

RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. FIFTH SEMESTER EXAMINATION, DECEMBER 2018

THIRD YEAR [BATCH 2016-19]

CHEMISTRY [Honours]

Paper : VI

Date : 24/12/2018

Time : 11 am – 1 pm

Full Marks : 50

[Attempt one question from each Unit]

Unit – I

[9 marks]

1. a) What is Crystal Field Stabilization Energy (CFSE)? Calculate the CFSE value of octahedral complexes of d^6 species in high and low spin state. Given : $\Delta_o = 25000 \text{ cm}^{-1}$ and average energy of pairing per electron (P) = 15000 cm^{-1} . [1+2]
b) More stable state of Cu is +2 while that of Au is +3. Explain in the light of CFT. [3]
c) Hydroxide is a weaker ligand than water, even though hydroxide is negatively charged and water is neutral. Explain. [3]
2. a) Which one of the following will have the higher Jahn-Teller distortion in octahedral environment? (i) Co(III) High-spin (ii) Co(II) low-spin. [1]
b) Co_3O_4 is a normal spinel while Fe_3O_4 is an inverse spinel. – Explain. [2]
c) Explain the following with the help of VBT:
(i) Co^{2+} -octahedral complexes are reducing agent, (ii) All octahedral complex of Ni^{2+} must be outer orbital complexes. [1.5+1.5]
d) What do you mean by the term "octahedral site stabilization energy (OSSE)"? Explain with an example. [1+2]

Unit – II

[8 marks]

3. a) How many absorption bands are expected in the electronic spectrum of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$? Assign the bands indicating Δ_o . [3]
b) Explain the following: (i) Intensity of LMCT is much higher than d-d transition.
(ii) $[\text{NiCl}_4]^{2-}$ is paramagnetic while $[\text{PdCl}_4]^{2-}$ is diamagnetic nature. [2+2]
c) Diamagnetic $[\text{Co}(\text{NH}_3)_6]\text{F}_3$ transforms to the paramagnetic when heated to 115°C . Why? [1]
4. a) The absorption spectrum of $\text{Ti}(\text{OH}_2)_6^{3+}$ has a band at $20,300 \text{ cm}^{-1}$. Do you expect ν_{max} to be less than, greater than or equal to $20,300 \text{ cm}^{-1}$ in the spectrum of $[\text{Ti}(\text{NCS})_6]^{3-}$? Explain your answer. [2]
b) Show the Orgel diagram of $\text{Co}^{2+}(\text{Td})$ and $\text{V}^{3+}(\text{Oh})$. How many d-d transitions do you expect from their? [4]
c) What is super exchange? Explain using an example. [2]

Unit – III

[8 marks]

5. a) Hydrolysis rate of Mg-ATP is faster than ATP. Comment. [2]
b) Explain the biological importance of Ca^{2+} and Mg^{2+} . [2]
c) Write a short note on Na^+ - ion pump. [3]
d) Explain why the intravenous fluids used in hospital procedures contains NaCl? [1]
6. a) Discuss the biological importance of creatine-phosphocreatine interconversions. [2]

- b) Name two of the ultratrace elements in biological systems. Explain the role of one of the ultratrace element. [2]
- c) heavy metals are in general toxic, explain with reasons. [2]
- d) Define active transport and passive transport in biological system. [2]

Unit – IV

[8 marks]

7. a) Suggest a reaction sequence accounting for why simple Fe-porphyrin complexes are unable to bind O_2 reversibly, but instead give products that include oxo-bridged dinuclear Fe(III) – porphyrin species. [3]
- b) Briefly describe the biological function of haemoglobin, indicating the role of metal ions present in the active site of the protein. [3]
- c) What is Bohr Effect? [2]
8. a) What is cis-platin? Explain its action of mechanism and medicinal use. [4]
- b) Write the mechanism of biological nitrogen fixation assisted by a metalloenzyme. [3]
- c) What is Co-operative effect? [1]

Unit – V

[9 marks]

9. a) What happens when metallic iron reacts with cyclopentadiene in presence of diethyl amine? give all the reactions involved and mention the role of diethylamine. Discuss the structure of the main product. [1+2+2]
- b) What is Zeise's salt and how it prepared? Explain the structure and bonding. [1+1+2]
10. a) Identify the first row transition metal for the following 18-electron species.
 $[M(CO)_3(PPh_3)]^-$, $[(\eta^4-C_8H_8)M(CO)_3]$ and $[\eta^5-(C_5H_5)M(CO)_3]_2$ [3]
- b) What happens when $[Co_2(CO)_8]$ reacts with i) NO ii) acetylene? [2]
- c) What are the different modes of binding of NO in metal nitrosyl? How would you identify the same using IR data? [2]
- d) Give an example of mono and penta-haptocyclopentadienyl complexes. [2]

Unit – VI

[8 marks]

11. a) The compound $[Fe_4(Cp)_4(CO)_4]$ is a dark-green solid. Its IR spectrum shows a single CO stretch at 1640 cm^{-1} . The 1H -NMR spectrum is a single line, even at low temperature. From this spectroscopic information and the CVE, propose a structure for $[Fe_4(Cp)_4(CO)_4]$. [3]
- b) What are the characteristic features of Wilkinson's catalyst? Discuss the steps of catalysis by this catalyst in hydrogenation of alkene. [1+2]
- c) 'CO-insertion' in $CH_3Mn(CO)_5$ is actually a methyl migration reaction — Explain. [2]
12. a) Predict the molecular geometries of the followings:-
 i) $[Fe_4C(CO)_{13}]$ ii) $[Rh_6C(CO)_{15}]$ [2]
- b) Draw the catalytic cycle for the Ziegler-Natta polymerization of propene. Explain each of the steps involved and predict the physical properties of the polymer produces. [3]
- c) $Cr_2Cl_9^{3-}$ is paramagnetic while $W_2Cl_9^{3-}$ is diamagnetic – explain. [2]
- d) Show any one application of metal clusters. [1]

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