RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

B.A./B.SC. FIFTH SEMESTER EXAMINATION, DECEMBER 2013

THIRD YEAR

Date : 21/12/2013 **CHEMISTRY (Honours)**

Time : 11 am – 1 pm Paper : VI Full Marks : 50

[*Answer **any one** question from each unit***]**

Unit - I

1. a) $[Fe(dipy)_3](ClO_4)_3$ complex has a magnetic moment of 2·2 BM. Is it an inner orbital or outer orbital complex? Give its crystal field stabilisation energy value. [3]

   b) $[FeF_6]^{3-}$ is colourless but $[Fe(SCN)_6]^{3-}$ is blood red – though both are d^5 complexes. [3]

   c) ''Both $[Ni(CN)_4]^{2-}$ and $Ni(CO)_4$ are diamagnetic —but they have different geometries'' —Explain. [3]

   d) ''Negetively charged F^- ion occupies the weaker end of the spectrochemical series while neutral CO is located in the stronger end.'' —Explain. [2]

   e) The corrected molar susceptibility of a paramagnetic material is $6{\cdot}20\times10^{-3}$ cgs units at 27°C. Find out the number of unpaired electrons. [2]

2. a) An aqueous solution of $Ni(NO_3)_2$ is green. Addition of aqueous NH_3 causes the colour of the solution to change to blue. If ethylenediamine is added to the green solution of $Ni(NO_3)_2$, the colour changes to violet. Account for the colours of these solutions. [3]

   b) Explain the following order of LMCT energies $VO_4^{3-} > CrO_4^{2-} > MnO_4^-$ [2]

   c) CrF_6^{3-} ion shows absorption bonds at 14,900 cm^{-1}, 22,700 cm^{-1} and 34,400 cm^{-1}. Assign the bands using orgel diagram. [3]

   d) The common oxidation state of silver is +1, but that of gold are +1 and +3. Justify from C.F.T. [3]

   e) How would you account for the magnetic moment of the following complexes? [2]

      i) $[CoCl_2(OPPh_3)_2]$ $\mu = 4{\cdot}91\,BM$

      ii) $Na_4[Co(NO_2)_6]$ $\mu = 1{\cdot}88\,BM$

Unit - II

3. a) Establish the relation between 'Stepwise formation Constant' and 'Overall formation Constant' in the formation of the complex ML_X. [3]

   b) How will you prepare cis- and trans- forms of $[PtCl_2(NH_3)_2]$ form NH_3, HCl and $[PtCl_4]^{2-}$? [2]

   c) Discuss the equilibrium between chromate and dichromate ions in aqueous solutions at different pH showing structural equilibrium between them. [2]

   d) What is the basis on which M^{2+} ions are arranged in the 'Irving-Williams Series'? Why Cu^{2+} ion is placed at the top position in the series? [3]

   e) ''Chromium (II) halides are very strong reducing agents''. Justify the statement giving suitable examples. [2]

4. a) How will you determine the metal-ligand ratio of a complex by mole ratio variation? [4]

   b) Strong field d^3 and d^6 complexes are generally inert. Explain. [2]

   c) The chemistry of Zirconium and Hafnium are very similar. Explain giving suitable examples. [3]

   d) Arrange M^{3+}/M^{2+} (M = Fe, Co and Ni) with increasing standard reduction potential values. Justify your answer. [3]

Unit - III

5. a) Discuss the biological function of haemoglobin indicating the role of metal ion present in the active site of the protein. [4]
   b) Discuss the role of copper in any one of the copper containing enzymes present in biological system. [3]
   c) Discuss with suitable examples, the 'Essential' and 'Benificial' metals in living systems. [3]
   d) Explain — 'Trivalent arsenic is more toxic than pentavalent arsenic'. [3]

6. a) What are photosystem I and photosystem II? Explain their roles in photosynthesis. [5]
   b) Define active transport and passive transport. Discuss the mechanism through which the nerve cells maintain the Na^+ and K^+ level inside and outside of the cells. [5]
   c) Write a note on diseases due to copper deficiency. [3]

Unit - IV

7. a) Identify the first row transition metal for the following 18-electron species—
   i) $[M(CO)_3(PPh_3)]^-$ ii) $[(\eta^5-C_5H_5)M(CO)_3]$ (assume single M-M bond) [2]
   b) Why ferrocene cannot be nitrated directly? How ferrocene can be nitrated? [3]
   c) Identify A and B :

$$PtCl_4 + C_2H_5OH \xrightarrow{\text{Reflux}} A \xrightarrow{KCl} B$$

   Discuss the structure and bonding of B. [7]

8. a) What is hydroformylation reaction? Why is it so called? [3]
   b) What is 'hepaticity'? Give examples of 'trihapto' and 'hexahapto' complexes. [3]
   c) Discuss the role of Ziegler-Natta catalyst in polymerisation? Give example. [4]
   d) Show the structure of : $Ti(\eta^1-C_5H_5)_2(\eta^2-C_5H_5)_2$ [2]