2026

CHEMISTRY

(Major)

Paper : CHE0600104

(Inorganic Chemistry—III)

Full Marks : 45

Time : 2 hours

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

1. Answer the following in short : 1×5=5

(a) State True or False :

Metal-halogen bonds are more labile than metal-nitrogen bonds.

(b) Give one example of a Fischer carbene complex.

(c) The rate of water exchange for $[Mo(H_2O)_6]^{3+}$ is very slow. Why?

(d) Draw the active site structure of Fe_2S_2 ferridoxin.

(e) What is the role of $CuCl_2$ in Wacker process?

2. Answer any *five* of the following questions : 2×5=10

(a) The second-order rate constants for formation of $[VX(OH_2)_5]^+$ from $[V(OH_2)_6]^{2+}$ and X^- for $X^- = Cl^-, NCS^-$ and N_3^- are in the ratio 1 : 2 : 10. What do the data suggest about the rate-determining step for the substitution reaction?

(b) If a substitution process is associative, why may it be difficult to characterize an aqua ion as labile or inert?

(c) Nickel complexes are observed to undergo substitution much faster than platinum complexes. Offer an explanation.

(d) Predict the products of the following reactions :

(i) $[Pt(CO)Cl_3]^- + NH_3 \longrightarrow$

(ii) $[Pt(NH_3)Br_3]^- + NH_3 \longrightarrow$

(e) Explain why ferrocene is more reactive than benzene towards electrophilic aromatic substitution.

(Continued)

(f) State the primary requirement for a metal-alkyl complex to undergo β-hydride elimination and draw the structure of the resulting products.

(g) Distinguish between Fischer and Schrock carbenes based on the oxidation state of the metal and the nature of the carbene carbon.

(h) What is chelation therapy? Name one chelating agent used in metal poisoning.

(i) What is the role of ATP in active transport? Give one example of an active transport system.

(j) What is the biological role of magnesium, and what happens when is it deficient?

3. Answer any *four* of the following questions : 5×4=20

(a) *(i)* Octahedral complexes of metal centres with high oxidation numbers or of *d* metals of the second and third series are less labile than those of low oxidation number and *d* metals of the first series of block. Account for this observation on the basis of a dissociative rate determining step. 3

(Turn Over)

(ii) The ligand exchange in $[Fe(phen)_3]^{3+}$ and in $[Fe(bpy)_3]^{2+}$ is much slower than the transfer of an electron from the bipyridine complex to the phenanthroline complex. Why does this rule out an inner sphere mechanism for the electron transfer? 2

(b) A Pt(II) complex of tetramethyldiethylenetriamine is attacked by Cl^- 10^5 times less rapidly than the diethylenetriamine analogue. Explain this observation in terms of an associative rate-determining step.

(c) The rate of loss of chlorobenzene, PhCl, from $[W(CO)_4L(PhCl)]$ increases with increase in the cone angle of *L*. What does this observation suggest about the mechanism?

(d) Describe the complete catalytic cycle for the hydrogenation of alkenes using Wilkinson's catalyst $[RhCl(PPh_3)_3]$. Include the specific roles of oxidative addition and reductive elimination steps in the mechanism.

(e) Discuss the Monsanto acetic acid process for the production of acetic acid. Provide the chemical equations for the catalytic cycle and explain the role of the iodide promoter.

(f) Explain the Dewar-Chatt-Duncanson model for the bonding of ethylene to a transition metal. Use diagrams to illustrate σ-donation and π-back-bonding, and describe how this affects the C—C bond length.

(g) Discuss the mode of action of *cis*-platin as anticancer drug.

(h) Discuss about the structure and function of haemoglobin.

4. Answer any *one* of the following questions : 10

(a) (i) Design two-step syntheses of *cis*- and *trans*-$[PtCl_2(NO_2)(NH_3)]^-$ starting from $[PtCl_4]^{2-}$. 5

(ii) What is synthetic gasoline? Discuss the Fischer-Tropsch process for preparing synthetic gasoline. 1+4=5

(b) How does each of the following modifications affect the rate of a square-planar complex substitution reaction?

(i) Changing a *trans* ligand from H to Cl

(ii) Changing the leaving group from Cl to I

(iii) Adding a bulky substituent to a *cis* ligand

(iv) Increasing the positive charge on the complex 10

(c) (i) Discuss the structure and function of carbonic anhydrase. 5

(ii) Define the term 'oxidative addition' in organometallic chemistry. Discuss its effect on the oxidation state, coordination number, and *d*-electron count of a transition metal complex. 1+4=5

(d) (i) Discuss about the classification and key component of the catalytic cycle of the nitrogenase enzyme. 5

(ii) Complete the following reaction :

$$(OC)_5MnCH_3 + CO \longrightarrow$$

What type of reaction is this? Write down the mechanism of this reaction. 1+1+3=5

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