3 (Sem-6/CBCS) CHE HC 1

2024

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. Choose the correct answer $1 \times 7 = 7$

(a)
$$\left[Cr(H_2O)_6 \right]^{2+} + \left[CrCl(NH_3)_5 \right]^{2+} \longrightarrow$$
 $\left[Cr(NH_3)_5 H_2O \right]^{2+} + \left[CrCl(H_2O)_5 \right]^{2+}$

$$[Fe(CN)_6]^{4-} + [Mo(CN)_8]^{3-} \longrightarrow$$

$$[Fe(CN)_6]^{3-} + [Mo(CN)_8]^{4-}$$

Which one of the following is correct statement?

(i) Both involve inner sphere mechanism

Contd.

- (ii) Both involve outer sphere mechanism
- (iii) Reaction I follows inner sphere mechanism and reaction II follows outer sphere mechanism
- (iv) Reaction I follows outer sphere mechanism and reaction II follows inner sphere mechanism
- (b) Wilkinson's catalyst is
 - (i) $[RhCl_3(PPh_3)_3]$
 - (ii) [RhCl₃(PPh₃)]
 - (iii) $[RhCl(PPh_3)_3]$
 - (iv) $[RhCl_2(PPh_3)_2]$
- (c) Which one of the following is not important for the formation of stable metal carbonyls?
 - (i) Metals with low oxidation states
 - (ii) Metals with small size
 - (iii) Lowering of carbon-oxygen bond order
 - (iv) EAN is obeyed

- (d) Which of the following is a wrong statement about industrially important catalytic processes?
 - (i) The proportion of H_2 gas in watergas mixtures can be increased.
 - (ii) All metals in Fischer-Tropsch catalytic processes have ability to chemically absorb carbon monoxide.
 - (iii) Nickel is best surface for methanation in Fischer-Tropsch processes,
 - (iv) Water gas cannot be obtained from natural gas.
- (e) Which of the following precipitates cannot be observed by use of group V reagents?
 - (i) $BaCO_3$
 - (ii) SrCO₃
 - (iii) CuCO₃
 - (iv) CaCO3
- (f) Which is true about $Mn(CO)_4NO$?
 - (i) The complex is paramagnetic and follows 18e- rule
 - (ii) The complex is diamagnetic and follows 18e rule

- (iii) The complex is paramagnetic and does not follow 18e- rule
- (iv) The complex is diamagnetic and does not follow 18e- rule
- (g) The n in symbol for hapticity (η^n) represents:
 - (i) number of ligands attached to the metal
 - (ii) number of atoms of the ligand within a bonding distance to the metal
 - (iii) charge on the ligand
 - (iv) co-ordination number of the metal
- 2. Answer the following: $2\times4=8$
 - (a) Draw the structure of $Fe_2(CO)_9$ and $CO_2(CO)_8$
 - (b) Common ion effect plays an important role in qualitative analysis. Explain.
 - (c) Define ground state trans-effect with an example.

- (d) What is the number of metal-metal bond in the following compounds?
 - (i) $Mn_2(CO)_{10}$
 - (ii) K2 Re2 Cl8
- 3. Answer **any three** of the following: $5 \times 3 = 15$
 - (a) Explain the mechanism of nucleophilic substitution reaction in square planar complexes.
 - (b) Explain EAN rule. Which of the following obey this rule:

$$Cr(CO)_6$$
; $Fe(\eta - C_5H_5)_2$

Draw the structure of

$$\eta^5 - C_5 H_5 - Re(CO)_2 C_5 H_5$$

- (c) Discuss the methods of removal of oxalate and phosphate ions during the qualitative analysis of salt mixture.
- (d) Draw the catalytic cycle of the hydroformylation of alkene. Discuss the reactions involved in various steps.
- (e) Explain the mechanism of outer sphere redox reaction of co-ordination compounds. 2+2+1=5

- 4. Answer **any three** of the following: 10×3=30
 - (a) (i) Discuss Eigen-Wilkins mechanism of ligand substitution reactions in octahedral complexes.
 - (ii) For the following substitution reactions:

trans $[NiCl(o-tolyl)(PEt_3)_2]^+ + py \longrightarrow trans$ $[Nipy(o-tolyl) (PEt_3)_2]^{2+} + Cl^- ... (1)$

trans [PdCl(o-tolyl) (PEt_3)₂]⁺⁺ py \longrightarrow trans [Pdpy(o-tolyl) (PEt_3)₂]²⁺ + Cl^- ... (2)

trans [PtCl(o-tolyl) (PEt_3)₂]⁺ + py \longrightarrow trans [Ptpy(o-tolyl) (PEt_3)₂]²⁺ + Cl⁻ ... (3)

The observed rates of reaction (1) is 50 times faster than reaction (2) which, in turn, is about 100,000 times faster than reaction (3). Explain.

- (iii) Define kinetically labile and inert complexes. The high spin complex ion $[Cr(H_2O)_6]^{2+}$ is labile but the low spin complex ion $[Cr(CN)]^{4-}$ is inert. Explain. 2+2=4
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- (b) Discuss synthesis, chemical properties of $(\eta C_5H_5)_2Fe$ and give a description of bonding in this important organometallic compound. 2+2+6=10
- (c) Discuss the role of organometallic compounds in catalysis with special reference to
 - (i) Synthesis gas by metal carbonyl complexes
 - (ii) Alkene hydrogenation by Wilkinson's catalyst. 5+5=10
- (d) Explain the preparation, structure and bonding of Zeise's salt. The IR stretching frequency of C = C bond in metal ethylene complex is found to be 1576 cm⁻¹ whereas the corresponding the corresponding frequency for free C_2H_4 is 1625 cm⁻¹. Explain.

1+2+5+2=10

- (e) (i) What is Zeigler-Natta catalyst?
 How is it prepared? Explain its
 major application. 2+2+1=5
 - (ii) What is Wacker process? Give one example. Mention the main three catalytic reaction sequence involved in it. 1+1+3=5

- (f) (i) Explain with suitable example how steric crowding at the reaction center influence the rate of substitution reactions in square planar and octahedral complexes.

 3+3=6
 - (ii) Discuss the mechanism of the following substitution reaction:

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