(c) Define quantum efficiency. What are the reasons for low and high quantum efficiency of a photochemical reaction? (5)

[This question paper contains 8 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 5845 **H**

Unique Paper Code : 2174001207

Name of the Paper. : GE: CHEMICAL KINETICS AND PHOTOCHEMISTRY

Name of the Course : **B.Sc. (Hons) / B.Sc. (Prog)**

Semester : II

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 out of **six.**
3. **All** questions carry equal marks.
4. Attempt all parts of a question together.
5. Use of non-programmable scientific calculator is allowed.

1. (a) What, is the difference between order and molecularity of a chemical reaction? Explain with the help of examples. (5)

   (b) What is half-life of a reaction? Derive the expression for the half-life of a first order reaction. (5)

   (c) What is the difference between photophysical and photochemical processes? Give examples of both. (5)

2. (a) For a certain reaction A → Prod, a straight-line plot is obtained between $\frac{1}{[A]_t}$ vs t. (5)

   (i) What does the slope and the intercept of this plot represent?

   (ii) What is the order of this reaction?

   (iii) What are the units for its rate constant?

(c) For thermal decomposition of ozone to oxygen, the following mechanism has been suggested.

$$O_3 \rightleftharpoons O_2 + O \quad (fast)$$
$$O_3 + O \rightarrow 2O_2 \quad (slow)$$

Using steady state approximation and other suitable approximation, derive the expression,

$$r = -\frac{k[O_3]^2}{[O_2]} \qquad (5)$$

6. (a) Explain the difference between the instantaneous and the average rate of a reaction. (5)

   For the reaction A → B, the concentration of the reactant changes from 0.03 M to 0.02 M in 25 min. Calculate the average rate of reaction in S.I. units.

   (b) Derive an expression for the half-life of an n^{th} - order reaction where $n \geq 2$. (5)

5. (a) Match the statements given in column I and column II (5)

Column I		Column II	
(a)	A catalyst alters the rate of reaction	(i)	cannot be a fraction or zero
(b)	Molecularity	(ii)	orientatione is not proper
(c)	Second half-life of a first order reaction	(iii)	by lowering the activation energy
(d)	Arrhenius equation	(iv)	is same as the first
(e)	Energetically favourable reactions are sometimes slow if	(v)	refers to the fraction of molecules with energy equal to or grater than the activation energy

(b) The rate of a reaction quadruples when the temperature changes from 293 K to 313 K. Calculate the energy of activation of the reaction if it does not change with temperature. (5)

(iv) Write the expression for the half-life of this reaction.

(v) Calculate the rate constant for this reaction is the initial concentration of A is 4.5×10^{-5} M and its half-life is 2.5×10^{4} s.

(b) Describe the ratio variation method and the graphical method of determination of order of a reaction. (5)

(c) What are primary and secondary photochemical processes? Which out of the two follows the law of photochemical equivalence? Which process is responsible for low or high quantum efficiency of the photochemical reactions? (5)

3. (a) For a first order reaction, show that the time required for 99% completion is twice the time required for 90% completion of the reaction. (5)

(b) Write the Arrhenius equation. How will the value of rate constant change when; (5)

(i) activation energy becomes exceptionally large,

(ii) activation energy becomes very small,

(iii) activation energy is zero,

(iv) temperature is extremely high.

(c) Explain **two** of the following terms: (5)

(i) Inter system crossing

(ii) photostationary state

(iii) quenching of fluorescence

4. (a) Write a short note on activated complex theory for bimolecular reactions. How does it compare with the collision theory? (5)

(b) State true or false: (5)

(i) A catalyst does not take part in a chemical reaction and so cannot appear in the rate law.

(ii) Activation energy of a reaction can never be zero.

(iii) Chlorophyll acts as a photosensitizer in photosynthesis.

(iv) For an exothermic reaction, the rate of reaction decreases with increase in temperature.

(v) Chemical kinetics study cannot help determine the mechanism of any reaction.

(c) Explain the photophysical phenomenon of fluorescence and phosphorescence with the help of the Jablonski Diagram. (5)