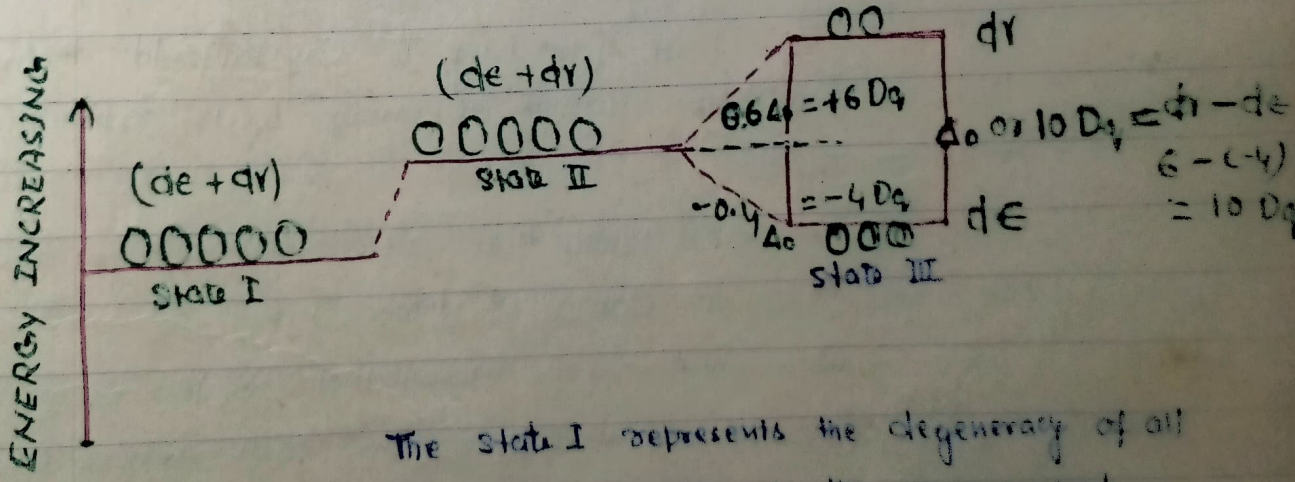
Spliting in Octahedral Complexes.

The three axes, x, y and z are pointed along the corners of a octahedron. It is all ready mentioned that $d\gamma$ orbitals (dx^2-y^2 & dz^2) are oriented along the axis and the $d\epsilon$ orbitals are oriented between the axes.

When the ligand approaches towards central metal ion the energy of $d\gamma$ orbitals increases rabidly than $d\epsilon$ orbital. It is due to the fact that $d\gamma$ orbital lies in the path of approaching ligand, the electron in these orbital experienced greater force of repulsion than those in $d\epsilon$ orbital.

Thus we find that under the influence of approaching ligands the five d-orbitals, which were originally degenerate in the free metallic cation are now (split) resolved in to two sets. One is $d\gamma$ level and other is $d\epsilon$ level.

The phenomenon of crystal field splitting in an octahedral complex has been shown below..



The state I represents the degeneracy of all the five d-orbitals. The state II represents the hypothetical degeneracy of all the orbitals at a higher energy level, if all the ligands approaches the central metal ion are at equal distance from each of the d-orbitals. i.e (ligand field is spherically symmetrical) the state III represents the c.f. spliting of d-orbitals.

Note:→ According to the purely electrostatic theory, the metal and the ligands surrounding it are considered as point charges. The force of electrostatic attraction between them is responsible for chemical bonding. Hence bond energy is given by expression;

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

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 show 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 the 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 $(-4\Delta_o)$ 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 $4Dq$.

Now 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 Stabilization 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.