CHEMISTRY

(FOR IIT, NEET, AIIMS)

Class – XII

Chapter 9: Coordination Chemistry

Topic : Crystal Field Theory (CFT)

➢Crystal Field Theory (CFT)

➢This theory was for the first time proposed by Orgel to explain nature of bonding in complexes.

➢It is an electrostatic model, where ligand-metal bond is considered to be ionic and arising purely from electrostatic interactions between metal ion and ligands.

➢Here, ligands are treated as point charges in case of anions or dipoles in case of neutral molecules.

➢In an isolated gaseous metal atom or ion, all the five d-orbitals have same energy i.e. they are degenerate. This degeneracy is maintained even in a spherically symmetrical magnetic field of negative charges surrounding the metal atom or ion.

➢However, if the magnetic field is due to ligands (anions or negative ends of polar molecules), it is asymmetrical and penta-degeneracy of five d-orbitals gets vanished and they get splited into two or more sets of orbitals having different energy.

➢This phenomenon is called Crystal Field Splitting of d- orbitals. Here, the pattern of splitting depends upon the nature of crystal field and is different in different types of crystal fields.

➢Crystal Field Splitting in Octahedral Magnetic Field

➢When ligands approach octahedrally to the CMI, the penta-degeneracy of its five d-orbitals gets vanished and they get splitted into two sets of orbitals, namely t_{2g} set (d_{xy}, d_{yz} and d_{xz}) having lower energy and e_g set ($d_x2\text{-}_y2$ and d_z2) having higher energy.

➢Here, the difference of the energy of the orbitals of e_g and t_{2g} set is called crystal field splitting energy (CFSE) and is represented by Δ_o.

➢In fact, axial d-orbitals (d_x2-$_y2$ and d_z2) lie in direct path of the ligands and therefore, they feel relatively more repulsion as compared to the non-axial d-orbitals (d_{xy}, d_{yz} and d_{xz}), which do not lie in direct path of the ligands. Thus, energy of axial d-orbitals (d_x2-$_y2$ and d_z2) gets increased more as compared to the average energy in spherical crystal field (barycentre) while, increase in energy of non-axial d-orbitals (d_{xy}, d_{yz} and d_{xz}) is relatively lesser as compared to that in spherically symmetrical crystal field.

➢Here, any electron entering in t_{2g} orbitals, lowers the energy of the complex ion by 2/5 Δ_o, while those entering in e_g orbitals increase the energy of complex ion by 3/5 Δ_o.

