

RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. FOURTH SEMESTER EXAMINATION, JUNE 2022

SECOND YEAR (BATCH 2020-23)

CHEMISTRY (HONOURS)

Date : 25/06/2022

Time : 11.00 am – 1.00 pm

Paper : X [CC10]

Full Marks : 50

[Use a separate Answer Book for each unit]

[Attempt one question from each unit]

Unit : I

[13 marks]

1. a) Give the d-orbital splitting patterns with explanation of complexes of formula ML_5 where M stands for the first row transition metal ion and L, a monodentate ligand.
b) Explain how Jahn-Teller theorem influences the structure of Cu(II) complexes.
c) Give expressions for CFSE of Fe^{2+} ion in weak and strong octahedral crystal fields.
d) 10Dq value of hexaaquamanganese(III) ion is estimated from the electronic spectrum analysis to be 21000 cm^{-1} . The energy required for pairing per electron is 28800 cm^{-1} . Derive the possible spin state of the complex. [5+3+2+3]
2. a) What is spin state isomerism? Explain with one example.
b) F^- is an ionic species but a weaker field ligand than neutral H_2O , while CO is neutral molecule yet a stronger field ligand than H_2O . Explain.
c) Which one is more nephelauxtic ligand: CO or CN^- and why?
d) Depict the M. O. configuration of $[Co(NH_3)_6]^{3+}$ showing the Δ_0 parameter. [(2+1)+(2+2)+3+3]

Unit : II

[12 marks]

3. a) Both Ni(IV) and Co(III) are $3d^6$ systems but $K_2[NiF_6]$ and $K_3[CoF_6]$ show magnetic behavior differently - Why?
b) With the help of an Orgel diagram, explain how many absorption bands are expected in the electronic spectra of $[Cr(H_2O)_6]^{3+}$. Label the energy levels and assign the transitions.
c) FeF_6^{3-} is colourless but $[Fe(SCN)_6]^{3-}$ is intensely deep red coloured-explain.
d) The electronic spectrum of $[Ti(H_2O)_6]^{3+}$ shows a broad band having peak at $20,100\text{ cm}^{-1}$ and a shoulder at $17,400\text{ cm}^{-1}$. Assign the ligand field transitions for both the peak and the shoulder in given species. [3+4+3+2]
4. a) Co^{2+} ($3d^7$) has a magnetic moment in the range of 4.8-5.2 B. M. in high spin octahedral complexes, while in tetrahedral environment the value is in the range 4.0 to 4.4 B. M. The reverse type of observation is true for Ni^{2+} complexes. Rationalize the given observations.
b) $[CrO_4]^{2-}$ is yellow while $[MoO_4]^{2-}$ or $[WO_4]^{2-}$ is colourless-why?
c) Electronic spectrum of $[CoF_6]^{3-}$ shows two maxima in the visible region – explain.
d) The corrected molar susceptibility of a paramagnetic material is 6.20×10^{-3} c.g.s units at 300 K. Find out the number of unpaired electrons. [4+2+4+2]

Unit : III

[13 marks]

5. a) What is common ion effect and solubility product? Explain their application during qualitative analysis of group-III metal ions.
b) How can you chemically prove that the two C_5H_5 rings in ferrocene can be freely rotated?
c) Comment on the stretching frequency data: $\bar{\nu}_{C-O}$ (cm^{-1}) $Ni(CO)_4 \sim 2060$; $Co(CO)_4^- \sim 1890$; $Fe(CO)_4^{2-} \sim 1790$.
d) What are the different modes of binding of CO in metal Carbonyl? How would you identify the same using IR data? [(2+2)+3+3+3]

6. a) What is haptic nomenclature? What are the advantages of haptic nomenclature? Give an example of mono, tri and penta-haptocyclopentadienyl complexes.
 b) What is Zeise's salt and how it is prepared? Explain the structure and bonding.
 c) The C_2H_4 moiety in Zeise's salt can be freely rotated, Explain your answer with evidence.
 d) Explain the redox behaviour of Ferrocene and cobaltocene. [(1+1+2)+(1+3)+3+2]

Unit : IV

[12 marks]

7. a) When $Mo(CO)_6$ reacts with an excess of CH_3CN , a pale yellow product A is formed. When compound A is refluxed with benzene, the pale yellow product B is formed which has the molecular formula $C_9H_6O_3Mo$ and shows a sharp singlet at $\delta = 5.5$ ppm in the 1H NMR spectrum. When compound A is refluxed with cyclooctatetraene in hexane, compound C is formed which has the molecular formula $C_{11}H_8O_3Mo$. Identify the compound A, B and C.
 b) $IrCl(CO)[P(C_6H_5)_3]_2$ (trans-carbonylchlorobis(triphenylphosphine)iridium(I), popularly known as Vaska's complex) can react with dihydrogen. What type of reaction it performed and what would be the geometry and oxidation state of the desired product?
 c) $[Ru(C_2H_5)Cl(PPh_3)_3]$ is stable only under a pressure of ethene- why?
 d) Why Zr and Hf have nearly same atomic radii?
 e) What are the probable spin only magnetic moment values for Fe^{3+} system? [3+3+2+2+2]
8. a) The compound $(C_5H_5)_2Fe(CO)_2$ shows two peaks of equal area in the 1H NMR spectrum but at lower temperature it shows four resonances of relative intensity 5:2:2:1. Explain.
 b) H_2O_2 can be oxidized to O_2 by MnO_4^- in acidic as well as basic medium- justify with proper reaction.
 c) What happens when a mixture of metal chloride is heated with potassium dichromate and conc. sulphuric acid?
 d) When $CH_3Mn(CO)_5$ is treated with ^{13}C labelled CO , $(COCH_3)Mn(CO)_5$ results as product but it has been observed that 25% of the product has no ^{13}CO , 25% has ^{13}CO trans to the alkyl group and 50% has ^{13}CO cis to alkyl group. Justify the experimental observation to predict the reaction mechanism.
 e) What happens when green vitriol is heated gradually from room temperature to $300^\circ C$ and then at more higher temperature ($700-800^\circ C$) [3+2+2+3+2]

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