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Summary

Description	The crystal field stabilization energy (CFSE) is defined as the stability achieved by placing a transition metal ion in the crystal field originated by a group of ligands arranged in a particular symmetry. It is the result of the splitting of the d orbitals in the ligand field. Some of the orbitals become higher and some lower in energy after splitting. The electrons occupying the lower set of orbitals result in the stabilization of the central metal ion of the coordination complex by the amount of energy called crystal field stabilization energy. The CFSE will depend on multiple factors including the geometry of the coordination compounds (which changes the d-orbital splitting patterns), number of d-electrons, spin pairing energy, crystal field splitting energy (Δ), and strength of ligand (Spectrochemical series).
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Chapter-27

Coordination Chemistry: Crystal Field Stabilization Energy (CFSE)

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The crystal field stabilization energy (CFSE) is defined as the stability achieved by placing a transition metal ion in the crystal field originated by a group of ligands arranged in a particular symmetry. It is the result of splitting of the d orbitals in the ligand field. Some of the orbitals become higher and some lower in energy after splitting. The electrons occupying the lower set of orbitals result in the stabilization of the central metal ion of the coordination complex by the amount of energy called crystal field stabilization energy.

The **CFSE will depend** on multiple factors including **geometry** of the coordination compounds (which changes the d-orbital splitting patterns), **number of d-electrons, spin pairing energy, crystal field splitting energy (Δ) and strength of ligand** (**Spectrochemical series**).

Spectrochemical series: Increasing order of strength of ligands:

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

Derivation of Crystal Field Stabilization Energy (CFSE) in terms of Δ_o and Dq for Octahedral Geometry:

Let us consider a **d^{p+q} ion** with p electrons in t_{2g} and q electrons in e_g orbitals, then from the CFT splitting diagram we can write,

Gain in energy due to q electrons in e_g orbitals (in terms of Δ_o) = $+ 0.6\ \Delta_o \times q$
and loss in energy due to p electrons in t_{2g} orbitals (in terms of Δ_o) = $- 0.4\ \Delta_o \times p$

Thus net change in energy in terms of Δ_o will be given for d^{p+q} ion

$$= [-0.4p + 0.6q]\ \Delta_o \text{ --------------- } (1)$$

Since, $\Delta_o = 10Dq$, thus change in energy in terms of Dq for d^{p+q} ion

$$= [-4p + 6q]\ Dq \text{ --------------- } (2)$$

If P be the mean pairing energy which is the energy required to pair two electrons against electron-electron repulsion in the same orbital and m = number of electron pairs, then for octahedral complexes

$$\text{CFSE} = [-0.4p + 0.6q]\ \Delta_o + mP \text{ -------- } (3)$$

Derivation of Crystal Field Stabilization Energy (CFSE) in terms of Δ_t for Tetrahedral Geometry:

Let us consider a d^{p+q} ion with p electrons in t_{2g} and q electrons in e_g orbitals, then from the CFT splitting diagram we can write,

Loss in energy due to q electrons in e_g orbitals (in terms of Δ_t) = - 0.6 Δ_t x q
and gain in energy due to p electrons in t_{2g} orbitals (in terms of Δ_t) = 0.4 Δ_t x p

Thus net change in energy in terms of $\Delta_t$will be given for d^{p+q} ion

= [0.4p - 0.6q] Δ_t --------------- (4)

If P be the mean pairing energy which is the energy required to pair two electrons against electron-electron repulsion in the same orbital and m = number of electron pairs, then, for Tetrahedral complexes

CFSE = [0.4p - 0.6q] Δ_t + mP -------- (5)

Crystal Field Stabilization Energy (CFSE) in terms of Δ_t, Δ_o and D_q for tetrahedral geometry

For d^{p+q} ion of tetrahedral complexes with p electrons in t_{2g} and q electrons in e_g orbitals,

CFSE = [-0.6q + 0.4p] Δ_t+ mP -------- (6) (in terms of Δ_t)
= [-0.6q + 0.4p] (4/9)Δ_o + mP ------- (7) (in terms of Δ_0)
= [-0.6q + 0.4p] (40/9) Dq + mP ------ (8) (in terms of Dq)