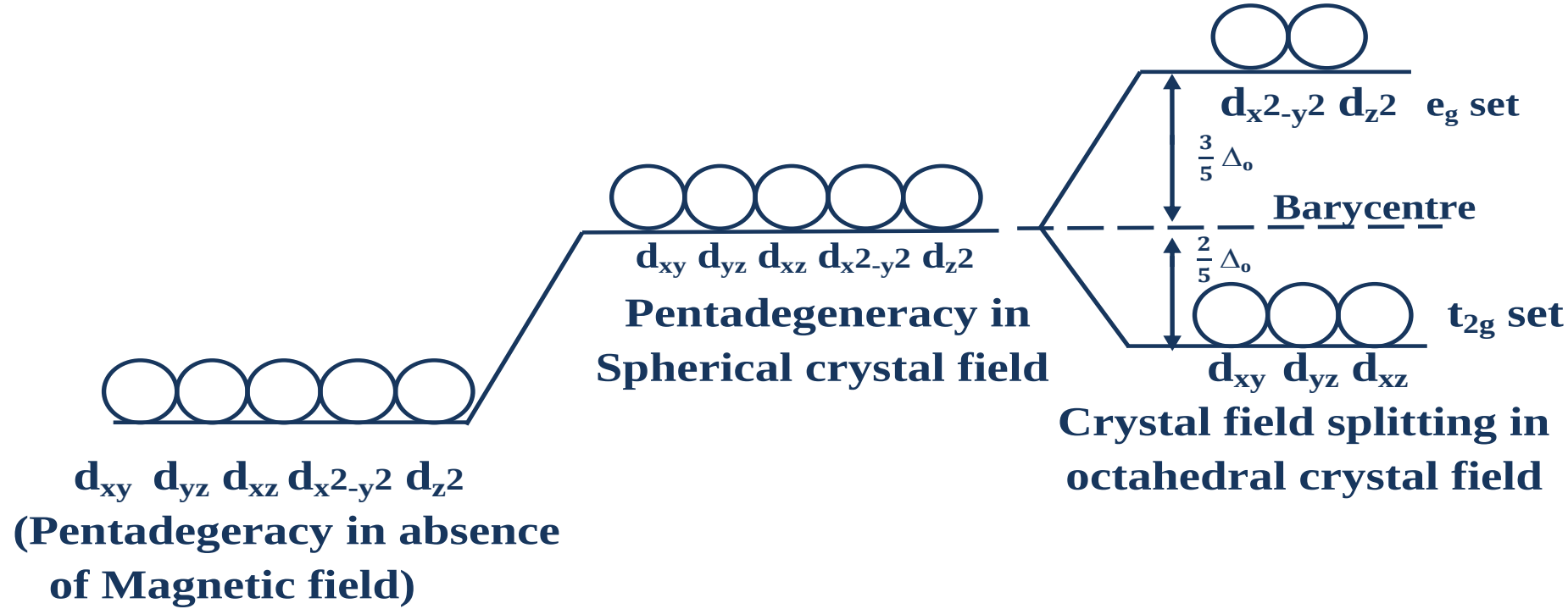


Fig.- Crystal Field Splitting of d-orbitals in octahedral magnetic field

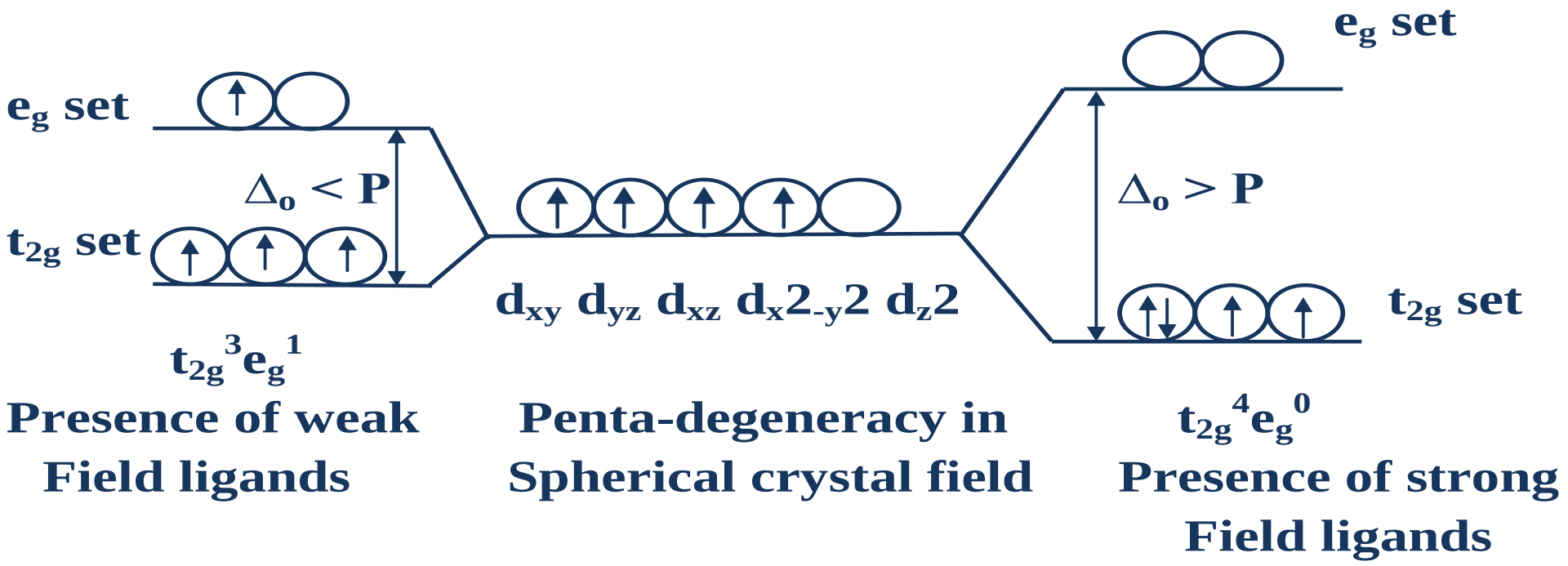
➢Crystal field splitting energy Δ_o depends upon the nature of crystal field produced by ligands and charge on the metal ion.

➢Electronic configuration of complexes

➢For strong field ligands, the value of CFSE is more than pairing energy, P (energy required for pairing of electron in orbital of lower energy). Hence, the electrons prefer to pair up in t_{2g} orbitals, instead of entering in e_g orbitals having higher energy.

➢On the other hand, for weak field ligands, the value of CFSE is lesser than the pairing energy, P. Hence, the electrons prefer to enter in e_g orbitals, instead of being paired in t_{2g} orbitals of lower energy.

➢For example, the electronic configuration of CMI having d^4 configuration in a complex ion with weak and strong field ligands can be expressed as under-



➢Spectrochemical Series

➢If different ligands are arranged in increasing order of their crystal field splitting energy i.e. field strength, a series is obtained which is called Spectrochemical Series.

