is
spherically symmetrical, the energy of all the d-orbitals
would be raised to the same extent, and they will
still be degenerate.

* But the d-orbitals differ in the orientation. As a
result, the energies of the larger extent than those
of the orbitals lying in between the split up into
the two sets of orbitals having different energies.

* This splitting of five degenerate d-orbitals of the
metal ion under the influence of approaching ligands,
into two sets of orbitals having different energies
is called crystal field splitting or energy level splitting.

The crystal field splitting depends on the number
and the arrangement of ligands around the
central metal ion.

orbit

## Crystal field splitting in Octahedral Complexes : (oh)

In the octahedral (oh) complex, the six ligands are arranged octahedrally around a central metal ion.

In this arrangement the dx^2-y^2 and d_{z^2} orbitals lie along the x, y, z axes and point directly towards the ligands.

So, they experience much more repulsion than those remaining d-orbitals dxy, dyz, dzz, which are directed in between the x, y and z axes.

Consequently the energies of dx^2-y^2 and d_{z^2} orbitals are increased much more in comparison to other d-orbitals.

The d-shell thus splits up into two degenerate sets, one consisting of more stable (lower energy) orbitals, dxy, dyz, dzx. and other less stable (higher energy) orbitals dx^2-y^2 and d_{z^2}.
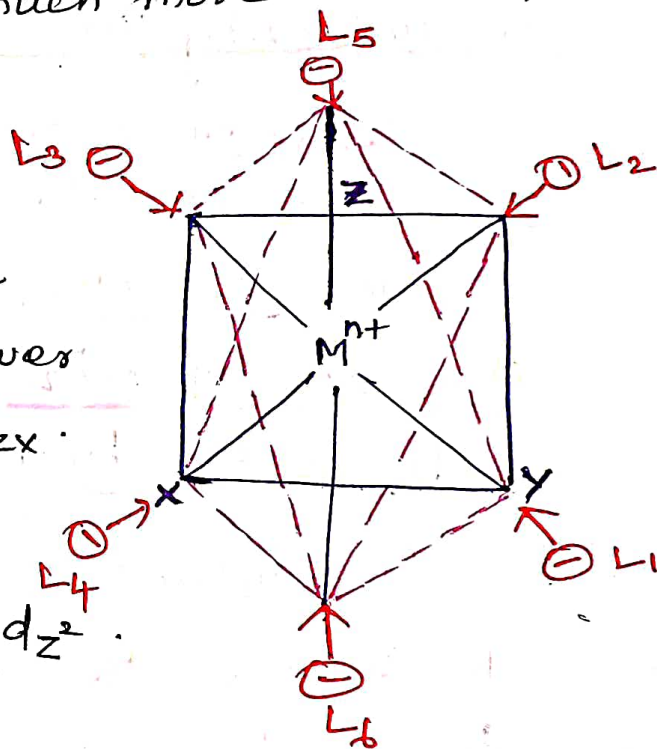
The energy difference between e_g and t_{2g} sets of orbitals is known as Crystal field stabilization energy (CFSE) and this is represented by the symbol Δ_o (or) D_q. where 'o' indicates an octahedral arrangements of ligands.

It is measured in terms of a parameter Dq. The magnitude of splitting is orbitarily set as 10.

Con...
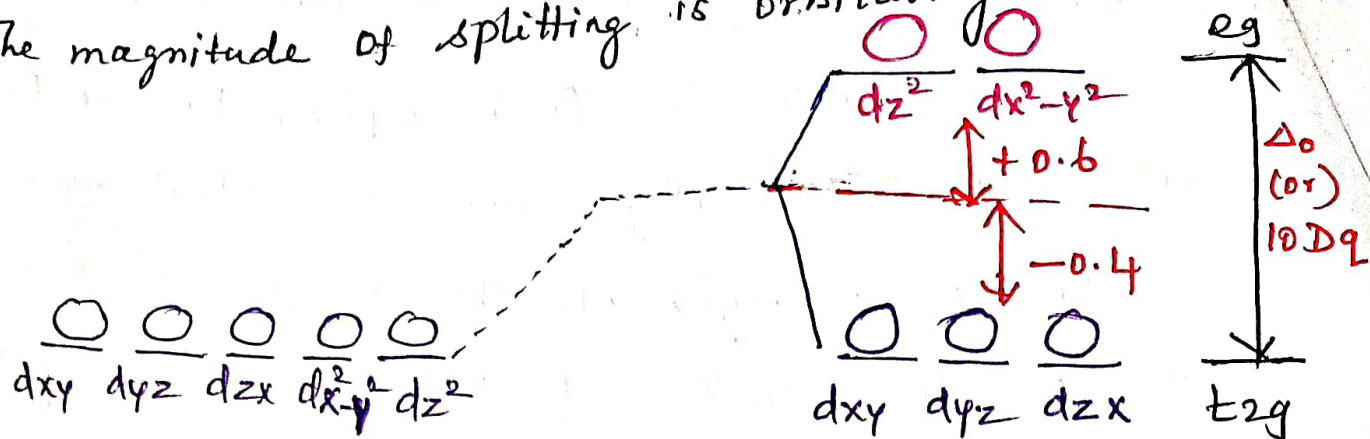
Electrons will tend to occupy the lower energy t_{2g} orbitals to achieve stability.

