

5051

8

(d) Integrated rate method for order determination

[This question paper contains 8 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 5051

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

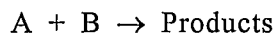
1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt any **Four** questions in all.
3. **All** questions carry equal marks.
4. Use of non-programmable scientific calculator is permitted.

1. (a) Explain (5)

(i) Thermodynamic principles can help predicting the feasibility of a reaction not the time the reaction will require for completion.

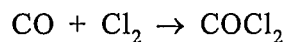
(ii) Order of an elementary step is always equal to its molecularity.

(b) The reaction (5)

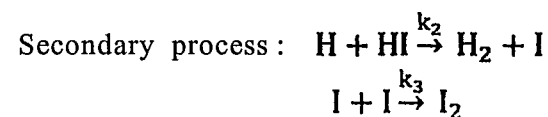
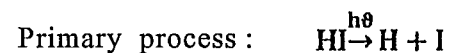


is a first order with respect to both A and B. Derive the integrated rate law when the initial concentration of both the reactants is equal.

(c) The following data was obtained for the reaction (5)



(c) 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.

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

(a) Photosensitized reactions

(b) Activated Complex Theory for Bimolecular Reactions

(c) Effect of temperature and pressure on rate of a reaction

At 460 nm, a blue filter transmits 72.7% of the light, and a yellow filter 40.7% of the light. Calculate the transmittance of the same wavelength of two filters in combination.

(5)

- (c) 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)

5. (a) (i) Differentiate between thermal reactions and photochemical reactions.

(ii) Beer's law fails in case of aqueous dilute $K_2Cr_2O_7$ solution. Justify.

(5)

- (b) Write the statement for Lambert Beer's Law and derive.

(5)

Write the differential rate expression. Using ratio variation method, determine the order with respect to each reactant. Find the value of the rate constant for the reaction.

Set Number	1	2	3	4
$[CO]_0 / \text{mole dm}^{-3}$	0.10	0.10	0.05	0.05
$[Cl_2]_0 / \text{mole dm}^{-3}$	0.10	0.05	0.10	0.05
Rate/mole $\text{dm}^{-3} \text{s}^{-1}$	1.2×10^{-3}	4.26×10^{-3}	6.0×10^{-3}	2.13×10^{-3}

2. (a) Describe, with a suitable example, the initial rates (van't Hoff differential) method for determination of order of a reaction.

(5)

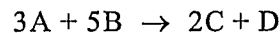
- (b) Define the term Half-life. For a first order reaction, show that the concentration of the reactant A after half-life times is

$$[A]_n = [A]_0 \left(\frac{1}{2} \right)^n$$

If the concentration of a reactant is doubled, what would be the half-life in a first order reaction?

(5)

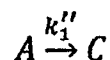
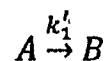
(c) For the hypothetical reaction



write the differential rate expression in terms of disappearance of A and B and appearance of C and D. Write the overall rate equation where the reaction is first-order with respect to each of A and half order with respect to B. What are the units of rate constant (k)? (5)

3. (a) Discuss the Collision Theory of Bimolecular Reactions. What are its limitations? (5)

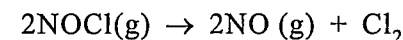
(b) For the concurrent elementary reaction,



Show that

$$\ln \frac{[A]_0}{[A]_t} = (k_1' + k_1'')t \quad \text{and} \quad \frac{[B]}{[C]} = k_1' / k_1'' \quad (5)$$

(c) For the reaction



the rate constant is $2.8 \times 10^{-5} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and $7.0 \times 10^{-1} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at 300 K and 400 K respectively. Calculate the activation energy of the reaction? (5)

4. (a) State and explain the two basic laws of photochemistry.

The reverse of Grothuss-Draper Law or first law of photochemistry is not true. Explain. (5)

- (b) How are Absorbance (A) and Transmittance (T) related?