

2022

Full Marks - 60

Time - 3 hours

The figures in the right-hand margin indicate marks

Answer *all* questions

**Part-I**

1. Fill in the blanks : 1 × 8
- a) \_\_\_\_\_ is the first organic compound which was synthesized in the laboratory.
  - b) The Hybridisation of a carbanion is \_\_\_\_\_ .
  - c) The absolute configuration of D(+)-Glyceraldehyde is \_\_\_\_\_ .
  - d) A racemic mixture is optically \_\_\_\_\_ .
  - e) Out of boat and twist boat, \_\_\_\_\_ is the most stable conformation of cyclohexane.
  - f) Elimination reaction generally occurs with the formation of \_\_\_\_\_ .

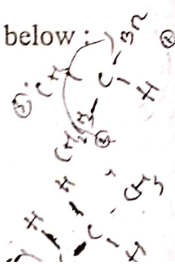
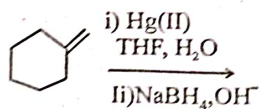
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- g) The number of delocalised  $\pi$  electrons in pyrrole is \_\_\_\_.
- h) \_\_\_\_ is the reactive species in sulphonation of benzene.

**Part-II**

2. Answer any *eight* of the following :  $1\frac{1}{2} \times 8$

- a) Define resonance energy.
- b) How inductive effect responsible for strength of an acid ?
- (c) What do you mean by 'relative configuration' ?
- d) Distinguish between enantiomers and diastereomers.
- e) Draw the structure of (2R)-2-bromobutane.
- f) What is nucleophilic elimination reaction ?
- (g) Write product(s) for the reaction below :



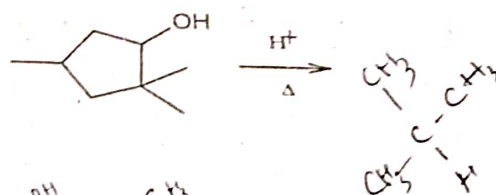
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- h) What is hydroxylation reaction ?
- i) What is Huckel's rule for aromaticity of a compound ?
- j) What do you understand by directing effect of a functional group attached to an aromatic ring ?

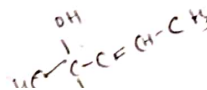
**Part-III**

3. Answer any *eight* of the following :  $2 \times 8$

- a) Explain the acidity characteristics of phenol based on resonance effect.
- (b) Draw the Newman projection for eclipsed form of 2-methyl propane.
- (c) Draw the structure of the (2S, 3E)-2-hydroxypent-3-enal.
- (d) Find product (s) for the reaction below :



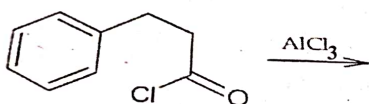
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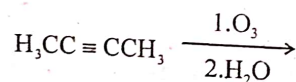
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- e) Briefly discuss radical substitution of halogen by hydrogen with a suitable example ?
- f) Why pyrrole behaves as a much weaker base than pyridine, though both are aromatic compounds.
- g) Find major product for the following reaction :



- h) With example, draw base catalysed hydration of a carbonyl compound.
- i) Draw energy profile diagram for an  $\text{E}_1\text{cB}$  mechanism.
- j) Write down the product for the following reaction :



*CH<sub>3</sub>CO + HCl*

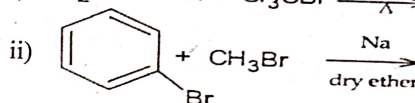
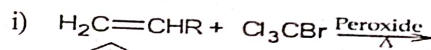
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**Part-IV**

4. a) What is a carbocation ? Taking suitable examples briefly explain the generation, structure and stability of the carbocation. 6

OR

- b) Predict the products and mechanism for the reactions below : 6



5. a) What do you mean by absolute and relative configuration ? Explain each with examples. 6

OR

- b) Explain term in brief relating to stereochemistry of molecules.

- i) Specific rotation  
ii) Chiral centres  
iii) Racemic mixture.

6

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[ 6 ]

6. a) While treating with HCl, propenoic acid gives the Anti-Markownikoff product, whereas 4-pentenoic acid gives the Markownikoff product. Explain why ? 3

b) Why (2Z, 4Z) -2, 4-hexadiene is less reactive than (2E, 4E) -2, 4-hexadiene in a Diels-Alder reaction ? 3

