g to the purely electrostatic theory, the metal and ligand bonding sidered as point charges. The force of electrostatic attraction between sponsible for chemical bondings. Hence bond energy is given by expression;

; Bond Energy = $\frac{q_1 q_2}{r^2}$

The crystal field splitting is thus the energy difference between d_γ and d_ϵ orbitals. and it is denoted by the Symbol Δ_o where script 'o' indicates octahedral complex or 10 Dq.

$\Delta_o = 10\ Dq$.

It can be shown from the Geometry of an octahedral system that energy of d_ϵ orbital is $0.4\Delta_o$ or $\frac{2}{5}\Delta_o$ or = 4 Dq less than that of the hypothetical degenerate d-orbitals, which result, if the crystal field splitting is ignored (state II). The energy of d_γ orbitals is $\frac{3}{5}0.6\Delta_o$ = 6 Dq, above that of the Hypothetical degenerate d-orbitals. It may be noted that according to purely Electrostatic theory which does not recognise any splitting of energy levels. All the five d-orbitals should have the same energy for the approach of ligands as represented in state II.

But According to Crystal field theory, there is definite splitting of energy levels, represented in state III.

We know that an electron always prefers to move in to an orbital of lower energy.

It is evident that in an octahedral Complex containing one d-electron, that electron will reside one of d_ϵ orbitals. this orbital is associated with energy $0.4\Delta_o$ = 4 Dq. less than that of Hypothetical degenerate orbital predicted by purely Electrostatic theory.

Thus the Complex (Δ_o) is more stable than predicted by purely Electrostatic Theory.

Hence $0.4\Delta_o = 4Dq$ is called Crystal field Stabilization Energy (C.F.S.E) of the complex under consideration.

Thus for each electron entering into $d\epsilon$ orbital, the C.F.S.E. is $0.4\Delta_o$ or $4Dq$.

Also for each electron entering into dr orbital, the destabilisation energy is $0.6\Delta_o = 6Dq$. In other words for each electron entering into dr orbital the stabilisation energy is $0.6\Delta_o = 6Dq$.

Hence, working on this basis, it is possible to calculate Crystal field Stabilisation energy for various metal ion in Octahedral Complexes:-

Distribution of Electrons in d-orbitals and C.F.S.E of Octahedral Complexes: → the distribution of electron in d-orbitals is based upon the following rules.

(i) Electrons prefer to occupy orbitals of lowest energy

(ii) Electron obey Hund's rule i.e. Pairing is not possible, until all the available orbitals of a given set contain one electron each

(iii) If energy to place an electron in the upper dr orbitals is greater than energy to pair electron (Pairing Energy = P) in the lower $d\epsilon$ level. ($10Dq > P$) the electron will pair up in $d\epsilon$ orbital.

(iv) If energy to place an electron in upper dr level is less than the pairing energy in the lower $d\epsilon$ orbital, ($i.e\ 10Dq < P$) the electron will occupy in dr-orbitals.

TION OF d-ELECTRONS IN $d\epsilon^{t_{2g}}$ & $d\gamma^{e_g}$ orbitals IN OCTAHEDRAL COMPLEXES:→

The distribution of d-electrons in dε and dγ orbital takes place on the basis of the nature of the ligands, i.e whether the ligands are weaker or stronger.

Thus two cases arise:—.

(i) When the ligands are Weaker:→ (High spin Complex.)

It has been that under the influence of weaker ligands the energy difference, Δ_o between dε and dγ orbitals is comparatively small ~~and~~ so, all the five d-orbitals of these two orbitals may be supposed to be degenerate. i.e in presence of weaker ligands all the d-orbitals have the same energy. and Consequently the distribution of d-electrons in dε & dγ sets takes place according to Hund's rule, which states, Electron will pair up only when each of the five d-orbitals is at least singly filled.

It may be clearly understood by means of the following example.