[Here, m = number of electron pair and P = Mean pairing energy, which is the energy required to pair two electrons against electron-electron repulsion in the same orbital]

Δ_{tet} is approximately 4/9 Δ_o
Δ_{tet} is approximately 40/9 Dq ($1\Delta_0 = 10$Dq)

Calculation of difference in CFSE value for Octahedral & Tetrahedral $3d^3$ (HS) complexes

- For a **HS d^3 (E.C. - t_{2g}^3, e_g^0)** ***octahedral*** **complexes**, the *Crystal Field Stabilization Energy* = [-0.4p + 0.6q] x Δ_o+ mP = -(3 × 0.4)Δo= **−1.2Δo ---- (1)**

For a **HS d^3 (E.C. - t_{2g}^1,e_g^2)** ***tetrahedral*** **complexes**, the

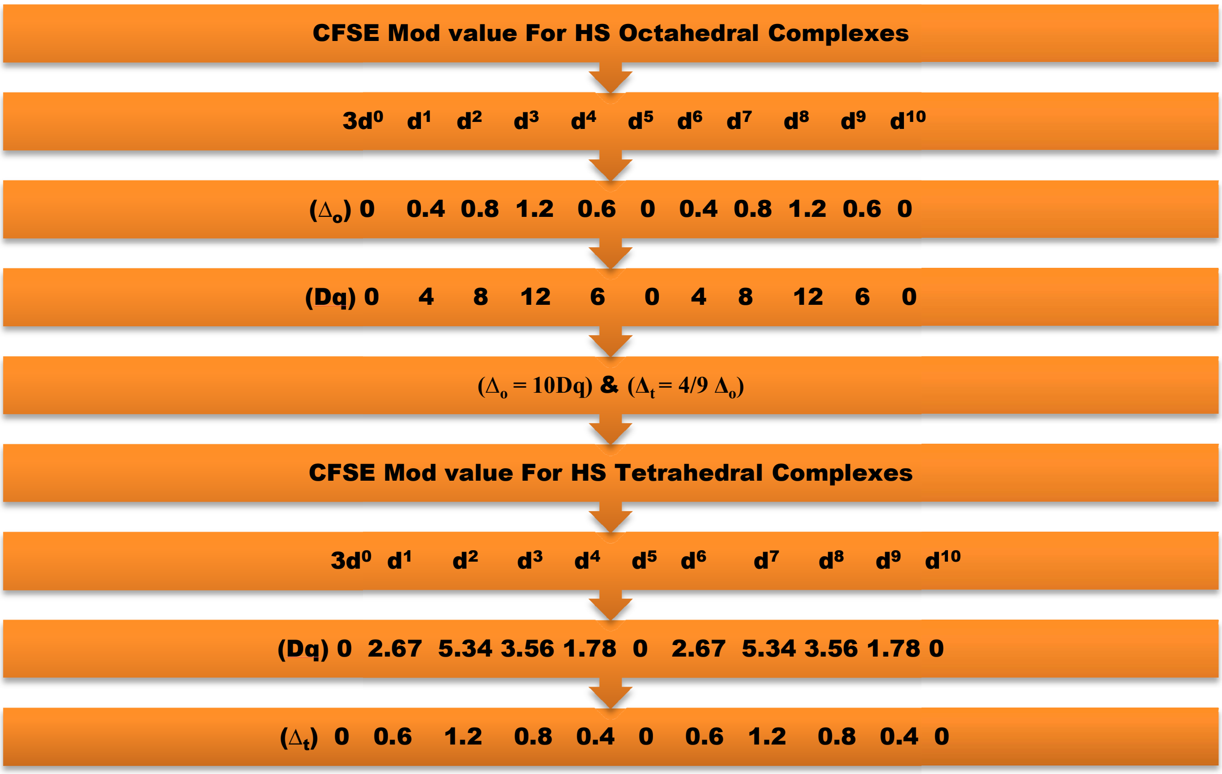
CFSE = **[-0.6q + 0.4p] x Δ_t+ mP = [-0.6x2 + 0.4x1] x Δ_t = −0.8Δ_t**

