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Roll No. | | | | | | | | | | | |

S. No. of Question Paper : **5317**

Unique Paper Code : **2174001207**

Name of the Paper : **GE : Chemical Kinetics and Photochemistry**

Name of the Course : **All Undergraduate Courses except with Chemistry Discipline**

Semester : **II/IV/VI**

Duration : **2 Hours** Maximum Marks : **60**

(Write your Roll No. on the top immediately on receipt of this question paper.)

Attempt any *four* questions.

All questions carry equal marks.

Use of non-programmable scientific calculator is permitted.

1. (*a*) Distinguish between : 5

(*i*) Rate of a reaction and rate constant

(*ii*) Elementary and complex reactions.

(*b*) The reaction : 5

$$A + B \rightarrow \text{Products}$$

is a first order with respect to both A and B. Derive the integrated rate law when the initial concentration of both the reactants is not equal.

P.T.O.

(c) In a reaction, the reactant (X) is initially at 0.12 M. It is reduces to 0.06 M in 10 hours and 0.03 M in 20 hours. What is the order of the reaction and what is the rate constant and its units ? Write the differential rate equation also. 5

2. (a) Describe the Integrated rate method for determination of order of a reaction. 5

(b) For a reaction with differential rate : 5

$$\frac{dx}{dt} = k_n \left([A]_0 - x \right)^n .$$

Show that the half-life is given by :

$$t_{\frac{1}{2}} = \frac{1}{k_n (n-1)} \frac{2^{n-1} - 1}{[A]_0^{n-1}} .$$

(c) On what factors the rate and rate constant of a reaction depends ? Tabulate the units of rate constants for zero, first and second order reactions. 5

3. (a) Write the expression for Arrhenius equation and explain the terms involved in it. For the decomposition of acetone dicarboxylic acid, the rate constants are 2.46×10^{-5} s^{-1} at 273 K and 1.63×10^{-3} s^{-1} at 303 K. Calculate the activation energy. 5

(b) Write a comparison between Collision Theory of Bimolecular Reactions and Activated Complex Theory for Bimolecular Reactions. 5

(*c*) Define the steady state approximation applicable to reactive intermediates. Justify the approximation by taking a consecutive reaction as an example where the first step is the rate determining step. 5

4. (*a*) The photochemical decomposition of HI involves the following steps : 5

Primary process : $HI \xrightarrow{h\theta} H + I$

Secondary process : $H + HI \xrightarrow{k_2} H_2 + I$

$I + I \xrightarrow{k_3} I_2$.

Show that the quantum yield of the reaction is 2 initially but gradually reduces as the reaction progresses.

(*b*) What do you mean by primary and secondary processes of a photochemical reaction ? Enumerate the various ways by which an activated molecule can get deactivated after the primary process. 5

(*c*) Explain why increase in reactant concentration decreases the quantum yield of fluorescence. Why phosphorescence is also referred to as delayed fluorescence ? 5

5. (*a*) Define a photosensitized reaction and give an example. Explain the role of uranyl ion in the determination of number of photons in a chemical actinometer. 5

(*b*) Explain the phenomenon of photo stationary state. The proposed mechanism of photochemical dimerization of Anthracene (A) is given below :

Primary process : (*i*) $A \xrightarrow{h\theta} A^*$

Secondary process : (*ii*) $A^* + A \xrightarrow{k_2} A_2$

(*iii*) $A_2 \xrightarrow{k_3} 2A$

(*iv*) $A^* \xrightarrow{k_4} A + h\theta'$.

Derive the expression for the rate of formation of the dimer. 5

(*c*) Calculate the number of moles of HCl produced by the absorption of 1 Joule of radiant energy of wavelength 480 nm in the photochemical reaction between H_2 gas and Cl_2 gas to produce HCl, if the quantum yield of the reaction is 1×10^{-6}. 5

6. Write short notes on any *three* : 3×5

(*a*) Quenching of Fluorescence

(*b*) Half Life Method for order determination

(*c*) Order and molecularity of a reaction

(*d*) Graphical method for order determination.