

International Institute of Information Technology, Hyderabad
Chemical kinetics and Reaction Dynamics - Monsoon 2023
Quiz : Oct 2023

Time: 45 mins

Max. marks=25

Evaluation will be based on brief explanation accompanying correct answers.

Answer each question coherently in one place - do not scatter the answer to disjoint sheets.

1. A laser is used to create a bright spot on a screen. The number of photons arriving on the spot follows zeroth order rate law. Show that the average number of photons that have arrived at a time t is what we get from macroscopic kinetics. Show that the average is the same as the variance.

Hints : Probability for number of photons arrived at time t is $P_n(t)$. Then $P_0(0) = ?$ and $P_{n \neq 0}(0) = ?$

From n photons at time t , transition probability for $(n + 1)$ th photon arriving in time Δt , $W_{n,n+1} = ?$ for zeroth order kinetics.

Formulate a master equation and solve it for $n = 0, 1, 2$. Generalise to any n .

To obtain the average, note that for positive integers n and m : $\sum_{n=0}^{\infty} \frac{f(n)}{(n-m)!} = \sum_{p=n-m=0}^{\infty} \frac{f(p)}{p!}$

Obtain the solution for rate law for zeroth order kinetics. Compare.

To obtain the variance, write $n^2 = n(n - 1) + 1$

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2. The rate constants for a gaseous reaction $A \rightarrow P$ are $3.40 \times 10^{-3} \text{ s}^{-1}$ and $4.40 \times 10^{-4} \text{ s}^{-1}$ at $[A] = 4.37 \times 10^{-4} \text{ mol dm}^{-3}$ and $1.00 \times 10^{-5} \text{ mol dm}^{-3}$, respectively. Use Lindemann-Hinshelwood mechanism to calculate rate constant for the activation step.

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3. A long polypeptide chain undergoes a transition from a helical conformation to a random coil. Consider a mechanism for a helix-coil transition that begins in the middle of the chain: $hhhh... \rightleftharpoons hchh... ; hchh... \rightleftharpoons cccc ...$ where h and c label an amino acid in a helical or coil part of the chain respectively. (a) Set up the rate equations for this mechanism. (b) Apply the steady-state approximation and show that, under these circumstances, the mechanism is equivalent to $hhhh ... \rightleftharpoons cccc...$

2 + 3

4. For the consecutive elementary reactions: $A \xrightarrow{k_a} I \xrightarrow{k_b} P$, (a) DERIVE a GENERAL expression for the concentration of the intermediate as a function of time and the initial concentration of A (method of solution of differential equation required).

(b) Find the maximal concentration of the intermediate in terms of other parameters.

2 + 2

5. Fill up the blanks in the following :

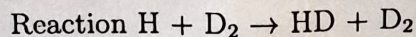
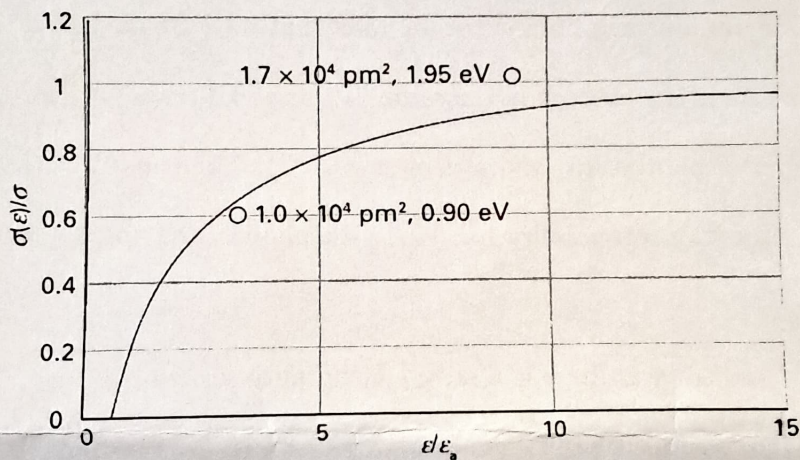
In nitrogen at 25°C and 1.0 bar, when $[N_2] \approx 40 \text{ mol m}^{-3}$, with $\sigma = 0.43 \text{ nm}^2$ and $m_{N_2} = 28.02 m_u$ the collision density is

$$= (4.3 \times \dots \text{m}^2) \times \sqrt{\frac{\dots \times (1.381 \times 10^{-23} \text{ JK}^{-1}) \times 298 \text{ K}}{\dots \times 28.02 \times (1.661 \times 10^{-27} \text{ kg})}} \times (\dots \text{mol}^{-1})^2 \times (\dots \text{mol.m}^{-3})^2 = 8.4 \times 10^{34} \dots$$

(units)

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6. In the plot below explain what the x- and y-axes are and write an algebraic expression for the curve :



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