[This question paper contains 2 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 5717 **L**

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= mol dm^{-3}; h = 6.6 x 10^{-34} J s^{-1}; R = 8.314 J K^{-1} mol^{-1}; c = 3 x 10^{8} m s^{-1}

1. a. Show that for a first-order reaction, the concentration of reactant A after n half-life times is given by

$$[A]_n = [A]_0(1/2)^n$$

b. The following results have been obtained during the kinetics studies of the reaction:

$$2NO + Cl_2 \longrightarrow 2NOCl$$

Set	[NO]/mol L^{-1}	[Cl_2]/mol L^{-1}	Initial rate/ mol L^{-1} min^{-1}
I	0.25	0.50	1.6 x 10^{-3}
II	0.50	0.50	3.2 x 10^{-3}
III	0.50	0.25	0.8 x 10^{-3}

Determine the order with respect to NO, Cl_2 and the overall reaction. Also, determine the rate constant of the reaction.

c. State the Beer-Lambert law. Write its mathematical form, explaining the various parameters involved. What are the limitations of this law? 5,5,5

2. a. Discuss in detail the factors affecting the rate of reaction.
b. For thermal decomposition of ozone to oxygen, the following mechanism has been suggested:

$O_3 \longrightarrow O_2 + O$ (fast)

$O_3 + O \longrightarrow 2O_2$ (slow)

Using steady state approximation and other suitable approximations, derive the differential rate Law expression.

P.T.O.

c. Absorbance measured in a 1 cm diameter cuvette containing 0.2 mol dm^{-3} solution of A is 0.75 for 520 nm. Determine the decrease in intensity of the incident light. 5,5,5

3. a. The rate constant of a second-order reaction is 5.70 x $10^{-5} dm^3 mol^{-1} s^{-1}$ at 25°C and 1.64 x $10^{-4} dm^3 mol^{-1} s^{-1}$ at 40°C. Calculate the activation energy and the Arrhenius pre-exponential factor.

b. Show that for zero-order reaction half life is proportional to the initial concentration of reactant.

c. Define the term Quantum efficiency. Discuss the reasons for some reactions having low and some reactions having very high quantum efficiency. 5,5,5

4. a. The rate constant of zero-order reaction is 0.25 $mol^{-1} L h^{-1}$. Determine the initial concentration of the reactant if after 30 minutes its concentration is 0.075M?

b. The reaction

$$aA + bB \longrightarrow \text{Product}$$

is first order with respect to A and first order with respect to B. Write down its differential rate law and integrated rate equation for equal concentration of A and B. What is the unit of rate constant of the above reaction?

c. Explain the photophysical phenomenon of absorption, vibrational relaxation and inter system crossing with the help of the Jablonski Diagram. 5,5,5

5. a. The decomposition of A into the product has value of k as 4.5 s^{-1} at 10 °C and energy of activation 60 kJ mol^{-1}. At what temperature would k be 9.0 s^{-1}.

b. Explain briefly the Van't Hoff differential method for finding out the order and rate constant of a reaction.

c. Absorption of UV radiation, decomposes acetone according to the reaction:

$$(CH_3)_2CO \xrightarrow{h\upsilon} C_2H_6 + CO$$

The quantum yield of the reaction at 280 nm is 0.4. A sample of acetone absorbs monochromatic radiation at 280 nm at the rate of 7.50 x 10^{-3} Js^{-1}. Calculate the rate of formation of CO. 5,5,5

6. a. Calculate the concentration of reactant A after 40 min if the reaction A ——> B follow second order reaction and the rate constant is 1.4 x 10^{-2} mol^{-1} L min^{-1}. The initial concentration of A is 0.2 mol L^{-1}.

b. Write a short note on collision theory for bimolecular reaction and its limitations.

a. Write a short note on photosensitised photochemical reactions. 5,5,5