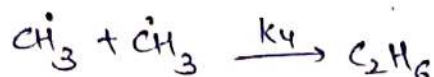
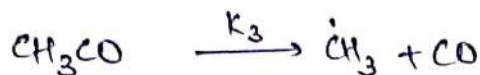
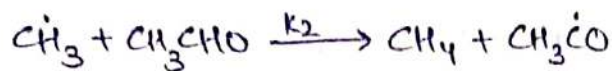
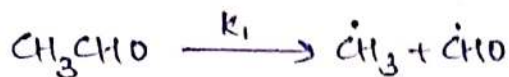


Assignment - 9 Solutions

1. Pyrolysis of acetaldehyde follows these elementary steps



Expression for decomposition of CH_3CHO :

$$-\frac{d[\text{CH}_3\text{CHO}]}{dt} = k_1[\text{CH}_3\text{CHO}] + k_2[\dot{\text{C}}\text{H}_3][\text{CH}_3\text{CHO}] \quad \text{--- (1)}$$

We have to calculate concentration of $\dot{\text{C}}\text{H}_3$ using steady state approximation.

$$\frac{d[\dot{\text{C}}\text{H}_3]}{dt} = k_1[\text{CH}_3\text{CHO}] - k_2[\dot{\text{C}}\text{H}_3][\text{CH}_3\text{CHO}] + k_3[\text{CH}_3\dot{\text{C}}\text{O}] - 2k_4[\dot{\text{C}}\text{H}_3]^2 \stackrel{\approx}{=} 0 \quad \text{(2)}$$

We again write expression for calculating $\text{CH}_3\dot{\text{C}}\text{O}$ intermediate concentration.

$$\frac{d[\text{CH}_3\dot{\text{C}}\text{O}]}{dt} = k_2[\dot{\text{C}}\text{H}_3][\text{CH}_3\text{CHO}] - k_3[\text{CH}_3\dot{\text{C}}\text{O}] = 0 \quad \text{--- (3)}$$

$$\text{From (3)} \quad [\text{CH}_3\dot{\text{C}}\text{O}] = \frac{k_2[\dot{\text{C}}\text{H}_3][\text{CH}_3\text{CHO}]}{k_3} \quad \text{--- (4)}$$

(4) in (2)

$$k_1[\text{CH}_3\text{CHO}] - k_2[\dot{\text{C}}\text{H}_3][\text{CH}_3\text{CHO}] + k_3 \cdot \frac{k_2[\dot{\text{C}}\text{H}_3][\text{CH}_3\text{CHO}]}{k_3} - 2k_4[\dot{\text{C}}\text{H}_3]^2 = 0$$

$$k_1[\text{CH}_3\text{CHO}] = 2k_4[\dot{\text{C}}\text{H}_3]^2$$

$$[CH_3] = \frac{k_1}{2k_4} \sqrt{[CH_3CHO]} \quad \text{--- (5)}$$

Put (5) in (1)

$$-\frac{d[CH_3CHO]}{dt} = k_1 [CH_3CHO] + \frac{k_2 k_1}{2k_4} [CH_3CHO]^{1/2}$$

2. According to Langmuire Adsorption isotherm

(i)

$$\theta = \frac{KP}{1+KP} \quad \text{--- (1)}$$

Reciprocating above equation

$$\frac{1}{\theta} = \frac{1}{KP} + 1 \quad \text{--- (2)}$$

Given $v \rightarrow$ volume of gas adsorbed on surface of solid.

Let $V \rightarrow$ volume corresponding to total coverage.

$$\therefore \theta (\text{fractional coverage}) = \frac{v}{V} \quad \text{--- (3)}$$

Put (3) in (2)

$$\frac{V}{v} = \frac{1}{KP} + 1 \quad \text{--- (4)}$$

we have to plot P/v graph versus P , \therefore we eliminate from V by multiplying eq. (4) by $\frac{P}{V}$ we get LHS

$$\frac{P \times V}{V \times v} = \frac{1}{KP} \times \frac{P}{V} + \frac{P}{BV} \Rightarrow \frac{P}{v} = \frac{1}{KV} + \frac{P}{V} \quad \text{--- (5)}$$

Thus, eq. (5) is straight line equation, where plot of $\frac{P}{v}$ versus P gives straight line, slope = $\frac{1}{V}$ & intercept = $\frac{1}{KV}$

(ii) We have to show for small coverages plot of $\ln\left(\frac{\theta}{P}\right)$ vs θ is also a straight line.

