(c) Pseudo unimolecular reactions.

(d) Steady state approximation.

[This question paper contains 8 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 4656 **J**

Unique Paper Code : 2174001207

Name of the Paper : All Undergraduate Courses except with Chemistry Discipline

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

Semester : II / IV / VI

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 any **Four** questions in all.
3. **All** questions carry equal marks.
4. Use of non-programmable scientific calculator is permitted.

1. (a) Explain (5)

(i) Order of a reaction cannot be predicted from its equation.

(ii) Elementary processes with molecularity greater than three are not known.

(b) The reaction (5)

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

is a first order with respect to A. Derive the integrated rate law. What are the units of rate constant for a first order reaction?

(c) The rate constant for a second-order reaction is $8.00 \times 10^{-5}\ M^{-1}\ min^{-1}$. How long will it take for a 1.0 M solution to be reduced to 0.5 M in the reactant? How much time will it take further until the solution is 0.25 M in reactant? (5)

(c) A radiation of wavelength 2500 Å was passed through a cell containing 10 ml of a solution which was 0.05 M in oxalic acid and 0.01 M in uranyl sulphate.

After absorption of 80 J of light energy, the concentration of oxalic acid was reduced to 0.04 M. Calculate the quantum yield for the decomposition of oxalic acid at the given wavelength. (5)

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

(a) Biological applications of photochemical reactions.

(b) Differential rate method (Initial rates) for order determination.

Explain why quantum efficiency of some photochemical reactions can be as low as 0.04 while for some it can be as high as 10^5. (5)

(c) What is the difference between internal conversion (IC) and Intersystem Crossing (ISC).

Why is phosphorescence also referred to as delayed fluorescence? (5)

5. (a) Explain how photochemical decomposition of oxalic acid can be used for determination of number of photons in a chemical actinometer. (5)

(b) Draw a neat labelled Jablonskii diagram and explain the various phenomena involved in it. (5)

2. (a) Describe the ratio variation method for determination of order of a reaction with the help of a suitable example. (5)

(b) Derive the expression for half-life for a zero order reaction.

A first order reaction is 40% complete after 6 minutes. How long will it take to be 90% complete? Calculate rate constant. (5)

(c) Write the Arrhenius equation. Explain the terms involved in the above expression.

What type of graph do you expect between log (k/k°) and 1/T? What is its slope? (5)

3. (a) What is threshold energy? How is it different from activation energy? Explain with suitable well labelled diagrams. (5)

(b) For the following reaction

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$$

Derive the integrated rate expressions

$$\ln \frac{x_{eq}}{x_{eq} - x} = k_f \frac{[A]_0}{x_{eq}} t$$

$$\ln \frac{x_{eq}}{x_{eq} - x} = (k_f + k_b)\, t \qquad (5)$$

(c) Define temperature co efficient of a reaction.

The activation energy of a reaction is 22.5 kcal mole^{-1}. Its rate constant is 1.8×10^{-5}. Calculate the Pre-exponential factor (A) at 40°C. (5)

4. (a) Explain the phenomenon of photo stationary state.

Given below is a mechanism of photo chemical dimerization of Anthracene(A).

Primary process : (i) $A \overset{h\vartheta}{\rightarrow} A^*$

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

(iii) $A_2 \overset{k_3}{\rightarrow} 2A$

(iv) $A^* \overset{k_4}{\rightarrow} A + h\vartheta'$

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

(b) What do you mean by quantum efficiency of a photochemical reaction?