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) $Co(Co_4)$

(iii) $Ni(Co)_4$

(iv) $Mn(Co)_5$

(Choose the correct option)

(b) Why is NH_4Cl 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-co-ordinate 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 ?

(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 cxchange for $\left[Mo(H_2O)_6\right]^{3+}$ 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: 5×3=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 : 2½×2=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: 10×3=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. 5

(b) (i) Discuss the mechanism of the following reaction with proper experimental evidences. 5

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

(ii) Establish the relationship between stepwise and overall formation constants for a complexation reaction between $[Cu(H_2O)_6]^{2+}$ and ethylenediamine. 5

(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 Et_2AlCl 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

(e) What are the interfering radicals ? How 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+1+6=10

(f) (i) Explain the synergistic bonding model in transition metal carbonyl complex clearly showing the orbital overlap diagrams. 5

(ii) Using MO theory explain the two electron-four centered (2e-4c) bonding in methyl-lithium tetramer. 5