OR

c) Why vinyl halide and aryl halides don't react in Friedel-Craft's reaction ? 3

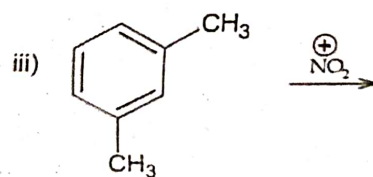
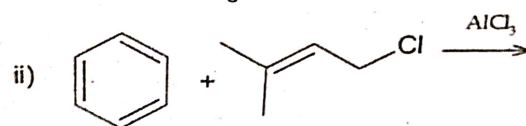
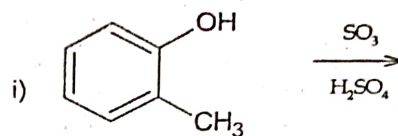
d) What is syn-elimination ? When such eliminations are favoured over trans-elimination ? 3

7. a) What is electrophilic aromatic substitution ? Why aromatic substrate with meta-directing group doesn't exhibit Friedel-Craft's reaction. 6

OR

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b) Write down products for the following reaction : 6



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## SEMESTER-II

### PAPER-CC-III (ORGANIC CHEMISTRY)

#### ONE MARK QUESTION

1. Zero inductive effect is exerted by:  
(a)  $-\text{C}_6\text{H}_5$  (b) H (c)  $-\text{CH}_3$  (d) Cl
2. A nucleophilic reagent is :  
(a) Lewis acid (b) Lewis base (c) Positive species (d) none
3. Optical isomerism is shown by:  
(a) 1-Butanol (b) 2-Butanol (c) 3-Pentanol (d) 4-Heptanol
4. Photochemical chlorination of alkane is initiated by a process of :  
(a) Pyrolysis (b) Substitution (c) Homolysis (d) Heterolysis
5. LPG mostly contains:  
(a) Methane (b) ethane (c) Butane (d) Propane
6. Presence of peroxide affects the addition of:  
(a) HBr (b) HCl (c) HI (d) all
7. Deviation from Markownikoff's rule occurs in the presence of:  
(a) Zinc (b) Peroxide (c) Hg-Zn/HCl (d) All of these
8. Lactic acid when heated with iodine and caustic soda gives :  
(a) Pyruvic acid (b) iodoform (c) Acetaldehyde (d) Lactic
9. What is the optical purity of a racemic modification?
10. The number of optical isomers possible for the compound  $\text{CH}_3\text{CHClCOOH}$ ?

#### 1.5 MARKS QUESTION

11. What is the origin of geometrical isomerism in alkene?
12. What is the number of isomers of dibromo derivative of alkene? (mol. Mass 186).
13. What makes butan-2-ol to be optically active unlike butan-1-ol?
14. Why alkyl free radical is less stable than allyl free radical?
15. How will you convert acetylene into 1-Butyne?
16. Toluene is nitrated more readily than benzene. why?
17. Discuss the boat and chair forms of cyclohexane.
18. What is inductive effect?
19. Describe resonance effect.
20. What are carbenes?

21. Write uses of mercaptans.
22. What is E-Z notation?
23. What is R-S designation?
24. What is racemic mixture? Give one example.
25. Write Wurtz-Fittig reaction.

## **2 MARKS QUESTION**

26. What is Walden inversion? Illustrate with a suitable example.
27. What is optical isomerism?
28. Distinguish between electrophiles and nucleophiles.
29. Distinguish between nucleophilicity and basicity.
30. What are free radicals. Give one example of formation of a free radical.
31. What is racemic mixture?
32. What are diastereomers? How do they differ from the enantiomers?
33. What do you mean by internal compensation? Give an example.
34. What will be the angle strain if a cyclooctane has an internal bond angle of  $135^\circ$
35. What is Huckel's Rule? Give example
36. Explain why is pyrrole an aromatic compound?
37. Write Wurtz reaction.

## **6 MARKS QUESTION**

38. Discuss Baeyer's strain theory to explain the relative stability of cycloalkanes.
39. Discuss the mechanism of Friedel-Craft's alkylation and acylation reaction.
40. What is optical activity? Give the stereoisomers of tartaric acid. How do you account for the lack of optical activity in meso form and racemic mixtures?
41. Define geometrical isomerism. What are the conditions necessary for geometrical isomerism? Compare the physical properties of geometrical isomers taking examples.
42. What are carbanions? How are they obtained? Explain the structure and relative stability of carbanions.
43. What are carbocations? How are they obtained? Explain the structure and relative stability of carbocations.
44. Discuss the mechanism of E1, E2 and E1cb reactions.
45. Discuss the mechanism of oxymercuration-demercuration reaction.
46. Explain Diels-Alder reaction with an example.

47. What are cycloalkanes? Discuss the relative stability of cycloalkanes.
48. Discuss the formation and chemistry of alkanes.
49. Explain Hyperconjugation and write its applications.
50. Discuss Fischer projection, Newmann and Sawhorse projection formula.
51. Describe the formation of alkenes by elimination reaction.
52. Explain Saytzeff and Hofmann eliminations.
53. Discuss the mechanism of Markownikoff and anti Markownikoff addition.
54. Discuss the reactions of alkynes with examples.
55. Draw and explain the energy diagrams of chair, boat and twist boat forms of cyclohexane.
56. Write a short note on ozonolysis.
57. Discuss 1,2 and 1,4-addition reactions in conjugated dienes.
58. Describe the conformational analysis of ethane.
59. Describe the conformational analysis of n-butane.
60. Explain halogenation, nitration and sulphonation of benzene with mechanism.

