RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. FIFTH SEMESTER EXAMINATION, DECEMBER 2017

THIRD YEAR [BATCH 2015-18]

Date : 23/12/2017 **CHEMISTRY [Honours]**

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

[Attempt <u>one question</u> from <u>each Unit</u>]

Unit – I

[13 marks]

1. a) Arrange the following species in the order of increasing Jahn-Teller distortion in an octahedral environment : (i) high spin Co (III), (ii) low spin Co (II), (iii) Cu (II) and (iv) Ti (III). [2]

   b) Draw a crystal field splitting diagram for a complex in a linear field assuming ligand lie along z-axis. [2]

   c) What is nephelauxtic effect? Which one of the following is most nephelauxitic : NH_3 or NH_2^- ? [2]

   d) The spin only magnetic moment of high-spin Mn^{2+} is quite in agreement with the experimentally determined value. Justify. [3]

   e) Account for the origin in color in Prussian blue. Justify with reason that Turnbull's blue readily isomerized to Prussian blue. [2+2]

2. a) Experimental magnetic moment of octahedral Ni(II) $(3\cdot3\beta)$ and tetrahedral Co(II) $(4\cdot5\beta)$ salts. Rationalize these data. [3]

   b) Draw the orgel diagram of a d^3 tetrahedral system with proper explanation with mention of possible electronic transition and 10Dq-parameter. [3]

   c) The spectrochemical series and nephelauxetic series are not quite parallel. Justify and illustrate. [3]

   d) $HgCl_2$ is colorless but HgI_2 is intensely colored. Explain. [2]

   e) Explain the changes in the spectrum of Ti(III) in water when aqueous KCN is slowly added to it. [2]

Unit – II

[12 marks]

3. a) Stability constants for $Cr(bipy)_3^{2+}$ are $\log K_1 = 4\cdot5$, $\log K_2 = 6\cdot0$ and $\log K_3 = 3\cdot5$. Justify the data above. [2]

   b) Mixing solutions of Fe(II) salts and potassium hexacyano chromate (III) results in a brick-red precipitate which turns green on heating. The brick-red and green compounds are isomeric to each other. How can you explain the observation? [2]

   c) A colourless acidic (H_2SO_4) solution when treated with H_2O_2 forms orange yellow colour which becomes colourless readily with NaF solution. Explain the observations with equation. [2]

   d) Define the terms with example : (i) Labile complex and unstable complex (ii) Stable complex and inert complex. [2]

   e) The reaction : $[Co(NH_3)_6]^{3+} + [Cr(H_2O)_6]^{2+} \rightarrow [Co(H_2O)_6]^{2+} + [Cr(H_2O)_6]^{3+} + 6NH_4^+$

   occurs with the rate constant $k = 10^{-3} M^{-1} sec^{-1}$ whereas the reaction

   $[Co(NH_3)_5Cl]^{2+} + [Cr(H_2O)_6]^{2+} \xrightarrow{H^+} [Co(H_2O)_6]^{2+} + [Cr(H_2O)_5Cl]^{2+} + 5NH_4^+$

   proceeds with the rate constant $k = 6\times10^5 M^{-1} sec^{-1}$. Explain why second reaction occurs with faster rate suggesting its mechanistic pathway. [2+2]

4. a) Explain the Irving-Williams order for stability of metal complexes in the light of CFT. [2]

   b) Discuss the π-bonding theory of trans effect. [2]

   c) Give a brief account of isopoly and heteropoly acids of Mo and W. [2]

d) How could you prepare *trans*-$[PtCl_2(NH_3)_2]$ starting from $PtCl_4^{2-}$ using NH_3 and Cl^- as the reagent. Justify your answer. [3]

e) Discuss the trends in the (i) stability of oxidation states and (ii) magnetic properties in passing from 3d through 4d to 5d transition metals. [3]

Unit – III

[13 marks]

5. a) To remove Pb^{2+} from the body it is better to use $Na_2CaEDTA$ than Na_2H_2 EDTA —Explain. [2]

b) State the biological function of carbonic anhydrase. [2]

c) Give the toxic action of mercury in human physiology. [2]

d) Why does the sodium ion pump is so named? Elucidate the relevance of the term pump and sodium ion in the name. [2]

e) Discuss the effect of copper(II) mismanagement in biosystem. [2]

f) Explain the function of **any one** of the following metalloproteins in biological systems : [3]
(i) Nitrogenase (ii) Hemoglobin

6. a) Give a brief account of the structural differences between cytochromes 'a', 'b' and 'c'. [3]

b) State the biological function of Fe – S proteins [2]

c) Illustrate the use of non-chelated metal compounds as drugs. [2]

d) Elucidate the role of *Cis*-platin in therapeutic use with necessary justification. [2]

e) Explain the role of magnesium(II) in biosystem. [3]

f) In which form arsenic is more toxic. [1]

Unit – IV

[12 marks]

7. a) Discuss the role of diethylamine in the preparation of ferrocene from an iron and cyclopentadiene. Give necessary equations. [2]

b) Using 18-electron rule, establish the possible structures of the following compounds : (i) $Fe_3(CO)_{12}$ and $CO_4(CO)_{12}$. [2]

c) For brown ring species $[Fe(H_2O)_5(NO)]^{2+}$ the room temperature magnetic moment is 3·9 B.M. Discuss the oxidation state of iron in the complex. [2]

d) In the following compounds coordinated NO is present. Indicate the actual species involved in the ligation and rationalize the N – O stretching frequencies mentioned below : $[Fe(CN)_5NO]^{2-}$: 1939 cm^{-1} ; $[Mn(CN)_5NO]^{3-}$: 1725 cm^{-1} ; $[Cr(CN)_5NO]^{4-}$: 1515 cm^{-1} [3]

e) Elucidate the structure of $Fe_2(CO)_9$. Cite evidences in support of you answer. [2]

f) Elucidate the fluxional nature of $Fe(CO)_5$ or $[\eta^5 - Cp)Fe(CO)_2]_2$. [1]

8. a) Discuss the structure of ferrocene and provide a chemical evidence that indicates free rotation of cyclopentadiene rings about the metal-ligand axis. [2+1]

b) Explain the role of Zeigler-Natta catalyst in polymerisation of olefins. [2]

c) Account for the formulation of the simplest carbonyls of Mn, Fe, Co and Ni as $Mn_2(CO)_{10}$, $Fe(CO)_5$, $Co_2(CO)_8$ and $Ni(CO)_4$. [3]

d) Illustrate different modes of binding of NO in a complex. [2]

e) What happens when ferrocene is treated with concentrated nitric acid? [2]

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