- **Now use the relation Δ_t = 4/9 Δ_o**
- So for tetrahedral d^3 HS, the Crystal Field Stabilization Energy **CFSE**

  = -0.8 x 4/9 Δ_o = -0.355 Δ_o ----- (2)
- **And the difference in Crystal Field Stabilization Energy (CFSE) between the two geometries will be: Eq. 1 – Eq.2 = (1.2 - 0.355) Δ_o = 0.845 Δ_o**

- **(N.B.: Ignore negative signs of CFSE to predict the difference between CFSE value of two geometries).**

Table-1: CFSE Value in terms of Δ_o and Δ_t for HS $3d^0$ to $3d^{10}$ Octahedral and Tetrahedral complexes



CFSE Mod value For HS Octahedral Complexes

$3d^0$ d^1 d^2 d^3 d^4 d^5 d^6 d^7 d^8 d^9 d^{10}

(Δ_o) 0 0.4 0.8 1.2 0.6 0 0.4 0.8 1.2 0.6 0

(Dq) 0 4 8 12 6 0 4 8 12 6 0

($\Delta_o = 10Dq$) & ($\Delta_t = 4/9\ \Delta_o$)

CFSE Mod value For HS Tetrahedral Complexes

$3d^0$ d^1 d^2 d^3 d^4 d^5 d^6 d^7 d^8 d^9 d^{10}

(Dq) 0 2.67 5.34 3.56 1.78 0 2.67 5.34 3.56 1.78 0

(Δ_t) 0 0.6 1.2 0.8 0.4 0 0.6 1.2 0.8 0.4 0

Table-2: CFSE Value in terms of Δ_o and Δ_t for LS $3d^0$ to $3d^{10}$ Octahedral and Tetrahedral complexes

CFSE Mod value For LS Octahedral Complexes

$3d^0$ d^1 d^2 d^3 d^4 d^5 d^6 d^7 d^8 d^9 d^{10}

(Δ_o) 0 0.4 0.8 1.2 1.6 2.0 2.4 1.8 1.2 0.6 0

(Dq) 0 4 8 12 16 20 24 18 12 6 0

($\Delta_o = 10Dq$) & ($\Delta_t = 4/9\ \Delta_o$)

CFSE Mod value For LS Tetrahedral Complexes

$3d^0$ d^1 d^2 d^3 d^4 d^5 d^6 d^7 d^8 d^9 d^{10}

(Δ_o) 0 0.27 0.54 0.8 1.08 0.90 0.72 0.54 0.36 0.18 0

(Δ_t) 0 0.6 1.2 1.8 2.4 2.0 1.6 1.2 0.8 0.4 0

Table 3: Comparative study for Crystal Field Stabilization Energies (CFSE) for octahedral and tetrahedral geometries, assuming high spin (HS) configurations. The units are Δ_0, and assuming that $\Delta_{tet} = 4/9\ \Delta_o$

$3d^n$	Octahedral	Tetrahedral	Difference
$3d^0$, d^5, d^{10}	0	0	0
$3d^1$, d^6	0.4	0.27	0.13
$3d^2$, d^7	0.8	0.53	0.27

Related Questions

Q.1. The electronic spectrum of $[Ti(H_2O)_6]^{3+}$ shows a single broad peak with a maximum at 20,300 cm^{-1}. The crystal field stabilization energy (CFSE) of the complex ion, in kJ mol^{-1}, is (1 kJ mol^{-1} = 83.7 cm^{-1})

(a) 145.5 (b) 242.5 (c) 83.7 (d) 97

→Ans. (*d*)

In $[Ti(H_2O)]^{3+}$, Ti^{3+} ion of d^1 configuration is present in the octahedral complex. Under octahedral crystal field, the configuration of Ti^{3+} will be, $t_{2g}^1 e_g^0$.

