

Numericals

Ex:1 For Mn^{+2} ion, $P = 28,000 \text{ cm}^{-1}$. Δ_o value for $[Mn(CN)_6]^{3-}$ ion is $38,500 \text{ cm}^{-1}$. Does this complex has high spin or low spin confⁿ? Also write the configuration.

Ans. The answer can be given in two way.

(i) P for Mn^{+2} is lower than Δ_o .

$$P < \Delta_o$$

$$28000 \text{ cm}^{-1} < 38500 \text{ cm}^{-1}$$

$\therefore [Mn(CN)_6]^{3-}$ ion is a L.S. state.

(ii) In $[Mn(CN)_6]^{3-}$ ion Mn is present as Mn^{3+} ion.

$$Mn (Z=25) = [Ar] 3d^5 4s^2$$

$$Mn^{3+} = [Ar] 3d^4$$

CFSE for d^4 ion in HS octahedral complex = $-0.6 \Delta_o$

$$= -0.6 \times 38500 \text{ cm}^{-1}$$

$$= -23100 \text{ cm}^{-1}$$

Now, CFSE for d^4 ion in LS state

$$= -1.6 \Delta_o + P$$

$$= (-1.6 \times 38500) + 28000$$

$$= -33600 \text{ cm}^{-1}$$

\therefore CFSE value for d^4 in LS complex is more negative than that of HS complex.

$\therefore [Mn(CN)_6]^{3-}$ ion in LS state: $t_{2g}^4 e_g^0$

Ex:2 calculate CFSE values in terms of Δ_o and P for HS and LS octahedral complexes of Fe(II) and Co(II).
 Predict whether the complexes are paramagnetic or diamagnetic?

Ans: Fe ($Z=26$) : $[\text{Ar}] 3d^6 4s^2$

Fe^{2+} : $[\text{Ar}] 3d^6$

Fe^{2+} in HS complex $P > \Delta_o$

distribution of d^6 e⁻s in t_{2g} and e_g :

$t_{2g}^4 e_g^2$ $\uparrow \uparrow e_g$

$\therefore m = 1$

$n = 4$

$\uparrow\uparrow \uparrow \uparrow t_{2g}$

$$\text{CFSE} = (-0.4 \times t_{2g} + 0.6 \times e_g) \Delta_o + mP$$

$$= (-0.4 \times 4 + 0.6 \times 2) \Delta_o + 1P$$

$$= -0.4 + P \text{ _____ Ans}$$

Due to the presence of 4 unpaired e⁻s the complexes are paramagnetic.

Fe^{2+} in LS complexes $P < \Delta_o$

distribution of d^6 e⁻s in t_{2g} and e_g :

$t_{2g}^6 e_g^0$ $\text{— — } e_g$

$m = 3$

$n = 0$

$\uparrow\uparrow \uparrow\uparrow \uparrow\uparrow t_{2g}$

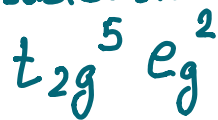
$$\begin{aligned}
 CFSE &= (-0.4 \times t_{2g} + 0.6 \times e_g) \Delta_o + mP \\
 &= (-0.4 \times 6 + 0.6 \times 0) \Delta_o + 1 \times P \\
 &= -2.4 \Delta_o + 3P \text{ ----- Ans.}
 \end{aligned}$$

Due to the absence of unpaired e⁻s the complexes are diamagnetic.



Co²⁺ in HS complex $P > \Delta_o$

Distribution of d⁷ e⁻s in t_{2g} and e_g:



Paramagnetic



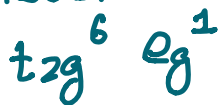
$$CFSE = (-0.4 \times t_{2g} + 0.6 \times e_g) \Delta_o + mP$$

$$= (-0.4 \times 5 + 0.6 \times 2) \Delta_o + 2P$$

$$= -0.8 \Delta_o + 3P \text{ ----- Ans.}$$

Co²⁺ in LS complex $P < \Delta_o$

Distribution of d⁷ e⁻s in t_{2g} and e_g



$$m=3, n=1$$

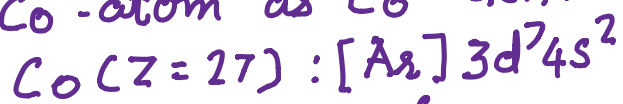


$$\begin{aligned}
 \text{CFSE} &= (-0.4 t_{2g} + 0.6 e_g) \Delta_o + mP \\
 &= (-0.4 \times 6 + 0.6 \times 1) \Delta_o + 3P \\
 &= -1.8 \Delta_o + 3P \quad \text{Ans.}
 \end{aligned}$$

Due to the one unpaired electron, the complexes are paramagnetic.

Ex:3 Calculate CFSE of $[\text{CoF}_6]^{3-}$.

