

SECOND SEMESTER M.Sc. DEGREE EXAMINATION, JUNE 2016

(CUCSS)

Chemistry**CH 2C 06—CO-ORDINATION CHEMISTRY****(2015 Admissions)**

Time : Three Hours

Maximum : 36 Weightage

Part A*Answer all questions.**Each question carries 1 weightage.*

1. Prove that for the formation of $[\text{Cu}(\text{NH}_3)_4]^{+*}$ from Cu^{+*} and NH_3 , $R_4 = k_1 \cdot k_2 \cdot k_3 \cdot k_4$.
2. What are the geometries exhibited by 5, 6 and 7-coordinate complexes ?
3. Calculate the CSFE for a high spin octahedral complex and tetrahedral complex of cobalt (II). Which is greater ? Why ?
4. Order the following ligands in spectrochemical series and nephelauxetic series: Cl^- , H_2O , NH_3 , CN^- , CO . Justify your answer.
5. The energy of charge transfer transition in $[\text{Co}(\text{NH}_3)_5\text{X}]^{+*}$ (X = halide ion) decreases in the order : $< \text{Cl}^- < \text{Br}^- <$
6. Explain Curie and Curie-Weiss laws.
7. Explain the terms (i) isomer shift and (ii) quadrupole splitting as applied to Mössbauer spectroscopy.
8. Describe the energy level diagram of an one electron system in a magnetic field and explain the resonance condition of EPR.
9. $\text{Cr}(\text{H}_2\text{O})_6^+$ is labile and $\text{Cr}(\text{CN})_6^{2-}$ is inert. Why ?
10. The aquation reaction $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ is faster than that of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{+*}$. Explain.
11. Describe photo-isomerisation and photoracemization reactions with examples.
12. What are prompt and delayed reactions in photochemistry ?

(12 x 1 = 12 weightage)

Part B*Answer any eight questions.**Each question carries 2 weightage.*

13. $[\text{CoF}_6]^-$ contains two unpaired electrons and $[\text{Co}(\text{NH}_3)_6]^{+*}$ is diamagnetic. Explain how valence bond theory can be used to explain the magnetic behaviour of these complexes.

Turn over

14. How formation constant of a metal complex is determined by pH-metry ?
15. Among Mn_3O_4 and Fe_3O_4 which would have normal spinel structure ? Why ?
16. Explain valence bond theory and its limitations with respect to the bonding in coordination compounds.
17. What is temperature independent magnetism ?
18. What are the selection rules for electronic spectra of transition metal complexes ?
19. What is group frequency concept used in IR spectroscopy ?
20. Explain the basic principle of Mössbauer spectroscopy.
21. What is trans effect ? Using trans effect, suggest a method for preparing three isomers of $[Pt(NH_3)(Py)BrCl]$ from $[PtCl_4]^-$.
22. Describe the A and D mechanisms of substitution reactions involving coordination complexes. How can you distinguish **between them** ?
23. Explain the mechanism of outer sphere redox reactions.
24. Write briefly on water photolysis.

(8 x 2 = 16 weightage)

Part C

*Answer any two questions.
Each question carries 4 weightage.*

25. How do Tanabe-Sugano diagrams differ from Orgel diagrams ? Draw Tanabe-Sugano diagram for $[V(H_2O)_6]^{+}$ and explain the electronic transitions.
26. How EPR spectra is used to study the nature of bonding in copper (H) complexes ?
27. Describe the base hydrolysis of $[Co(NH_3)_5Cl]^{+}$ and give experimental evidence in support of the mechanism.
28. Account for the photoreactive excited states of Cr(III) complexes. Giving suitable examples discuss the photoaquation reactions of Cr(III) complexes

(2 x 4 = 8 weightage)