

RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

B.A./B.SC. FIFTH SEMESTER EXAMINATION, DECEMBER 2012

THIRD YEAR

CHEMISTRY (Honours)

Date : 21/12/2012

Time : 11 am – 1 pm

Paper : VI

Full Marks : 50

Group – A

Answer four questions taking one from each unit.

Unit-I

1. a) What is meant by CFSE of a transition metal complex? Formulate expressions for CFSE for the following complex ions:
 $[Mn(H_2O)_6]^{+2}$, $[Mn(CN)_6]^{-4}$, $[Co(NH_3)_6]^{+3}$ and $[CoCl_4]^{-2}$ 2+1x4=6
- b) Which major phenomenon is responsible for antiferromagnetism in transition metal complexes? 3
- c) Which one of the following will have intense colour and why?
trans- $[Cr(NH_3)_4Cl_2]^+$ and Cis- $[Cr(NH_3)_4Cl_2]^+$ 1+2=3
- d) Many complexes exhibiting CT bands in the visible region are unstable in sunlight. Explain. 1
2. a) Diamagnetic complexes of Co(III) such as $[Co(NH_3)_6]^{+3}$ and $[Co(NO_2)_6]^{-3}$ are orange yellow. In contrast, paramagnetic $[CoF_6]^{-3}$ and $[Co(H_2O)_3F_3]$ are blue. Explain qualitatively the difference in colour. 3
- b) Explain the following: 2x3=6
- (i) Addition of concentrated hydrochloric acid to pink coloured aqueous solution of Co^{+2} trans forms to deep blue.
- (ii) NiF_6^{-2} is diamagnetic while CoF_6^{-3} is paramagnetic with magnetic moment higher than 4.90 B.M.
- c) $[Ni(H_2O)_6]^{+2}$ is a regular octahedron but $[Co(H_2O)_6]^{+2}$ is a slightly distorted octahedron –why? 2
- d) Explain the term critical crystal field splitting value. 2

Unit-II

3. a) Name two ores of titanium with their chemical compositions. Outline the chemistry of isolation of pure titanium from one of its ores mentioning the chemical reactions involved therein. 2+4
- b) Describe the preparation and uses of potassium dichromate. 2+1
- c) Suggest the effective routes for the synthesis of cis and trans $[PtCl_2(NH_3)(PPh_3)]$ using the following reagents: PPh_3 , NH_3 and $[PtCl_4]^{-2}$. 3
4. a) A polyvalent metal ion forms an octahedral complex with a neutral bidentate ligand (A-A). Write down the complex formation equilibria in aqueous solution. Give expressions for stepwise and overall stability constants and establish the relation between them. 1+2+2
- b) Substitution reactions of $[Cr(CO)_6]$ are very slow, consistent with a low spin d^6 complex. But the isoelectronic complex $[V(CO)_5(NO)]$ is very reactive. –Comment. 3
- c) Give the structures of all the isomers of the complex $[Co(en)(NH_3)_2Cl_2]^+$ 2
[en=ethylenediamine]
- d) Compare the oxidising properties of chromate, molybdate and tungstate. 2

Unit-III

5. a) Briefly discuss the biological functions of haemoglobin and cytochromes mentioning the roles of the metal ions present in the active sites of these two proteins. 3+3=6
b) Write a brief account on Na^+ and K^+ ions transport in haemoglobin and point out the role of metal ion involved. 4
c) Explain with examples 'Essential' and 'Beneficial' metals in living systems. 3
6. a) State the biological functions of the following (**any two**): 3x2=6
(i) Fe-S proteins (ii) carbonic anhydrase and (iii) catalase.
b) Write a short note on 'Chelation Therapy'. 4
c) Which oxidation state of arsenic is more toxic? 1
d) Write a brief account on 'Ionophores'. 2

Unit – IV

7. a) Name the main reaction product of iron(II) chloride with cyclopentadiene in presence of excess dimethyl amine. Give balanced equation for the reaction. Discuss the structure of the resulting compound. 1+2+2
b) Using 18-electron rule as a guide rationalise stoichiometry of the products of the following reactions:
$$\text{Co}_2(\text{CO})_8 + 2\text{NO} \rightarrow 2\text{Co}(\text{CO})_3(\text{NO}) + 2\text{CO}$$
$$\text{Fe}(\text{CO})_5 + 2\text{NO} \rightarrow \text{Fe}(\text{CO})_2(\text{NO})_2 + 3\text{CO}$$
 2
c) What is 'insertion reaction'? Give an example. 3
d) Why different products are obtained when Friedel –Craft reaction is carried out in ferrocene in absence and in presence of H_3PO_4 using acetyl chloride? 2
8. a) Discuss the structure and bonding pattern in 'Zeise salt'. 3
b) Discuss sigma bonded organometallic compounds with respect to their formation and stabilities. 4
c) $[\text{Co}_3(\text{CO})_{10}]^-$ exhibits three distinct types of νCO in the regions 2080-2000, 1850 and 1600 cm^{-1} . Explain. 3
d) Explain 'Hydroformylation reaction.' 2

