SECTION - A   2 x 4 = 8

1) **Read the passage given below and answer the following questions:**

Iron forms many complexes in its +2 and +3 oxidation states such as
$[Fe(H_2O)_6]^{2+}(A); [Fe(CN)_6]^{4-}(B) [Fe(H_2O)_6]^{3+}(C); [Fe(CN)_6]^{3-}(D)$,etc., They
exhibit, different magnetic properties and undergo different hybridisation of iron.

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) Which of the following statements is correct?

(a) (B) is paramagnetic while (C) is diamagnetic.

(b) Both (B) and (D) are outer orbital complexes.

(c) Both (A) and (C) are paramagnetic.

(d) (A) is outer orbital complex and (C) is inner orbital complex.

(ii) The complex having maximum magnetic moment is

(a) (A)   **(b) (B)**   **(c) (C)**   **(d) (D)**

(iii) The spin only magnetic moment of complexes (A), (B), (C) and (D) are respectively (in BM)

(a)   **(b)**   **(c)**   **(d)**

$2\sqrt{6}, 0, \sqrt{35}, \sqrt{30}, 2\sqrt{6}, \sqrt{35}, \sqrt{3}\sqrt{15}, 2\sqrt{6}, \sqrt{3}, 0\sqrt{3}, \sqrt{8}, 0, \sqrt{15}$

(iv) Which of the given complexes are outer orbital complexes?

(a) (A) and (B) only   **(b) (B) and (C) only**   **(c) (A) and (C) only**   **(d) (B) and (D) only**

Answer : (i) (c): (A) : sp^3d^2 hybridisation (outer orbital)

No. of unpaired electrons = 4

(B) : d^2sp^3 hybridisation (inner orbital)

No. of unpaired electrons = 0

(C) : $sp^3 d^2$ hybridisation (outer orbital)

No. of unpaired electrons = 5

(D) : d^2sp^3 hybridisation (inner orbital)

No. of unpaired electron = 1

(ii) (c): It has 5 unpaired electrons.

(iii) (a): Magnetic moments of (A), (B), (C) and (D) are respectively.

$\sqrt{4(4+2)}, 0, \sqrt{5(5+2)}, \sqrt{1(1+2)}$

(iv) (c)

2) **Read the passage given below and answer the following questions:**

Valence bond theory considers the bonding between the metal ion and the ligands as purely covalent. On the other hand, crystal field theory considers the metal-ligand bond to be ionic arising from electrostatic interaction between the metal ion and the ligands. In coordination compounds, the interaction between the ligand and the metal ion causes the five d-orbitals to split-up. This is called crystal field splitting and the energy difference between the two sets of energy level is called crystal field splitting energy. The crystal field splitting energy (Δ_o) depends upon the nature of the ligand. The actual configuration of complexes is divided by the relative values of Δ_o and P (pairing energy)

If $\Delta_o < P$, then complex will be high spin.

If $\Delta_o > P$, then complex will be low spin.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Which of the following ligand has lowest Δ_o value?

(a) CN^- (b) CO   (c) F^- (d) NH_3

(ii) The crystal field splitting energy for octahedral (Δ_o) and tetrahedral (Δ_t) complex is related as

(a) $\Delta_t = \frac{1}{2}\Delta_o$ (b) $\Delta_t = \frac{4}{9}\Delta_o$

(c) $\Delta_t = \frac{3}{5}\Delta_o$ (d) $\Delta_t = \frac{2}{5}\Delta_o$

(iii) On the basis of crystal field theory, the electronic configuration of d^4 in two situations: (i) $\Delta_o > P$ and (ii) $\Delta_o < P$ are

(i)   (ii)

(a) $t_{2g}^4 e_g^0$ $t_{2g}^3 e_g^1$

(b) $t_{2g}^3 e_g^1$ $t_{2g}^4 e_g^0$

(c) $t_{2g}^3 e_g^1$ $t_{2g}^3 e_g^1$

(d) $t_{2g}^4 e_g^0$ $t_{2g}^4 e_g^0$

(iv) Using crystal field theory, calculate magnetic moment of central metal ion of $[FeF_6]^{4-}$.

(a) 1.79 B.M.   (b) 2.83 B.M.   (c) 3.85 B.M.   (d) 4.9 B.M.

Answer : (i) (c): Spectrochemical series:

$$(I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < O^{2-} < H_2O < NCS$$

(ii) (b)

(iii) (a) : When $\Delta_o > P$, the electrons paired up in the t_{2g} level rather than going to the e_g level, so when $\Delta_o > P : t_{2g}^4 e_g^0$

and $\Delta_o < P : t_{2g}^3 e_g^1$

(iv) (d): Fe^{2+}: $3d^6 \Rightarrow t_{2g}^4 e_g^2$

(Since, F^- is a weak field ligand)

Hence four unpaired electrons are present.

Magnetic moment (μ)= $\sqrt{n(n+2)} = \sqrt{4(4+2)} = 4.9 \text{ B} \cdot \text{M}$