

[This question paper contains 6 printed pages.]

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Your Roll No.....



Sr. No. of Question Paper : 4540

Unique Paper Code : 32171201

Name of the Paper : Organic Chemistry – I

Name of the Course : **B.Sc. (H) Chemistry**

Semester : II

Duration : 3 Hours

Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt **six** questions in all
3. **All** questions carry equal marks.

1. Give reasons for the following statements. Attempt any **five** :

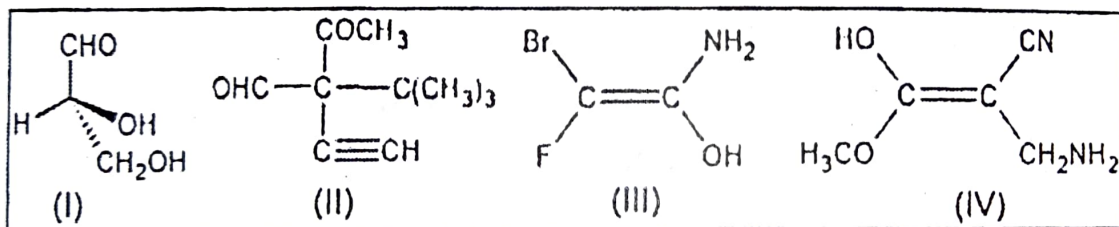
(a) Methyl group in Toluene is ortho-para directing.

(b) Chair conformation of cyclohexane is more stable than boat conformation.

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- (c) Both racemic mixture and meso compound are optically inactive.
- (d) Phenols are less acidic than carboxylic acids.
- (e) Terminal alkynes are acidic in nature.
- (f) Alkenes are more reactive than alkynes towards electrophilic addition reactions. (2.5×5=12.5)

2. (a) Assigning priorities, determine the configuration (E/Z or R/S) for the following compounds.



- (b) An alkene on reductive ozonolysis yields a mixture of two isomers with molecular formula C_3H_6O . Identify the structure of the alkene and the products. Write the product of reaction between the alkene with HBr. (8,4.5)

3. (a) Comment on the aromaticity of the following compounds

(i) Naphthalene

- (ii) Cyclopentadienyl cation
- (iii) Cycloheptatriene
- (iv) Pyridine

(b) A compound (4.25 g in 100 mL)'s solution in chloroform was taken in a polarimeter tube of length 5 cm and its optical rotation (at 25°C) was observed to be -1.2 . Calculate the specific rotation.
(8,4.5)

4. (a) Carry out the following conversions :

- (i) Propane to 2,3-Dimethyl butane
- (ii) Propyne to Pent-2-yne
- (iii) But-1-yne to Butan-2-one
- (iv) But-1-ene to But-2-ene

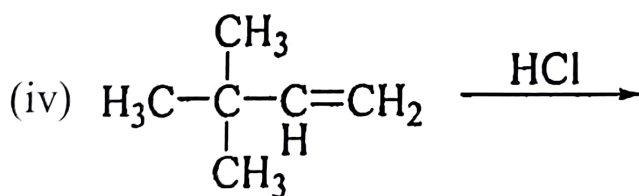
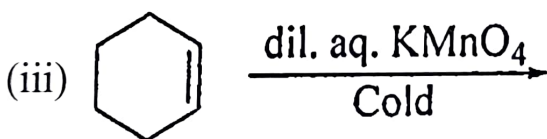
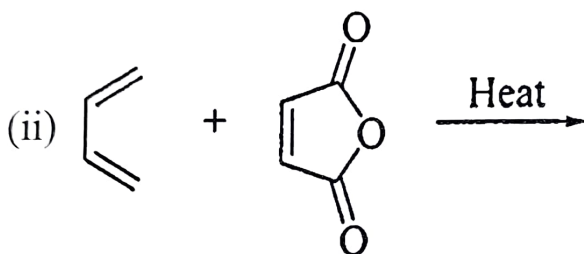
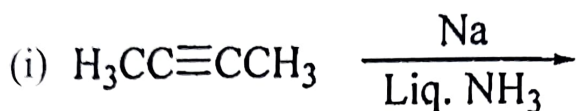
(b) Write down the mechanism involved in Friedel Craft's alkylation of benzene with propyl chloride.
(8,4.5)

5. (a) Draw the Fischer projection for all the possible stereoisomers of butane-2,3-diol. State the correlation among these stereoisomers? Comment on the optical activity of these isomers.

(b) In halogenation of alkanes why chlorination is more reactive but less selective than bromination?

(c) Why peroxide effect is observed in case of addition of HBr? (5,4.5,3)

6. (a) Complete the following reaction with product(s) (including stereochemistry wherever applicable)



(b) Calculate the percentage of isomers formed on monochlorination of n-butane.

