SOLUTIONS

EXERCISE # S-II

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1. Rate = $k[A]^2[B]$

Given : $[A] = 0.2$ M

$[B] = 2 \times 10^3$ M

Since [B] is very large in comparison to [A]

therefore [B] will remain almost constant with the progress of reaction.

$\therefore$ Rate = $k'[A]^2$ where $k' = k[B]$

$= 5 \times 10^{-5} \times 2 \times 10^3 = 0.1$

$\therefore$ For 2^{nd} order reaction

$$t_{1/2} = t_{1/2} = \frac{1}{k'[A]}$$

$$= \frac{1}{0.1 \times 0.2} = 50 \text{ min.}$$

2. $2P_{(g)} \longrightarrow 4Q_{(g)} + R_{(g)} + S(l)$

$t = 0$	P^o	0	0	0
$t = 30$ min	$P^o - x$	$2x$	$\frac{x}{2}$	32.2 mmHg
$t = \infty$ min	0	$2P^o$	$\frac{P^o}{2}$	32.2 mmHg

At $t = \infty$

Total pressure = $2P^o + \frac{P^o}{2} + 32.5 = 617 \Rightarrow P^o = 233.8$ mm.

At $t = 30$ min

Total pressure = $P^o - x + 2x + \frac{x}{2} + 32.5 = 317 \Rightarrow x = 33.8$ mm.

$$\therefore \quad k = \frac{1}{t}\ln\left(\frac{P^o}{P^o - x}\right) = \frac{1}{30}\ln\left(\frac{233.8}{233.8 - 33.8}\right) = 5.2 \times 10^{-3} \text{ min.}$$

After $t = 75$ min.

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$x = P^{o}(1 - e^{-kt}) = 233.8(1 - e^{-5.2\times10^{-3}\times75}) = 75.56$ mmHg

$\therefore$ Total pressure $= P^{o} - x + 2x + \dfrac{x}{2} + 32.5 = 379.64$ mmHg

3. $A \longrightarrow B + C$

	A	B	C
t = 0	a_0 M	0	0
t = 20 min	$a_0 - x$	x	x
t = ∞	0	a_0	a_0

At $t = \infty$

Rotation $r_\infty = a_0 \times 40 + a_0 \times (-80) = -20 \Rightarrow a_0 = 0.5$

At $t = 20$ min

Rotation $r_t = (a_0 - x) \times 60 + x \times 40 + x \times (-80) = 5$

$60 \times a_0 - 100\,x = 5 \Rightarrow x = 0.25$

$\because$ At $t = 20$ min $x = \dfrac{a_0}{2}$

$\therefore$ Half life = 20 min

4.

$$A \begin{cases} \xrightarrow{k_1} B \\ \xrightarrow{k_2} C \end{cases} \quad \& \quad \frac{k_1}{k_2} = \frac{1}{9}$$

t=0 a_0

t=1hr. a_0

$\therefore$ $k_2 = 9\,k_1$

$= 9 \times 1.3 \times 10^{-5}\ \text{sec}^{-1}$

After $t = 1$hr.

$x = [A]_0\left(1 - e^{-(k_1+K_2)t}\right)$

$= 0.374\, a_0$

$$\therefore \quad \frac{[C]}{[A]} = \frac{\dfrac{k_2}{k_1 + k_2} \times x}{(a_0 - x)} = \frac{\dfrac{9}{10} \times 0.374}{(a_0 - 0.347\, a_0)}$$

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5. Rate = k_3[CoCl] [Cl_2] ...(1)

$\because \quad \frac{k_2}{k_{-2}} = \frac{[CoCl]}{[Cl][Co]}$ (from 2nd reaction equilibrium)

$\therefore \quad [CoCl] = \frac{k_2}{k_{-2}}[Cl]\,[Co]$ ...(2)

$\because \quad \frac{k_1}{k_{-1}} = \frac{[Cl]^2}{[Cl_2]}$

$\therefore \quad [Cl] = \sqrt{\frac{k_1}{k_{-1}}[Cl_2]}$ ...(3)

$\therefore$ From (1), (2) & (3)

Rate $= k_3 \frac{k_2}{k_{-2}} \times \sqrt{\frac{k_1}{k_{-1}}} \times [Co] \times [Cl_2]$

$= k_3 \times \frac{k_2}{k_{-2}} \times \sqrt{\frac{k_1}{k_{-1}}} \times [Co] \times [Cl_2]^{3/2}$

6. At T = 43.3°C

$\log k = \frac{3163}{(273+43.3)} + 12 = 28$

$k = 10^{22}\ M^{-1}\ min^{-1}$

For 2nd order reaction

$t_{1/2} = \frac{1}{a_0 \times k} = \frac{1}{0.001 \times 10^{22}} = 10^{-19}\ min^{-1}$

7. For reaction (i)

$A \longrightarrow$ product

$\frac{k_{300}}{k_{310}} = \frac{1}{2}$ & $k_{310} = \frac{0.693}{30} = 0.0231\ min^{-1}$

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$\because \quad \ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$

$\ln(2) = \frac{E_a}{8.314}\left[\frac{1}{300} - \frac{1}{310}\right]$

$E_a = 53.59$ kJ/mole

For reaction (ii)

$\left(k_{(ii)}\right)_{310K} = \left(k_{(i)}\right)_{310K} \times 2 = 0.0231 \times 2 \;\&\; E_{a(ii)} = \frac{E_{a(i)}}{2} = \frac{53.59}{2}$ kJ / mole

$\therefore \quad \ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$

$\ln\left(\frac{0.0231 \times 2}{k_1}\right) = \frac{53.59}{2 \times 8.314}\left[\frac{1}{300} - \frac{1}{310}\right]$

$k = 0.0327 \text{ min}^{-1}$

8. $\because$ Rate α k α $\frac{1}{\text{time}}$

$\therefore \quad \frac{k_{20^\circ C}}{k_{3^\circ C}} = \frac{3 \times 64}{64} = 3$

(a) $\because \quad \ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$

$\therefore \quad \ln(3) = \frac{E_a}{8.314}\left[\frac{1}{276} - \frac{1}{293}\right]$

$E_a = 43.45$ kJ/mole

(b) $\ln\left(\frac{k_2}{k_1}\right) = \ln\left(\frac{t_1}{t_2}\right) = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$

$\ln\left(\frac{64}{t_2}\right) = \frac{43.45 \times 10^3}{8.314}\left[\frac{1}{293} - \frac{1}{313}\right]$

$\therefore \quad t_2 = 20.47$ hr.

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9.

$$\begin{array}{lccc} & & \xrightarrow{k_1} & B \\ t=0 & \underset{1\,mole}{A} & & \frac{k_1}{k_1+k_2}\times 1\,mole \\ & & \xrightarrow{k_2} & C \\ t=\infty & 0 & & \frac{k_2}{k_1+k_2}\times 1\,mole \end{array}$$

$$\therefore \quad E_{a_{overall}} = \frac{k_1}{k_1+k_2}E_{a_1} + \frac{k_2}{k_1+k_2}E_{a_2}$$

10. $$E_{a_{overall}} = \frac{k}{k+2k+\ldots}\times E + \frac{2k}{k+2k+\ldots}\times 2E + \ldots$$

$$= \frac{2}{n(n+1)}\times E + \frac{2\times 2}{n(n+1)}\times 2E + \ldots = \frac{2E}{n(n+1)} + \frac{8}{n(n+1)}E + \ldots = \frac{(2n+1)}{3}E$$