

Model Questions (SEM-IV)

CC-4-10-TH

Crystal field theory

1. What are the important limitations of valence bond theory? [3]
2. What is crystal field theory? How does it differ from the valence bond theory? How does this theory account for the fact that $[\text{CoF}_6]^{3-}$ is paramagnetic but $[\text{Co}(\text{NH}_3)_6]^{3+}$ is diamagnetic though both are octahedral? [2+3+3]
3. How do the d-orbitals split when a transition metal ion is placed in octahedral field of ligands? [4]
4. Give the number of unpaired electrons in a strong and weak octahedral field for (i) Cr^{2+} (ii) Co^{2+} (iii) Fe^{3+} [3x2]
5. Explain the effect of the nature of ligands from the magnitude of delta. [4]
6. Discuss carefully and concisely the splitting of d-orbitals in case of (i) Octahedral complexes (ii) Tetrahedral complexes and (iii) Square planar complexes. [3x2]
7. Giving a net diagram to explain how the d-orbital energy levels split when transition metal ion is placed in the centre of a tetrahedral field. [4]
8. Which complex has larger crystal field splitting (Δ) [4x1]
 - (i) $[\text{Co}(\text{CN})_6]^{3-}$ or $[\text{Co}(\text{NH}_3)_6]^{3+}$
 - (ii) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ or $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$
 - (iii) $[\text{Co}(\text{NH}_3)_6]^{3+}$ or $[\text{Rh}(\text{NH}_3)_6]^{3+}$
9. What relationship exists between Δ (crystal field splitting energy) and the pairing energy (P) in determining whether a given complex will be high spin or low spin- explain with reason. [4]
10. How does crystal field theory explain the colour of co-ordination complexes? [3]
11. Define crystal field stabilization energy. Calculate its value for the following systems:
 - (i) d^5 octahedral (both low and high spin) [3x2]
 - (ii) d^9 octahedral (both low and high spin)
 - (iii) d^4 and d^6 tetrahedral
12. Discuss the σ and π metal-ligand bonding in transition metal complexes with reference to octahedral transition metal complexes. [6]

13. Why is molecular orbital theory preferred over crystal field theory in explaining metal-ligand bonding in transition metal complexes? [4]
14. Discuss σ and π bonding in square planar complexes by constructing a composite molecular orbital diagram for $[\text{PtCl}_4]^{2-}$. [4]
15. Bring out clearly how the crystal field theory explains satisfactorily the magnetic properties of complexes of transition metals. [4]
16. Give example of complex compounds in which $\Delta_o \neq 0$ but CFSE = 0. [2]
17. Given Δ_o for H_2O is 13900cm^{-1} , what would the CFSE of $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ in high spin and low spin configurations? (Mean pairing energy(P) = 23500cm^{-1}) [3]
18. Both $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ ions appear almost colourless in dilute aqueous solutions, though one is low spin and the other is high spin- explain. [2]
19. What is tetragonal distortion? Which d^n configurations lead to Jahn-Teller distortions in octahedral complexes? Explain with examples. [2+6]
20. Explain the nature of J-T distortion expected for a tetrahedral complex of a d^9 metal ion. [6]
21. Explain whether the following complexes will have any orbital contribution to their μ_{eff} values: d^2 (Oh), d^4 (Td) and d^7 (Td). [3x2]
22. Explain why: [2 marks each]
- Co^{2+} (aq) forms a tetrahedral tetrachloro complex when treated with conc. HCl but Ni^{2+} (aq) does not do so.
 - $[\text{CuCl}_4]^{2-}$ has a flattened tetrahedral structure while $[\text{CoCl}_4]^{2-}$ is a regular tetrahedron.
 - Electronic spectrum of $[\text{CoF}_6]^{3-}$ shows two bands having maxima around 11500cm^{-1} and 14500cm^{-1} .
 - Trans- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ is more intensely coloured than $[\text{Co}(\text{en})_2\text{F}_2]^+$.
 - A deep blue solution containing Co(II) in conc. HCl gradually turns pale pink on addition of excess water.
 - The fluoro complexes of Cu(III) and Au(III) are $[\text{CuF}_6]^{3-}$ (paramagnetic) and $[\text{AuF}_4]^-$ (diamagnetic).
 - A green aqueous solution of Ni(II) turns colourless on addition of CN^- .
 - An aqueous solution of Co(III) sulphate is diamagnetic but becomes paramagnetic when a large excess of fluoride is added.
 - The CrO_4^{2-} ion is a d^0 complex and is yet coloured.

