Assignment 8 solution

1.

$$R \xrightarrow{k_1} P_1$$
$$R \xrightarrow{k_2} P_2$$
$$R \xrightarrow{k_3} P_3$$

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^n wrt t b/w limits $t=0$ & $t=t$

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

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 $k_1+k_2+k_3 = k$

$$\boxed{[P_1] = \frac{k_1[R_0]}{k}\left[1-e^{-kt}\right]} \quad \text{—(2)}$$

Similarly

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

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

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

3. Decomposition of ozone:

$$O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O$$

$$O_3 + O \xrightarrow{k_2} 2O_2$$

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

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

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

applying S.S.A

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

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

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

Rate of Rx^n = Rate of product formation

$$\therefore \frac{1}{2}\frac{d[O_2]}{dt} = k_2[O_3][O]$$

$$= k_2[O_3] \times \frac{k_1[O_3]}{k_2[O_3] + k_{-1}[O_2]}$$

$$= \frac{k_1k_2[O_3]^2}{k_2[O_3] + k_{-1}[O_2]}$$

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

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

$\therefore$ Rate of Rx^n is Ist order wrt ozone.

4.

$$L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M \xrightarrow{k_2} N$$

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

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

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

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

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

(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

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

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

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

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

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

Assignment 8 Solution

4.

$$P \xrightarrow{k_1} Q \qquad P \xrightarrow{k_2} R$$

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

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

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

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

$$= \frac{15 \times \cancel{10^{-2}}\ min^{-1}}{(5+15)\times \cancel{10^{-2}}\ min^{-1}}\left\{1 - e^{-(20\times10^{-2})\,\cancel{min^{-1}} \times 10\,\cancel{min}}\right\} 4\ mol\,L^{-1}$$

$$= \frac{15}{20}\left[1 - e^{-200\times10^{-2}}\right] \times 4\ mol\,L^{-1}$$

$$= \frac{\cancel{15}^{\,3}}{\cancel{20}_{\,\cancel{5}}}\left[1-e^{-2}\right] \times \cancel{4}\ mol\,L^{-1} = 3[1-0.135] = 2.59\ mol\,L^{-1}$$

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

5. $\quad A \xrightarrow{k_1} B \xrightarrow{k_2} C$

(a) Derivation for expression for tmax.

w.k.t $\quad [B] = \dfrac{k_1\ [A]_0}{k_2 - k_1}\left[e^{-k_1 t} - e^{-k_2 t}\right]$ —— ①

at tmax, [B] is maximum $\therefore \dfrac{d[B]}{dt} = 0$

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

$$\frac{d[B]}{dt} = \frac{k_1[A_0]}{k_2-k_1}\left[e^{-k_1t}(-k_1) + e^{-k_2t}(k_2)\right] = 0$$

$$\Rightarrow \quad k_2 e^{-k_2t} = k_1 e^{-k_1t}$$

$$\frac{e^{-k_2t}}{e^{-k_1t}} = \frac{k_1}{k_2}$$

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

taking natural log both sides

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

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

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

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

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

(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)

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

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

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