

C 4756

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Name.....

Reg. No.....

**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  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  from  $\text{Cu}^{2+}$  and  $\text{NH}_3$ ,  $R_4 = k_1 \cdot k_2 \cdot k_3 \cdot k_4$ .
2. What are the geometries exhibited by 5, 6 and 7-coordinate complexes ?
3. Calculate the CFSE 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:  $\text{Cl}^-$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{CN}$ ,  $\text{CO}$ . Justify your answer.
5. The energy of charge transfer transition in  $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$  (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.  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  is labile and  $\text{Cr}(\text{CN})_6^{3-}$  is inert. Why ?
10. The aquation reaction  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  is faster than that of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ . 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.  $[\text{CoF}_6]^{3-}$  contains two unpaired electrons and  $[\text{Co}(\text{NH}_3)_6]^{3+}$  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  $\text{Mn}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4$  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  $[\text{Pt}(\text{NH}_3)(\text{Py})\text{BrCl}]$  from  $[\text{PtCl}_4]^-$ .
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  $[\text{V}(\text{H}_2\text{O})_6]^{3+}$  and explain the electronic transitions.
26. How EPR spectra is used to study the nature of bonding in copper (II) complexes ?
27. Describe the base hydrolysis of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^+$  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 )