2019/TDC/EVEN/CHMHC-201T/069

TDC (CBCS) Even Semester Exam., 2019

CHEMISTRY

(2nd Semester)

Course No.: CHMHCC-201T

(Organic Chemistry-I)

Full Marks: 50
Pass Marks: 20

Time: 3 hours

The figures in the margin indicate full marks for the questions

Answer five questions, taking one from each Unit

UNIT-1

1. (a) Write the IUPAC name of the following compounds: 1×2=2

(b) Explain why CH_4 is tetrahedral but C_2H_4 and $H-C \equiv C-H$ are planer.

(2)

(3)

(c) Arrange the following amines in terms of increasing base strength. Justify your answer: 1+11/2=21/2

$$NH_2$$
 NH_2 Me NMe_2 Me NMe_2 Me NMe_2 Me

(d) The following compound has isomers, one isomer has dipole moment 0D and other has a dipole moment 2.95D. Propose structures for the two isomers that are consistent with these data and explain why:

ClCH=CHCl

11/2

3

- (e) Give the products of the following reactions-
 - (i) under condition that favour an S_N2 reaction;
 - (ii) under condition that favour an S_N1 reaction: 1+1=2

$$H_3CCH=CHCH_2Br + CH_3O \xrightarrow{CH_3OH} ?$$

(a) Give the hybridization of the central atom of the following species and draw the shape of these species:

(b) Arrange the following carbanion in terms of increasing stability:

Neopentyl, Benzyl, Phenyl

(c) Which of the following indicated bonds have greater bond strength and why? $1\times2=2$

(i)
$$CH_3$$
— CH_2 — CH_2 or CH_3 — CH — CH_3
 H

- (ii) $H_3C_{\overline{\uparrow}}CH_3$ or $CH_3-CH_2_{\overline{\uparrow}}CH_3$
- (d) Draw curved arrows to show the flow of electrons responsible for the conversion of the following reactants into the product: ½×2=1

(i)
$${}^{\Theta}OH + H_2C - CH_3 \longrightarrow$$
Br $H_2O + H_2C = CH_2 + Br^-$

(ii)
$$\text{Br} + \text{H}_2^{\bullet}\text{C} = \text{CH}_2 \longrightarrow \text{H}_2\text{C} - \dot{\text{C}}\text{H}_2$$

$$\text{Br}$$

(e) Give the configuration of the following reaction:

$$H_3C$$
 C_2H_5
 C_2H_5

Which of the following is a better base or better nucleophile and why?

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(Turn Over)

1

2

1

(Continued)

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(4)

Unit—2

3. (a) Provide the major products of the following reactions: 1×4=4

(i) Br
$$\longrightarrow$$
I + 2Na \longrightarrow A

(ii)
$$CH=CH_2 \xrightarrow{H_2} B$$

(iii)
$$\langle D \rangle$$
 Br + Na + CH₃I $\longrightarrow C$

(iv)
$$CH_3$$
— CH_2 — $C = C$ — CH_3 $\xrightarrow{H_2}$ D

catalyst

(b) Which alkyl halide would you expect to be more reactive in an E2 reaction and why? 1½×2=3

(ii)
$$CH_2$$
— CH_2 — CH_5 or CH_2 — CH_2 — CH_2 — CH_2 — CH_3

(Continued)

(c) Carry out the following transformation with appropriate reagent/reaction condition(s) and provide mechanism of the reactions:

HCECH
$$\longrightarrow$$
 CH₃CH₂CH₂—C—H

4. (a) Complete the following reactions and provide plausible mechanism: $2 \times 2 = 4$

(i)
$$A + HBr \longrightarrow CH_3$$

(ii)
$$CH_3 \xrightarrow{1) O_3} B$$

(b) Propose a mechanism for the following reaction: 1½

(c) If 2-fluoropentane were to undergo E1 reaction, would you expect the major product to be one predicted by Zaitsev's rule? Explain.

