[This question paper contains 2 printed pages.]

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Sr. No. of Question Paper : 5041

Unique Paper Code : 2174001207

Name of the Paper : GE – Chemical Kinetics and Photochemistry

Name of the Course : **B.Sc. (H)**

Semester : VIII

Duration : 2 Hours

Maximum Marks : 60

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt **four** questions in all, question No. **1** is compulsory.
3. The answers should be numbered in accordance to the number in the question paper.
4. Use of scientific calculator, log tables and graph paper is permitted.

($R = 8.314$ J K^{-1} mol^{-1}; $k = 1.38 \times 10^{-23}$ J K^{-1}; $N_A = 6.023 \times 10^{23}$ mol^{-1}; $h = 6.626 \times 10^{-34}$ J s)

1. Answer any *five* of the following

   (a) The acid hydrolysis of methyl acetate is a pseudo-first order reaction. Explain. 3

   (b) Some reactions, in spite of having low activation energy, proceeds at very slow rate. 3

   (c) Differentiate between order and molecularity of a reaction giving examples. 3

   (d) Why a first order reaction never completes? 3

   (e) Describe the conditions for the applicability of Lambert-Beer law for a coloured solution. 3

   (f) Why is the fluorescence spectrum always observed at a lower wavelength (higher energy) than phosphorescence? 3

2. (a) Describe various factors affecting the rate of a chemical reaction. 5

   (b) Using integrated rate expressions, derive equations for half-life of first and second order reactions. 5

   (c) The rate constant of a first order decomposition of ethylene oxide into CH_4 and CO follows the equation $\log k(\text{in s}^{-1}) = 14.34 - (1.25 \times 10^4)/T$. Calculate

   (a) the activation energy

   (b) the rate constant at 700 K

   (c) the frequency factor, A. 5

3. (a) For the first order opposed by first order reaction

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

with the initial concentration of A and B as $[A]_0$ and zero respectively, show that integrated rate expression is given by

$$\ln \frac{x_{eq}}{x_{eq} - x} = (k_1 + k_{-1})t$$

where x is the concentration of B at time t and x_{eq} is the concentration at equilibrium. 5

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(b) Describe van't Hoff differential method for determining the order of a reaction and derive expression. 5

(c) The decomposition of N_2O_5 is an important process in tropospheric chemistry. The half-life for the first order decomposition of this compound is 2.05×10^4 s. How long will it take for a sample of N_2O_5 to decay to 60% of its initial value? 5

4. (a) Derive integrated rate expression for second order reaction assuming reactants to be different. 5

(b) What is activation energy of a chemical reaction? Show on the energy profile diagram of a reaction. Using the Arrhenius equation derive integrated expression for activation energy. 5

(c) A first order reaction has rate constant 2.2×10^{-5} min^{-1} at 85 °C and 3.07×10^{-5} min^{-1} at 137 °C. Calculate the activation energy for the reaction. 5

5. (a) Draw labelled Jablonski diagram for photochemical absorption of light and explain the fluorescence and phosphorescence processes using the different states. 5

(b) State and explain the laws of photochemistry. Also, give reasons for low and high quantum yield in photochemical reactions. 5

(c) In a particular reaction the time required to complete half of the reaction was found to increase 16 times when the initial concentration of the reactant was reduced to one fourth. Determine the order of the reaction and also give unit of rate constant. 5

6. (a) HCl can be synthesized by irradiating a mixture of H_2 and Cl_2. Show that the reaction mechanism 5

$$Cl_2 + h\nu \xrightarrow{k_1} 2Cl$$

$$Cl + H_2 \xrightarrow{k_2} 2H + HCl$$

$$H + Cl_2 \xrightarrow{k_3} HCl + Cl$$

$$Cl \text{ (at the walls)} \xrightarrow{k_4} \frac{1}{2} Cl_2$$

Confirms the following rate law

$$\frac{d}{dt}[HCl] = \frac{k_1 k_2}{k_4} I_{abs}[H_2]$$

(b) A light of wavelength 250 nm was passed through a cell containing 10 mL of solution containing 0.05 molar oxalic acid and 0.01 molar uranyl sulphate. After absorption of 120 Joules of radiation energy, the concentration of oxalic acid was reduced to 0.03 molar. Calculate the quantum yield for the photochemical decomposition of oxalic acid at the given wavelength. 5

(c) Lambert-Beer's law, derive expression for absorbance, write its limitations and physical significance of absorption coefficient. 5