II Semester M.Sc. Degree Examination, July 2017 (CBCS) CHEMISTRY C – 201 : Inorganic Chemistry – II

Time : 3 Hours

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

- 1. Answer any ten of the following :
 - a) How is the overall stability constant of a complex related to its stepwise stability constant ?
 - b) For Cu^{2+}/NH_3 system, the log of the stepwise stability constant are log K₁ = 4.25, log K₂ = 3.55, log K₃ = 2.85 and log K₄ = 2.15. Calculate the overall stability constant of [Cu (NH₃)₄]²⁺ species.
 - c) The formation of $[Cu (en)_3]^{2+}$ not observed in solution. Why?
 - d) How do the pi-bonding ligands help in the stabilization of metal complex?
 - e) Which of the two, [Co (Cl)₄]²⁻ and [Co (I)₄]²⁻ is expected to have higher Δ_t and why ?
 - f) What are hetero crowns and spherandes ? Give an example.
 - g) Complete the following reactions :
 - i) $[Co (CN)_6]^{3-} + H_2O \xrightarrow{hv} ?$
 - ii) Co $[(NH_3)_6]^3 + H_2O \xrightarrow{hv} ?$
 - h) 'Aquation reaction in Rh³⁺ and Ir³⁺ complexes is very difficult' substantiate.
 - i) On the basis of molecular orbital, explain why the Mn-O distance in $[MnO_4]^{2-}$ is longer by 3.9 pm than in $[MnO_4]^{-}$.
 - j) What are the possible magnetic moments of Co(II) in tetrahedral and octahedral complexes ?
 - k) Illustrate antiferromagnetic coupling.
 - I) What do you mean by nephelauxetic ratio? How does it relates with delocalization of metal ligand bond?

Max. Marks: 70

(2×10=20)

- 2. a) Discuss the structure and different modes of bonding of NO with transition metal complexes.
 - b) Give the ground state terms for d^2 and d^7 systems.
 - c) Explain Laporte and spin selection rule.
- 3. a) With a suitable example, explain the kinetic and thermodynamic stability of metal complexes.
 - b) Discuss the determination of binary formation constant by an ion-exchange method.
 - c) Point out the uses and limitations of CFT.
- 4. a) In what Tanaube Sugano diagrams are different from Orgel diagrams ? Draw Orgel diagram for an octahedral chromium (III) complex. Explain the possible transitions.
 - b) $[Co (NH_3)_6]^{2+}$ has absorption band at 9000 cm⁻¹ and 21100 cm⁻¹. Calculate Δ_0 and B for d⁷ ion.
 - c) The complexes $[Co (NH_3)_5 X]^{2+} (X = CI, Br, I)$ have charge transfer to metal bands. Which of these complexes would you expect to have the lowest-energy charge-transfer band? Why? (4+3+3=10)
- 5. a) Depict MO diagram involving sigma orbital for an octahedral complex and discuss the salient features of the diagram.
 - b) Discuss any two spectral evidences for metal ligand covalency in complexes.
 - c) Explain the self-assembly concept and its application in molecular and supra molecular Chemistry. (4+3+3=10)
- 6. a) Discuss the determination of magnetic susceptibility of metal complexes by Gouy method.
 - b) Calculate the crystal field stabilization energies for a d⁸ system in octahedral and tetrahedral complexes.
 - c) Represent the different polyhedrons for co-ordination number 7 and 8. (4+3+3=10)

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- 7. a) Mention the importance of spin-orbit coupling and report a Jabolnskii diagram for an octahedral complex of Cr³⁺.
 - b) Illustrates the variation of redox potentials in photochemical processes.
 - c) Write a note on light-harvesting Antennae. (4+3+3=10)
- 8. a) Explain the inter-and intra-molecular photo process.
 - b) K_4 [NiF₆] is diamagnetic while K_3 [CoF₆] is paramagnetic. Account for this.
 - c) State Kasha's rule. Discuss the main principle of Kasha's rule and Stokes shifts. (4+3+3=10)