So, CFSE = $[(-0.4) \times 1 + (+0.6) \times 0]\,\Delta_0$

$= -0.4 \times \Delta_0 = -0.4 \times 20{,}300\ cm^{-1}$

$[\because \Delta_0 = 20{,}300\ cm^{-1}]$

$= -0.4 \times \frac{20{,}300}{83{,}7}$ kJ mol^{-1}

$[\because = 1\ kJ\ mol^{-1} = 83.7\ cm^{-1}]$

$= -97.103$ kJ mol^{-1}

⇒ CFSE = 97 kJ mol^{-1}

Q.2. The crystal field stabilization energy (CFSE) of $[CoF_3(H_2O)_3]$ ($\Delta_0 < P$) is

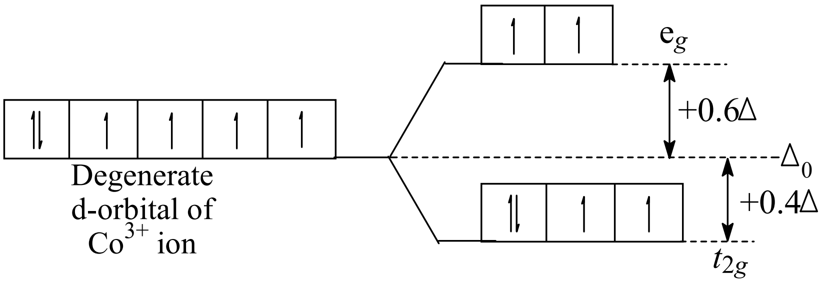
(a) $-0.8\,\Delta_0$ (b) $-0.8\Delta_0 + 2P$

(c) $-0.4\,\Delta_0$ (d) $-0.4\Delta_0 + P$

→Ans. (c)

$[CoF_3(H_2O)_3]$ is an octahedral complex.

In this complex (compound) all ligands are weak field ligand. For weak field ligands $\Delta_0 < P$ (pairing energy), so the electronic configuration of Co (III) will be $t_{2g}^4\ e_g^2$.



Here, CFSE can be calculated as:

CFSE = $[-0.4\,p + 0.6q]\,\Delta_0$

Where, Δ_0 = crystal field splitting energy in octahedral complex

p = Number of electrons in t_{2g} orbitals = 4 & q = Number of electrons in e_g orbitals = 2

Hence CFSE = $[-0.4 \times 4 + 0.6 \times 2]\,\Delta_0$

$= [-1.6 + 1.2]\,\Delta_0 = [-0.4\,\Delta_0]$

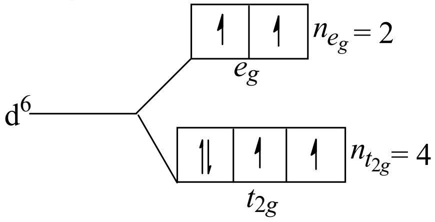
Hence, the crystal field stabilization energy (CFSE) of $[CoF_3(H_2O)_3]$ will be – $0.4\,\Delta_0$.

Q.3. The values of the crystal field stabilization energies for a high spin d^6 metal ion in octahedral and tetrahedral fields respectively, are

(a) -0.4 Δ_0 and -0.27 Δ_t **(b) -1.6 Δ_0 and -0.4 Δ_t**
(c) -2.4 Δ_0 and -0.6 Δ_t **(d) -0.4 Δ_0 and -0.6 Δ_t**

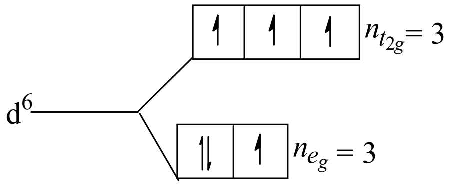
→***Ans.* (*d*)**

Crystal field stabilization energy (CFSE) for high spin d^6 metal ion.
Crystal field splitting in octahedral field.



