

RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

B.A./B.Sc. FIFTH SEMESTER EXAMINATION, DECEMBER 2014

THIRD YEAR

CHEMISTRY (Honours)

Paper : VI

Date : 23/12/2014

Time : 11 am – 1 pm

Full Marks : 50

[Answer one question from each Unit)

Unit – I

1. a) The ion CrF_6^{3-} shows absorption bands at 14900, 22700 and 34,400 cm^{-1} respectively. Assign the band. Find out $10D_q$ value. What is the expected colour? [4]
b) Account for the weak field character of halides and strong field nature of CO in the light of MO theory. [4]
c) Rationalise the observed magnetic moments of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ($\mu = 5.0 \text{ BM}$) and $[\text{CoCl}_4]^{2-}$ ($\mu = 4.4 \text{ BM}$) respectively. [3]
d) Co_3O_4 are mixed valence oxides with normal spinel structure, explain. [2]
2. a) Fe^{2+} can produce deep red complex with 2, 2'-bipyridine while SCN^- fails to do so— Justify. [3]
b) Rationalise the fact that Δ_o increases in the order— $\text{Co}(\text{H}_2\text{O})_6^{2+}$, $\text{Co}(\text{H}_2\text{O})_6^{3+}$, $\text{Rh}(\text{H}_2\text{O})_6^{3+}$. [3]
c) Account for the following order of lattice enthalpies of the octahedral fluorides of 3d(M^{2+}) ions : $\text{Mn}^{2+} < \text{Fe}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} > \text{Zn}^{2+}$. [3]
d) For the $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ ion, the mean pairing energy P is found to be 23500 cm^{-1} . The magnitude of Δ is 13900 cm^{-1} . Calculate the crystal field stabilization energy for the complex in configuration corresponding to high spin and low spin states. Which is more stable? [2]
e) The complex ions $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{MnCl}_4]^{2-}$ have μ_{eff} value very close to the μ_s value explain. [2]

Unit – II

3. a) Electron transfer between $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$ is much faster than between $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Co}(\text{NH}_3)_6]^{2+}$. Explain. [3]
b) Give a comparative study on chromates, Molybdates and Tungstates. [3]
c) Rationalise the overall stability constants of Ni(II) complexes from the given data $[\text{Ni}(\text{NH}_3)_6]^{2+}$ ($\log \beta_6 = 8.6$), $[\text{Ni}(\text{en})_3]^{2+}$ ($\log \beta_3 = 18.3$), $[\text{Ni}(\text{dien})]^{2+}$ ($\log \beta_2 = 19.1$). [3]
d) Two isomers of $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ react with thiourea (tu) giving different products. Identify them suggesting reason for the difference. [3]
4. a) How does the OH^- group in $[\text{Co}(\text{OH})\text{Cl}(\text{en})_2]^+$ influence aquation reaction? Name the type of mechanism involved therein. [3]
b) Substitution reactions at square-planar complexes proceed with retention of stereochemistry, but sometimes exceptions are observed, explain with reason give example. [3]
c) Write the Irving-Williams series of stability constants for complexes of M(II) ($M = \text{Mn, Fe, Co, Ni, Cu and Zn}$). Explain the order with the help of a suitable theory of your choice. [3]
d) Establish a relation between stepwise stability constant and overall stability constant. [3]

Unit – III

5. a) Cytochrome C is a redox protein but myoglobin is an oxygen storage protein. Justify the statement. [2]
b) Mention the function of globin chain in hemoglobin. [2]

- c) Give the short account of the following :
 i) Ferredoxins ii) Ionophores [2+2]
 d) Show the structure of active site of carbonic anhydrase and describe its role in transporting CO₂. [3]
 e) Name the chelating agents used for removing toxic effects of As and Cu. [2]
6. a) Write the mechanism of biological nitrogen fixation assisted by a metalloenzyme. [4]
 b) Which platinum drug shows antitumour activity? How does it destroy tumour cells? [3]
 c) Draw the active site structure of cytochromes C and explain with reason, rate of electron transfer with cytochromes C $\approx 10^3$ times slower than analogous compounds of iron. [3]
 d) The first row transition elements (except Ti) are all very abundant in living system but second or third row transition elements are almost (except Mo and W) absent. Suggest an explanation. [3]

Unit – IV

7. a) For each of the following species, indicate the number of electrons in the valence shell of the metal. Which of these complexes would you expect to be stable enough to be characterized?
 i) $(\eta^6 - \text{C}_6\text{H}_6)_2\text{Fe}$ ii) $\text{CP}_2\text{NbH}(\text{C}_2\text{H}_4)$ iii) $\text{Re}(\text{CO})_5$ [3]
 b) What is meant by a hydroformylation reaction? Give an example of such a reaction. What are the main features of the reaction mechanism? Give an example of a catalyst that works very efficiently for the purpose even at 25°C and 1 atm pressure. [4]
 c) Show the mode of linking of NO in $[\text{IrCl}_2(\text{NO})(\text{PPh}_3)_2]$ and $[\text{RuCl}(\text{NO})_2(\text{PPh}_3)_2]^+$. Is there any fluxionality in the Ru complex? [3]
 d) Rationalise the following reaction : $\text{Co}_2(\text{CO})_8 + 2\text{NO} \rightarrow 2\text{Co}(\text{CO})_3(\text{NO}) + 2\text{CO}$. [2]
8. a) Comment on the stretching frequency data : $\bar{\nu}_{\text{C-O}}(\text{cm}^{-1})$ $\text{Ni}(\text{CO})_4 \sim 2060$; $\text{Co}(\text{CO})_4^- \sim 1890$ and $\text{Fe}(\text{CO})_4^{2-} \sim 1790$. [3]
 b) What do you mean by hapticity? Illustrate with simultaneous η^1 and η^5 binding of cyclopentadienyl in the same complex. [3]
 c) In the reaction $(\text{OC})_5\text{MnCH}_3 + \text{CO} \rightarrow (\text{OC})_5\text{Mn}\overset{*}{\text{C}}\text{OCH}_3$ ($\overset{*}{\text{C}} = ^{14}\text{C}$) the acyl CO is derived from $(\text{OC})_5\text{MnCH}_3$, comment. [2]
 d) Do you expect any rotation of the ethylene molecule in Zeise's salt without hampering the stability of the complex? If possible explain it. [2]
 e) Write the favourable factor for the oxidative addition reaction. [2]

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