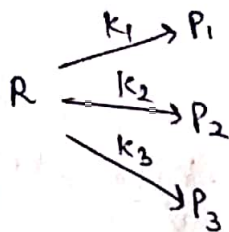


# Assignment 8 solution

1.



Rate of decay of R is given by  $-\frac{dR}{dt} = k_1[R] + k_2[R] + k_3[R]$

$$\frac{-d[R]}{dt} = (k_1 + k_2 + k_3)[R]$$

Integrating above eq<sup>n</sup> w/ t b/w limits  $t=0$  to  $t=t$

$$[R] = [R]_0 e^{-(k_1 + k_2 + k_3)t} \quad \text{--- (1)}$$

Similarly, rate expressions for all three products,

$$\frac{d[P_1]}{dt} = +k_1[R] = k_1[R]_0 e^{-(k_1 + k_2 + k_3)t}$$

$$\int_0^{[P_1]} d[P_1] = k_1[R]_0 \int_0^t e^{-(k_1 + k_2 + k_3)t} dt$$

$$[P_1] = \frac{k_1[R]_0}{-(k_1 + k_2 + k_3)} \left| e^{-(k_1 + k_2 + k_3)t} \right|_0^t$$

$$[P_1] = \frac{k_1[R]_0}{k_1 + k_2 + k_3} \left[ 1 - e^{-(k_1 + k_2 + k_3)t} \right]$$

writing  $k_1 + k_2 + k_3 = k$

$$[P_1] = \frac{k_1[R]_0}{k} \left[ 1 - e^{-kt} \right] \quad \text{--- (2)}$$

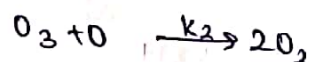
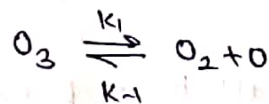
Similarly

$$[P_2] = \frac{k_2}{k} [1 - e^{-kt}] \quad \& \quad [P_3] = \frac{k_3}{k} [1 - e^{-kt}]$$

$$[P_1] : [P_2] : [P_3] = \frac{k_1}{k} [1 - e^{-kt}] : \frac{k_2}{k} [1 - e^{-kt}] : \frac{k_3}{k} [1 - e^{-kt}]$$

$$\underline{[P_1] : [P_2] : [P_3] = k_1 : k_2 : k_3}$$

3. Decomposition of ozone:



forward  $\frac{-d[O_3]}{dt} = \frac{d[O_2]}{dt} = \frac{d[O]}{dt} = k_1 [O_3]$

Backward  $-\frac{d[O_2]}{dt} = -\frac{d[O]}{dt} = \frac{d[O_3]}{dt} = k_{-1} [O_2][O]$

2nd Step  $-\frac{d[O_3]}{dt} = -\frac{d[O]}{dt} = \frac{k_2}{2} \frac{d[O_2]}{dt} = k_2 [O_3][O]$

applying S.S.A

$$\therefore \frac{d[O]}{dt} = 0$$

$$k_1 [O_3] - k_{-1} [O_2][O] - k_2 [O_3][O] = 0$$

$$[O] = \frac{k_1 [O_3]}{k_{-1} [O_2] + k_2 [O_3]} \quad \text{--- (1)}$$

Rate of Rxn = Rate of product formation

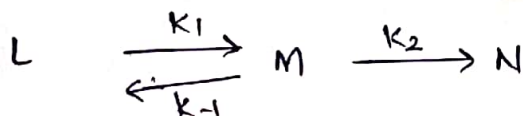
$$\begin{aligned}\therefore \frac{1}{2} \frac{d[O_2]}{dt} &= k_2 [O_3] [O] \\ &= k_2 [O_3] \times \frac{k_1 [O_2]}{k_2 [O_3] + k_{-1} [O_2]} \\ &= \frac{k_1 k_2 [O_3]^2}{k_2 [O_3] + k_{-1} [O_2]}\end{aligned}$$

Now, using the approximation  $k_{-1} [O_2] \ll k_2 [O_3]$

$$\frac{1}{2} \frac{d[O_2]}{dt} = \frac{k_1 k_2 [O_3]^2}{k_2 [O_3]} = k_1 [O_3]$$

$\therefore$  Rate of Rxn is 1st order w.r.t. ozone.

4.



$$k_1 = 10^5 \text{ L mol}^{-1} \text{ sec}^{-1}, k_2 = 10 \text{ sec}^{-1} \text{ \& } k_{-1} = 10^4 \text{ sec}^{-1}$$

$$\text{Rate of formation of N, } \frac{d[N]}{dt} = k_2 [M] \quad \text{--- (1)}$$

$$\frac{d[M]}{dt} = k_1 [L] - k_{-1} [M] - k_2 [M] = 0 \quad (\text{S.S.A})$$

$$\Rightarrow k_1 [L] = (k_{-1} + k_2) [M]$$

$$[M] = \frac{k_1}{k_{-1} + k_2} [L] \quad \text{--- (2)}$$

(2) in (1)