Relative rates of hydrogens $3^\circ:2^\circ:1^\circ$ towards chlorination at room temperature are 5.0:3.8:1.

(8,4.5)

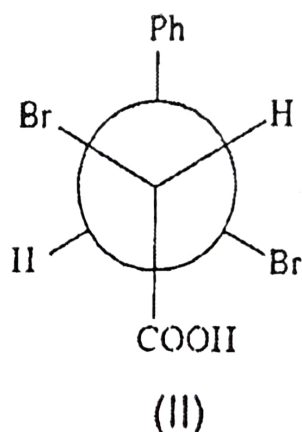
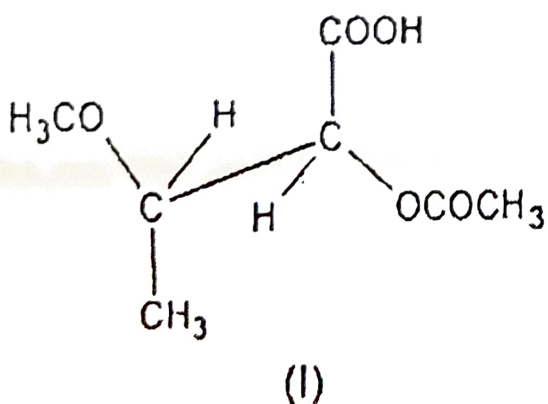
7. (a) Comment on the stereochemistry of the products formed when cis and trans isomers of but-2-ene reacts with bromine solution. Explain the reaction with mechanism.

(b) State limitations of Wurtz reaction. How Corey-House synthesis overcomes these limitations? Give with suitable examples.

(c) Which is more acidic, p-nitrophenol or o-nitrophenol? Give reasons. (5,4.5,3)

8. (a) How will you chemically distinguish between 1-butyne and 2-butyne?

(b) Convert the following structures to standard Fischer projections:



(c) Explain why 1,3-pentadiene is more stable than 1,4-pentadiene?

(d) Why nitration of toluene is faster than nitration of benzene? (2,4,3,3.5)

9. Write short notes on the following : **(any four)**

(a) E1 and E2 reactions (including mechanism)

(b) D,L system of configuration (including limitations)

(c) Oxymercuration – Demercuration Reaction (including mechanism)

(d) Allylic Halogenation using NBS (including mechanism)

(e) Nucleophilic addition reactions in alkynes

(3.5,3,3,3)

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(4)

Your Roll No. 2023



Sr. No. of Question Paper : 4660

Unique Paper Code : 32171202

Name of the Paper : Physical Chemistry II :
Chemical Thermodynamics
and its Applications

Name of the Course : **B.Sc. (Hons) Chemistry**

Semester : II

Duration : 3 Hours

Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt **six** questions in all. Question number **1** is compulsory.
3. Use of scientific calculators is allowed.

1. Answer any **five** : (5×3=15)

(a) Define the term residual entropy. Explain the reason for residual entropy in NO.

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- (b) Show mathematically that the magnitude of the work involved in a reversible expansion of an ideal gas from volume V_1 to V_2 is larger than the corresponding work involved in an irreversible expansion against a constant pressure of p_2 .
- (c) Why is the value of C_p always greater than C_v ?
- (d) Define integral enthalpy of solution and dilution.
- (e) Heat of neutralization of HCl and NH_4OH is less than $-57.36 \text{ KJ mol}^{-1}$. Explain.
- (f) State and explain zeroth law of thermodynamics. What are its applications?
- (g) Justify that ' K_p° of a reaction depends only on temperature and is independent of partial pressures of the components and that of the total pressure of the system'.
2. (a) Starting from the T and P dependence of entropy, derive :

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

- (b) What do you understand by the terms 'state function' and 'path function'? Show that the volume of a fixed amount of an ideal gas is a state function.
- (c) 10 g of a solute is dissolved in 80 g acetone at 303 K. The vapour pressure of solution is found to be 271 Torr. Calculate the molar mass of solute if vapour pressure of pure acetone is 283 Torr at 303 K. (4,4,4)
3. (a) The heat of dissociation per mole of gaseous water at 18°C and 1 bar pressure is 241.75 kJ mol⁻¹; calculate its value at 68°C. Given that :
- $$C_p(\text{H}_2\text{O}) = 33.56 \text{ J K}^{-1} \text{ mol}^{-1}$$
- $$C_p(\text{H}_2) = 28.83 \text{ J K}^{-1} \text{ mol}^{-1}$$
- $$C_p(\text{O}_2) = 29.12 \text{ J K}^{-1} \text{ mol}^{-1}$$
- (b) Derive the Gibb's-Duhem equation and show that for a two-component system, if the chemical potential of one component increases then the chemical potential of the other component must decrease.