23. $10 Dq$ of $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$ is known from electronic spectrum to be 21000cm^{-1} . The pairing energy of Mn(III) is 28800cm^{-1} . Predict whether the complex is high spin or low spin. [4]
24. Cr(III) under forcing conditions form $[\text{CrCl}_6]^{3-}$ but the corresponding complexes are never found in Mn(III) and Fe(III)-why? [4]
25. Why does $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ have pale colour as compared to the complexes of other oxidation states of these metals? [3]
26. Aqueous solution of octahedral $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and tetrahedral $[\text{CoCl}_4]^{2-}$ are coloured yellow, pink and blue respectively. Explain the facts with proper reason. [3x2]
27. Determine the likely configuration of the central metal ions considering the weak field and strong field characters of the ligands. [4x2]
- $[\text{Co}(\text{NH}_3)_6]^{3+}$
 - $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
 - $[\text{Fe}(\text{CN})_6]^{3-}$
 - $[\text{Cr}(\text{NH}_3)_6]^{3+}$
28. Explain why a solution of CuCl_2 in aq. HCl is deep greenish blue whereas similar aq. HCl solution of CuCl is colourless. [2]
29. Why $\text{K}_3[\text{CuF}_6]$ is paramagnetic while $\text{K}[\text{AgF}_4]$ is diamagnetic? [3]
30. Explain when Δ and CFSE are zero. [3]
31. KReO_4 is colourless whereas KMnO_4 is intense purple- explain. [3]
32. Hexaquoiron(III) is nearly colourless but on addition of potassium thiocyanate a blood red colour develops- explain. [2]
33. $[\text{NiCl}_4]^{2-}$ is tetrahedral paramagnetic while $[\text{PdCl}_4]^{2-}$ and $[\text{PtCl}_4]^{2-}$ are diamagnetic square planar-explain. [3]
34. Arrange the following species in the order of increasing Jahn-Teller distortion in an octahedral environment: [4x2]
- high spin Co(III)
 - low spin Co(II)
 - Cu(II)
 - Ti(III)
35. Explain why Ti^{3+} forms coloured aqueous solution while Ti^{4+} gives colourless solution.

[2]

36. $K_2[NiF_6]$ is diamagnetic while $K_3[CoF_6]$ is paramagnetic although both Ni(IV) and Co(III) are d^6 systems – Explain. [2]

37. What is spectrochemical series? [3]

38. How are the magnetic properties of metal ions of d^4 to d^7 configurations explained by crystal field theory? [4x2]

39. Differentiate between ligand field theory and crystal field theory. [4]

40. What are selection rules? How are they useful? [2+3]

41. What are Racah parameters? What is their importance? [2+2]

42. Discuss with the help of Orgel diagrams the absorption spectra of octahedral aqua complexes of d^1, d^2, d^3 and d^6 metal ions. [4x4]

43. What is hole formalism? How is it useful in explaining the spectra of d^2 and d^8 metal ions? [2+4]

44. What is charge transfer spectrum? Explain with suitable examples. [2+4]

MO Theory

1. . Compare the most common oxidation states and highest oxidation state of Cr, Mn and Fe.
2. Lanthanides behave more or less identically with respect to chemical properties while d-block elements differ widely in this respect. - Explain.
3. Why Thallium form iodide only in +1 oxidation state?
4. Lanthanides exhibit +3 oxidation state in general while actinides can show variable oxidation state – Explain.
5. Eu^{2+} and Tb^{4+} are stable in addition to their common oxidation states. - Explain.
6. Compare the most common oxidation states and highest oxidation state of Ni, Pd and Pt metals.
7. Electronic absorption bands of lanthanides ions are shaper compared to those of transition metal ions. – Explain.
8. Complexes of Cu (II) are quite common but those of Au (II) are unstable. Explain.

9. Compare Cr^{2+} , Mn^{2+} , Fe^{2+} and Co^{2+} ions with respect to their redox properties.
10. State electronic absorption spectral features of lanthanides.