CFSE = $[-0.4n_{t2g} + 0.6n_{e_g}]\Delta_0$
$= [-0.4 \times 4 + 0.6 \times 2]\ \Delta_0 = -0.4\ \Delta_0$

Crystal field splitting in tetrahedral field



CFSE = $(-0.6\ n_{e_g} + 0.4n_{t_{2g}})\Delta_t$
$= (-0.6 \times 3 + 0.4 \times 3)\ \Delta_t$
$= (-1.8 + 1.2)\ \Delta_t = -0.6\ \Delta_t$

Here, $n_{t_{2g}}$ = number of electrons in t_{2g} and n_{e_g} = number of electrons in e_g.

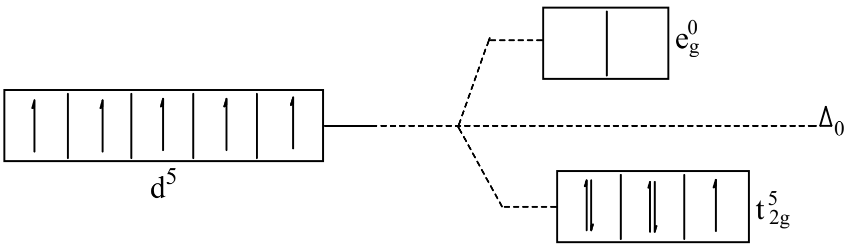
Q.4. The spin-only magnetic moment and crystal field stabilization energy [CFSE] of $[Fe(CN)_6]^{3-}$ respectively, are [Note : Ignore the pairing energy]

a) 1.73 BM and -2.0Δ_0 **b) 2.84 BM and – 1.6Δ_0**
c) 0 BM and -2.4Δ_0 **d) 5.92 BM and 0**

→***Ans.* (*a*)**

In $[Fe(CN)_6]^{-3}$, oxidation state of iron in $[Fe(CN)_6]^{-3}$ is (+3). E.C. $Fe^{3+} = 3d^5$.

It forms a low spin complex (CN^- is a strong field ligand).



∴ Number of unpaired electrons (n) = 1
Spin only magnetic moment
$\mu_s = \sqrt{n(n+2)}$ BM $= \sqrt{3} = 1.73$ BM
CFSE = (Number of electrons in $t_{2g} \times -0.4\Delta_0$) + (Number of electrons' in $e_g \times 0.6\Delta_0$).
$= (5 \times -0.4)\ \Delta_0 = -2.0\ \Delta_0$.

Q.5. The correct order of the spin only magnetic moments of the following complexes is

(I) $[Cr(H_2O)_6]Br_2$ **(II) $Na_4[Fe(CN)_6]$**

(III) $Na_3[Fe(C_2O_4)_3](\Delta_0 > P)$ **(IV) $(Et_4N)_2[CoCl_4]$**

a) (II) ≈ (I) > (IV) > (III) **b) (I) > (IV) > (III) > (II)**

c) (III) > (I) > (IV) > (II) **d) (III) > (I) > (II) > (IV)**

→***Ans.*** **(b)**

I. In $[Cr(H_2O)_6]Br_2$, chromium is in Cr^{2+} having electronic configuration $[Ar]3d^4$.
H_2O is a weak field ligand.
It has octahedral geometry

$$\therefore \quad 3d^4 = t_{2g}^3\ e_g^1$$

Unpaired electrons = 4

$$\mu_s = \sqrt{4 \times 6}$$
$$= \sqrt{24}\ \text{BM.}$$

II. Na 4[Fe(CN)6] → $Fe^{2+} = [Ar]3d^6$
CN^- is a strong field ligand
Octahedral geometry

$$\therefore \quad 3d^6 = t_{2g}^6\ e_g^0$$

Unpaired electrons = 0

$$\mu_s = 0$$

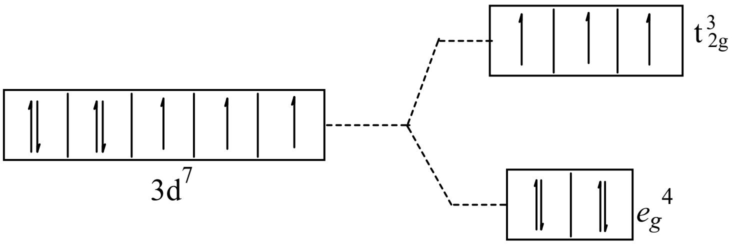
III. $Na_3[Fe(C_2O_4)_3]$ → $Fe^{3+} = [Ar]3d^5$