Each electron entering the t_{2g} orbitals stabilizes the complex by $0.4 \Delta_0$ units and each electrons entering the higher energy orbitals (e_g) introduces in the comple an instability unit of $0.6 \Delta_0$.

The greater the amount of CFSE of the complex is, greater is its stability.

Since $\Delta_0 = 10 Dq$, each electron entering t_{2g} orbital stabilizes by $4 Dq$ & each electron entering e_g orbital destabilizes by $6 Dq$.

The magnitude of Δ_0 depends upon the following factors

1. Size of the metal ion.
2. Oxidation state of the metals.
3. Nature of the ligand.
4. Stereochemistry of the complex.

Let us consider a d^x ion containing $t_{2g}^{p}\ e_{g}^{q}$ configuration, where 'p' is the number of electrons in t_{2g} level and 'q' is the number of electrons in e_g level. and $x = p+q$.

For this system, the CFSE is given by

$$CFSE = [-4p + 6q]\, Dq$$

∧ In the above expression, the pairing energy (P) is not taken into account. If we take that also into account their.

$$CFSE = [-4p + 6q]\, Dq + mp$$

where 'm' is the total number of pairs of electrons in t_{2g} and e_g levels put together.

The following table gives of CFSE for various Configuration are given below.

(1) High Spin (spin-free / weak field) octahedral Complexes

Configuration	P	Q	m	CFSE
d^0	0	0	0	$0\, Dq$
d^1	1	0	0	$-4\, Dq$
d^2	2	0	0	$-8\, Dq$
d^3	3	0	0	$-12\, Dq$

Configuration	P	Q	m	CFSE
d^4	3	1	0	$-6Dq$
d^5	3	2	0	$0Dq$
d^6	4	2	1	$-4Dq+P$
d^7	5	2	2	$-8Dq+2P$
d^8	6	2	3	$-12Dq+3P$
d^9	6	3	4	$-6Dq+4P$
d^{10}	6	4	5	$0+5P$

2. Low spin (spin paired / strong field) octahedral complexes

Configuration	P	Q	m	CFSE
d^0	0	0	0	$0Dq$
d^1	1	0	0	$-4Dq$
d^2	2	0	0	$-8Dq$
d^3	3	0	0	$-12Dq$
d^4	4	0	1	$-16Dq+P$
d^5	5	0	2	$-20Dq+2P$
d^6	6	0	3	$-24Dq+3P$
d^7	6	1	3	$-18Dq+3P$
d^8	6	2	3	$-12Dq+3P$
d^9	6	3	4	$-6Dq+4P$
d^{10}	6	4	5	$-0Dq+5P$

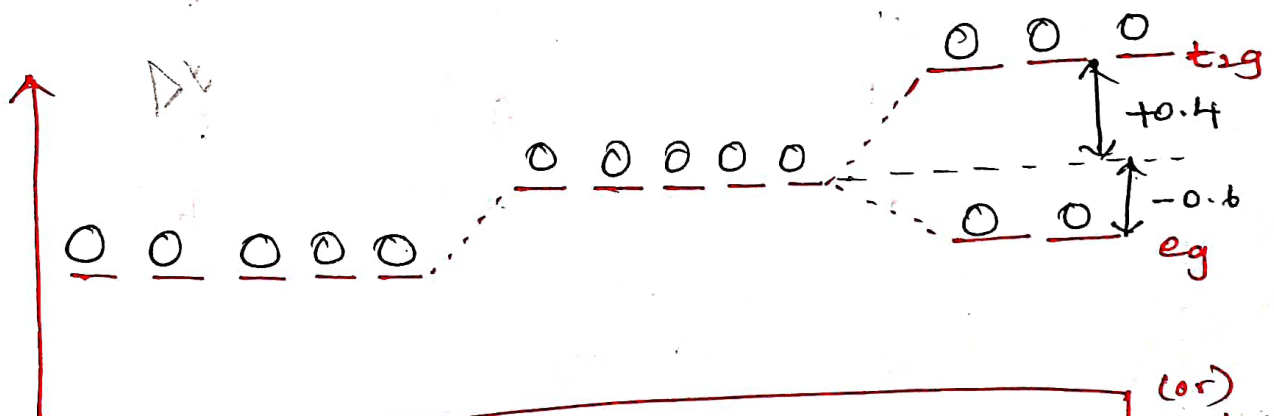# Crystal field splitting in tetrahedral complex:

