

[This question paper contains 2 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 6483

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Unique Paper Code : 2174001207

Name of the Paper : CHEMICAL KINETICS AND PHOTOCHEMISTRY

Name of the Course : B.Sc. (H)

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 out of the **six** questions.
3. Attempt **all parts** of a question together.
4. **All** questions carry equal marks.
5. The use of a scientific calculator and log tables are permitted.

$$M = \text{mol dm}^{-3}; h = 6.6 \times 10^{-34} \text{ J s}^{-1}; R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}; c = 3 \times 10^8 \text{ m s}^{-1}.$$

1. a. By what factor does the rate of the reaction increases if the half-life period decreases from 20 min to 5 min by the use of a catalyst.
b. For the following elementary reaction. What is the order and molecularity and derive the rate law.
$$2\text{HI} \longrightarrow \text{H}_2 + \text{I}_2$$

c. Determine absorbance of a 0.5 molar oxalic acid solution, if extinction coefficient of oxalic acid is $0.8 \text{ mol}^{-1} \text{ dm}^3 \text{ m}^{-1}$ and the solution is irradiated by light of 250 nm was passed through a curette of 1 cm width. 5,5,5
2. a. Calculate the activation energy of a reaction whose reaction rate at 27°C doubles when temperature rises to 37°C temperature.
b. Write short note on Activated Complex theory for biomolecular reactions.
c. Define the term 'Quantum efficiency. Justify the statement that the quantum efficiency of a primary process is always one. 5,5,5

P.T.O.

3. a. Explain Vant Hoff differential rate equation method used for the determination of order of a reaction.
 b. The activation energy of a non-catalysed reaction at 37°C is $83.68 \text{ kJ mol}^{-1}$ and the activation energy of the same reaction catalyzed by an enzyme is $25.10 \text{ kJ mol}^{-1}$. Calculate the ratio of the rate constants of the enzyme-catalysed and the non-catalysed reaction.
 c. Define Frank Condon principle of electronic transition. Explain the reason of vertical transition in Jabolinski diagram of separation vs energy graphs. 5,5,5

4. a. What is the difference between rate constant and rate of reaction ? Give the units of rate constant for zero, first and second order reaction.
 b. From the following data for the decomposition of N_2O_5 in carbon tetrachloride solution at 48°C , show that the reaction is of the first order and calculate the rate constant.

Time/ min	10	15	20	25	∞
Vol. of O_2 evolved (in ml)	6.30	8.95	11.40	13.50	34.75

- c. Calculate the number of photons given in 10 minutes by a 500 watt monochromatic source of 480 nm wavelength. 5,5,5
5. a. Why the reactions of third and higher orders are usually not very common?
 b. The half life of a first order chemical reaction $\text{A} \longrightarrow \text{B}$ is 10 min. What percent of reactant remains after 40 min.
 c. i) What is Stark-Einstein law of photochemical equivalence?
 ii) Explain Photosensitisation with example. 5,5,5
6. a. Explain the effect of temperature on the rate of a chemical reaction?
 b. Define the term Activation energy. The activation energy of a reaction is 40 kJ mol^{-1} and the value of rate constant at 40°C is $1.8 \times 10^{-5} \text{ s}^{-1}$. Calculate the frequency factor A
 c. Differentiate between Primary process and secondary process in photochemistry with suitable examples. 5,5,5