

LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – CHEMISTRY

THIRD SEMESTER – NOVEMBER 2009

CH 3809 - COORDINATION CHEMISTRY

Date & Time: 05/11/2009 / 9:00 - 12:00 Dept. No.

Max. : 100 Marks

PART – A

Answer *all* the questions

(10 x 2 = 20)

1. Which complex has larger crystal field splitting: $[\text{Co}(\text{NH}_3)_6]^{3+}$ or $[\text{Rh}(\text{NH}_3)_6]^{3+}$? Give reasons.
2. Calculate CFSE of d^7 , high and low octahedral system.
3. What is the ground term of $3d^4$ configuration?
4. Why is lattice energy of an octahedral complex more than expected?
5. Why the magnetic moment of Co(II) octahedral complexes are much higher than that of tetrahedral complexes?
6. Explain why CrO_4^{2-} ion is coloured?
7. Explain S_N^1 CB mechanism with an example.
8. What is Wilkinson catalyst? What type of reaction can make use of this catalyst?
9. What is Nephelauxetic effect? What is its significance?
10. Why are transition metal aryls more stable than transition metal alkyls?

PART – B

Answer any *six* questions

(8 x 5 = 40)

11. Define JahnTeller effect. Which d^n configurations lead to strong JahnTeller distortion in octahedral and tetrahedral complexes?
12. What is quenching of orbital angular momentum and what are the consequences of it on the μ_{eff} of transition metal complexes?
13. Discuss the bonding in ferrocene on the basis of molecular orbital energy level diagram.
14. Explain the variations in the stretching frequency of the isoelectronic species, $\text{Cr}(\text{CO})_6$, $\text{V}(\text{CO})_6^-$ and $\text{Mn}(\text{CO})_6^+$.
15. Explain the fluxional isomerism with two examples.
16. What is trans effect? Explain the theory of trans effect in the following order of ligands $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$.
17. Discuss the utility of Orgel diagrams. What are their limitations? Draw Orgel diagram for d^1 configuration.
18. Why do electronic spectra of $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ show only two absorption bands against the three predicted for the system?
19. Discuss the effect of zero field effects in the EPR spectrum of coordination compounds with an example.

20. Explain the crystal structures of Fe_3O_4 , MgAl_2O_4 as spinel or inverse spinel.
21. Explain various mechanisms proposed for substitution reactions of coordination compounds.
22. Write short notes on
 - a) Wacker's process
 - b) Fischer Tropsch process

PART – C

Answer any four questions.

(4 x 10 = 40)

23. Explain the d orbital splitting of square planar complexes using crystal field theory. Why does the metal with d^8 configuration in a strong field form square planar complexes?
24. Account for the field strengths of fluoro and cyano ligands in octahedral transition metal complexes using MO theory..
25. Explain the features of Tanabe- Sugano and Orgel diagram. Construct Orgel diagram for d^1 and d^9 , tetrahedral and octahedral complexes.
26. a) Discuss in detail the mechanisms of outer and inner sphere electron transfer in metal complexes. (10)
b) Why is the electron transfer in the system $[\text{Co}(\text{NH}_3)_6]^{2+} - [\text{Co}(\text{NH}_3)_6]^{3+}$ slower than that in the system $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$.
27. Describe the essential structural features of haemoglobin and explain its cooperativity in its oxygenation.
