

Section D

7. (a) What are basic types and structures of liquid crystals ? How are they different from a solid crystal and pure liquids ? Give a detailed comparison. 7
- (b) Discuss dielectric properties of nematic liquid crystals. Obtain an expression of dielectric anisotropy. 5
8. (a) Discuss Freedericksz and DAP effects of dielectric deformations in a nematic liquid crystal. 6
- (b) Write short notes on the following : 6
- (i) Lyotropic liquid crystals
- (ii) Schlieren textures.

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Total Pages : 04

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PHYSICAL CHEMISTRY SPECIAL-VI CHEM-404

Time : Three Hours]

[Maximum Marks : 60

Note : Attempt *Five* questions in all, selecting at least *one* question from each Section. All questions carry equal marks.

Section A

1. (a) Discuss, how pre-exponential factors show temperature dependence. 5
- (b) Discuss Marcus's extension of RRK treatment of the unimolecular reactions. What shortcomings of RRK theory were overcome by Marcus and in what way is it an improvement ? 7
2. (a) Discuss the treatment by Rice, Ramsperger and Kassel to the unimolecular reaction : 9



where both k_2 and k_1/k_{-1} were treated as dependent on ε^* energy.

- (b) Write a brief note on London-Eyring-Polanyi method to calculate energy of the reaction intermediates.

3

Section B

3. (a) Discuss the principle and working of cross molecular beam experiment. How are molecular beams formed and detected in this experiment ? 8
- (b) Describe relationship between reaction cross section and reaction rate. 2
- (c) Describe dependence of collision cross section on translational energy. 2
4. (a) For a bimolecular reaction : 7



taking place in solution, obtain the rate expression

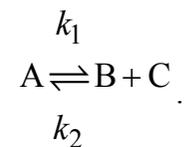
$$\ln k = \ln k_0 - \frac{z_A z_B e^2}{4\pi\epsilon_0 \epsilon d_{AB} kT} - \frac{\mu_\ddagger^2 - \mu_A^2 - \mu_B^2}{16\pi\epsilon_0 \epsilon d_{AB}^3 kT}$$

What is the influence of ionic strength on the reaction ?

- (b) Discuss the influence of substrate concentration on enzyme catalyzed reactions and derive Michaelis-Menten equation. Recast the equation to obtain a linear plot. 5

Section C

5. (a) What are branching chain reactions ? Why do they always lead to explosions ? Illustrate and describe temperature-pressure range for branching chain explosion in Hydrogen-Oxygen reaction. 6
- (b) What are different techniques of studying fast reactions ? Discuss different variants of flow methods for studying fast reactions. 6
6. (a) What do you understand by the term relaxation ? What are relaxation methods in fast reaction ? Deduce the relationship between rate constants and relaxation time (τ) for the system : 5



- (b) Which is the better method for studying fast reactions; temperature jump or pressure jump method and why ? 3
- (c) Discuss flash photolysis method of studying fast reactions. Explain the role of tetra ethyl lead in fuel in internal combustion engines as an antiknock agent. 4