2022

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Answer *all* questions

**Part-I**

1. Answer the following : 1 × 8
- a) Represent first law of Thermodynamics, when work done on the system.
  - b) Which of the following is/are intensive property Viscosity, volume, energy.
  - c) The entropy is regarded as a measure of the \_\_\_\_\_ of a system.
  - d) Write entropy condition for reversible process.
  - e) The partial molar free energy is known as \_\_\_\_\_.
  - f) Write the unit of  $K_p$ .
  - g) Give an example of binary solution.
  - h) Colligative properties does not depends on \_\_\_\_\_ of the solute.

**Part-II**

2. Answer any *eight* of the following : 1½ × 8
- a) Represent the relation between enthalpy, internal energy and pressure.



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- b) Define open system with an example.
- c) Represent second law of Thermodynamics, mathematically.
- d) Write the conditions for spontaneity of a reaction.
- e) Write Gibb's Helmholtz equation for an isochoric process.
- f) Give an idea on partial molar entropy.
- g) Write the fugacity expression at very low pressure.
- h) Write Henry's law.
- i) Write the Van,t Hoff equation for osmotic pressure of a dilute solution.
- j) Entropy of a solution of solid in water is  $-41.6\text{KJmol}^{-1}$ . When NaOH is dissolved in water, the temperature of the water will be ?

**Part-III**

3. Answer any *eight* of the following :  $2 \times 8$
- a) Differentiate bond energy and bond dissociation energy.
  - b) Calculate  $q$ , for the isothermal expansion of one mole of an ideal gas at  $27^\circ\text{C}$  from a volume of  $10\text{dm}^3$  to a volume of  $20\text{dm}^3$  against a constant external pressure of 1 atm.

[ 3 ]

- c) Give an idea on residual entropy.
- d) Derive Maxwell's thermodynamic relation  $(\partial T/\partial V)_s = -(\partial P/\partial S)_v$
- e) Give an idea on work function.
- f) Write the variation of partial molar free energy with temperature.
- g) Write the integrated Van,t Hoff equation.
- h) Write the significance of the  $K_p$  and  $K_c$ .
- i) Define Osmosis and osmotic pressure.
- j) 1.20 g of a non-volatile organic substance was dissolved in 100g of acetone at  $20^\circ\text{C}$ . The vapour pressure of the solution was found to be 182.5 torr. Calculate the molar mass of the substance. (Vapour pressure of acetone at  $20^\circ\text{C}$  is 185.0 torr.)

**Part-IV**

4. a) Define the term internal energy change and enthalpy change of a system. Derive the relation between them for an ideal gas. 6

OR

- b) What is bond energy ? Explain how do you calculate enthalpy of reaction from bond energy.

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5. a) Derive an expression for the enthalpy change accompanying the isothermal expansion of an ideal gas. 6

OR

- b) Explain how the absolute entropy of a substance is determined with the help of the third law of thermodynamics ?
6. a) What is chemical potential ? Derive Gibb's-Duhem equation for a binary solution. 6

OR

- b) State the law of chemical equilibrium. How can it be derived on thermodynamic consideration ?
7. a) State and explain Raoult's law and Henry's law. Show that if in any solution, the solvent obeys Raoult's law, the solute obey Henry's law. 6

OR

- b) Derive the relation between the boiling point elevation of a solution and the mole fraction of the dissolved solute. How is the expression used for determining molar mass of non-volatile solute ? 6

## CHEMISTRY-CC-IV

### PART I ( 1 mark)

1. State zeroth law of thermodynamics.
2. Define heat. Write its unit.
3. Define heat capacity. Write its unit.
4. Define  $C_p$  and  $C_v$ .
5. Define Internal energy. Write its unit.
6. Define entropy. Write its unit.
7. Define enthalpy. Write its unit.
8. What is an isobaric process?
9. What is an isochoric process?
10. Define enthalpy of fusion.
11. Define enthalpy of vapourisation.
12. State first law of thermodynamics.
13. Write the mathematical expression of first law of thermodynamics.
14. State the third law of thermodynamics.
15. What is residual entropy?
16. What is inversion temperature?
17. What is fugacity?
18. What do you mean by the standard state of a substance?
19. Define bond energy.
20. Define bond dissociation energy.
21. Define resonance energy.
22. Define partial molar property.
23. Define chemical potential.
24. State Le Chatelier's principle.
25. Define an ideal solution. Give an example.
26. What is osmosis?
27. What are isotonic solutions?
28. State Carnot theorem.
29. Under what condition  $\Delta H = \Delta U$  ?
30. What happens to the internal energy of a system, if work is done (i) by the system and (ii) on the system?

