

II Semester M.Sc. Degree Examination, July 2017  
(NS – 2010 – 11 Scheme) (Repeaters)

CHEMISTRY

C – 201 : Inorganic Chemistry – II (Coordination Chemistry)

Time : 3 Hours

Max. Marks : 80

*Instruction : Answer Question No. 1 and any five of the following.*

1. Answer any ten of the following.

(10×2=20)

- Distinguish between kinetic and thermodynamic stability of metal complexes.
- What is the general trend in the relative magnitudes of stepwise stability constants of a complex? What are the reasons for the trend?
- Explain the anomalous magnetic behaviour of  $\text{Sm}^{3+}$ .
- Why does electronic absorption bands of  $[\text{NiCl}_4]^{2-}$  show greater intensities than  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ ?
- Deduce the microstates for  $\text{Co}^{2+}$  and  $\text{Mn}^{2+}$ .
- Distinguish the bonding between hydride and dihydrogen complex.
- What is Faraday effect in MCD?
- What are the possible ways in which  $\text{O}_2$  can bind to the metal complexes? Give one example for each.
- Calculate the spin only magnetic moment for the following complexes :  $\text{K}_3[\text{Fe}(\text{CN})_6]$  and  $\text{CoCl}_4^{2-}$ .
- What are Pascal constants? Mention their utility.
- How can nephelauxetic effect? Explain the bonding between metal and ligands.
- What are the limitations of CFT?

- Discuss briefly the effect of nature of metal and ligand on the stability of metal complexes.
- What is Jahn-Teller effect? Which are the systems that are susceptible to this effect?
- Write briefly on angular overlap model.

(4+4+4=12)

P.T.O.



3. a) Describe the determination of formation constants by spectrophotometric method.
- b) What are chelate and macrocyclic effects? How do these influence the stability of metal complexes? Explain with suitable examples.
- c) What are stepwise and overall formation constants? Prove that the formation of  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  from  $\text{Cu}^{2+}$  and  $\text{NH}_3$ ,  $\beta_4 = K_1 \cdot K_2 \cdot K_3 \cdot K_4$ . (4+5+3=12)
4. a) Draw the Orgel diagram for  $\text{Co}^{2+}$  ( $d^7$ ) system and give its salient features. Explain the merits of Tanabe-Sugano diagrams over Orgel diagrams.
- b) The absorption spectrum of  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  displays spin allowed bands at 17400, 24600 and 37800  $\text{cm}^{-1}$ . Assign the transitions and calculate  $10 Dq$ ,  $B^1$  and  $\beta$  ( $B$  for  $\text{Cr}^{3+} = 1030 \text{ cm}^{-1}$ ). Comment on the metal-ligand bonding.
- c) Write briefly on selection rules in electronic spectroscopy. (5+4+3=12)
5. a) What are the different types of charge transfer transitions encountered in metal complexes? How do they differ from d-d spectra?
- b) Write the structures of  $\text{Mn}_2(\text{CO})_{10}$  and  $\text{Fe}_3(\text{CO})_9$  and explain the bonding involved. How is terminal and bridging carbonyls distinguished by IR spectroscopy?
- c) Though  $\text{N}_2$  and  $\text{CO}$  are isoelectronic and contain triple bond,  $\text{CO}$  forms stable metal complexes while  $\text{N}_2$  does not. Explain. (4+5+3=12)
6. a) What are stereochemical non-rigid molecules? Explain the fluxional behaviour exhibited by  $(\text{Cp})(\text{CO})\text{Fe}(\mu\text{-CO})_2\text{Fe}(\text{CO})(\text{Cp})$ .
- b) Explain how ORD helps in assigning absolute configuration of metal complexes.
- c) Discuss the type of bonding present in supramolecular structure. (4+4+4=12)
7. a) The spin only magnetic moment value of  $\text{Ni}^{2+}$  is 2.83 B.M. whereas, experimental value for  $\text{Ni}(\text{II})$  octahedral complexes range from 2.8 to 3.3 BM and for tetrahedral around 4.0 BM. How do you account for these observations?
- b) Discuss briefly on spin crossover encountered in transition metal complexes.
- c) Set up the molecular diagram for  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  without  $\pi$ -bond. What are the salient features of this diagram? (3+4+5=12)