RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. FIFTH SEMESTER EXAMINATION, DECEMBER 2016

THIRD YEAR [BATCH 2014-17]

Date : 22/12/2016 **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) Complexes of monovalent silver (C.N = 2) are diamagnetic, of bivalent silver (C.N = 4 and C.N = 6) are paramagnetic (~1·7B) and of trivalent silver again diamagnetic. Explain the fact in the light of valence bond theory. [4]

   b) Which complexes of the following pairs has the larger value of Δ_0 and why? [3]

   i) $[Co(CN)_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$ ii) $[Co(NH_3)_6]^{3+}$ and $[Rh(NH_3)_6]^{3+}$

   iii) $[Co(H_2O)_6]^{2+}$ and $[Co(H_2O)_6]^{3+}$

   c) $V(H_2O)_6^{3+}$ has absorption bands at 17800 and 25700 cm^{-1}. Assign the bands using Orgel diagram. Calculate the value of Dq. [3+1]

   d) Using CFSE, indicate spinels to be normal or inverse : $MnCr_2O_4$, $NiFe_2O_4$. [2]

2. a) Chromium (II) fluoride and manganese (II) fluoride both have a central metal ion are surrounded by six fluoride ligands. The Mn – F bond lengths are equidistant, but four of Cr – F distances are long and two are short. —Explain. [2]

   b) The reduction of violet $[Cr(H_2O)_6]^{3+}$ gives bright blue $[Cr(H_2O)_6]^{2+}$. Provide an explanation. How many d-d transitions do you expect for both? [3]

   c) The spectrum of $[Ti(H_2O)_6]^{3+}$ shows an absorption max at 20,000 cm^{-1}. Calculate Δ_0 in KJ/mol. [2]

   d) Predict the spin only magnetic moment of $[Mn(NCS)]^{4-}$. Comment on the following moments: $K_3[CoF_6]$ has $\mu = 4\cdot2$ B.M. but $K_3[CuF_6]$ has $\mu = 2\cdot8$ B.M and $K_2[NiF_6]$ is diamagnetic. [1+3]

   e) The heat of hydration of Cr^{2+} ion is 460 Kcal/mole. For $[Cr(H_2O)_6]^{2+}$, $\Delta_0 = 13,900\,cm^{-1}$. Calculate what heat of hydration would be, if there was no CFSE. [2]

Unit – II

[12 marks]

3. a) How would prepare *cis* and *trans* - $[PtCl_2(NO_2)(NH_3)]^-$ starting from $[PtCl_4]^{2-}$? [3]

   b) CrO_4^{2-} is yellow while WO_4^{2-} is colourless —why? [2]

   c) For the reaction trans $PtL_2Cl_2 + Y \rightarrow$ trans $PtL_2ClY + Cl^-$ the rate constant 'K' varies as follows :

	Y	L	$K(10^{-3}M^{-}S^{-1})$
i)	PPh_3	Py	249000
ii)	SCN^-	Py	180
iii)	I^-	Py	107

   What is the mechanism of the reaction and why? [3]

   d) What will you observe when $TiOSO_4$ in dilute H_2SO_4 solution is treated with H_2O_2 and then NaF solution? (Give the reaction) [2]

   e) $[NiXL_5]^+ + H_2O \rightarrow [NiL_5(H_2O)]^{2+} + X^-$ is much faster if L is NH_3 instead of H_2O —Explain [2]

4. a) How the stabilization of abnormally low and high oxidation states of 3d-block metal ions can be done through the suitable choice of ligands? [2]

b) Explain the following (i) Elements in the middle of transition series have higher melting points
(ii) The decrease in atomic size of transition elements in a series is very small.
(iii) Most of transition metal ions exhibit characteristic colors in aqueous solutions. [3]

c) The inert complexes are not necessarily thermodynamically stable and that labile complexes are not necessarily thermodynamically unstable. Explain with suitable examples. [3]

d) What is Bjerrum method (Potentiometric method)? How do you determine the formation constant of a complex using this method? [4]

Unit – III

[13 marks]

5. a) Define active transport and passive transport write down the mechanism through which the nerve cells maintain the concentrations of Na^+ and K^+ inside and outside of the cells. [2+4]

b) What is cis-platin? State its medicinal use. [1+2]

c) Explain the slow rate of electron transport in cytochrome-C, and draw its active site structure. [2+2]

6. a) Discuss the role of photosystem I and photosystem II in photosynthesis. [4]

b) Briefly describe the biological function of haemoglobin, indicating the role of metal ions present in the active site of the protein. [3]

c) Would chelation therapy be useful in case of lead poisoning? Explain your answer. [2]

d) Provide an explanation for why the toxicity of mercury is greatly increased by the action of enzymes containing cobalamin. [2]

e) Blood is red in colour —Why? [2]

Unit – IV

[12 marks]

7. a) Consider the 18 electron rule as a guide, for the following molecule $\{(\mu-CO)_2[\eta^5CpRh]_3(CO)\}$, give the formal oxidation state of the metal, d electron count, total valence electrons (TVE), the number of M-M bonds and draw the most probable structure. [4]

b) The V – C bond distance in $[V(CO)_6]^-$ and $V(CO)_6$ are 1·93 and 2·00Å respectively. Justify the difference in bond distances in these compounds. [2]

c) Both N_2 and CO are isoelectronic but CO is a good π-acid ligand while N_2 is very weak. Explain. [2]

d) Discuss the bonding pattern in 'Zeises Salt'. Explain its stability if the alkene moiety is allowed to rotate along metal-alkene bond. [3+1]

8. a) Account for the following trend in IR-frequencies : [3]
$[Cr(CN)_5(NO)]^{4-}$ $\gamma(NO) = 1515\,cm^{-1}$; $[Mn(CN)_5(NO)]^{3-}$ $\gamma(NO) = 1725\,cm^{-1}$;
$[Fe(CN)_5(NO)]^{2-}$ $\gamma(NO) = 1939\,cm^{-1}$

b) Dimeric form of $V(CO)_6$ exists at 10K —why? [2]

c) What is Ziegler-Natta catalyst? Where it is used? [2+1]

d) How will you identify experimentally the presence of terminal and bridging CO group in a metal carbonyl? [2]

e) Arrange the following in the decreasing order of back donation and explain your answer
$Cr(CO)_6$; $[Ti(CO)_6]^{2-}$; $[Mn(CO)_6]^+$; $[Ir(CO)_6]^{3+}$; $[V(CO)_6]^-$. [2]

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