## PART II (1.5 marks)

31. Write the limitations of the first law of thermodynamics.
32. What is a cyclic process? What is the value of  $\Delta U$  in a cyclic process?
33. State the second law of thermodynamics.
34. State and explain Carnot theorem.
35. Define free energy. Write its significance.
36. Write the conditions for spontaneity of a reaction.
37. What is enthalpy of combustion?
38. What is enthalpy of formation?
39. State Raoult's law. Write its applications.
40. State Henry's law. Write its applications.
41. What are colligative properties? Give some examples of colligative properties.
42. What is Joule-Thomson coefficient?
43. What is the relation between  $C_p$  and  $C_v$ .
44. What is Joule-Thomson effect?
45. Calculate the maximum efficiency of an engine operating between  $85^\circ\text{C}$  and  $35^\circ\text{C}$ .
46. What is Work function? Write its significance.
47. The heat of combustion of butane is  $-2220 \text{ kJ mol}^{-1}$ . How much heat would be produced on burning 1g of it?

## PART III (2 marks)

48. What are extensive and intensive variables? Give examples.
49. What are state function and path function? Give examples.
50. Explain open system and closed system with examples.
51. Give the molecular and statistical interpretation of entropy.
52. Differentiate between reversible and irreversible process.
53. Differentiate between isothermal and adiabatic process.
54. What is the difference between  $\Delta G$  and  $\Delta G^0$ ?
55. What are exothermic and endothermic reactions? Explain with one example from each.
56. Two carnot engines A and B have their sources at 400 K and 350 K and sinks at 350 K and 300 K, respectively. Which engine A or B is more efficient?
57. Differentiate between bond energy and bond dissociation energy.
58. Write the significance of  $K_p$  and  $K_c$ .

59. What is Entropy? Calculate the change in entropy when two moles of an ideal gas expands reversibly from a volume of 5L to 50 L at 25°C.
60. What are the criteria of spontaneity? Predict whether at 27°C, the following reaction is spontaneous or not ?  $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{l})$  , Given  $\Delta H = +9080 \text{ J mol}^{-1}$  and  $\Delta S = + 35.7 \text{ J K}^{-1}\text{mol}^{-1}$
61. If  $dG = VdP - SdT$ , Show that  $\left(\frac{\partial S}{\partial P}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_P$
62. Calculate the standard entropy change for a reaction if the value of  $\Delta H^0 = 28.40 \text{ kJ mol}^{-1}$  and equilibrium constant is  $1.8 \times 10^{-7}$  at 298 K.

#### PART IV ( 6 marks)

63. Define the terms internal energy change and enthalpy change of a system. Derive the relation between them for an ideal gas.
64. What is bond energy? Explain how do you calculate enthalpy of reaction from bond energy?
65. Derive Gibbs-Duhem equation.
66. Derive an expression for the entropy change accompanying the isothermal expansion of an ideal gas.
67. What is chemical potential? Discuss the variation of chemical potential with temperature and pressure.
68. State the law of chemical equilibrium. How can it be derived on thermodynamic considerations?
69. Derive van't Hoff equation. Integrate the equation and discuss the effect of temperature on  $K_P$ .
70. Derive the expression for work done in reversible isothermal expansion of an ideal gas.
71. Explain how the absolute entropy of a substance is determined with the help of the third law of thermodynamics?
72. Derive Kirchoff's equation for the effect of temperature on heat of reaction.
73. Derive the relation between the boiling point elevation of a solution and the mole fraction of the dissolved solute. How is the expression used for determining molar mass of non-volatile solute?
74. State Le Chatelier principle and explain its applications.
75. Write short notes on Maxwell relations.
76. Derive Gibbs-Helmholtz equation. Explain its significance.
77. Derive the expression relating the variation of entropy with temperature, volume and pressure for an ideal gas.

78. Derive the expression relating the variation of Gibbs free energy with temperature, volume and pressure for an ideal gas.
79. Derive Gibbs-Helmholtz equation. Write its applications. The free energy change for a given process is  $-80 \text{ kJ}$  at  $20^\circ\text{C}$  and  $-60 \text{ kJ}$  at  $30^\circ\text{C}$ . Calculate the change in enthalpy of the process at  $25^\circ\text{C}$ .
80. What is Free energy function? Discuss the variation of this with Pressure. Calculate the free energy change when one mole of an ideal gas expands reversibly and isothermally at  $37^\circ\text{C}$  from initial volume of  $10 \text{ dm}^3$  to  $200 \text{ dm}^3$ .