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.

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

$$C_{(g)} + 4H_{(g)} \longrightarrow CH_{4(g)}$$

[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+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

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 SN_1 reactions

(*e*) Kinetics of $S_E^{2\text{-}Ar}$ 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

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

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