3 (Sem-6/CBCS) CHE HC 1

2025

CHEMISTRY

(Honours Core)

Paper: CHE-HC-6016

(Inorganic Chemistry-IV)

Full Marks: 60

Time: Three hours

The figures in the margin indicate full marks for the questions.

- 1. Answer the following questions: 1×7=7
 - (a) Which of the following complex is oxidizing agent?
 - (i) $Fe(Co)_5$
 - (ii) Co(Co₄)
 - (iii) Ni (Co)₄
 - (iv) $Mn(Co)_5$

(Choose the correct option)

- (b) Why is NH₄Cl added before precipitating Group III cations?
- (c) What is Schlenk equilibrium?
- (d) In the base catalysed substitution of Cl^- by $(OH)^-$ in $\left[Co(NH_3)_5Cl\right]^{2+}$, the first step in the mechanism is
 - (i) conversion of an amine to amido group
 - (ii) Substitution of Cl by (OH)
 - (iii) dissociation of Cl- to give a 5-coordinate intermediate
 - (iv) association of OH to give a 7 co-ordinate intermediate.

(Choose the correct option)

- (e) Calculate the Effective Atomic Number (EAN) of cobalt in the complex $\left[Co(NO_2)(NH_3)_5 \right] Cl_2$
- (f) What is the hapticity (η) of the cyclopentadienyl ligand in ferrocene?

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(g) Which metal complex undergoes faster outer-sphere electron transfer,

 $\left[Fe(bipy)_3\right]^{2+}$ or $\left[Fe(bipy)_3\right]^{3+}$ and why?

- 2. Answer the following questions: 2×4=8
 - (a) Draw the structures of the following: $CO_2(CO)_8$, $Mn_2(CO)_{10}$
 - (b) What do you understand by the term "labile" and "inert"?
 - (c) Rate of water exchange for $[Mo(H_2O)_6]^{3+}$ is very slow. Why?
 - (d) Why do Group I cations precipitate as chlorides while Group II cations precipitate as sulfides?
- 3. Answer **any three** of the following questions: $5 \times 3 = 15$
 - (a) Discuss the Eigen-Wilkins mechanism of ligand substitution in octahedral complexes.

- (b) The complex $CO_2(CO)_8$ can be used for the catalytic synthesis of aldehyde from an alkene having one carbon less. Propose a mechanism for this process taking a suitable example. What are the disadvantages of using this catalyst?
- (c) Discuss the mechanism of acetylation of ferrocene using Friedel-Crafts catalyst.
- (d) Discuss in detail the transeffect and its theories in substitution reactions of square planner complexes.
- (e) Explain why: $2\frac{1}{2} \times 2 = 5$
 - (i) Transition metal carbonyls and other organometallic compounds almost always obey 18 electron rule.
 - (ii) Although aromatic, ferrocene is much more reactive compared to benzene.

- 4. Answer **any three** of the following questions: $10 \times 3 = 30$
 - (a) (i) Discuss how stereochemical investigation of a substitution reaction helps in predicting the shape of a reaction intermediate. 5
 - (ii) The C-O stretching frequencies $[Ni(CO)_4], [CO(CO)_4]^-$ for and $[Fe(CO)]^{2-}$ are 2060, 1890 and 1790 cm^{-1} respectively Account for this.
 - (b) (i) Discuss the mechanism of the following reaction with proper experimental evidences. 5

$$\left[\operatorname{CoCl}(NH_3)_5\right]^{2+} + OH^- \rightarrow \left[\operatorname{Co}(OH)(NH_3)_5\right]^{2+} + Cl^-$$

(ii) Establish the relationship between stepwise and overall formation constants for a complexation reaction between $\left[Cu(H_2O)_6 \right]^{2+}$ and ethylenediamine.

- (c) What is synthesis gas? What are the reaction products derived from synthetic gas? Discuss the mechanism of water gas shift reaction using a homogeneous catalyst. What are the advantages and disadvantages of homogeneous and heterogeneous catalyst?

 1+3+4+2=10
- (d) (i) Give the mechanism of ethene polymerization using Ziegler-Natta catalyst? What is the role of Et₂AlCl in the process? 3+2=5
 - (ii) What is Zeise's salt? How it is prepared from K_2PtCl_4 ? Discuss the Dewar-Chatt-Duncanson bonding model in Zeises salt.

1+1+3=5

do they interfere in systematic separation of cationic radicals? Why is it necessary to remove them before 3rd group analysis? Why don't they interfere in 1st or 2nd group analysis? How are borate, and phosphate removed after Group II analysis? 1+1+1+6=10

- (f) (i) Explain the synergistic bonding model in transition metal carbonyl complex clearly showing the orbital overlap diagrams.
 - (ii) Using MO theory explain the two electron-four centered (2e-4c) bonding in methyl-lithium tetramer.

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