$\Delta_0 > p$ (Given), that is oxalate ($C_2O_4^{2-}$) treated as stronger ligand.
Octahedral geometry

$$\therefore \quad 3d^5 = t_{2g}^5\ e_g^0$$

Unpaired electrons = 1; **$\mu_s = \sqrt{3} = 1.73$ BM**

IV. $(Et_4N)_2[CoCl_4]^{2-}$; $Co^{2+} = [Ar]3d^7$
Cl^- is a weak field ligand.
In this complex, coordination number is 4
Tetrahedral geometry
Splitting of *d* – orbitals in tetrahedral field is



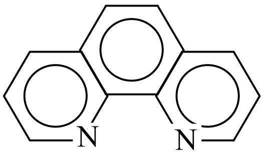
Unpaired electrons = 3

$$\mu_s = \sqrt{15}\ \text{BM}$$

∴ Spin only magnetic moment order is I > IV > III > II

Q.6. The complex ion that will lose its crystal field stabilization energy upon oxidation of its metal to +3 state is (ignore pairing energy)

(Phen =



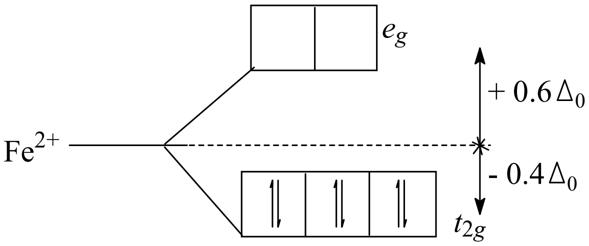
a) $[Co(phen)_3]^{2+}$ **b)** $[Ni(phen)_3]^{2+}$
c) $[Zn(phen)_3]^{2+}$ **d)** $[Fe(phen)_3]^{2+}$

→ ***Ans***. (*d*)

The complex ion that will lose its crystal field stabilization energy upon oxidation of its metal to +3 state is $[Fe(phen)_3]^{2+}$.

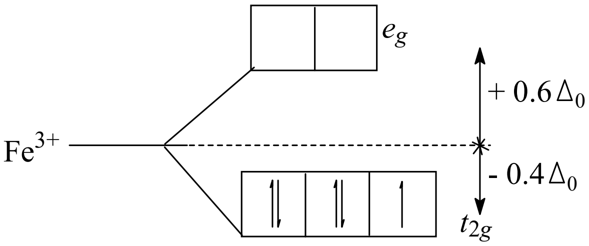
$$[Fe(phen)_3]^{2+} \xrightarrow{-e^-} [Fe(phen)_3]^{3+}$$

In $[Fe(phen)_3]^{2+}$, electronic configuration of Fe^{2+} is $3d^6 4s^0$. Phenanthrene is a strong field symmetrical bidentate ligand. **The E.C. of Fe^{2+} is as follows:**



$$\mathbf{CFSE = 6 \times - 0.4\ \Delta_0 = - 2.4\ \Delta_0.}$$

The splitting of orbital and arrangement of electrons **(E.C.)** in Fe^{3+} is as follows:



$$\mathbf{CFSE = 5 \times - 0.4\ \Delta_0 = - 2.0\ \Delta_0}$$

Fe^{2+} upon oxidation of its metal to (+3) state lose its CFSE from -2.4 Δ_0 to - 2.0 Δ_0.

Reference Books:

1. *Introduction to Coordination Chemistry*, Geoffrey A. Lawrance

2. *Coordination Chemistry*, Joan Ribas Gispert

3. *Coordination Chemistry, 20: Invited Lectures* Presented at the 20th International Conference on Coordination Chemistry, Calcutta, India, 10-14 December 1979, D. Banerjea

4. *Comprehensive Coordination Chemistry III*, Gerard Parkin, Edwin C Constable, Lawrence Que Jr.