The d-orbital Contains 10 electron:, Hence in this case electron. no. 1,2,3 go to dε level, and 4,5 go to the dγ level, then 6,7,8, (three electron) go to dε level and the remaining two electrons 9 & 10 will occupy dγ sets.

$$d\epsilon^{1,2,3} \longrightarrow d\gamma^{4,5} \longrightarrow d\epsilon^{6,7,8} \longrightarrow d\gamma^{9,10}$$

For example, If we Consider the octahedral Complex i.e $[CoF_6]^{3-}$, which Contains Weaker ligands, The distribution of Six d-electrons of Co^{+3} ion (Co^{+3} — $3d^6$) in dε & dγ sets will be $d\epsilon^4, d\gamma^2$. ~~Into~~ Complex which Contains weaker ~~field~~

ligans are refered as Weak field or low field Complex.

In the formation of such type of Complexes $\Delta_o < P$, where P is average pairing energy, which is the energy required to pair two electrons in the same orbital, & Δ_o is Octahedral Crystal field splitting Energy.

(ii) When the ligands are stronger:→ (Strong field) or high spin complex.

$P > \Delta_o$

Now we consider the octahedral Complexes Containing stronger ligands, the distribution of d-electrons in $d\epsilon$ and $d\gamma$ sets does not obey Hund's rule.

Thus in stronger field the first six electrons numbered as 1,2,3,4,5 & 6, these electrons will go to $d\epsilon$ set and the remaining four electrons numbered as, 7,8,9 & 10 enters into $d\gamma$ set.

this Can be shown as:—

$$d\epsilon^{1,2,3,4,5,6} \longrightarrow d\gamma^{7,8,9,10}.$$

Let us Consider on the distribution of $\overset{1}{\text{Six}}\ d^1$ electron of Co^{+3} ion ($Co^{+3} \longrightarrow 3d^6$) in the Complex ion $[Co(NH_3)_6]^{3+}$ which Contains Stronger ligand, Thus it is Quite obvious that the distribution will be takes as $d\epsilon^6 d\gamma^0$ i.e $t_{2g}^6 e_g^0$ (where t_{2g} stands for tolply regenerate and e_g stands for doubly regenerate orbitals).

The Complex which Contains stronger field ligand like NH_3 is Called Strong field Complex or High field Complex.

For these Complex, $\Delta_o > P$

i.e the C.F. splitting in Octahedral Complex is ~~greater~~ lesser than the pairing Energy.

Strength of Ligands :

The strength of ligand is considered in the following order :—

$Co > CN^- > NO_2^- > en > NH_3 > H_2O > F^- > OH^- > Cl^- > Br^- > I^-$

Strong field ligand — Weak ligand field

(a) In a weak field ligand $10Dq > P$, Hence pairing does not occur in de orbitals. i.e C.F.S.E > Pairing Energy

(b) In the case of strong field ligand $P < 10Dq$, Hence pairing occurs in de orbitals. i.e Pairing Energy < C.F.S.E

In an octahedral complex with d^1 - configuration. the d-electron will occupy, t_{2g} (the lower) de orbital. irrespective of the field strength and crystal field stabilization energy is $-4Dq$.

For d^2 configuration, the two electron will occupy separate two de orbitals and C.F.S.E is $-8Dq$. Similarly for d^3 Configuration CF.S.E is $-12Dq$ and de level is just half field.

Thus Complex with d^1, d^2 and d^3 configuration. will be irrespective of ligand field strength and will be paramagnetic with 1, 2, 3 unpaired electron.

For d^4 (electron) Configuration, there are two possibilities :—

(2) If ligand is weak field ligand then $P > 10Dq$.
and 4th electron will go in to dr level and Pairing will not occur in de orbitals.

$$\therefore C.F.S.E. = \{8 \times (-4Dq)\} + 1(+6Dq)$$

$$= -12Dq + 6Dq = -6Dq \text{ or } .6\Delta_o$$

or.

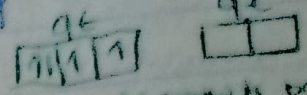
$$\text{or } C.F.S.E = [[3 \times -.4] + 1(.6)]\Delta o$$

or $3 \times -.4\Delta o + 1 \times .6\Delta o = -1.2\Delta o - 1.6\Delta o$

$= -.6\Delta o$

(2) If ligand is strong field ligand then $P < 10Dq$ and electron will prefer to go into t_{2g} orbital and pairing takes place.

$$C.F.S.E. = 4 \times (-4Dq) + P$$
$$= -16Dq + P$$



one electron is paired hence P.P

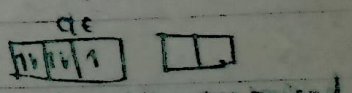
Thus for d^4 configuration, electronic arrangement in weak and strong fields.

