Crystal field stabilization energy in octahedral complexes:-

In an octahedral complex, the d-orbitals of the central metal ion are split into two sets of orbitals having different energies. The separation b/w these two steps is Δ_o or 10 Dq. The t_2g set has an energy of $-0.4\Delta_o$ and the eg set has an energy of $+0.6\Delta_o$ relative to Bary centre - & + signs indicate decrease & increase in energy related to Bary centre

Crystal - field stabilization energy is given by :- In an octahedral complex with e.c $t_{2g}^{x}\ eg^{y}$. The C.F.S.E is given by C.F.S.E = $[(0.4 \times x) + (0.6 \times y)]\Delta_o$ x = no. of e's in t_{2g} & y = no. of e's in eg. The Crystal field stabilization.

Scanned by CamScanner

Metal ions	Low spin	High spin
d^1		CFSE $= [-0.4\times1]\Delta_0$ $= -0.40\,\Delta_0$
d^2		CFSE $= [-0.4\times2]\Delta_0$ $= -0.80\,\Delta_0$
d^3		CFSE $= [-0.4\times3]\Delta_0$ $= -12\,\Delta_0$
d^4	CFSE $= [-0.4\times4]\Delta_0 + P$ $= -1.6\,\Delta_0 + P$	CFSE $= [-0.4\times3 + 0.6\times1]\Delta_0$ $= [-1.2 + 0.6]\Delta_0$ $= -0.6\,\Delta_0$
d^5	CFSE $= [-0.4\times5]\Delta_0 + 2p$ $= -2.0\,\Delta_0 + 2p$	CFSE $= [-0.4\times3 + 0.6\times2]\Delta_0$ $= [-1.2 + 1.2]\Delta_0$ $= 0$
d^6	CFSE $= [-0.4\times6]\Delta_0 + 2P$ $= -2.4\,\Delta_0 + 2P$	CFSE $= [-0.4\times4 + 0.6\times2]\Delta_0$ $= -0.4\,\Delta_0$
d^7	CFSE $= [-0.4\times6 + 1\times0.6]\Delta_0 + P$ $= [-2.4 + 0.6]\Delta_0 + P$ $= -1.8\,\Delta_0 + P$	CFSE $= [-0.4\times5 + 0.6\times2]\Delta_0$ $= -0.8\,\Delta_0$
d^8	CFSE $= [-0.4\times6 + 2\times0.6]\Delta_0$ $= [-2.4 + 1.2)\Delta_0$ $= -1.2\,\Delta_0$	CFSE $= [-0.4\times6 + 0.6\times2]\Delta_0$ $= [-2.4 + 1.2]\Delta_0$ $= -1.2\,\Delta_0$
d^9	CFSE $= [-0.4\times6 + 3\times0.6]\Delta_0$ $= [-2.4 + 1.8]\Delta_0$ $= \cdot 06\,\Delta_0$	CFSE $= [-0.4\times6 + 0.6\times3]\Delta_0$ $= [-2.4 + 1.8]\Delta_0 = -0.6\Delta_0$
d^{10}	CFSE $= [-0.4\times6 + 4\times0.6]\Delta_0$ $= 0$	CFSE $= 0$

Scanned by CamScanner

Crystal Field Stabilization Energy in Tetrahedral Complexes:-

In a tetrahedral complex, the d-orbitals of the metal cation are split into two sets of different energies, e of lower energy and t_2 of higher energy. The separation b/w these two sets is equal to Δ_t. The eg set has an energy of $-0.6\Delta_t$ and the t_2g set has an energy $+0.4\Delta_t$ relative to the barycentre. For a d^n tetrahedral complex with $e_g^p t_{2g}^q$ configuration.

$$CFSE = [-0.6p + 0.4q]\Delta t \qquad \left(\because \Delta t = \frac{4}{9}\Delta o\right)$$

$$= [-0.6p + 0.4q] \times \frac{4}{9}\Delta o$$

$$= [-0.27p + 0.18q]\Delta o$$

Since tetrahedral complexes are high spin and no pairing of d-electrons occurs ($\Delta_t < P$). Therefore, no pairing energy is include in the above equation. The CFSE values of tetrahedral complexes of d^1 to d^{10} metal ions:-

d^1 $CFSE = [-0.6 \times 1]\Delta t = -0.6\Delta_t$.

d^2 $CFSE = [-0.6 \times 2]\Delta_t = -1.2\Delta t$

d^3 $CFSE = [-0.6 \times 2 + (0.4) \times 1]\Delta_t = -0.8\Delta t$

d^4 $CFSE = [-0.6 \times 2 + (0.4) \times 2]\Delta t = -0.4\Delta t$.

d^5 $CFSE = [-0.6 \times 2 + (0.4) \times 3]\Delta t = 0\Delta t$

d^6 $CFSE = [-0.6 \times 3 + (0.4) \times 3]\Delta t = [-1.8 + 1.2]\Delta t = -0.6\Delta t$.

d^7 $CFSE = [-0.6 \times 4 + (0.4) \times 3]\Delta t = [-2.4 + 1.2]\Delta t = -1.2\Delta t$

d^8 $CFSE = [-0.6 \times 4 + (0.4) \times 4]\Delta t = [-2.4 + 1.6]\Delta t = -0.8\Delta t$

d^9 $CFSE = [-0.6 \times 4 + (0.4) \times 5]\Delta t = [-2.4 + 2.0]\Delta t = -0.4\Delta$

d^{10} $CFSE = [-0.6 \times 4 + (0.4) \times 6]\Delta t = 0$

Since, the magnitude of crystal Field splitting in tetrahedral is small and always lesser then the pairing energy, therefore, pairing of electrons is not energetically favourable.

