

Total number of printed pages-7

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 hapticity of C_5H_5 (cyclopentadienyl) 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)**
2×4=8

(a) What is π -acidity ?

(b) Give examples of two oxidation-reduction reactions occurring through the transfer of atoms or groups of atoms.

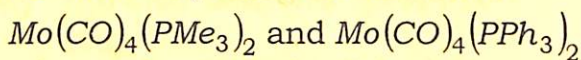
(c) Distinguish between thermodynamic stability and kinetic stability.

(d) $[Mn(CO)_4NO]$ and $[Fe(CO)_4CN^-]$ 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 ν_{CO} value in the IR spectrum? Rationalize your answer.



(h) Why are transition metal aryls more stable than the transition metal alkyls ?

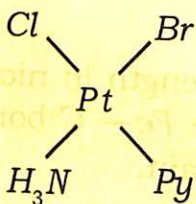
3. Answer **any three** of the following :

5×3=15

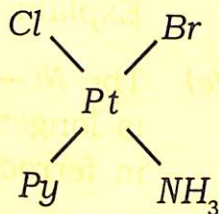
(a) How does vibrational spectra help to understand bonding in metal carbonyls ?

(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



and



(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) ? $3+2=5$

(h) What is meant by hapticity of a ligand ? Show clearly that the hapticity of a ligand varies from one organometallic compound to another. $2+3=5$

4. Answer **any three** of the following : $10 \times 3 = 30$

(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

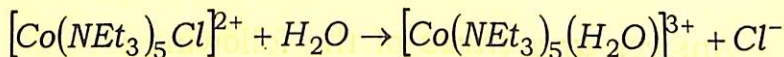
(ii) Synergic effect

(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



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

(e) Discuss the structure of mononuclear, binuclear and polynuclear metal carbonyls. 10

- (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. $2+3+5 = 10$
-

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3 (Sem-6/CBCS) CHE HC 2

2022

CHEMISTRY

(Honours)

Paper : CHE-HC-6026

(Organic Chemistry-V)

Full Marks : 60

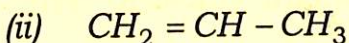
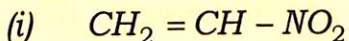
Time : Three hours

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

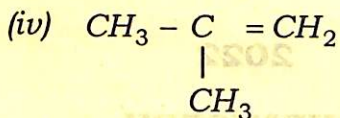
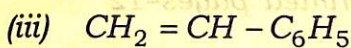
1. Answer the following questions : **(any seven)**
1×7=7

(a) Give an example of edible dye.

(b) Which one of the following is most reactive for anionic polymerization ?



Contd.



(c) Which of the following is laevorotatory ?

(i) Glucose

(ii) Fructose

(iii) Sucrose

(iv) Cellulose

(d) Fill in the blank :

The auxochrome group in the picric acid is _____ .

(e) The electronic transition, which requires maximum energy is

(i) $\sigma - \sigma^*$

(ii) $\pi \rightarrow \pi^*$

(iii) $n \rightarrow \pi^*$

(iv) $n \rightarrow \sigma^*$

(f) Which of the following compounds absorb UV radiation ?

(i) Heptane

(ii) Benzene

(iii) Butadiene

(iv) Acetone

(g) Which of the following compounds does not show mutarotation ?

(i) Glucose

(ii) Fructose

(iii) Maltose

(iv) Sucrose

(h) How many stereoisomers should an aldohexose have ?

(i) Ribose and xylose are

(i) epimers

(ii) anomers

(iii) disaccharide

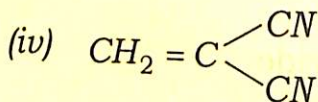
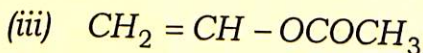
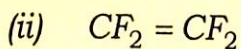
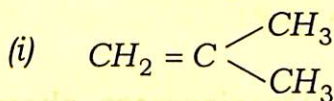
(iv) optically inactive

(j) What are the constituents of starch ?