(c) One mole of an ideal gas is allowed to expand isothermally at 27°C until its volume is tripled. Calculate ΔS_{sys} and ΔS_{univ} under the following conditions :

(i) The experiment is carried out reversibly

(ii) Free expansion. (4,4,4)

4. (a) Show that for adiabatic reversible expansion of an ideal gas from P_1, V_1 to P_2, V_2 ; the work done is

$$\text{given by : } w = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$$

(b) Derive the relations :

$$(i) \left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P ;$$

$$(ii) \left(\frac{\partial \mu_i}{\partial T} \right)_{n, n_j's} = -S_{i, pm}$$

(c) Consider two pure gases A and B each at 298 K and 1 bar pressure. Calculate the free energy change, entropy change and enthalpy change relative to the unmixed state for a mixture of 10 mol of A and 10 mol of B. Is the process spontaneous? (4,4,4)

5. (a) Using the expression of α (coefficient of thermal expansion) and κ (isothermal compressibility coefficient), show that

$$\left(\frac{\partial\alpha}{\partial P}\right)_T + \left(\frac{\partial\kappa}{\partial T}\right)_P = 0$$

- (b) State Henry's law for solubility of a gas in a liquid. Also derive its thermodynamic relation.
- (c) Derive the expression of Joule-Thomson effect ($\mu_{J.T}$) and show that for van der waals gas

$$\mu_{J.T} = \frac{1}{C_p} \left[\frac{2a}{RT} - b \right] \text{ where } a \text{ and } b \text{ are van der waals constants. } C_p \text{ is heat capacity at constant pressure.} \quad (4,4,4)$$

6. (a) Determine the enthalpy of formation of gaseous isoprene (C_5H_8) from the given data :

Enthalpy of sublimation of graphite = 718.39 kJ mol⁻¹

Enthalpy of dissociation of hydrogen = 435.97 kJ mol⁻¹

Bond enthalpy data: $\epsilon_{C-H} = 413.38$ kJ mol⁻¹, $\epsilon_{C-C} = 347.69$ kJ mol⁻¹ and $\epsilon_{C=C} = 615.05$ kJ mol⁻¹

- (b) State and explain the third law of thermodynamics. Write the expression for third law entropy of a gas above its boiling point by writing all the steps from solid to gas above boiling point clearly.
- (c) Derive the relation

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T + 1 = 0 \quad (4,4,4)$$

7. (a) State Le Chatelier's principle as applicable to chemical reactions. With the help of this rule predict qualitatively the effect of
- (i) changing the pressure
 - (ii) changing the temperature on chemical reactions at equilibrium.
- (b) 10 dm³ of O₂ at 101.325 kPa and 298 K is heated to 348 K. Assuming ideal behaviour, calculate the heat absorbed, ΔH and ΔU of this process at i) constant pressure, and ii) at constant volume. Given $C_{p,m} \text{ (J K}^{-1} \text{ mol}^{-1}\text{)} = 25.72 + 0.013 \text{ (T/K)} - 3.86 \times 10^{-6} \text{ (T/K)}^2$

(c) Derive the following relations :

$$\text{Show that } C_p - C_v = T \left(\frac{\partial p}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_p \quad (4,4,4)$$

8. (a) Consider the reaction $A_2B_3(g) \rightleftharpoons AB_2(g) + AB(g)$ at 298 K and having initial amount of $A_2B_3(g)$ as 1.0 mol. At equilibrium, the extent of reaction is found to be 0.3 mol for a total pressure of 1 bar. Calculate K_p° and ΔG_r° for the reaction.

(b) Explain the concept of coupled reactions with a suitable example.

(c) Determine the values of q , w , ΔU and ΔH during isothermal and reversible expansion for one mole of a certain gas which obeys the equation of state $p(V - b) = RT$ (parameter b is a constant).

(4,4,4)

9. (a) State Le Chatelier's principle as applicable to chemical reactions.

(b) The vapour pressures of pure CCl_4 ($M = 154 \text{ g mol}^{-1}$) and $SnCl_4$ ($M = 170 \text{ g mol}^{-1}$) at 25°C are 114.9 and 238.3 torr, respectively. Assuming ideal behaviour, calculate the total vapour pressure of a solution containing 10 g of CCl_4 and 15 g of $SnCl_4$.

P.T.O.

(c) Derive thermodynamically the relation

$$\frac{1}{T_b} = \frac{1}{T_b^*} + \frac{R \ln x_1}{\Delta_{\text{vap}} H_{1,m}}$$

where T_b is the boiling point of the solution, x_1 is the mole fraction of the solvent and T_b^* is the boiling point of the pure solvent. (4,4,4)