Q.1. Calculate the crystal field splitting energy in kJ/mol for $[Co(NH_3)_6]^{3+}$, if the complex ion absorbs at 470 nm.

Ans:-

$$E = \frac{hc}{\lambda}$$

$h = 6.626 \times 10^{-34} \text{ Js}$

$c = 3 \times 10^8 \text{ m/s}$

$\lambda = 470 \text{ nm} = 470 \times 10^{-9} \text{ m}$

$$E = \frac{(6.626 \times 10^{-34} \text{ Js}) \times (3 \times 10^8 \text{ m/s})}{470 \times 10^{-9} \text{ m}}$$

$$E = 4.23 \times 10^{-19} \text{ J}$$

or $E = (4.23 \times 10^{-19} \text{ J}) \times (6.022 \times 10^{23} \text{ mol}^{-1})$

$= 254692.16 \text{ J/mol}$

$= 254.69 \text{ kJ/mol}.$

Q2. A tetrahedral complex absorbs at 545 nm. What is the respective octahedral crystal field splitting (Δ_0). What is the colour of the complex?

Ans:-

$$\Delta_t = \frac{hc}{\lambda}$$

$$= \frac{(6.626 \times 10^{-34} \text{ Js})(3 \times 10^8 \text{ m/s})}{545 \times 10^{-9} \text{ m}}$$

$$= 3.65 \times 10^{-19} \text{ J}$$

However, the tetrahedral splitting (Δ_t) is $\sim \frac{4}{9}$ that of the octahedral splitting (Δ_0)

$$\Delta_t = 0.44 \Delta_0$$

$$\Delta_0 = \frac{\Delta_t}{0.44} = \frac{3.65 \times 10^{-19} \text{ J}}{0.44} = 8.30 \times 10^{-18} \text{ J}$$

This is the energy needed to promote one electron in

one complex. Often the crystal field splitting is given per mole, which requires the number to be multiplied by Avogadro's Number (6.022×10^{23}).

This complex appears red, since it absorbs in the complementary green colour (determined via the colour wheel).

Q3. Find out the number of unpaired electrons for the following complexes :-

(a) $[V^{III} F_6]^{3-}$　(b) $[Fe^{II} (CN)_6]^{4-}$　(c) $[Fe^{III} (CN)_6]^{3-}$　(d) $[Rh^{III} Cl_6]^{3-}$
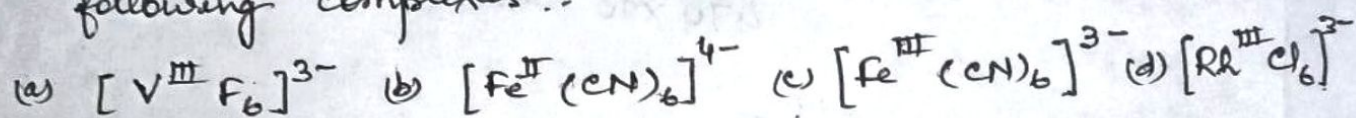
Solution:-

(a) V^{3+} is a $3d^2$ system. Thus in this case the question of the formation of HS or LS complex does not arise & the distribution of two 3-d electrons is as follows:-

$V^{3+} (3d^2) \longrightarrow t_{2g}^2 e_g^0$ which gives the number of unpaired electrons (n) equal to 2.

(b) In $[Fe(CN)_6]^{4-}$ ion, Fe is present as Fe^{2+} with $3d^6$ configuration. Since CN^- ion is a strong ligand, $[Fe(CN)_6]^{4-}$ ion is a low-spin complex and hence the distribution of electrons will be as follows:

$Fe^{2+} (3d^6) \longrightarrow t_{2g}^6 e_g^0$ hence $n = 0$

(c) $Fe^{3+} (3d^5) \longrightarrow t_{2g}^5 e_g^0$ hence $n = 1$

(d) Cl^- ion is a weak ligand. Thus $[Rh Cl_6]^{3-}$ is a HS. complex and consequently

$Rh^{3+} (4d^6) \longrightarrow t_{2g}^4 e_g^2$ hence $n = 4$

Q. For Mn^{3+} ion, the electron pairing energy, P is about 28000 cm^{-1}. Δ_0 values for the complexes $[Mn(H_2O)_6]^{3+}$ and $[Mn(CN)_6]^{3-}$ are $21,000$ cm^{-1} and 38500 cm^{-1} respectively. Do these complexes have high spin - or low-spin configurations? Also write down the configurations corresponding to these states.

Answer:- For the complex ion, $[Mn(H_2O)_6]^{3+}$, since

$P > \Delta_0$ ($P = 28000$ cm^{-1} and $\Delta_0 = 21,000$ cm^{-1}), this complex ion is a high-spin complex and its configuration is $t_{2g}^3 e_g^1$. Note that Mn^{3+} ion is a d^4 system.

For the complex ion, $[Mn(CN)_6]^{3-}$, since $P < \Delta_0$ ($P = 28,000$ cm^{-1} and $\Delta_0 = 38,500$ cm^{-1}), the complex is a low-spin complex and its configuration is $t_{2g}^4 e_g^0$.