PG – 704

Second Semester M.Sc. Degree Examination, June 2016
(NS) (2010-11 and Onwards)
CHEMISTRY
C 201 : Inorganic Chemistry – II (Co-ordination Chemistry)

Time : 3 Hours | Max. Marks : 80

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

1. Answer **ten** questions of the following : **(2×10=20)**

   a) For a co-ordination compound formation, $\Delta G^{\circ} = -10.56\ kJmol^{-1}$. Calculate the stability constant at 25° C (Given : $R = 8.314\ JK^{-1}\ mol^{-1}$).

   b) Explain why $[Cu\ (en)\ (H_2O)_2]^{2+}$ is stabler than $[Cu\ (NH_3)_2\ (H_2O)_2]^{2+}$.

   c) What is spectrochemical series ? Why is it called so ?

   d) Which of the following would undergo Jahn Teller distortion ?
   $[Cu(H_2O)_6]^{2+}$, $[FeF_6]^{3-}$, $[Co(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$.

   e) Indicate the possible modes of bonding of isocyanide to metals.

   f) Explain the Cotton effect.

   g) Some values of the Racah parameter are 920, 760 and 1050 cm^{-1}. Assign these values to the ions, Cr^{3+}, V^{2+} and Mn^{4+}. Explain your choice.

   h) Obtain the total number of microstates for carbon and V^{3+}.

   i) Copper acetate has a lower magnetic moment at room temperature with respect to its spin-only value. Why ?

   j) What is meant by spin cross over ? Why spin cross over systems are not possible in tetrahedral complexes ?

   k) Predict the geometries of metal complexes with co-ordination numbers 7 and 8.

   l) Account for the fact that NO is capable of forming both linear and angular M-NO groups in nitrosyl complexes.

2. a) Nature of the metal ion affects the stability of metal complexes. Enumerate with suitable examples.

   b) Describe the spectrophotometric method of determination of stability constant of a metal complex.

   c) The stepwise stability constant values for Cu^{2+}/NH_3 system are as follows : $\log k_1 = 4.28$, $\log k_2 = 3.55$, $\log k_3 = 2.99$ and $\log k_4 = 2.36$. Calculate the overall stability constant of $[Cu\ (NH_3)_4]^{2+}$. **(3+6+3)**

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3. a) Illustrate any two experimental evidences for covalency in M-L bonding of complexes.

   b) Sketch the MO energy level diagram for $[FeF_6]^{3-}$ involving σ bonding only. Give its salient features.

   c) Identify all the isomers of (i) $[M(aa)_2bc]$ and (ii) $[M(aa)_2b_2]$ where (aa) is a bidentate ligand. Which of them are optically active ? **(4+4+4)**

4. a) Distinguish between CD and ORD. Discuss the use of CD in determining the absolute configuration of metal complexes.

   b) Write the structures of $Mn_2(CO)_{10}$ and $Fe_3(CO)_{12}$ and discuss the bonding of CO in there complexes. Explain why metal atoms/ions occur in lower oxidation states in carbonyl complexes.

   c) Give a brief account of stereochemical non-rigidity. **(5+4+3)**

5. a) How does ^3F state of Ni^{2+} free ion transform in an octahedral field ? Assign the possible transitions. Calculate the values of Dq, B' and β for $[Ni(H_2O)_6]^{2+}$ which exhibits absorption bands at 8700, 14500 and 25000 cm^{-1} (Given : B for free Ni^{2+} ion = 1040 cm^{-1}).

   b) Giving suitable examples, explain the characteristics of different types of charge transfer transitions. Explain why compounds exhibiting charge transfer transitions are intensely colored ?

   c) State and explain the selection rules of electronic spectroscopy. **(4+5+3)**

6. a) Discuss the spectral and magnetic properties of lanthanides.

   b) Distinguish between ferromagnetism and antiferromagnetism. Explain the effect of temperature on magnetic susceptibility of ferromagnetic and antiferromagnetic compounds.

   c) For $[Ni(H_2O)_6]^{2+}$ complex, $\mu_{eff} > \mu_s$, while for $[Cr(H_2O)_6]^{3+}$ the μ_{eff} is comparable to μ_s value. Explain. **(4+5+3)**

7. a) Discuss the bonding in dinitrogen and phosphine metal complexes.

   b) Give a brief account of self assembly in supramolecular chemistry.

   c) Mention the limitations of CFT. **(6+3+3)**