In the weak field there are 4 unpaired electron while in the strong field there are only two unpaired electrons. The arrangement with maximum number of unpaired electrons is called 'High spin', or spin free, & one with minimum number of unpaired Electron is called 'Low spin' or spin paired arrangement'.-

For d^5 configuration, in a weak field three electrons occupy the t_{2g} orbitals and the other two, goes into e_g orbitals. (One electron in each), C.F.S.E is zero, because the presence of two electrons in unfavorable e_g - level, exactly balances. $C.F.S.E = -4Dq \times 3 + 6Dq \times 2 = -12 + 12 = 0$

In Case of strong field ligand 5th Electron will go into t_{2g} orbital and pairs a t_{2g} orbital.

$$C.F.S.E = -20Dq + 2P.$$



three t_{2g}-orbitals are paired
Hence pairing E = 2P.

For d^6 - configuration in weak field, the 6th electron will pair up one t_{2g} orbital. ~~one t_{2g} orbital~~.

$$\therefore C.F.S.E = -4Dq + P$$

Now In strong field ligand the 6th electron will pair up a t_{2g} orbital. and $C.F.S.E = -24Dq + 3P$

Similarly for d^7, d^8, d^9 and d^{10} Configuration the d-electrons of the metal can be distributed and their C.F.S.E can be calculated.

In General Δ_o C.F.S.E = $(-0.4x + 0.6y)\Delta_o + mP$

P = mean pairing energy which is the energy required to pair two electrons against electron-electron repulsion in the same orbit.

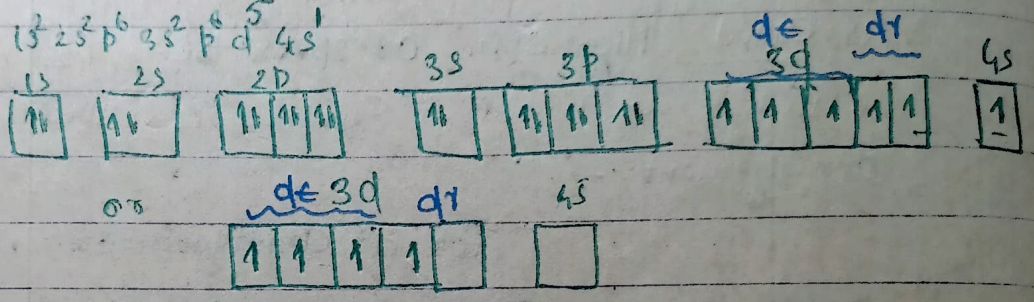
m = No. of unpaired electrons.

Can be distributed and their C.P.S.E can be Calculated.

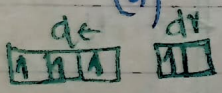
Question → For the $[Cr(H_2O)_6]^{3+}$ ion, the mean pairing energy, P is found to be 23,500 cm^{-1}, the magnitude of Δ_o is 13,900 cm^{-1} Calculate the C.F.S.E for this Complex ion Corresponding to high spin and low spin state. Which state is more stable.

Ans Cr is present as Cr^{+3} ion. Which is d^4 ion.

$_{24}Cr \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 d^5 4s^1$



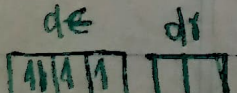
(a) For d^4 ion in a high spin state (Maximum unpaired condition)



C.F.S.E = $-0.4 \times 3 + 1 \times 0.6$

$= -1.2 + 0.6 = -0.6\Delta_o$

$= -0.6 \times (13,900)\ cm^{-1} = -8,340\ cm^{-1}$



For a d^4 ion in low spin state (Minimum unpaired)

C.F.S.E = $(-0.4 \times 4)\Delta_o + P$

$= -1.6\Delta_o + P$

$= (-1.6 \times 13900 + 23500)\ cm^{-1}$

$= -22240 + 23500$

$= +1260\ cm^{-1}$

Since ($\Delta_o = 13,900\ cm^{-1}$) is less than P (= 23500), Hence the high spin Configuration would be more stable.