(Turn Over)

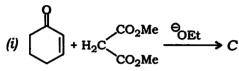
11/2

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(d) Provide the product(s) of the following reactions: $1 \times 3 = 3$



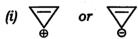
(ii)
$$H_2C=CH-CH=CH_2$$

 $+ H_3C-C-C=C-COCH_3 \xrightarrow{\Delta} D$
 CH_3
 O_2

(iii)
$$H_3C$$
— $C=CH$ — CH_3 $\xrightarrow{O_3}$ $E+F$

UNIT-3

- (a) State Hückel's rule of aromaticity. 11/2
 - (b) Which ion in each of the following pairs is more stable and why? $(\frac{1}{2}+1)\times 2=3$



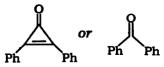
- (c) Predict the product of the following reaction and provide mechanism:

$$+ Br_2 \xrightarrow{FeBr_3} Product$$

Why is hydrated FeBr₃ inactive as a Lewis acid catalyst? 2+1=3

- (d) Describe synthesis of anthracene from 21/2 benzene.
- 6. (a) How the following compound could be prepared from benzene? Provide the mechanism of the following reaction: 21/2

- (b) When phenol is treated with Br2, a mixture of monobromo, dibromo and tribromo phenol is obtained. Design a synthesis that would convert phenol primarily to ortho-bromo phenol.
- (c) Starting from benzene, explain how you can synthesize 2-ethyl-naphthalene.
- (d) Prove chemically that naphthalene contains two benzene ring fused in orthoposition.
- (e) Which of the following compounds has greater dipole moment and why? 1/2+1=11/2



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(Turn Over)

2

2

2

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(Continued)

Unit-4

- 7. (a) Draw Fischer projection of the following compound(s): 1×2=2
 - (i) (2S, 3R)-3-chloro-2-pentanol
 - (ii) (S)-3-chloro-1-pentanol
 - (b) Write whether H_a , H_b hydrogens in each of the following compounds are homotropic, enantiotropic or diastereotropic: $\frac{1}{2} \times 4 = 2$

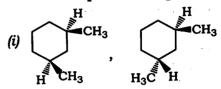
(ii)
$$H_{a}$$
 H_{a}

(iii) H_{b}
 H_{a}

(iii) H_{a}

- (iii) H_3C — CH_2 —C— CH_3 H_b H_3C — H_a
- (c) Discuss with an example, the resolution method through the formation of diastereomers.
- (d) Write the structure of meso-tartaric acid in Newman projection and Fischer projection. Show that it contains an S₂ axis.

8. (a) Give the stereochemical relationship between the pair of compounds: 1×3=3



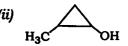
(iii) OH CH

- (b) Define optical rotation and specific rotation. 1+1=2
- (c) Convert the following perspective formula to Fischer projection: 1×2=2

(d) Draw projections of the following compounds to show the presence of geometric cis-trans isomers and optical isomers:

1½×2=3





UNIT-5

- 9. (a) Explain with example, Baeyer strain theory. 2½
 - (b) Explain why, in case of cyclohexane, chair conformer is more stable than boat conformer. 2½
 - (c) Draw most stable conformation of the following compounds: 1×3=3
 - (i) cis-1-tert-butyl-4-methyl cyclohexane
 - (ii) Butane-2,3-di-ol (in Newman projection)
 - (iii) cis-cyclohexane-1,3-diol
 - (d) Explain why in 1-methyl-1-phenyl cyclohexane the conformer with axial phenyl and equatorial methyl is more stable than other conformer.

- 10. (a) Draw the most stable conformer of cyclopentane. Explain why planar conformation is not stable. 1+1½=2½
 - (b) Why does cyclobutane have less ring strain than cyclopropane? 1½
 - (c) Draw Newman projections of various conformations of *n*-butane and arrange them according to their decreasing stability. Also draw the potential energy diagram (energy vs. torsion angle) of *n*-butane. 1+2½=3½
 - (d) Draw two conformers of 1,2-cis-dimethyl cyclohexane. State which one is more stable and why. 1+1½=2½

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2019/TDC/EVEN/CHMHC-202T/070

TDC (CBCS) Even Semester Exam., 2019

CHEMISTRY

(2nd Semester)

Course No.: CHMHCC-202 T

(Physical Chemistry—II)

Full Marks: 50 Pass Marks: 20

Time: 3 hours

The figures in the margin indicate full marks for the questions

SECTION-A

(Marks: 20)

Answer ten questions, taking two from each Unit

UNIT-I

- 1. What are exact and inexact differentials? Give one example each from thermodynamics.
- 2
- 2. Write the mathematical statement for the first law of thermodynamics.

