

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.

Ans. Let the probability for number of photons arrived at time t be $P_n(t)$. Then $P_n(0) = \begin{matrix} 1 & \text{if } n = 0 \\ 0 & \text{if } n \neq 0 \end{matrix}$

The transition probability for $(n+1)$ th photon arriving in time Δt is, $W_{n,n+1} = k\Delta t \dots (\frac{1}{2})$ mark

In time Δt , the state of n molecules may become the state of $n+1$ molecules with probability $P_n(t)W_{n,n+1}$

$\therefore P_n(t + \Delta t) = P_n(t) + P_{n-1}(t)W_{n-1,n} - P_n(t)W_{n,n+1} \dots (\frac{1}{2})$ mark

or, $P_n(t + \Delta t) = P_{n-1}(t)k\Delta t - P_n(t)k\Delta t$

or, $\dot{P}_n = \frac{P_n(t+\Delta t) - P_n(t)}{\Delta t} = kP_{n-1}(t) - kP_n(t) \quad \forall n = 0, 1, \dots, n$

For $n = 0$

eqn. becomes, $\dot{P}_0(t) = -kP_0(t)$ with the initial condition $P_0(0) = 1 \dots (\frac{1}{2})$ mark

soln. : $P_0(t) = e^{-kt} \dots (\frac{1}{2})$ mark

For $n = 1$, $\dot{P}_1 = kP_0(t) - kP_1(t) = ke^{-kt} - kP_1(t)$ with the initial condition $P_1(0) = 0 \dots (\frac{1}{2})$ mark

use the method of integrating factors, multiply both sides by $e^{\int k dt} = e^{kt}$,

$$\implies \frac{d(e^{kt}P_1)}{dt} = k \implies e^{kt}P_1(t) - P_1(0) = kt$$

obtain $P_1(t) = kte^{-kt} \dots (\frac{1}{2})$ mark

for $n = 2$, $\dot{P}_2 = kP_1(t) - kP_2(t) = k^2te^{-kt} - kP_2(t)$

$$\implies \frac{d(e^{kt}P_2)}{dt} = k^2t \implies e^{kt}P_2(t) - P_2(0) = \frac{1}{2}k^2t^2$$

obtain $P_2(t) = \frac{1}{2}k^2t^2e^{-kt} = e^{-kt} \frac{(kt)^2}{2!}$.

Generalising, $P_n(t) = e^{-kt} \frac{(kt)^n}{n!}$ [such a distribution is called Poisson distribution] $\dots (\frac{1}{2})$ mark

$\therefore \langle n \rangle(t) = \sum_0^\infty nP_n = \sum_0^\infty ne^{-kt} \frac{(kt)^n}{n!} = kte^{-kt} \sum_0^\infty \frac{(kt)^{n-1}}{(n-1)!} = kte^{-kt} \sum_{m=n-1=0}^\infty \frac{(kt)^m}{m!} = kt \dots (\frac{1}{2})$ mark

The phenomenological kinetics is $\frac{dn}{dt} = k \implies n(t) = n(0) + kt = kt$, same as the statistical average $\dots (\frac{1}{2})$ mark

Variance = $\langle n^2 \rangle - \langle n \rangle^2$

$$\begin{aligned} \langle n^2 \rangle(t) &= \sum_0^\infty n^2 P_n = \sum_0^\infty n(n-1+1)P_n = e^{-kt} \sum_0^\infty n(n-1) \frac{(kt)^n}{n!} + \langle n \rangle = kte^{-kt} \sum_0^\infty \frac{(kt)^{n-1}}{(n-1)!} = \langle n \rangle + e^{-kt} (kt)^2 \sum_0^\infty \frac{(kt)^{n-2}}{(n-2)!} \\ &= \langle n \rangle + e^{-kt} (kt)^2 \sum_{p=n-2=0}^\infty \frac{(kt)^p}{p!} = \langle n \rangle + (kt)^2 = \langle n \rangle + \langle n \rangle^2 \dots (\frac{1}{2}) \text{mark} \end{aligned}$$

\therefore Variance = mean. This is a characteristic of Poisson distribution.