$$\text{from eq. (1)} \quad \theta(1+KP) = KP$$

$$\theta + KP\theta = KP$$

$$\theta = KP - KP\theta$$

$$\theta = KP(1 - \theta)$$

$$\frac{\theta}{P} = K(1 - \theta)$$

Taking natural log both sides

$$\ln\left(\frac{\theta}{P}\right) = \ln K + \ln(1 - \theta)$$

If $\theta \ll 1$, mathematically $\ln(1 - \theta) \approx -\theta$ so we get

$$\ln\left(\frac{\theta}{P}\right) = \ln K - \theta$$

So, plot of $\ln\left(\frac{\theta}{P}\right)$ versus θ will also be a straight line with slope = -1 & intercept = $\ln K$.

$$3. \quad K = 1.25 \text{ kPa}^{-1}, \quad \theta = 20\% = 0.2$$

Surface coverage (θ) is given as

$$\theta = \frac{KP}{1+KP}$$

Solving above equation for pressure

$$\theta(1+KP) = KP$$

$$P = \frac{\theta}{K(1-\theta)} = \frac{0.2}{1.25 \times 10^3 \text{ Pa}^{-1} (1-0.2)}$$

$$P = 2 \times 10^{-4} \text{ Pa}$$

4. $V_{\text{mono}} = 130 \text{ cm}^3$ (monolayer volume)

22.4 L of any gas = 1 mol of its molecules

$$\therefore \text{no. of molecules present in } V_{\text{mono}} = \frac{6.022 \times 10^{23} \text{ mol}^{-1} \times 130 \times 10^{-3} \text{ dm}^3}{22.4 \text{ dm}^3 \text{ mol}^{-1}}$$
$$= 3.49 \times 10^{21}$$

Area of cross-section of one molecule = 0.162 nm^2
 $= 0.162 \times 10^{-18} \text{ m}^2$

\therefore area covered by 3.49×10^{21} molecules = $0.162 \times 10^{-18} \text{ m}^2 \times 3.49 \times 10^{21}$
 $= 565.38 \text{ m}^2$

5. (1) Adsorption of O_3 without dissociation



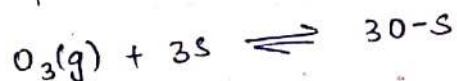
$$\theta = \frac{bP_{\text{O}_3}}{1 + bP_{\text{O}_3}}$$

(2) Adsorption via dissociation into O_2 & O



$$\theta = \frac{(bP_{\text{O}_3})^{1/2}}{1 + (bP_{\text{O}_3})^{1/2}}$$

(3) Adsorption via dissociation into $\text{O} + \text{O} + \text{O}$



$$\theta = \frac{(bP_{\text{O}_3})^{1/3}}{1 + (bP_{\text{O}_3})^{1/3}}$$

6. Langmuir adsorption isotherm:

$$\theta = \frac{KP}{1+KP} \quad (1)$$

mass adsorbed, $m_1 = 0.63 \text{ mg}$ at $P_1 = 36.0 \text{ kPa}$

$m_2 = 0.21 \text{ mg}$ at $P_2 = 4.0 \text{ kPa}$

we have to calculate fractional coverage θ_1 & θ_2 at P_1 & P_2

$$\theta = \frac{m_{\text{adsorbed}}}{m_{\text{mono}}}, \text{ from (1) } K = \frac{\theta}{P(1-\theta)}$$

Setting expression for K at one pressure = K at 2nd pressure

$$\frac{\theta_1}{P_1(1-\theta_1)} = \frac{\theta_2}{P_2(1-\theta_2)}$$

$$\frac{\frac{m_1}{m_{\text{mono}}}}{P_1 \left(1 - \frac{m_1}{m_{\text{mono}}}\right)} = \frac{\frac{m_2}{m_{\text{mono}}}}{P_2 \left(1 - \frac{m_2}{m_{\text{mono}}}\right)}$$

$$\text{So, } \frac{P_1(m_{\text{mono}} - m_1)}{m_1} = \frac{P_2(m_{\text{mono}} - m_2)}{m_2}$$

$$(m_{\text{mono}} P_1 - P_1 m_1) m_2 = m_1 (P_2 m_{\text{mono}} - P_2 m_2)$$

$$m_{\text{mono}} = \frac{P_1 - P_2}{\frac{P_1}{m_1} - \frac{P_2}{m_2}} = \frac{(36 - 4) \text{ kPa}}{\left(\frac{36}{0.63} - \frac{4}{0.21}\right) \text{ kPa mg}^{-1}}$$

$$= 0.84 \text{ mg}$$

$$\theta_1 = \frac{0.63}{0.84} = 0.75$$

$$\theta_2 = \frac{0.21}{0.84} = 0.25$$