

II Semester M.Sc. Examination, June 2015 (CBCS) CHEMISTRY C – 201 : Inorganic Chemistry – II (Coordination Chemistry)

Time : 3 Hours

Instruction : Answer question 1 and any five of the remaining.

- 1. Answer ten questions of the following :
 - a) Which of the following metal complexes is expected to be subject to a John Teller distortion ? Explain
 - i) [CrF₆]^{2–} ii) [Cu(H₂O)₆]²⁺
 - b) Distinguish between kinetic and thermodynamic stability of metal complexes.
 - c) Account for the fact that CO stabilizes the low oxidation states of metal ions.
 - d) Calculate the CFSE of an octahedral Cr(III) complex for which

 $\Delta_0 = 23,100 \text{ cm}^{-1} \text{ and P} = 17,200 \text{ cm}^{-1}.$

- e) Predict the geometries of complexes whose coordination numbers are 5 and 7.
- f) Mention the limitations of OFT.
- g) Some value of Racah parameters are 920, 760 and 1050 cm⁻¹. Assign these values to the ions, V²⁺, Cr³⁺ and Mn⁴⁺. Explain your choice.
- h) Arrange the given Russell Saunders terms in increasing order of energy : ${}^{3}P$, ${}^{1}G$, ${}^{1}P$ and ${}^{3}F$. Explain your answer.
- i) Explain why lanthanides exhibit sharp absorption bands.
- j) What is meant by spin cross over ? Mention a system exhibiting it.
- k) For Hg[Co(SCN)₄], the value of corrected molar magnetic susceptibility was found to be 16.44×10^{-6} cgs at 300 K. Calculate its effective magnetic moment.
- I) State and explain Kasha's rule.

(2×10=20)

Max. Marks: 70

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- 2. a) What are metal chelates ? Explain with suitable examples.
 - b) Describe the formation constant of a metal complex by pH metric method.
 - c) The stepwise stability constant values for Cu^{2+}/NH_3 system are as follows : log k₁ = 4.25, log k₂ = 3.56, log k₃ = 2.96 and log k₄ = 2.35. Calculate the overall stability constant of [$Cu(NH_3)_4$]²⁺. (3+4+3)
- a) Explain any two experimental evidences for partial covalency in M L bonding of complexes.
 - b) Sketch the MO energy level diagram for $[CoF_6]^{3+}$ involving σ bonding only.
 - c) Discuss how CFT explains color of a complex. (4+3+3)
- 4. a) Show the splitting pattern of d-orbitals in octahedral and tetrahedral complexes. Explain why 10 Dq value of an octahedral complex is greater than that of a tetrahedral complex.
 - b) Discuss the bonding and structure of a metal nitrosyl.
 - c) Describe the stereochemical non-rigidity in $Fe_2Cp_2(CO)_4$. (4+3+3)
- 5. a) Calculate the values of B' and β for $[Cr(H_2O)_6]^{3+}$ which exhibits absorption bands at 10040, 16500 and 20920 cm⁻¹. Assign these transitions (Given : B for free Cr³⁺ ion = 650 cm⁻¹)
 - b) Giving suitable examples, mention different types of charge transfer transitions. Explain why compounds exhibiting charge transfer transitions are intensely colored.
 - c) In what way Tanabe Sugano diagrams are different from Orgel diagrams?

(4+3+3)

- 6. a) Discuss the magnetic properties of actinide metal complexes.
 - b) Sketch the graph and explain the effect of temperature on magnetic susceptibility of ferromagnetic and antiferromagnetic compounds.
 - c) The complexes $[Mn(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{3+}$ and $[MnCl_4]^{2-}$ have magnetic moments of nearly 5.9 BM. What does this tell you about electrons arrangement in these complexes ? Why is the spin-only formula so precise in these complexes ? (3+4+3)
- 7. a) Discuss the preparation and bonding in phosphine complexes.
 - b) Give a brief account of self assembly in supramolecular chemistry.
 - c) Explain why an electronic transition for $[Mr(H_2O)_6]^{2+}$ is spin forbidden but for $[Co(H_2O)_6]^{2+}$ is spin allowed ? (3+4+3)
- 8. a) With the help Jablonskii diagram, indicate the various photophysical processes.
 - b) With suitable examples, explain photo substitution and photo-redox reactions.
 - c) Draw the possible geometrical and optical isomers $[Pt(NH_3)_2CI_2]$. (3+4+3)

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