The tetrahedral arrangement of a central metal ion surrounded by four ligands is shown in figure.

we find that in tetrahedral arrangement no d-orbitals points exactly towards the ligand, d_{xy}, d_{yz} and d_{xz} are pointing approximately by in the directions of the approaching ligands.
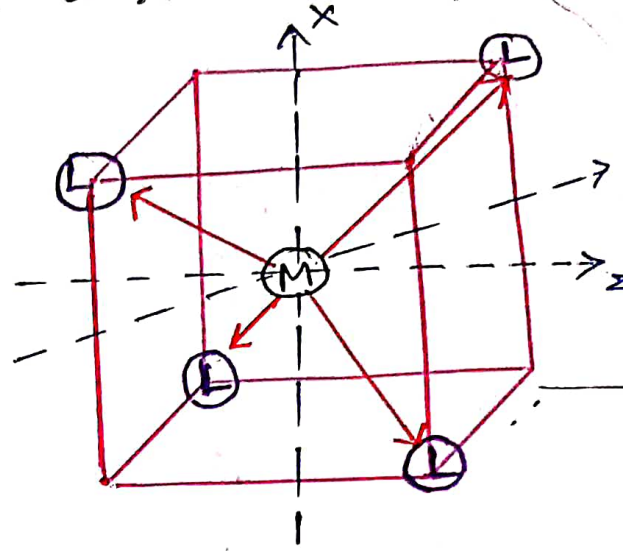
$d_{x^2-y^2}$ and d_{z^2} are lying in between approaching ligands. So the energies of d_{xy}, d_{yz} and d_{xz} increase more than those of $d_{x^2-y^2}$ and d_{z^2}.

Thus we find that the d orbital splitting is just the reverse of what happened in octahedral complexes.

$$\Delta_t \qquad \text{(energy level diagram)}$$

$$t_{2g} \qquad +0.4$$

$$e_g \qquad -0.6$$

The CFSE of tetrahedoal complex $\Delta t = 0.45 \Delta_0$ (or) $\Delta_t = \frac{4}{9}\Delta_0$

Thus the crystal field splitting in a tetrahedral complex will be about half the magnitude of octahedral complex. Hence crystal field effects favours the formation of octahedral complex over that of tetrahedral complex.

Calculation of CFSE in tetrahedral complex

$$CFSE = (-0.6q + 0.4P)\Delta_t$$

$$CFSE = (-6q + 4p)Dq$$

Configuration	q (eg)	p (t₂g)	CFSE
d^0	0	0	0 Dq
d^1	1	0	-6 Dq
d^2	2	0	-12 Dq
d^3	2	1	-8 Dq
d^4	2	2	-4 Dq
d^5	2	3	0
d^6	3	3	-6 Dq
d^7	4	3	-12 Dq
d^8	4	4	-8 Dq
d^9	4	5	-4 Dq
d^{10}	4	6	0

Magnetic Properties:

* If an orbital contains paired electrons, the magnetic moment of one electron is cancelled by the equal and opposite magnetic moment of the other. Such substances get repelled by an applied magnetic field and are called diamagnetic.

* A substance having orbitals with one or more unpaired electrons, however, has a definite magnetic moment and it is attracted by a magnetic field. Such substances are said to be paramagnetic.

* It has been shown that magnetic moment of a substance containing 'n' unpaired electrons is approximately equal to $\sqrt{n(n+2)}$ Bohr magnetons.

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

Magnetic moment (BM)	No. of unpaired electrons (n)
0	0
1.73	1
2.83	2
3.87	3
4.90	4
5.92	5

Example:

(1) Calculation of magnetic moment of $[Fe(CN)_6]^{3-}$

CN − Strong ligand.