This ion is octahedral and contains Co-atom as Co^{3+} ion.



Here F^- ions are weak ligands, the distribution of six d-e's in Co^{3+} ion is $t_{2g}^4 e_g^2$

CFSE of d^6 ion

$$= (-0.4 \times 4 + 0.6 \times 2) \Delta_o$$

$$= -0.4 \Delta_o \quad \text{Ans}$$

Ex:4 Calculate CFSE of $[\text{Fe}(\text{CN})_6]^{4-}$

This ion is octahedral and contains

Fe atom as Fe^{2+} ion.



Here CN^- ions are strong ligands, the distribution of six d-e's in Fe^{2+} ion is:



$$\text{CFSE of } d^6 \text{ ion} = (-0.4 \times 6 + 0.6 \times 0) \Delta_o$$

Ex: 4 Calculate CFSE for $[\text{Fe}(\text{CN})_6]^{4-}$ ion. $= -2.4 \Delta_o$ _____ Ans.

Answer: $-2.4 \Delta_o$

Ex: 5 Calculate CFSE for $[\text{Cu}(\text{NH}_3)_6]^{2+}$ ion.

Answer: $-0.6 \Delta_o$

Ex: 6 Calculate CFSE and number of unpaired e's for the following complex ion:



Answer: Number of unpaired e's = 5

$$\text{CFSE} = 0.0$$



Answer: Number of unpaired e's = 3

$$\text{CFSE} = -1.2 \Delta_o$$

Ex: 7 Determine CFSE of a d^6 octahedral complex having $\Delta_o = 25000 \text{ cm}^{-1}$ and $P = 15000 \text{ cm}^{-1}$.

$$P = 15000 \text{ cm}^{-1}, \Delta_o = 25000 \text{ cm}^{-1}$$

$$\therefore P < \Delta_o$$

$\therefore d^6$ octahedral complex is a LS complex.

CFSE for d^6 ion in LS state

$$= -2.4 \Delta_o + 3P$$

$$= (-2.4 \times 25000 + 3 \times 15000)$$

$$= -15000 \text{ cm}^{-1} \text{ _____ Ans.}$$

Ex: 8 For $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ ion, the mean pairing energy (P) is found to be equal to 23500 cm^{-1} . The magnitude of Δ_o is 13900 cm^{-1} . (a) Calculate the CFSE for this complex ion corresponding to HS

and LS state (b) Which state is more stable?

Cr^{2+} ion d^4 e's in HS state $\text{CFSE} = -8340 \text{ cm}^{-1}$
and d^4 e's in LS state $\text{CFSE} = +1260 \text{ cm}^{-1}$

There are two concepts for determine the stability of complex.

(i) $\text{CFSE of HS state} < \text{CFSE of LS state}$

\therefore HS state is more stable than LS state.

(ii) $P (23500 \text{ cm}^{-1}) > \Delta_o (13900 \text{ cm}^{-1})$

$\therefore [\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ is more stable in HS state.

Ex: 9 Using CFT give the electronic configuration of Rh^{2+} rhodium(II) ($Z=45$) in an octahedral field for which the crystal field splitting parameter (Δ_o) is greater than the P . Calculate CFSE for this configuration in terms of Δ_o and P .

Ans: (i) $t_{2g}^6 e_g^1$

(ii) $\text{CFSE in LS} = -1.8 + 3P$

Ex: 10 $10 Dq$ of $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$ is known from electronic spectrum to be $21,000 \text{ cm}^{-1}$. The pairing energy of Mn(III) is $28,800 \text{ cm}^{-1}$. Predict whether the given complex ion is high spin or low spin.

Answer can be given by two methods.

(i) $P (28,800) > 10 Dq (21,000)$

\therefore Given complex ion is high spin octahedral complex ion.

(ii) In the given complex Mn^{3+} ion is $3d^4$ ion.

Let us calculate CFSE for Mn^{3+} ion in its HS and LS complex.

$$\begin{aligned}
 \text{CFSE for } d^4 \text{ ion in} \\
 \text{HS complex} &= -6 D_q \\
 &= -6 \times \frac{21000}{10} \\
 &\quad (\because 10 D_q = 21000 \text{ cm}^{-1}) \\
 &= -12600 \text{ cm}^{-1}
 \end{aligned}$$

$$\begin{aligned}
 \text{CFSE for } d^4 \text{ ion in} \\
 \text{LS complex} &= -16 D_q + P \\
 &= -16 \times \frac{21000}{10} + 28800 \\
 &= -4800 \text{ cm}^{-1}
 \end{aligned}$$

From the above calculation value of CFSE for d^4 ion in HS complexes is more negative than that in LS complexes.

$\therefore [\text{Mn}(\text{H}_2\text{O})_6]^{3+}$ ion is a HS octahedral complex.