Numericals

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

Ans. The answer can be given in two way.

(i) P for Mn^{+2} is lowen than Δo.

$P < \Delta o$

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

$\therefore [Mn(CN)_6]^{3-}$ 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 $= -0.6\ \Delta o$

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

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

Now, CFSE for d^4 ion in LS state

$= -1.6\ \Delta o + P$

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

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

$\therefore$ 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 diamegnetic ?

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

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

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

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

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

$\therefore m = 1$

$n = 4$

↑ ↑ e_g

↑↓ ↑ ↑ t_{2g}

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

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

$= -0.4 + P$ _____ 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 :

$t_{2g}^6\ e_g^0$

$m = 3$

$n = 0$

— — e_g

↑↓ ↑↓ ↑↓ t_{2g}

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

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

$Co\ (Z = 27) : [Ar]\ 3d^7 4s^2$

$Co^{2+} : [Ar]\ 3d^7$

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

Distribution of d^7 e⁻s in t_{2g} and e_g:

$t_{2g}^5\ e_g^2$ ↑ ↑ e_g

Paramagnetic ↑↓ ↑↓ ↑ t_{2g}

$$CFSE = (-0.4 \times t_{2g} + 0.6 \times e_g)\Delta_o + mP$$
$$= (-0.4 \times 5 + 0.6 \times 2)\Delta_o + 2P$$
$$= -0.8\,\Delta_o + 3P \text{ ——— Ans.}$$

Co^{2+} in LS complex $P < \Delta_o$

Distribution of d^7 e⁻s in t_{2g} and e_g

$t_{2g}^6\ e_g^1$ ↑ — e_g

$m = 3,\ n = 1$

↑↓ ↑↓ ↑↓ t_{2g}

$$CFSE = (-0.4\,t_{2g} + 0.6\,eg)\Delta_o + mP$$
$$= (-0.4 \times 6 + 0.6 \times 1)\Delta_o + 3P$$
$$= -1.8\,\Delta_o + 3P \quad \text{——— Ans.}$$

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

Ex:3 Calculate CFSE of $[CoF_6]^{3-}$.

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

$Co(Z=27) : [Ar]\,3d^7 4s^2$

$Co^{3+} : [Ar]\,3d^6 4s^0$

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

$$= (-0.4 \times 4 + 0.6 \times 2)\Delta_o$$
$$= -0.4\,\Delta_o \text{ ——— Ans}$$

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

This ion is octahedral and contains Fe atom as Fe^{2+} ion.

$Fe(Z=26) : [Ar]\,3d^6 4s^2$

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

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

$t_{2g}^6 e_g^0$.

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

$= -2.4\Delta_o$ _____ Ans.

Ex: 4 Calculate CFSE for $[Fe(CN)_6]^{4-}$ ion.

Answer: $-2.4\Delta_o$

Ex: 5 Calulate CFSE for $[Cu(NH_3)_6]^{2+}$ ion.

Answer: $-0.6\Delta_o$

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

(i) $[Fe(H_2O)_6]^{3+}$

Answer: Number of unpaired e⁻s = 5

CFSE = 0.0

(ii) $[Co(NH_3)_6]^{3+}$

Answer: Number of unpaired e⁻s = 3

CFSE = $-1.2\Delta_o$

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

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

$\therefore P < \Delta_o$

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

CFSE for d^6 ion in LS state

$= -2.4\Delta_o + 3P$

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

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

Ex: 8 For $[Co(H_2O)_6]^{2+}$ 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 CFSE = −8340 cm^{-1}

and d^4 e⁻s in LS state CFSE = +1260 cm^{-1}

There are two concepts for determine the stability of complex.

(i) CFSE of HS state < CFSE of LS state

∴ HS state is more stable than LS state.

(ii) P (23500 cm^{-1}) > Δo (13900 cm^{-1})

∴ $[Cr(H_2O)_6]^{3+}$ 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 (Δo) is greater than the P. Calculate CFSE for this configuration in terms of Δo and P.

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

(ii) CFSE in LS = −1.8 + 3P

Ex: 10 10 Dq of $[Mn(H_2O)_6]^{3+}$ is known from electronic spectrum to be 21,000 cm^{-1}. The pairing energy of Mn(III) is 28,800 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) > 10Dq (21,000)

∴ 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.

CFSE for d^4 ion in

HS complex $= -6Dq$

$= -6 \times \frac{21000}{10}$

$(\because 10Dq = 21000\ cm^{-1})$

$= -12600\ cm^{-1}$

CFSE for d^4 ion in

LS complex $= -16Dq + P$

$= -16 \times \frac{21000}{10} + 28800$

$= -4800\ cm^{-1}$

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

$\therefore [Mn(H_2O)_6]^{3+}$ ion is a HS octahedral complex.