

C 63028

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Name.....

Reg. No.....

SECOND SEMESTER M.Sc. DEGREE EXAMINATION, JUNE 2019

(CUCSS)

Chemistry

CH 2C 06—CO-ORDINATION CHEMISTRY

(2015 Admissions)

Time : Three Hours

Maximum : 36 Weightage

Section A

Answer all questions.

Each question carries 1 weightage.

1. K_3 value is found to be greater than K_2 value for Fe(II) complexes of 1, 10-phenanthroline. Why ?
2. A tris-diaminoethane complex will generally be more stable than the-corresponding monodentate ligand. Why ?
3. Nickel and Platinum are in the same family of Periodic Table but $[\text{NiCl}_4]^{2-}$ and $[\text{PtCl}_4]^{2-}$ differ considerably in their geometries. Why ?
4. Interionic repulsion is found to be weaker in complexes than in free ions. Why ?
5. Deduce the spectroscopic ground term of d^1 and Co^{3+} .
6. State Curie law and Curie-Weiss law.
7. Arrange the following in the order of increasing CO stretch frequencies and explain your answer $[\text{Mn}(\text{CO})_6]^+$, $[\text{Ti}(\text{CO})_6]^{2-}$, $[\text{Cr}(\text{CO})_6]$, $[\text{V}(\text{CO})_6]$.
8. Define Doppler broadening of Mossbauer spectroscopy.
9. Steric crowding favours dissociative mechanism of substitution in metal complexes. Justify the statement with suitable examples.
10. Write down the Fuoss-Eigen equation and explain the terms.
11. Complexes containing Cl^- , NCS^- , N_3^- and CN^- ions as ligands favour inner sphere electron transfer reactions. Why ?
12. What is photorecimization ? illustrate,

(12 x 1 = 12 weightage)

Turn over

Section B

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

13. Write down the stepwise and overall formation constants for the reaction $\text{Cu}^{2+} + 4\text{NH}_3 \rightleftharpoons \text{Cu}(\text{NH}_3)_4^{2+}$. Also calculate P_4 value for the reaction if $\log k_1 = 4$, $\log k_2 = 3.2$, $\log k_3 = 2.7$ and $\log k_4 = 2$.
14. Describe the spectrophotometric method for determining Binary formation constant.
15. Name and draw the structures of the following complexes :
(a) $[\text{Ni}(\text{CO})_4]$; (b) $[\text{Ni}(\text{CN})_4]^{2-}$; (c) $[\text{CoCl}_4]^{2-}$; (d) $[\text{Ni}(\text{NH}_3)_6]^{2+}$.
16. Explain how does a Pi donor ligand influences the magnitude of the splitting parameter in a pi bonded octahedral complex.
17. What do you mean by spin only magnetic moment ? Calculate the spin only magnetic moment for (a) $[\text{Fe}(\text{CN})_6]^{4-}$; (b) $[\text{Ru}(\text{NH}_3)_6]^{3+}$; (c) $[\text{Cr}(\text{NH}_3)_6]^{2+}$.
18. Write down the favourable conditions for LMCT and MLCT.
19. Explain hyperfine structure of EPR spectrum taking Cu(II) complex as example.
20. Sketch the Mossbauer spectra for the complexes $\text{K}_4[\text{Fe}(\text{CN})_6]^{1-}$ and $\text{K}_3[\text{Fe}(\text{CN})_6]^{4-}$. Explain the features of the spectra.
21. What is trans effect ? How is 'cis' and trans $[\text{Pt}(\text{NH}_3)_4]^{2+}$ synthesized by the application of trans effect ?
22. Give a brief note on SN^1CB mechanism.
23. Distinguish between outer sphere and inner sphere reactions with examples.
24. Discuss the reducing and oxidizing character of $[\text{Ru}(\text{bipy})_3]^{2+}$.

(8 x 2 = 16 weightage)

Section C

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

25. Discuss the merits of MOT over CFT and sketch the MO diagram for $[\text{CoF}_6]^{3-}$ and predict its magnetic behaviour.
26. What are Orgel diagrams ? Draw the Orgel diagrams for $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and explain how does their electronic spectra differ each other ?
27. With suitable examples, discuss the applications of IR spectroscopy in structural studies of metal complexes.
28. Give an account of photochemical reactions of metal complexes.

(2 x 4 = 8 weightage)