

AE-765

M. Sc. (Final)
Term End Examination, 2016-17

CHEMISTRY

Group - B

Paper - IV

Physical Organic Chemistry and
Heterocyclic Chemistry

Time : Three Hours] [Maximum Marks : 100
[Minimum Pass Marks : 36

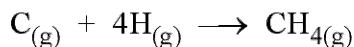
Note : Selecting at least **two** questions from each Section, answer **five** questions in all. The figures in the right-hand margin indicate marks.

Section-A

1. What are the mechanistic significance of Entropy, Enthalpy and Gibbs' free energy ? If for two reactions ΔG° values are -795 kJ/mol and $+105$ kJ/mol, predict which reaction will take place spontaneously and why.

(2)

Define bond enthalpy. How bond enthalpy of C—H in methane can be determined? The main reaction is



[when heat of formation of CH_4 , heat of dissociation of H_2 all amount to 398 kcal/mole] 10+10

2. What are the main conditions essential for the formation of a covalent bond?

To form molecular orbital, what are the rules for linear combinations of atomic orbitals?

Draw a diagram for ψ_g and ψ_u molecular orbitals showing curves among energy, distance and atoms.

Mention the importance of ionisation potential and electron affinity in the formation of a covalent bond. 5+5+5

3. Explain any **four** of the following : 4×5

- (a) Solvent effects from the curve-crossing model
- (b) Acidity functions and their applications
- (c) Ambivalent nucleophiles
- (d) Marcus theory of electron transfer
- (e) Hammond's postulate

(3)

4. (a) What are free radicals? Discuss their stability. Explain regioselectivity in radical reactions. 12

(b) Give an account of reactivity related specificity and periselectivity in pericyclic reactions. 8

5. (a) Discuss qualitative understanding of solvent solute effects on reactivity. 10

(b) Mention and discuss examples of solvent sensitive reaction rates. 10

OR

Write brief notes on any **three** of the following : 20

(a) Frontier molecular orbital theory

(b) Arrhenius equation

(c) Bell-Evans-Polanyi principle used in steric and solvent effects in reaction mechanism

(d) Structural and electronic effects on $\text{S}_{\text{N}}1$ reactions

(e) Kinetics of $\text{S}_{\text{E}}^{2-\text{Ar}}$ reaction.

Section-B

6. Give an account of six membered heterocycles with reference to molecular geometry, barrier to ring inversion, pyramidal inversion and 1,3-diaxial interaction. 20

(4)

7. Give synthesis and reactions including medicinal applications of Benzopyrroles, Benzothiophenes and Benzofurans (any **two**). 20

8. Explain any **two** of the following : 20

- (a) Empirical resonance energy, delocalisation energy and Dewar resonance energy.
- (b) Hantzsch-Widman system of nomenclature for monocyclic and fused heterocycles.
- (c) Hetero-aromatic reactivity and tautomerism in aromatic heterocycles.

9. Give an account of the synthesis and reactions of Coumarins, Benzopyrylium and Quinolizinium salts (any **two**). 20

10. (a) Give an account of principles of heterocyclic synthesis involving cyclisation reactions and cycloaddition reactions. 10

(b) Give syntheses of any **two** of the following : 10

- (i) Oxiranes
- (ii) Oxetanes
- (iii) Aziridines
- (iv) Azetidines