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.

Ans. activation : $A + A \xrightarrow{k_a} A^*$; deactivation : $A + A^* \xrightarrow{k'_a} 2A$; reaction : $A^* \xrightarrow{k_b} P$

$$\begin{aligned} \frac{1}{k} &= \frac{k'_a}{k_a k_b} + \frac{1}{k_a [A]} \dots (1) \text{mark} \\ \therefore \frac{1}{k_{a1}} - \frac{1}{k_{a2}} &= \frac{1}{k_a} \left(\frac{1}{[A]_1} - \frac{1}{[A]_2} \right) [\dots (\frac{1}{2}) \text{mark}] \\ \therefore k_a &= \frac{\frac{1}{[A]_1} - \frac{1}{[A]_2}}{\frac{1}{k_{a1}} - \frac{1}{k_{a2}}} = \frac{\frac{1}{1.00 \times 10^{-5}} - \frac{1}{4.37 \times 10^{-4}}}{\frac{1}{4.40 \times 10^{-4}} - \frac{1}{3.40 \times 10^{-3}}} [\dots (1) \text{mark}] = 10 \cdot \frac{43.7-1}{34-4.4} \cdot \frac{34 \times 4.4}{43.7} = 10 \times \frac{42.7}{29.6} \cdot \frac{34 \times 4.4}{43.7} = 49.384 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1} \dots (1) \text{mark for correct numerical value and (1)mark for units} \end{aligned}$$

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: $hhhh \dots \rightleftharpoons hchh \dots$; $hchh \dots \rightleftharpoons cccc \dots$ 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 $hhhh \dots \rightleftharpoons cccc \dots$

Ans. Let us say there are a total of n helices. In a sequence of steps for transition from a helical conformation to a coil conformation, let us consider the steps when a system with $m-1$ 'c' and $n-m+1$ 'h' is converted to m 'c' s and $n-m$ 'h' system.

Let us denote this as a conversion $X_{m-1} \xrightleftharpoons[k']{k} X_m$ and the next step is $X_m \xrightleftharpoons[k']{k} X_{m+1}$.

The rate equations are $\frac{d[X_m]}{dt} = k[X_{m-1}] - (k' + k)[X_m] + k'[X_{m+1}] \dots 2 \text{ marks}$

Notice that the rate constant for both elementary steps is taken to be k . This is a fair assumption.

Applying steady state, $\frac{d[X_m]}{dt} = 0$, we have $\frac{k[X_{m-1}] + k'[X_{m+1}]}{k' + k} = [X_m] \dots [A] \dots 1 \text{ marks}$

The overall rate is for the formation of n 'c' system from n 'h' system, $X_0 \xrightleftharpoons[k'_{\text{overall}}]{k_{\text{overall}}} X_n \dots 2 \text{ marks}$

\therefore overall rate = $k_{\text{overall}}[X_0] - k'_{\text{overall}}[X_n]$

Iterating Eq. [A], we can convert any $[X_m]$ to terms containing only X_0 and X_n

\therefore under these circumstances, the mechanism is equivalent to $hhhh \dots \rightleftharpoons cccc \dots$

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).

Ans. $\frac{d[A]}{dt} = -k_a[A] \dots (1)$

$\frac{d[I]}{dt} = k_a[A] - k_b[I] \dots (2)$

$[A] + [I] + [P] = [A]_0$

(1) $\implies [A] = [A]_0 e^{-k_a t} \dots (3) \dots (\frac{1}{2}) \text{mark}$

(2) & (3) $\implies \frac{d[I]}{dt} + k_b[I] = k_a[A]_0 e^{-k_a t} \dots (4) [\dots (1)] \text{mark}$

multiply both sides by $e^{k_b t} \implies \frac{d(e^{k_b t}[I])}{dt} = k_a[A]_0 e^{(k_b - k_a)t}$

integrate from 0 to t and get, $e^{k_b t} [I] = \frac{k_a}{k_b - k_a} [A]_0 [e^{(k_b - k_a)t} - 1]$

$$\Rightarrow [I] = \frac{k_a}{k_b - k_a} (e^{-k_a t} - e^{-k_b t}) [A]_0 \text{ (.....(1))mark}$$

