[This question paper contains 2 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 5308 **L**

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.

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

1. Answer any *five* of the following 5×3

   (a) The rate of complex reactions is low. Explain why?

   (b) Differentiate between thermochemical and photochemical reactions.

   (c) Distinguish between fluorescence and phosphorescence.

   (d) What is meant by activation energy and threshold energy barrier of a reaction? How these are related to each other?

   (e) The $t_{1/2}$ of a reaction is halved as the initial concentration of reactant is doubled. What is the order of the reaction.

   (f) Why the quantum efficiency for the photochemical reaction

   $H_2\ (g) + Br_2\ (g) \rightarrow 2HBr$

   is low while for the reaction

   $H_2\ (g) + Cl_2\ (g) \rightarrow 2HCl$

   is very high?

2. (a) Derive integrated rate expression for a second order reaction assuming reactants are similar. Give graphical representation for the variation of concentration with time for second-order kinetics. 5

   (b) What are consecutive reactions? Derive the integrated rate law expression for the formation of final product in a consecutive reaction. 5

   (c) Nitrogen pentoxide (N_2O_5) gas decomposes according to the reaction

   $$2N_2O_5 \rightarrow 4NO_2(g) + O_2(g)$$

   At 328 K, the rate of reaction under certain conditions is $0.75 \times 10^{-4}\ \text{mol dm}^{-3}\text{s}^{-1}$. Neglecting the concentrations of intermediates, determine the values of

   $-\frac{d[N_2O_5]}{dt}$, $\frac{d[NO_2]}{dt}$ and $\frac{d[O_2]}{dt}$ 5

3. (a) Derive expressions to determine order of reaction using (i) differential rate equation method (ii) half-life method. 5

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(b) In a certain rection 8% of the reactant decomposes in 30 minutes, 24 % in 90 minutes and 48% in 180 minutes. What would be the order of reaction and what are the dimensions of the rate constant. 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 Arrhenius equation for showing the effect of temperature on reaction rate. 5

(b) Describe the Activated Complex theory and show that it leads to the following equation for rate constant

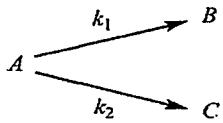
$$k_2 = \left(\frac{RT}{N_A h}\right)\exp\left(-\frac{(\Delta H^\circ)^\#}{RT}\right)\exp\left(\frac{(\Delta S^\circ)^\#}{R}\right)$$ 5

(c) Calculate the activation energy of the reaction whose rate constant is tripled by a 10 °C rise in temperature in the vicinity of 27 °C temperature. 5

5. (a) Draw and describe the Jablonski diagram (labelled) for photochemical absorption of light. 5

(b) State and derive Lambert- Beer's law for light absorption by solutions. Derive expression for absorbance and also plot absorbance versus concentration graph. 5

(c) Reactant A forms products B and C in a parallel reaction in ratio 8:3, respectively. 5



If initial concentration 0.8 M becomes 0.3 M in 25 minutes. Determine the rate constants k_1 and k_2.

6. (a) Define quantum yield. How it can be determined experimentally using uranyl oxalate actinometer? Give two reasons each for high and low quantum yield. 5

(b) HBr can be synthesized by irradiating a mixture of H_2 and Br_2 via mechanism

(i) $Br_2 + h\nu \xrightarrow{k_1} 2Br$

(ii) $Br + H_2 \xrightarrow{k_2} H + HBr$

(iii) $H + Br_2 \xrightarrow{k_3} HBr + Br$

(iv) $H + HBr \xrightarrow{k_4} H_2 + Br$

(v) $2Br \xrightarrow{k_5} Br_2$

Show that rate law for the formation of HBr is given by

$$\frac{d}{dt}[HBr] = \frac{2k_2(k_1/k_5)^{1/2} I_{abs}^{1/2}[H_2]}{1+\{k_4[HBr]/k_3[Br_2]\}}$$ 5

(c) A sample of HI gas was irradiated by light of wavelength 253.7 nm when 450 Joules of energy was found to decompose 2.6×10^{-3} moles of HI. Calculate the quantum yield for the decomposition of HI. 5