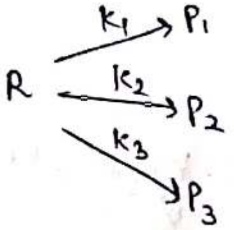
Assignment 8 solution

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

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

Similarly, rate expressions for all three products,

$$\frac{d[P_1]}{dt} = +k_1[R] = k_1[R_0]e^{-(k_1+k_2+k_3)t}$$

$$\int_0^{[P_1]} d[P_1] = k_1[R_0]\int_0^t e^{-(k_1+k_2+k_3)t}\,dt$$

$$[P_1] = \frac{k_1[R_0]}{-(k_1+k_2+k_3)}\Big| e^{-(k_1+k_2+k_3)t}\Big|_0^t$$

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

writing $k_1+k_2+k_3 = k$

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

Similarly

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

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

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

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

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

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

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

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

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)

$$\frac{d[M]}{dt} = K_2[M] = \frac{K_2 \cdot K_1}{K_{-1}+K_2}[L]$$

$$\therefore \quad K_{obs} = \frac{K_2 \cdot K_1}{K_{-1}+K_2}$$

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

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4.
$$P \xrightarrow{k_1} Q \qquad P \xrightarrow{k_2} R$$

$k_1 = 5\times10^{-2}\ \text{min}^{-1}$

$k_2 = 15\times10^{-2}\ \text{min}^{-1}$

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

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

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

$$= \frac{15}{20}\left[1-e^{-20\times10^{-2}}\right]\times4\,\text{mol}\,L^{-1}$$

$$= \frac{15}{20}\left[1-e^{-2}\right]\times4\,\text{mol}\,L^{-1} = 3[1-0.135] = 2.59\,\text{mol}\,L^{-1}$$

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

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

(a) Derivation for expression for t_{max}.

we kt $\quad [B] = \dfrac{k_1\,[A]_0}{k_2-k_1}\left[e^{-k_1t} - e^{-k_2t}\right]$ —— (1)

at t_{max}, [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)

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

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

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