

Reg. No..... Name.....

M. Sc. DEGREE END SEMESTER EXAMINATION MARCH 2017**SEMESTER - 2: CHEMISTRY/APPLIED CHEMISTRY****COURSE: P2CHET05, P2CPHT05: CO-ORDINATION CHEMISTRY***(Supplementary for 2014 admission)*

Time: Three Hours

Max. Marks: 75

SECTION A*Answer any ten questions, each question carries 2 marks*

1. Distinguish between LMCT and MLCT.
2. Why lanthanides give fewer complexes than actinides and d-block elements?
3. What is CFSE? Calculate the CFSE of d^7 high spin and d^7 low spin situations.
4. Compare the molar atomic volume and density of Cerium and Europium with other lanthanides and explain the logic behind it.
5. The measured magnetic moment of copper(II) acetate dehydrate at room temperature is less than the spin only value. Explain why?
6. Which electronic transition would you expected to be more intense and why? ${}^3A_{2g} \rightarrow {}^3T_{2g}$ in a Ni(II) octahedral (or) ${}^3T_1 \rightarrow {}^3T_2$ in a Ni(II) tetrahedral complex.
7. Arrive at the ground state term symbol of Cr^{3+} and Mn^{2+}
8. Differentiate between ferromagnetism and antiferromagnetism.
9. Differentiate between macrocyclic effect and chelate effect with examples.
10. What is nephelauxetic ratio? Point out its significance.
11. What is spectrochemical series? Why OH^- comes before water in the series, in spite of the negative charge?
12. What is transition moment integral? Explain its significance.
13. Arrive at the ground state term symbol of V^{3+} and Mn^{2+}

(2 x 10 = 20)

SECTION B*Answer any five questions. Each question carries 5marks*

14. Explain the Gouy method for determination of magnetic susceptibility.
15. What are Orgel diagrams? Draw the Orgel diagrams of d^2 and d^4 ions in octahedral and tetrahedral ligand field?
16. What is absolute configuration of a coordination compound? Discuss the role of CD and ORD in reaching absolute configuration.
17. Discuss the crystal field splitting of d levels in TBP and Sq. Pyramidal complexes.
18. Jahn-Teller distortion observed in t_{2g} state is very small compared to e_g state. Why? Site examples of complex systems involving slight distortion, maximum distortion and no distortion.
19. Explain how IR spectroscopy used to identify the different bonding modes of CO in metal carbonyls. The C-O stretching frequency for $[Ni(CO)_4]$, $[Co(CO)_4]^-$ and $[Fe(CO)_4]^{2-}$ are 2060, 1890 and 1790 cm^{-1} respectively. Account for the observation.

20. What are ligand field and charge transfer excited states of metal complexes? Illustrate the reactions initiated by excitation of these states in metal complexes?
21. Discuss briefly the mechanism of outer-sphere electron transfer reactions? How can Marcus theory be used to explain it?

(5 x 5 = 25)

SECTION C

Answer **any Two** questions. Each question carries **15 marks**

22.(a). The electronic spectrum of $[\text{CoF}_6]^{3-}$ shows an absorption peak at $13,000 \text{ cm}^{-1}$. Assign the peak with the help of Orgel diagram.

(b). Explain the origin of the pale pink color of $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$.

23.(a). For Mn^{2+} ion the electro pairing energy is about $28,000 \text{ cm}^{-1}$. Δ_o value for the complexes $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Mn}(\text{CN})_6]^{3-}$ are $21,000 \text{ cm}^{-1}$ and $38,000 \text{ cm}^{-1}$ respectively. Do these complexes have high spin or low spin configuration? Also write the configuration corresponding to these states.

(b). The Racah parameter, B, for $[\text{Co}(\text{CN})_6]^{3-}$ is 460 cm^{-1} and the same for $[\text{Co}(\text{NH}_3)_6]^{3+}$ is 615 cm^{-1} . Explain.

24. (a). Discuss the postulates of MO theory as applied to co-ordination compounds. How are group orbitals constructed for the formation of MO in an octahedral complex?

(b). Explain why the two spin allowed ligand field transitions of $[\text{Cr}(\text{NCS})_6]^{3-}$ are at lower energy than those of $[\text{Cr}(\text{NH}_3)_6]^{3+}$.

25. (a). What is trans effect? Keeping trans effect, suggest method for preparing three different isomers of $[\text{Pt}(\text{NH}_3)(\text{py})(\text{Br})(\text{Cl})]$ from $[\text{PtCl}_4]^{2-}$.

(b). What is base hydrolysis? Explain its mechanism using $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ as an example.

(15 x 2 = 30)
