



ACH 551

IV Semester M.Sc. Degree Examination, September/October 2022 (CBCS – 2016 – 17 Syllabus) (Freshers and Repeaters) APPLIED CHEMISTRY Coordination Chemistry

Time: 3 Hours Max. Marks: 70

Instructions: i) Answer all questions in Part – A and any four questions from Part – B.

ii) Figures to the **right** indicate marks.

PART - A

Answer all sub-divisions.

 $(9 \times 2 = 18)$

- 1. a) Find the ground term for the configurations of 3d⁵(Mn²⁺) and 3d³(Cr³⁺).
 - b) What is nephelauxetic effect? Place the following ligands in order of increasing nephelauxetic effect: H₂O, Br⁻, en, F⁻, CN⁻.
 - c) Account for the color intensity difference of Octahedral $\left[\text{Co}(\text{H}_2\text{O})_6\right]^{2^+}$ and tetrahedral $\left[\text{CoCl}_4\right]^{2^-}$.
 - d) Among actinides, in terms of magnetic properties, Pu(III) and Am(III) appear as exceptions. Why?
 - e) Spin-state isomerism is not observed in tetrahedral and square planar complexes. Justify.
 - f) The free sulphate ion shows two IR active bands at 1104 and 613 cm⁻¹, but in the complex [Co(NH₃)₅SO₄]Br, each band is split into two peaks. Why?
 - g) Differentiate between labile and inert complexes.
 - h) How Cis and trans-isomers of [Pt(NO₂)NH₃Cl₂] are prepared?
 - i) Predict the products of acid hydrolysis of $[Cr(C_2O_4)_3]^{3-}$.

PART - B

Answer any four questions.

 $(4 \times 13 = 52)$

- 2. a) Explain solar energy conversion by taking [Ru(biph)₃]^{2+/3+} complex as an example. Discuss its applications.
 - b) Explain the mechanism of photoredox reactions.
 - c) Discuss why $[Mn(H_2O)_6]^{2+}$ exhibits extremely weak absorption bands in its absorption spectrum. (5+4+4=13)
- 3. a) Discuss the selection rules for electronic transitions with suitable examples.
 - b) Explain the advantages of Tanbe-Sugano diagram over Orgel diagram. Represent a Tanbe-Sugano diagram for the d⁶ configuration and predict its spin allowed transitions/energies.
 - c) How are charge transfer bands different from d-d bands? Discuss their origin, types and characteristics. (4+5+4=13)
- 4. a) Indicate the changes that occur in the IR spectra of carbonate and perchlorate groups upon complexation.
 - b) Describe Faraday's method for the determination of magnetic susceptibility of a compound.
 - c) Calculate magnetic moments for $[Mn(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$ complexes. Why spin only values are precise in these cases? (4+5+4=13)
- 5. a) Discuss the ESR spectrum of bis-salicylideneiminocopper (II) complex.
 - b) Discuss the application of Mossbauer spectroscopy in determination of structures of iron complexes.
 - c) Calculate a value for μ_{eff} of [Ni(H₂O)₆]²⁺ taking into account spin-orbit coupling (Given $\lambda = -315$ cm⁻¹ and $\Delta_0 = 8500$ cm⁻¹). (4+5+4=13)



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- 6. a) Explain the mechanism of anation reactions.
 - b) Discuss the mechanism involved in those reactions where there is no M-L bond cleavage.
 - c) Discuss base hydrolysis of octahedral complexes. (5+4+4=13)
- 7. a) What are two electron transfer reactions? How this reaction is useful in the preparation of coordination compounds?
 - b) Complete the following reaction and write its mechanism:

$$\left[\operatorname{Co}\!\left(\operatorname{NH}_3\right)_{\!5}\operatorname{CI}\right]^{2+} + \left[\operatorname{Cr}\!\left(\operatorname{H}_2\operatorname{O}\right)_{\!6}\right]^{2+} \xrightarrow{\quad H^+ \quad} ?$$

c) Discuss the factors affecting nucleophilic substitution reactions on square planar complexes. (4+5+4=13)