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 $n^2 = n(n-1) + 1$ 5

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

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

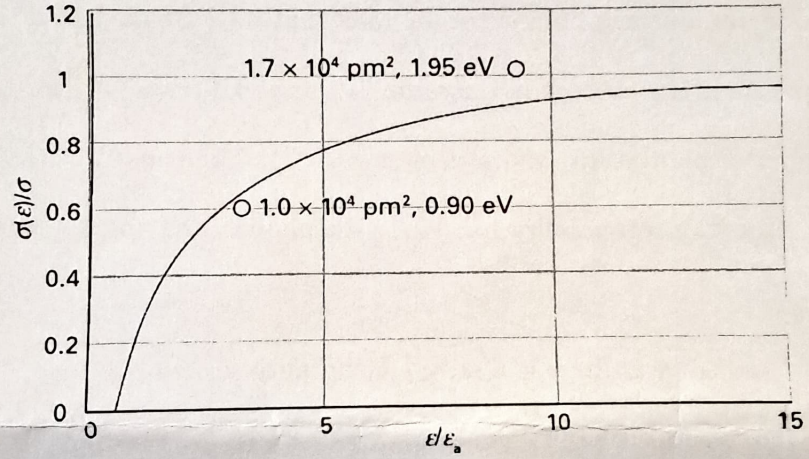
5. Fill up the blanks in the following :

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

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

(units) 3

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



Reaction $H + D_2 \rightarrow HD + D_2$ 3