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

$$\text{Ans. } \frac{d[I]}{dt} = 0 \Rightarrow k_a e^{-k_a t_{\max}} - k_b e^{-k_b t_{\max}}, \text{ or, } t_{\max} = \frac{1}{k_a - k_b} \ln \frac{k_a}{k_b} \text{ (.....(1))mark}$$

$$\text{Also, from eq. (4) above, } \frac{d[I]}{dt} = 0 \Rightarrow k_b [I]_{\max} = k_a [A]_0 e^{-k_a t_{\max}}$$

$$\therefore [I]_{\max} = \frac{k_a}{k_b} [A]_0 e^{-\frac{k_a}{k_a - k_b} \ln \frac{k_a}{k_b}} = \frac{k_a}{k_b} \left(\frac{k_a}{k_b} \right)^{-\frac{k_a}{k_a - k_b}} = \left(\frac{k_a}{k_b} \right)^{-\frac{k_b}{k_a - k_b}} \text{ (.....(1))mark}$$

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 $m_{N_2} = 28.02 \text{ m}_u$ the collision density is

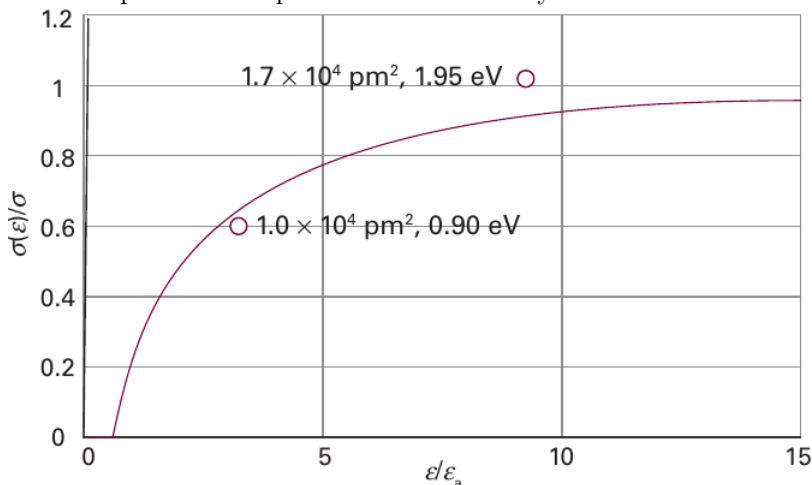
$$= (4.3 \times \dots \text{m}^2) \times \sqrt{\frac{\dots \times (1.381 \times 10^{-23} \text{ JK}^{-1}) \times 298 \text{ K}}{\dots \times 28.02 \times (1.661 \times 10^{-27} \text{ kg})}} \times (\dots \text{mol}^{-1})^2 \times (\dots \text{mol.m}^{-3})^2 = 8.4 \times 10^{34} \dots$$

(units)

$$\text{Ans. } (4.3 \times 10^{-19} \text{ m}^2) \times \sqrt{\frac{4 \times (1.381 \times 10^{-23} \text{ JK}^{-1}) \times 298 \text{ K}}{\pi \times 28.02 \times (1.661 \times 10^{-27} \text{ kg})}} \times (6.022 \times 10^{23} \text{ mol}^{-1})^2 \times (40 \text{ mol.m}^{-3})^2 = 8.4 \times 10^{34} \text{ m}^{-3} \text{ s}^{-1} \text{ (}\frac{1}{2}\text{mark)}$$

for each)

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



Ans. x-axis : relative kinetic energy of H and D₂ relative to the minimum energy required for a reactive collision, ε_a($\frac{1}{2}$)mark

y-axis : Variation of the reactive cross-section with energy relative to the hard sphere collision cross-section, $\sigma = \pi d^2$($\frac{1}{2}$)mark

$$\Rightarrow \sigma(\varepsilon) = \left(1 - \frac{\varepsilon_a}{\varepsilon}\right) \sigma \text{ (.....(2)marks)}$$