2. Give answer of the following : **(any four)**

2×4=8

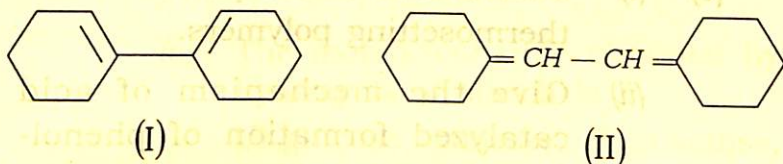
- (a) Write the expected products by showing the reaction of hydrolysis of lactose.
- (b) Glucosides neither give positive test with Fehling solution or Tollen's reagent nor undergo mutarotation. Explain.
- (c) Indicate the mechanism, cationic, anionic or free radical—by which the following monomers will undergo polymerization :



- (d) Give the method of preparation and uses of PVC and neoprene.

(e) How do you explain the greater stability β -D(+)-glucopyranose ?

(f) Why is the λ_{max} for the diene (I) low than diene (II).



(g) "Though azobenzene is a coloured compound it is not used as a dye." Explain why.

(h) Fill in the blanks :

(i) Amylose is a _____ polymer of _____.

(ii) Amylopectin is a _____ polymer of _____.

3. Answer **any three** of the following :

5×3=15

(a) (i) Draw the cyclic anomeric forms of D-fructose.

(ii) Give the mechanism for hydrolysis of glycoside under acidic condition.

1+4=5

(b) Explain the following : $2\frac{1}{2} \times 2 = 5$

(i) Chemical shift

(ii) Spin-spin coupling

(c) (i) Differentiate thermoplastic and thermosetting polymers.

(ii) Give the mechanism of acid catalyzed formation of phenol-formaldehyde resin.

$2\frac{1}{2} \times 2 = 5$

(d) How many proton signals would be expected in NMR spectra of each of the following compounds ? $2\frac{1}{2} \times 2 = 5$

(i) $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{OH}$

(ii) $\text{CH}_3 - \text{O} - \text{CH}_2 - \text{CH}_3$

(e) Differentiate the following by giving one example of each :

$2\frac{1}{2} \times 2 = 5$

(i) Reducing sugar and non-reducing sugar

(ii) Sugar and non-sugar

(f) Find out the correct answer of the following : $1 \times 5 = 5$

(i) Glucose cannot be clarified as (hexose, an oligosaccharide, an aldose, a monosaccharide)

(ii) The monosaccharide obtained by hydrolysis of starch is (D-glucose, maltose, D-galactose, D-ribose)

(iii) The product which is not derived from cellulose is (rayon, insulin, gun cotton, paper)

(iv) Carbohydrates are stored in the body as (sugars, starch, glucose, glycogen)

(v) Hydrolytic conversion of sucrose into glucose and fructose is called (induction, insertion, inversion, inhibition)

(g) (i) A very strong characteristic absorption for $-C=C-$ stretching vibration is observed for *cis-2-butene* but not for *trans-2-butene*. Explain briefly. 2

(ii) A compound A having molecular formula C_3H_6O gave the following IR spectral data :

2720cm^{-1} and 2820cm^{-1} (doublet) and 1730cm^{-1} (singlet).

Deduce the structure of the compound A and also explain the spectral data. 3

(h) (i) What is a leuco base ? How can it be converted into a dye ?

(ii) How will you synthesize alizarin from anthraquinone ?

$2\frac{1}{2} \times 2 = 5$

4. Answer **any three** of the following :

$10 \times 3 = 30$

(a) (i) What is Ziegler-Natta polymerization ? Discuss its special importance in the synthesis of addition polymers.

$1 + 4 = 5$

(ii) What is Nylon-66 ?

2

(iii) Write the structures of monomer unit for the following polymers :

3

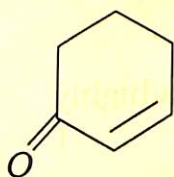
Polyvinyl chloride, Teflon and Rubber

(b) (i) A pleasant smelling liquid having molecular formula $C_9H_{10}O_2$ shows three singlets in the NMR spectrophotometry at δ 7.31 (5H), 5.08 (2H) and 2.06 (3H) and an IR peak at 1730cm^{-1} but none near 3350cm^{-1} . Identify the compound.

