



SOLUTIONS

EXERCISE # S-II

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

Given : $[A] = 0.2 \text{ M}$

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

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

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

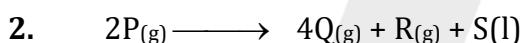
∴ Rate = $k'[A]^2$ where $k' = k[B]$

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

∴ For 2nd order reaction

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

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



$t = 0$	P°	0	0	0
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$t = 30 \text{ min}$	$P^\circ - x$	$2x$	$\frac{x}{2}$	32.2 mmHg
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$t = \infty \text{ min}$	0	$2P^\circ$	$\frac{P^\circ}{2}$	32.2 mmHg
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At $t = \infty$

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

At $t = 30 \text{ min}$

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

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

After $t = 75 \text{ min.}$



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$$x = P^o(1 - e^{-kt}) = 233.8(1 - e^{-5.2 \times 10^{-3} \times 75}) = 75.56 \text{ mmHg}$$

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



$$t = 0 \quad a_0 \text{ M} \quad 0 \quad 0$$

$$t = 20 \text{ min} \quad a_0 - x \quad x \quad x$$

$$t = \infty \quad 0 \quad a_0 \quad a_0$$

At $t = \infty$

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

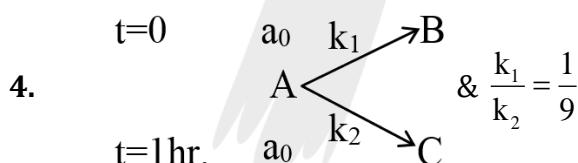
At $t = 20 \text{ min}$

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

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

$$\therefore \text{At } t = 20 \text{ min} \quad x = \frac{a_0}{2}$$

\therefore Half life = 20 min



$$\therefore k_2 = 9k_1$$

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

After $t = 1\text{hr.}$

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

$$= 0.374 a_0$$

$$\therefore \frac{[C]}{[A]} = \frac{k_2}{k_1 + k_2} \times x = \frac{9}{10} \times 0.374$$

$$= \frac{(a_0 - 0.347 a_0)}{(a_0 - x)}$$



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

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

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

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

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

∴ From (1), (2) & (3)

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

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

6. At $T = 43.3^\circ C$

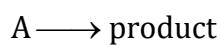
$$\log k = \frac{3163}{(273+43.3)} + 12 = 28$$

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

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)



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



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

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

$$E_a = 53.59 \text{ kJ/mole}$$

For reaction (ii)

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

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

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

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

8. \therefore Rate $\propto k \propto \frac{1}{\text{time}}$

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

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

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

$$E_a = 43.45 \text{ kJ/mole}$$

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

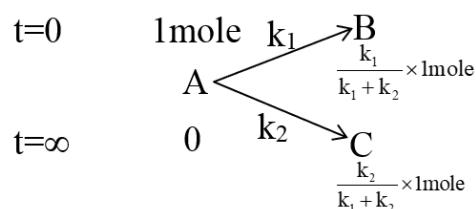
$$\ln\left(\frac{64}{t_2}\right) = \frac{43.45 \times 10^3}{8.314} \left[\frac{1}{293} - \frac{1}{313} \right]$$

$$\therefore t_2 = 20.47 \text{ hr.}$$



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9.



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

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

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