

1. For complexes $[\text{Fe}(\text{CN})_6]^{3-}$ or $[\text{Fe}(\text{CN})_6]^{4-}$ answer the following questions:

(a) Which complex will show the higher value for Δ_o , give a brief reason for your answer?

Ans: Higher the charge on the metal ion higher will be Δ_o

In $[\text{Fe}(\text{CN})_6]^{4-}$ the iron is in +2 oxidation state while in $[\text{Fe}(\text{CN})_6]^{3-}$ iron is in +3 oxidation state thus $[\text{Fe}(\text{CN})_6]^{3-}$ will show higher Δ_o value.

(b) Calculate the wavelength most intensely absorbed light for $[\text{Fe}(\text{CN})_6]^{4-}$ complex ($\Delta_o = 392 \text{ kJ/mol}$) [Avogadro's no. = $6.02214 \times 10^{23} \text{ mol}^{-1}$]

Ans: $\Delta_o = 392 \text{ kJ/mol}$

$$\Delta_o = [(392 \text{ kJ/mol} \times 1000 \text{ J}) / 1 \text{ kJ}] / 6.02214 \times 10^{23} = 6.5093 \times 10^{-19} \text{ J}$$

$$\Delta_o = h\nu$$

$$\text{As } \nu = c/\lambda$$

$$\text{So, } \Delta_o = hc/\lambda$$

$$\lambda = hc / \Delta_o = [6.6261 \times 10^{-34} \text{ Js} \times 2.9979 \times 10^8 \text{ m/s}] / 6.5093 \times 10^{-19} \text{ J}$$

$$\lambda = 305.17 \times 10^{-9} \text{ m} = \mathbf{305 \text{ nm}}$$

(c) What will be the color of a dilute aqueous solution of $[\text{Fe}(\text{CN})_6]^{4-}$?

Ans: Almost colorless as it absorbs in the UV region. Refer to the artist's wheel.

2. The material NiFe_2O_4 will prefer spinel or inverse spinel structure? Use the crystal field theory to explain.

Ans. Ni(II) prefers octahedral geometry over tetrahedral due to stabilization through LFSE.

Octahedral ($t_{2g}^6 e_g^2$): LFSE: $-1.2 \Delta_o$

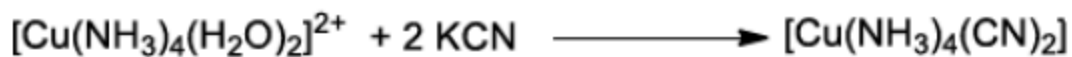
Tetrahedral ($e^4 t_2^4$): LFSE: $-0.8 \Delta_t$

Fe(III) is similar for both octahedral and tetrahedral (LFSE = 0 units)

So NiFe_2O_4 will be an inverse spinel.

3. If we add two equivalents of KCN into a solution containing $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ complex sample, it produces $[\text{Cu}(\text{NH}_3)_4(\text{CN})_2]$. Based on the crystal field theory, predict the Cu d -orbital splitting and coordination geometry for both the complexes?

Ans.



Axially
elongated

Axially
Compressed