Pairing Energy:- Energy required to cause pairing of electrons in the same orbital is called the pairing Energy (P). It is expressed in cm^{-1}. The value of P is 23500 cm^{-1}. It may be obtained from the analysis of electronic Spectra

if Δ_o is greater then P, it favours low spin complexes

If $\Delta_o < P$, it favours high spin complex.

If $\Delta_o = P$, high spin & low spin complexes equally exist

Scanned by CamScanner

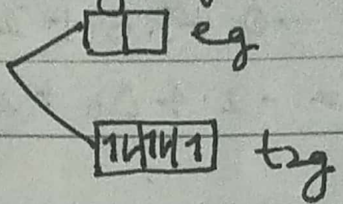
Examples:

Pairing energy ~~for~~

$[Fe(CN)_6]^{3-}$ where CN^- is a strong field ligand so pairing of ēs take place.

Here $Fe^{3+} = d^5$

(Low spin complex)



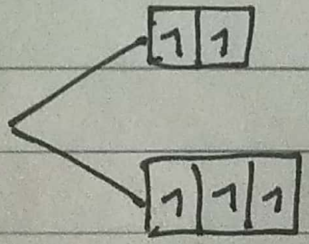
$t_{2g}^5 e_g^0$

$$CFSE = (5 \times -0.4\Delta_o) + 2P$$
$$= -2.0\Delta_o + \boxed{2P} \rightarrow$$ where 2p is pairing energy for two ē pairs.

But when we take,

$[Fe(H_2O)_6]^{3+}$ It is a high spin complex, as $H_2O \rightarrow$ weak field ligand NO pairing of ēs occur

$Fe^{3+} = d^5$



$t_{2g}^5 e_g^0$

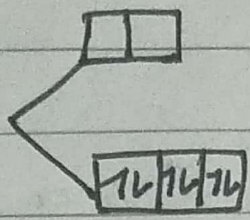
$$CFSE = -0.4 \times 3 + 0.6 \times 2$$
$$= -1.2 + 1.2 = 0 + 0P$$

Similarly $[Co(CN)_6]^{3-}$ ⇒ Low spin complex with strong field ligand.

Co(III) = d^6

↓

$t_{2g}^6 e_g$

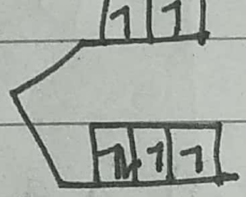


$$CFSE = -0.4\Delta_o \times 6 + 2P$$

$$= -2.4\Delta_o + \enclose{circle}{2P} \rightarrow \text{Pairing energy.}$$

When $[Co(Cl)_6]^{3-}$ High spin complex.
Cl^- is a weak field ligan

Co(III) = d^6



$$CFSE = -0.4\Delta_o \times 4 + 0.6\Delta_o \times 2$$

$$= -1.6\Delta_o + 1.2\Delta_o = -0.4\Delta_o$$

Factors affecting crystal field splitting parameter :-

There are several factors that affect the magnitude of splitting of d - orbitals by surrounding ligands.

(i) Oxidation state of metal cation :→ The higher the oxidation state of metal cation, the greater will be magnitude of Δ. The higher oxidation state of metal causes the ligands to approach more closely to it and therefore the ligand cause more splitting of metal d - orbitals.

e.g. Δ_o for $[Co(H_2O)_6]^{2+} = 9200\,cm^{-1}$

Δ_o for $[Co(H_2O)_6]^{3+} = 20760\,cm^{-1}$

(ii) Same oxidation state of metal cation but no. of d-electrons is different :- In general for a given series of transition elements in complexes having metal cation with same oxidation states but with different no. of electrons in d-orbitals, the magnitude of Δ_o decreases with increase in no. of d-electrons. It is due to the fact that the higher ~~the~~ no. of d - electrons prevent the ligand to come closer the metal cation. e.g.

Δ_o for $[Co(H_2O)_6]^{2+} = 9200\,cm^{-1}$ $(3d^7)$

Δ_o for $[Ni(H_2O)_6]^{2+} = 8500\,cm^{-1}$ $(3d^8)$

(iii) Nature of the ligands :- ligands which causes only small splitting are called weak field ligands and those which causes a large splitting are called strong field ligands. It is possible to arrange the ligands according to the magnitude of Δ observed with a given metal ion. The series of arrangement of ligands is called spectrochemical series

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < N_3^- < F^- < NCO^- < OH^- < C_2O_4^{2-} < O^{2-} < H_2O < acac^- < NCS^- < CH_3CN < gly < pyridine < NH_3 < en < bipy < phen < NO_2^- < PPh_3 < CN^- < CO.$

iv) Geometry of the complex :- The magnitude of Δ varies with the geometry of the complex. e.g. Δ values for tetrahedral complex is about 40-50% less than that of Octahedral complexes.

v) Type of d-orbitals :- The magnitude of Δ varies little through first transition series (3d) for a particular oxidation state of central metal cation but becomes considerably large i.e. 30-50% in second (4d) and third (5d) transition series for a particular ligand. This may be explained on the basis that 4d or 5d orbital are bigger in size as compared to 3d orbital and thus can extend further out from the central metal ion and interact more strongly with the ligand.