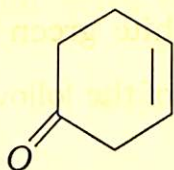
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(ii) What kind of transition of the compound CH_3OCH_3 gives rise to the 185nm absorption? 1

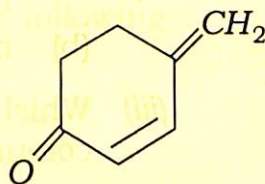
(iii) Which one of the following would be expected to absorb light of longest and shortest wavelength and why? 4



Str.(A)



Str.(B)



Str.(C)

(c) (i) Explain the following : $2 \times 2 = 4$

(a) H-bonding raises the wavelength of absorption.

(b) -I effect raises the wave number of absorption.

(ii) How will you distinguish the following by spectroscopy? $3 \times 2 = 6$

(A) Salicylic acid and *p*-hydroxybenzoic acid (by IR).

(B) $\text{ClCH}_2\text{CH}_2\text{Cl}$ and CH_3CHCl_2 (by $^1\text{H NMR}$)

(d) (i) Give the structural formula of the following : $2 \times 3 = 6$

(a) Fluorescein

(b) Congo red

(c) Methyl Orange

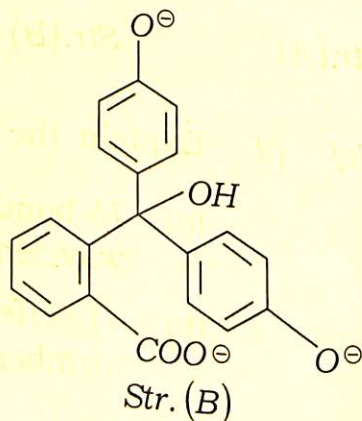
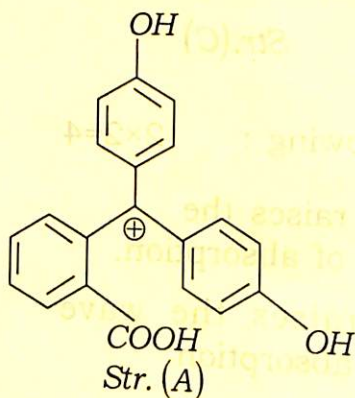
(ii) What Chromophore is group present in— $1 \times 2 = 2$

(a) fluorescein in alkaline medium ;

(b) malachite green ?

(iii) Which one of the following is highly coloured ?

1



(iv) What is Witt's theory of colour and constitution of dye? 1

(e) (i) Give the concept of poly-dispersion in polymers. 2

(ii) How will you synthesize polystyrene from benzene? 3

(iii) State the differences between addition and condensation polymerization. 3

(iv) Give reasons why PVC is soft and flexible whereas bakelite is hard and brittle. 2

(f) Write notes on the following : $2 \times 5 = 10$

(i) Co-polymerisation

(ii) Rubber

(iii) Configuration of polymer chains

(iv) Polymer classification

(v) Electrically conducting polymers

(g) (i) Explain why the polysaccharide do not mutarotate. 2

(ii) Give the structures of sucrose, lactose and maltose. 3

(iii) Fill in the blanks : $1 \times 5 = 5$

(A) *D*-glucose is an epimer of _____ .

(B) Ketoses have less number of _____ than aldoses.

(C) Mild oxidation of glucose gives _____ .

(D) _____ is present mostly as furanose.

(E) The common form of glucose as represented by Haworth projection is known as _____ .

(h) (a) Why is ESR spectrum recorded in derivative mode ? 1

(b) How many ESR lines are observed in methyl radical ? Explain. 2

(c) In which region of the δ -scale usually aromatic hydrogens absorb in a ^1H NMR spectrum and why ? 3

(d) How would you expect the ^1H NMR spectrum of ethanol to vary when it is recorded as—

(i) pure ethanol ;

(ii) ethanol in presence of small amount of water ? 4
