



**LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034**

**M.Sc. DEGREE EXAMINATION – CHEMISTRY**

**FOURTH SEMESTER – APRIL 2015**

**CH 4956 - ADVANCED COORDINATION CHEMISTRY**

Date : 22/04/2015

Dept. No.

Max. : 100 Marks

Time : 09:00-12:00

**Part-A**

*Answer all questions. Each question carries two marks.*

*(10x2=20)*

1. Organometallic compounds are formed by transition metal ions in the low oxidation state. Comment.
2.  $\text{Cl}^-$  occupies the lower end of the spectrochemical series, yet the  $10Dq$  value in  $[\text{RuCl}_6]^{3-}$  is comparable to that of  $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$ . Offer a reasonable explanation.
3. Jahn-Teller distortion arising from the electronic degeneracy of  $t_{2g}$  orbitals in octahedral complexes escapes experimental detection. Comment.
4. Mention the causes of tetragonal distortion in transition metal complexes.
5. For a complex of a transition metal ion  $\Delta_o \sim P$  at room temperature. Comment upon its magnetic properties.
6. Differentiate thermodynamic and kinetic coordination template effects.
7. How do you differentiate LMCT and MLCT transitions?
8. What are the causes of ZFS in transition metal complexes?
9. How does angular overlap alter the magnitude of  $e_\sigma$  and  $e_\pi$ ?
10. What are slipped sandwiches? Cite an example.

**Part-B**

*Answer any eight questions. Each question carries five marks.*

*(8x5=40)*

11. Explain the structural features and biological roles of Fe-S proteins.
12. Illustrate transmetallation reaction with an example.
13. How are cyano, isocyano, nitro and nitrito complexes differentiated by IR spectroscopy?
14. Explain photoisomerization and photosubstitution reaction in transition metal complexes with illustrative examples.
15. What is nitrogen fixation? Explain its mechanism.
16. What are coupled chemical reactions? How are they classified? How do you ascertain such processes from cyclic voltammetry?
17. Give an account of electrochemical synthesis of coordination compounds.
18. Give an account of the structural features of biological electron transfer agents.
19. Write a note on chelate therapy.
20. Explain the principle of AC polarography. How is the reversibility of a redox couple evaluated by this technique?
21. What are optically transparent thin layer electrodes? Mention their importance.
22. What is static dynamic Jahn-Teller distortion? How is it studied by esr spectroscopy?

### Part-C

*Answer any four questions. Each question carries ten marks.*

**(4x10=40)**

- 23a. Explain the electronic spectral features of low-spin and high-spin  $O_h$  complexes of  $d^6$  metal ion. **(4)**
- b. Explain the electronic spectral features of tetragonally distorted  $O_h$  complex of low-spin  $d^6$  metal ion and the method of evaluating the crystal field parameters. **(6)**
- 24a. Derive Marcus-Hush equation to compute the rate constant of electron transfer reaction. **(7)**
- b. How do you differentiate inner- and outer-sphere electron transfer reactions? **(3)**
- 25a. Explain hyperfine and superhyperfine splitting. **(3)**
- b. The epr spectrum of a high spin Mn(II) complex, doped onto a diamagnetic host, consists of 30 epr lines when there is no hyperfine splitting by the ligand. Interpret the spectrum with the help of a qualitative hyperfine splitting diagram. **(7)**
- 26a. Give an account of the NMR spectra of paramagnetic transition metal complexes. **(5)**
- b. How is low-spin and high-spin Fe(III) complexes differentiated by Mossbauer spectroscopy? Explain with examples. **(5)**
27. Explain the principles of angular overlap model. Show that  $\Delta_t = 4/9 \Delta_o$  with the help of this model.
- 28a. Illustrate coordination template effect with examples. **(4)**
- b. What are compartmental ligands? Explain the method of synthesizing macrocyclic and macroacyclic compartmental ligands with illustrative examples. **(6)**

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