RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. FOURTH SEMESTER EXAMINATION, AUGUST 2021

SECOND YEAR (BATCH 2019-22)

Date : 11/08/2021 **CHEMISTRY (Honours)**

Time : 11.00 am – 1.00 pm **Paper : X [CC 10]** Full Marks : 50

[Attempt one from each unit]

UNIT - I [1×13]

1. a) Arrange $[Rh(CN)_6]^{3-}$, $[RhI_6]^{3-}$, $[Ir(CN)_6]^{3-}$ and $[CoI_6]^{3-}$ with increasing crystal field splitting amount of d-orbitals with justification. [4]
   b) CrF_2(s) shows some Cr-F bonds are longer than the other Cr-F bonds-why? [2]
   c) Citing an example, explain the term 'spin state isomerism' of a co-ordination compound. [3]
   d) For an octahedral complex, which of the following d-electron configuration will give maximum crystal field stabilization energy?
   (i) d^6 (HS), (ii) d^4 (LS), (iii) d^5 (LS) and (iv) d^7 (HS) [4]

2. a) What is Octahedral Site Stabilization Energy (OSSE)? Give its an importance. [3+1]
   b) What is the 'Nephelauxetic parameter (ß)? Justify the following order of the Nephelauxetic power of the ligands: OH-< H2O< NH3<CO [2 + 2]
   c) If the values of 10Dq and pairing energy (P) of $[MnL_6]^{3-}$ complex, respectively, are 42000 cm-1 and 28800 cm-1; what will be the nature and CFSE value of the complex? [2+3]

UNIT - II [1×12]

3. a) Both Ni(IV) and Co(III) are d^6-systems but $K_2[NiF_6]$ is diamagnetic while $K_3[CoF_6]$ is paramagnetic-Explain. [3]
   b) Absorption band of $[Cu(NH_3)6]^{2+}$ showed two band peaks at small energy gap- why? [3]
   c) State the necessary conditions for either LMCT or MLCT band in a complexes. [2]
   d) How many electronic transitions will be observed for the $[CrL_6]^{3+}$ (where L = weak field ligand) complex ion? Assign the bands. Which one will indicate CF-splitting value? [4]

4. a) $[Cr(H_2O)_6]^{3+}$ ion is pale blue-green (€ =20 mol-1L Cm^{-1}) but CrO_4^{2-} ion is intense yellow (€ = 8000 mol^{-1}. L. Cm^{-1}). Explain. [4]
   b) Using qualitative Orgel diagram, explain the electronic spectral transitions for $3d^6$ ion in weak octahedral field. [4]
   c) Explain why is the magnetic moments of bis-(acetato)aquacopper(II) abnormally low, that of bis-(acetato) aquachromium(II) diamagnetic? [4]

UNIT - III [1×13]

5. a) What is common ion effect and solubility product? Explain their application during qualitative analysis of group-II metal ions. [2+2]
   b) How can you chemically prove that the two C_5H_5 rings in ferrocene can be freely rotated? [3]
   c) Comment on the stretching frequency data: $\bar{\nu}_{c-o}$ (cm^{-1}) $Ni(CO)_4$ ~ 2060; Co(CO)4- ~ 1890 ; $Fe(CO)_4^{2-}$ ~ 1790 . [3]

d) What are the different modes of binding of NO in metal nitrosyl? How would you identify the same using IR data? [3]

6. a) Give an example of mono and penta-haptocyclopentadienyl complexes. [2]

b) What is Zeise's salt and how it prepared? Explain the structure and bonding. [1+1+2]

c) For brown ring species $[Fe(H_2O)_5NO]^{2+}$ the room temperature magnetic moment is 3·9 B.M. Discuss the oxidation state of iron in the complex. [2]

d) The C_2H_4 moiety in Zeise's salt can be freely rotated, Explain your answer with evidence. [3]

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

UNIT - IV [1×12]

7. a) What do you mean by Carbonyl hopping? [2]

b) Why does ^{19}F-NMR spectrum of PF_5 contain one signal at room temperature but two signals at low temperature? [2]

c) How a solvent can affect the rate of reductive elimination of a complex? [2]

d) Discuss briefly the preparation of acetic acid by Monsanto Acetic Acid Process. [3]

e) Highlight the catalytic activity of Wilkinson catalyst. [3]

8. a) Write a short note on zerovalent iron. [2]

b) Write the structure of (i) Mohr's salt; (ii) Sodium nitroprusside. [1+1]

c) Write a short note on Ziegler-Natta catalyst. [3]

d) Write the product when Cis-$[Ir(CO)_2I_2]^-$ reacts with methyl iodide. Also show the mechanistic pathway. [1+2]

e) What is Bery-pseudorotation? Explain with a proper example. [2]

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