$$\frac{d[M]}{dt} = k_2[M] = \frac{k_2 \cdot k_1}{k_{-1} + k_2} [L]$$

$$\therefore k_{obs} = \frac{k_2 \cdot k_1}{k_{-1} + k_2}$$

Putting values of these rate constants

$$k_{obs} = \frac{10 \text{ sec}^{-1} \times 10^5 \text{ L mol}^{-1} \text{ sec}^{-1}}{10^4 \text{ sec}^{-1} + 10 \text{ sec}^{-1}}$$

$$= \frac{10^6 \text{ L mol}^{-1} \text{ sec}^{-1}}{10010 \text{ sec}^{-1}}$$

$$= \frac{1000000 \text{ L mol}^{-1} \text{ sec}^{-1}}{10010}$$

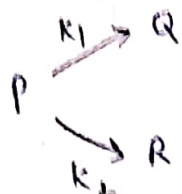
$$= 99.9 \text{ L mol}^{-1} \text{ sec}^{-1}$$

$\therefore$  Rate constant for formation of  $M = 99.9 \text{ L mol}^{-1} \text{ sec}^{-1}$ .



## Assignment 8 Solution

Q.



$$k_1 = 5 \times 10^{-2} \text{ min}^{-1}$$

$$k_2 = 15 \times 10^{-2} \text{ min}^{-1}$$

$$[P]_0 = 4 \text{ mol L}^{-1} \quad t = 10 \text{ minutes}$$

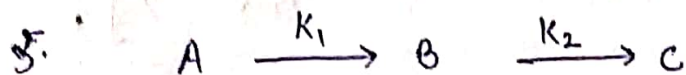
$$[R] = \frac{k_2}{k_1 + k_2} [P]_0 \left\{ 1 - e^{-(k_1 + k_2)t} \right\}$$

$$= \frac{15 \times 10^{-2} \text{ min}^{-1}}{(5 + 15) \times 10^{-2} \text{ min}^{-1}} \left\{ 1 - e^{-(20 \times 10^{-2}) \text{ min}^{-1} \times 10 \text{ min}} \right\} 4 \text{ mol L}^{-1}$$

$$= \frac{15}{20} \left[ 1 - e^{-2} \right] \times 4 \text{ mol L}^{-1}$$

$$= \frac{15}{5} \left[ 1 - e^{-2} \right] \times 4 \text{ mol L}^{-1} = 3[1 - 0.135] = 2.59 \text{ mol L}^{-1}$$

Concentration of product 'R' after 10 minutes is  $2.59 \text{ mol L}^{-1}$



(a) Derivation for expression for  $t_{\text{max}}$ .

$$\text{whet } [B] = \frac{k_1 [A]_0}{k_2 - k_1} \left[ e^{-k_1 t} - e^{-k_2 t} \right] \quad \text{--- (1)}$$

at  $t_{\text{max}}$ ,  $[B]$  is maximum  $\therefore \frac{d[B]}{dt} = 0$

Taking derivative of eq (1) & equating it to zero

B

$$\frac{d[B]}{dt} = \frac{k_1[A_0]}{k_2 - k_1} \left[ e^{-k_1 t} (-k_1) + e^{-k_2 t} (k_2) \right] = 0$$

$$\Rightarrow k_2 e^{-k_2 t} = k_1 e^{-k_1 t}$$

$$\frac{e^{-k_2 t}}{e^{-k_1 t}} = \frac{k_1}{k_2}$$

$$e^{(k_1 - k_2)t} = \frac{k_1}{k_2}$$

taking natural log both sides

$$(k_1 - k_2)t = \ln \frac{k_1}{k_2}$$

$$\therefore t_{\max} = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2}$$

(b) Expression for  $[B]_{\max}$

at  $t = t_{\max}$ , B reaches its maximum value.

$$\therefore [B]_{\max} = \frac{k_1 [A_0]}{k_2 - k_1} \left\{ \exp\left(\frac{-k_1 \ln(k_1/k_2)}{k_1 - k_2}\right) - \exp\left(\frac{-k_2 \ln(k_1/k_2)}{k_1 - k_2}\right) \right\}$$

(c) given  $k_1 = \frac{\ln 2}{4}$  &  $k_2 = \frac{\ln 2}{2}$

$$t_{\max} = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2} \quad \text{--- (1)}$$

$$k_1 - k_2 = \frac{\ln 2}{4} - \frac{\ln 2}{2}$$

$$= \ln 2 \left( \frac{1}{4} - \frac{1}{2} \right)$$

$$= -\frac{1}{4} \ln 2 \quad \text{--- (2)}$$

$$\frac{k_1}{k_2} = \frac{\ln 2}{4} \times \frac{2}{\ln 2} = \frac{1}{2} \quad -(2)$$

(2) & (3) in (1)

$$t_{\max} = \frac{-4}{\ln 2} \ln \frac{1}{2}$$

$$= \frac{-4}{\ln 2} \ln(2)^{-1}$$

$$= \frac{+4}{\ln 2} \ln 2 = 4 \text{ minutes}$$