1. Pyrolysis of acetaldehyde follows these elementary steps

$$CH_3CHO \xrightarrow{k_1} \dot{C}H_3 + \dot{C}HO$$

$$\dot{C}H_3 + CH_3CHO \xrightarrow{k_2} CH_4 + CH_3\dot{C}O$$

$$CH_3\dot{C}O \xrightarrow{k_3} \dot{C}H_3 + CO$$

$$\dot{C}H_3 + \dot{C}H_3 \xrightarrow{k_4} C_2H_6$$
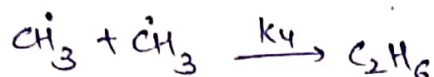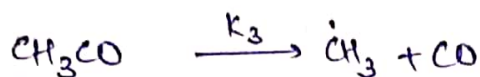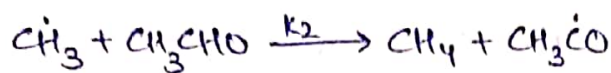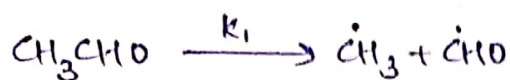
Expression for decomposition of CH_3CHO:

$$- \frac{d[CH_3CHO]}{dt} = k_1[CH_3CHO] + k_2[\dot{C}H_3][CH_3CHO] \quad - \quad (1)$$

we have to calculate concentration of $\dot{C}H_3$ using steady state approximation.

$$\frac{d[\dot{C}H_3]}{dt} = k_1[CH_3CHO] - k_2[\dot{C}H_3][CH_3CHO] + k_3[CH_3\dot{C}O] - 2k_4[\dot{C}H_3]^2 \simeq 0 \quad (2)$$

We again write expression for calculating $CH_3\dot{C}O$ intermediate concentration.

$$\frac{d[CH_3\dot{C}O]}{dt} = k_2[\dot{C}H_3][CH_3CHO] - k_3[CH_3\dot{C}O] = 0 \qquad\qquad - (3)$$

From (3) $\qquad [CH_3\dot{C}O] = \dfrac{k_2[\dot{C}H_3][CH_3CHO]}{k_3} \qquad\qquad - (4)$

(4) in (2)

$$k_1[CH_3CHO] - k_2[\dot{C}H_3][CH_3CHO] + k_3 \cdot \frac{k_2}{k_3}[\dot{C}H_3][CH_3CHO] - 2k_4[\dot{C}H_3]^2 = 0$$

$$k_1[CH_3CHO] = 2k_4[\dot{C}H_3]^2$$

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

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 Langmuir Adsorption isotherm

(i)

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

Reciprocating above equation

$$\frac{1}{\theta} = \frac{1}{KP} + 1 \qquad - ②$$

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

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

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

Put (3) in (2)

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

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

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

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.

from eq. (a) $\theta(1+KP) = KP$

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

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

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

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

Taking natural log both sides

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

If $\theta \ll 1$, mathematically $\ln(1-\theta) \simeq -\theta$ 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. $K = 1.25 \, kPa^{-1}$, $\theta = 20\% = 0.2$

Surface coverage (θ) is given as

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

Solving above equation for pressure

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

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

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

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

$22.4 L$ of any gas $= 1$ mol of its molecules

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

$$= 3.49 \times 10^{21}$$

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

$$= 0.162 \times 10^{-18} \text{ m}^2$$

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

$$= 565.38 \text{ m}^2$$
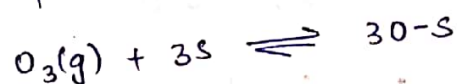
5. (1) Adsorption of O_3 without dissociation

$$O_3(g) + S \rightleftharpoons O_3 - S$$

$$\theta = \dfrac{b P_{O_3}}{1 + b P_{O_3}}$$

(2) Adsorption via dissociation into O_2 to

$$O_3(g) + 2S \rightleftharpoons O_2 - S + O - S$$

$$\theta = \dfrac{(b P_{O_3})^{1/2}}{1 + (b P_{O_3})^{1/2}}$$

(3) Adsorption via dissociation into $O + O + O$

$$O_3(g) + 3S \rightleftharpoons 3O - S$$

$$\theta = \dfrac{(b P_{O_3})^{1/3}}{1 + (b P_{O_3})^{1/3}}$$

5

6. Langmuir adsorption isotherm:

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

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

$\qquad\qquad m_2 = 0.21\,mg$ at $P_2 = 4.0\,kPa$

we have to calculate fractional coverage $\theta_1 \& \theta_2$ at $P_1 \& P_2$

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

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

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

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

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

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

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

$$\approx 0.84\,mg$$

$\theta_1 = \dfrac{0.63}{0.84} = 0.75$ & $\theta_2 = \dfrac{0.21}{0.84} = 0.25$