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C 82840 (Pages : 3) Name.....

Reg. No.....

SECOND SEMESTER M.A./M.Sc./M.Com. DEGREE EXAMINATION, JUNE 2020

(CUCSS)

Chemistry

CH 2C 06—CO-ORDINATION CHEMISTRY

(2015 Admissions)

Time : Three Hours Maximum : 36 Weightage

Section A

Answer **all** *questions.*

Each question carries a weightage of 1.

1. Explain, why stepwise equilibrium constant values decrease as the number of ligands attached to the metal increases ?

2. Chelate effect is an entropy effect. Justify the statement.

3. Arrange the ligands NH_3, H_2O,OH^-,Cl^- and CO in increasing order of crystal field strength and justify your answer.

4. Give a note on Nephelauxetic effect and series.

5. The magnetic moment of Gd^{3+} is less than Dy^{3+}. Why ?

6. For Co (II) complexes, generally the observed magnetic moment is higher than that calculated by the spin only formula. Why ?

7. How many peaks do you expect in the ESR spectrum of $[Mn\ (H_2O)_6]^{2+}$? Explain your answer.

8. Which among the following have the highest CO stretch frequency in IR spectrum ? (i) $Ni(CO)_4$, (ii) $[Co(CO)_4]^-$ (iii) $Fe(CO)_4]^{2-}$. Justify your answer.

9. $[Co(NH_3)_5X]^{2+}$ undergoes acid hydrolysis as well as base hydrolysis. What are the products obtained by the above two hydrolysis ?

10. Distinguish between inert and labile complexes with examples.

11. Write down the elementary steps involved in the mechanism of the reaction :

$$[Cr(H_2O)_6]^{2+} + [Co(H_2O)_5Cl]^{2+} \rightarrow [Cr(H_2O)_5Cl]^{2+} + [Co(H_2O)_6]^{2+}$$

12. What is photoisomerisation ? Illustrate.

(12 × 1 = 12 weightage)

Turn over

Section B

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

18. Write down the stepwise and overall formation constants for the reaction

$Cu^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+}$. Also Calculate β_4 value for the reaction if $\log k_1 = 4$, $\log k_2 = 3$, $\log k_3 = 2.7$ and $\log k_4 = 2$.

14. Describe the pH-metry method for determining Binary formation constant.

15. Sketch the *d*-orbital splitting pattern of metal ion in $[NiCl_4]^{2-}$. Sketch the change in *d* orbit splitting when Cl^- ion is completely replaced by CN^- ion.

16. Explain how does a Pi acceptor ligand influences the magnitude of the splitting parameter a pi bonded octahedral complex.

17. What do you mean by spin only magnetic moment ? Calculate the spin only magnetic moment a) $[Fe(CN)_6]^{4-}$; b) $[Ru(NH_3)_6]^{3+}$; c) $[Cr(NH_3)_6]^{2+}$.

18. State and explain the selection rules for d-d transition.

19. Explain hyperfine structure of EPR spectrum taking Cu(II) complex as example.

20. Sketch the Mössbauer spectra for the complexes $K_4[Fe(CN)_6]^{4-}$ and $K_3[Fe(CN)_6]^{4-}$. Explain t features of the spectra.

21. What is trans effect ? Propose the synthesis for 'cis' and trans $[PtCl_2(NO_2)\,NH_3]^-$.

22. Discuss the Eigen-Wilkins mechanism of substitution reactions in octahedral complexes.

23. Comment on the difference in the activation energies of the electron transfer reactions betwe the following pairs :

(a) $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ 19.6kJ

(b) $[Co(NH_3)_6]^{2+}$ and $[Co(NH_3)_6]^{3+}$ 56.5kJ

24. Discuss the reducing and oxidizing character of $[Ru(bipy)_3]^{2+}$.

(8 × 2 = 16 weightag

Section C

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

25. Discuss the merits of MOT over CFT and sketch the MO diagram for $[Co(NH_3)_6]^{2+}$ and predict it magnetic behavior.

26. Give a comparison between Orgel diagrams and Tanabe Sugano diagrams with special reference to their importance in the interpretation of electronic spectra.

27. With suitable examples, discuss the applications of NMR spectroscopy in structural studies of metal complexes.

28. Brief out the methods for distinguishing Outer and Inner sphere redox reactions.

(2 × 4 = 8 weightage)