3 (Sem-6/CBCS) CHE HC 1

2022

CHEMISTRY

(Honours)

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: (any seven) $1 \times 7 = 7$
 - (a) Name the co-catalyst used in Wacker process.
 - (b) In qualitative analysis of basic radicals, hydrochloric acid is preferred to nitric acid for preparing a solution of given substance. This is because —
 - (i) nitric acid contains nitrogen
 - (ii) chlorides are easily converted to sulphides

Contd.

- (iii) hydrochloric acid is not an oxidising acid
- (iv) nitrates are not decomposed to sulphides

(Choose the correct option)

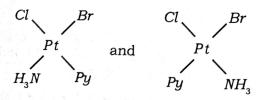
- (c) Arrange the metallocenes of Ti, V, Cr, Mn, Fe, Co and Ni, in the increasing order of their stability.
- (d) Give the structure of the following organometallic compound: Bis[(tricarbonyl)(η^5 -cyclopentadienyl)] dimolybdenum.
- (e) The total number of metal-metal bonds in $Ru_3(CO)_{12}$ and $Co_4(CO)_{12}$ are ____ and ___ respectively.

 (Fill in the blanks)
- (f) Find the hepticity of C_5H_5 (cyclopentadenyl) rings in $Fe(C_5H_5)_2(CO)_2$.
- (g) Why is Zn not precipitated as its sulphide in acidic medium?
- (h) What are aquation reactions?
- (i) Give the chemical formula and geometry of Vaska's complex.

- (j) Name the metals that are used as catalysts in the Fischer-Tropsch synthesis of gasoline.
- 2. Answer the following questions: (any four)
 - (a) What is π -acidity?
 - (b) Give examples of two oxidationreduction reactions occurring through the transfer of atoms or groups of atoms.
 - (c) Distinguish between thermodynamic stability and kinetic stability.
 - (d) $[Mn(CO)_4NO]$ and $[Fe(CO)_4CN^{-1}]$ both have trigonal bipyramidal structure. In the Mn complex, NO occupies an equatorial position while in the Fe complex, CN^- is at axial position. Explain.
 - (e) The Ni C bond length in nickelocene is longer than the Fe C bond length in ferrocene. Explain.
 - (f) Why is it essential to add dil. HCl before proceeding to the test for the basic radicals of group II?

- (g) Which of the following complexes have lower v_{CO} value in the IR spectrum? Rationalize your answer. $Mo(CO)_4(PMe_3)_2$ and $Mo(CO)_4(PPh_3)_2$
- (h) Why are transition metal aryls more stable than the transition metal alkyls?
- 3. Answer **any three** of the following :

- (a) How does vibrational spectra help to understand bonding in metal carbonyls?
- (b) Discuss the role of Wilkinson's catalyst in hydrogenation of alkenes.
- (c) What is trans effect? Using the concept of trans effect, how will you arrive at the following products? 1+4=5



(d) Explain Zeigler-Natta polymerization reaction.

- (e) What do you mean by labile and inert complexes? How does the d-electron configuration affect the labile/inert nature of complexes? 2+3=5
- (f) What are metal olefin complexes?

 Discuss the bonding and structure of Zeise's salt.

 1+4=5
- (g) How will you establish that the substitution in square planar complexes proceeds through an associative mechanism? Why are Ni (II) and Pd (II) square planar complexes more labile than square complexes of Pt (II)?
- (h) What is meant by hepticity of a ligand? Show clearly that the hepticity of a ligand varies from one organometallic compound to another. 2+3=5
- Answer **any three** of the following: 10×3=30
 - (a) What is hydroformylation reaction? Name three catalysts used in this reaction. Discuss the mechanism of a hydroformylation reaction using a suitable example. Why is such a reaction industrially important?

1+3+4+2=10

- (b) Write notes on the following: $2\frac{1}{2} \times 4 = 10$
 - (i) Reductive carbonylation
 - (ii) Synergic effect
 - (iii) 18 electron rule
 - (iv) Polarization theory of trans effect
- (c) Give the methods of preparation and properties of organometallic compounds of aluminum. Discuss the structure of organoaluminium compounds, 5+5=10
- (d) Discuss Eigen-Wilkins mechanism of ligand substitution reaction in octahedral complexes. Sketch the reaction profile for the reaction

$$\left[\operatorname{Co}(\operatorname{NE}t_3)_5\operatorname{Cl}\right]^{2+} + H_2O \to \left[\operatorname{Co}(\operatorname{NE}t_3)_5(H_2O)\right]^{3+} + \operatorname{Cl}^{-}$$

Clearly indicate intermediates and transition states. 5+5=10

(e) Discuss the structure of mononuclear, binuclear and polynuclear metal carbonyls.

- (f) Describe various reactions of ferrocene, which establish its aromatic character. How can you say that aromaticity of ferrocene is even more than that of benzene?
 8+2=10
- (g) Discuss the inner sphere and outer sphere mechanism in electron transfer reactions giving suitable examples. 5+5=10
- (h) What are interfering radicals and how do they interfere in qualitative tests while performing salt analysis? Discuss the methods of removal of phosphate and oxalate anions during salt analysis.
 2+3+5 = 10

7