$x - 6 = -3$
$x = -3 + 6$
$x = +3$

$Fe - 3d^6 \, 4s^2$
$Fe^{3+} - 3d^5$

$Fe^{3+} (d^5)$ [↑|↑|↑|↑|↑]
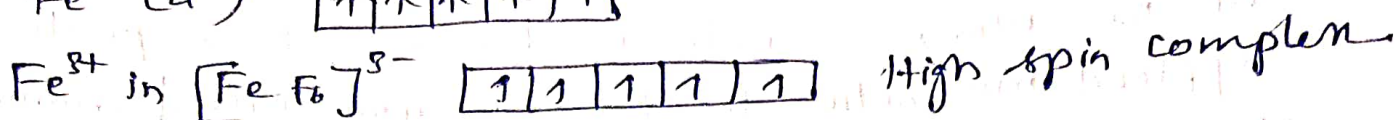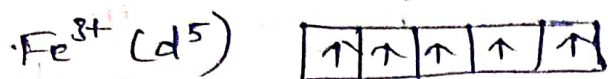
Fe^{3+} in $[Fe(CN)_6]^{3-}$: [↑↓|↑↓|↑| |] Low spin complex.
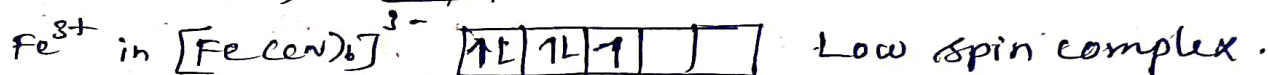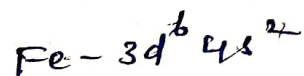
$n = 1$ ∴ $\mu = \sqrt{n(n+2)} = \sqrt{1(1+2)} = \sqrt{3} = 1.73 \, BM.$

Complex is Paramagnetic in nature.

(2) Calculation of magnetic moment value of the
Complex $[Fe\ F_6]^{3-}$

F^- — weak ligand

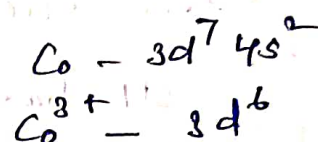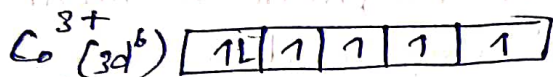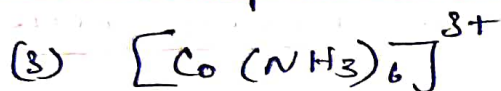$x + 6 = -3$
$x - 6 = -3$
$x = 6 - 3$
$x = +3$ //

$Fe^{3+}\ (d^5)$ ⬆⬆⬆⬆⬆

Fe^{3+} in $[Fe\ F_6]^{3-}$ ⬆⬆⬆⬆⬆   High spin complex.

$n = 5$

∴ $\mu = \sqrt{n(n+2)} = \sqrt{5(5+2)} = \sqrt{5(7)} = \sqrt{35} = 5.928$

∴ The complex is Paramagnetic.

(3) $[Co\ (NH_3)_6]^{3+}$

$Co^{3+}\ (3d^6)$ ⬆⬇⬆⬆⬆⬆

$Co — 3d^7\ 4s^2$
$Co^{3+} — 3d^6$

NH_3 is a strong ligand.

∴ Co^{3+} in $[Co\ (NH_3)_6]^{3+}$ is ⬆⬇⬆⬇⬆⬇⬜⬜
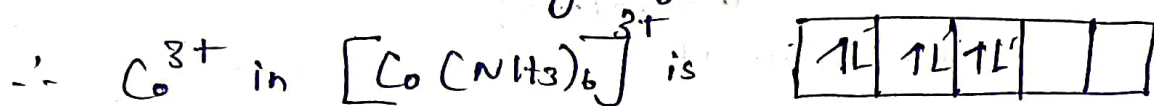
$n = 0$ ∴ $\mu = \sqrt{n(n+2)} = \sqrt{0(0+2)} = 0$

$\mu = 0$.

∴ The complex is diamagnetic.

(4) $[Fe\ (CN)_6]^{4-}$ CN — strong ligand.

$Fe^{2+}\ (3d^6)$ ⬆⬇⬆⬆⬆⬆

$x - 6 = -4$
$x = 6 - 4$
$x = +2$ //

∴ In $[Fe\ (CN)_6]^{3-}$ ⬆⬇⬆⬇⬆⬇⬜⬜
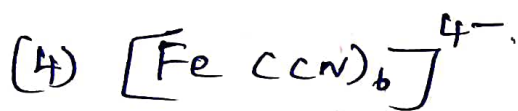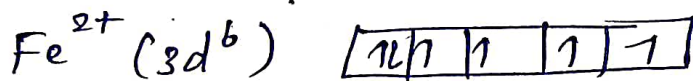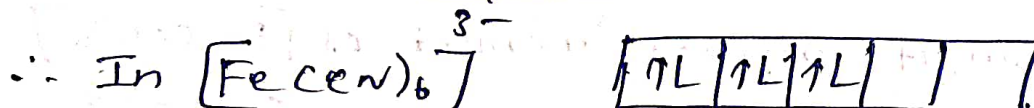
$n = 0$ ∴ $\mu = \sqrt{n(n+2)} = \sqrt{0(0+2)} = 0$

∴ $\mu = 0$

And the Complex is diamagnetic in nature.