➢An Spectrochemical Series of some most common ligands is as under-

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

➢This series has been determined experimentally by absorption of light by complexes containing different ligands.

➢Crystal Field Splitting in Tetrahedral Magnetic Field

➢When ligands approach tetrahedrally to the CMI, the penta-degeneracy of its five d-orbitals gets vanished and they get splitted into two sets of orbitals, namely t_2 set (d_{xy}, d_{yz} and d_{xz}), having higher energy and e set (d_x2-$_y2$ and d_z2) having lower energy. Here, the difference of the energy of the orbitals of t_2 and e set is called crystal field splitting energy (CFSE) and is represented by Δ_t.

➢Here, none of the d-orbitals lie in direct path of the ligands, but non-axial d-orbitals (d_{xy}, d_{yz} and d_{xz}) are more closure to the ligands and therefore, they feel relatively more repulsion as compared to the axial d-orbitals (d_x2-$_y2$ and d_z2). Thus, energy of non-axial d-orbitals (d_{xy}, d_{yz} and d_{xz}) gets increased more as compared to the average energy in spherical crystal field (barycentre) while, increase in energy of axial d-orbitals (d_x2-$_y2$ and d_z2) is relatively lesser as compared to that in spherically symmetrical crystal field. Thus, pattern of crystal field splitting in tetrahedral crystal field gets inverted as compared to that in octahedral crystal field.

➢Here, any electron entering in e-orbitals, lowers the energy of the complex ion by 3/5 Δ_t, while, those entering in t_2 orbitals, increases the energy of complex ion by 2/5 Δ_t.

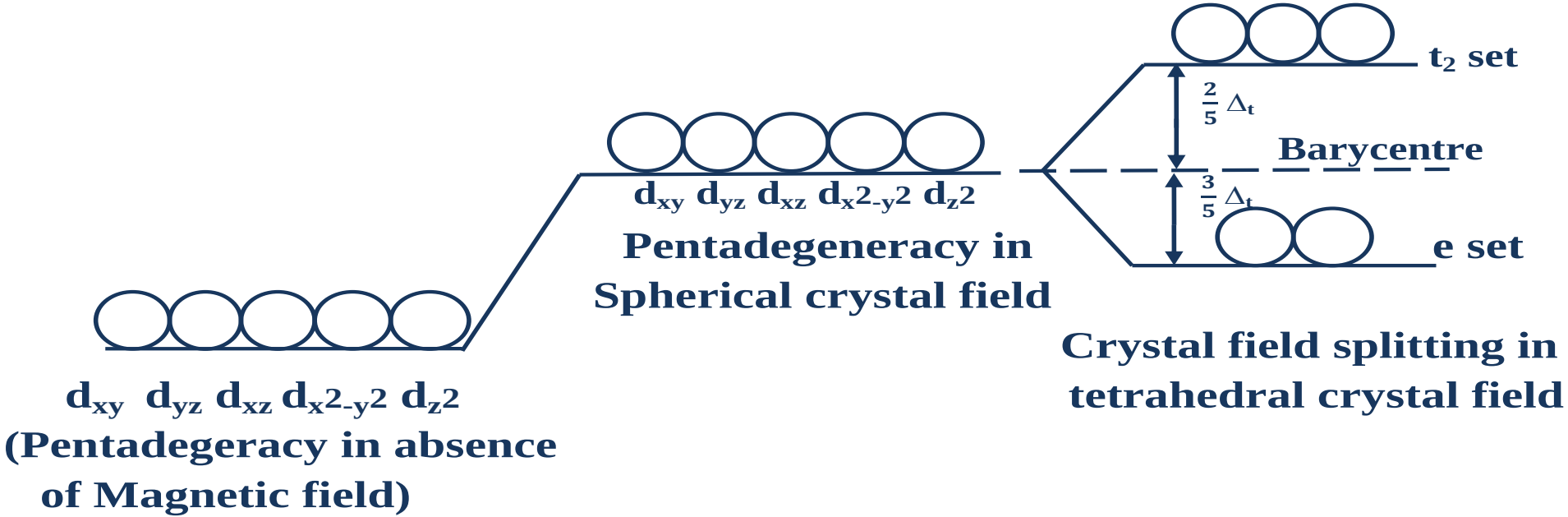


Fig.- Crystal Field Splitting of d-orbitals in tetrahedral magnetic field

- Crystal field splitting energy, Δ_t for tetrahedral complexes is relatively lesser as compared to that of octahedral complexes.

- For same metal ion, same ligands and same distance of ligands from the metal ion, Δ_t is related to Δ_o as under-

$$\Delta_t = \frac{4}{9} \Delta_o$$

- Here, the crystal field splitting energy is not sufficiently large for forced pairing of electrons in orbitals of lower energy. It is the reason why, low spin configurations are rarely observed in tetrahedral complexes.

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