

This question paper contains 4 printed pages]

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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.

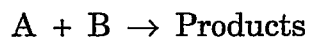
Use of non-programmable scientific calculator is permitted.

1. (a) Distinguish between : 5

(i) Rate of a reaction and rate constant

(ii) Elementary and complex reactions.

(b) The reaction : 5



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 reduced 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

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

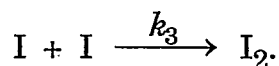
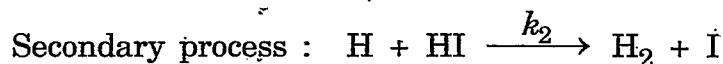
Show that the half-life is given by :

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

- (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  $2.46 \times 10^{-5} \text{ s}^{-1}$  at 273 K and  $1.63 \times 10^{-3} \text{ s}^{-1}$  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

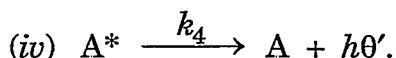
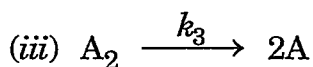
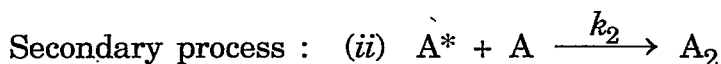
4. (a) The photochemical decomposition of HI involves the following steps : 5



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 :



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  $1 \times 10^{-6}$ . 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.