2

(Turn Over)

(2)

(3)

3. Define adiabatic flame temperature and explosion temperature.

2

2

UNIT-II

4. Give the statement of the second law of thermodynamics in terms of entropy.

5. Define inversion temperature. What is its significance? 1+1=2

6. Show that

$$\left(\frac{\partial S}{\partial P}\right)_{T} = -\left(\frac{\partial V}{\partial T}\right)_{P}$$

UNIT-III

- 7. Explain the term 'partial molar property'.
- 8. Show that

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P, N} = -\overline{S}_i$$

where the terms have their usual meanings. 2

9. Show the variation of chemical potential with temperature, graphically.

UNIT-IV

- **10.** Fugacity is a sort of 'fictitious pressure'. Explain.
- 11. Define the degree of advancement of a chemical reaction.
 - 12. What is reaction potential? Complete the following sentence:

 1+1=2

 The decrease of reaction potential is

defined as the ____.

UNIT-V

- 13. State Raoult's law. Define ideal solutions.
- 14. Mention two differences between osmosis and diffusion.
- **15.** Define ebullioscopic constant and cryoscopic constant. 1+1=2

2

(4)

SECTION—B

(Marks: 30)

Answer five questions, taking one from each Unit

UNIT-I

16. (a) Prove thermodynamically

$$C_P - C_V = R$$

for one mole of an ideal gas.

(b) Compare isothermal and adiabatic expansions of an ideal gas and show that

$$P_{\rm adia} < P_{\rm iso}$$

where P indicates pressure of the ideal gas after expansion.

- 17. (a) Deduce Kirchhoff's equations.
 - (b) Calculate the bond enthalpy of C—H bond in methane from the following thermodynamic data:
 - (i) Heat of formation of methane is -75 kJ
 - (ii) Heat of sublimation of carbon is 720 kJ
 - (iii) Bond enthalpy of hydrogen gas is 435 kJ

(5)

UNIT--II

- **18.** (a) State Lewis and Randall's statement for the third law of thermodynamics.
 - (b) Explain the concept of residual entropy.
 - (c) Show that Joule-Thomson effect is isoenthalpic.
- 19. (a) Derive the first thermodynamic equation of state using Maxwell relations.
 - (b) Show that

$$-\Delta A_T = w_{\text{max}}$$

where the terms have their usual meanings.

(c) In the solid state at 0 K, nitric oxide, NO, is capable of existing in two orientations, viz., NONO and NOON, which have practically equal probabilities. Calculate the molar entropy of NO at 0 K.

UNIT-III

- 20. Define chemical potential. What is its significance? Derive an expression to show the variation of chemical potential with pressure.
 2+1+3=6
- 21. Deduce Gibbs-Duhem equations. Mention one important conclusion that can be drawn from Gibbs-Duhem equations. 4+2=6

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(Turn Over)

1

2

3

2

2

2

(Continued)

2

3

(6)

UNIT--IV

- **22.** (a) Derive thermodynamically the relation between Gibbs free energy of reaction and reaction quotient.
 - (b) The extent of dissociation of PCl₅ at a certain temperature is 20% at 1 atm pressure. Calculate the pressure at which this substance is half dissociated at the same temperature.
- 23. (a) Derive the integrated van't Hoff equation.
 - (b) The equilibrium constant of a reaction doubles on raising the temperature from 25 °C to 35 °C. Calculate ΔH° for the reaction.
 - (c) Explain coupling of exoergic and endoergic reactions.

UNIT-V

- **24.** (a) State and explain the law which explains the effect of pressure on the solubility of a gas.
 - (b) Define van't Hoff factor. Find a relation between van't Hoff factor and degree of dissociation, taking one mole of a uni-univalent electrolyte as an example. 1+2=3

25. (a) Apply thermodynamics to derive a relationship between osmotic pressure and vapour pressure lowering of an ideal solution.

(b) At 37 °C, osmotic pressure of blood is 7.65 atm. How much glucose should be used per litre for an intraveinous injection that is to have the same osmotic pressure as blood?

4

2

2

2