FREUNDLICH ADSORPTION ISOTHERM

- Empirical equation describing the variation of extent of adsorption with pressure at constant temperature.
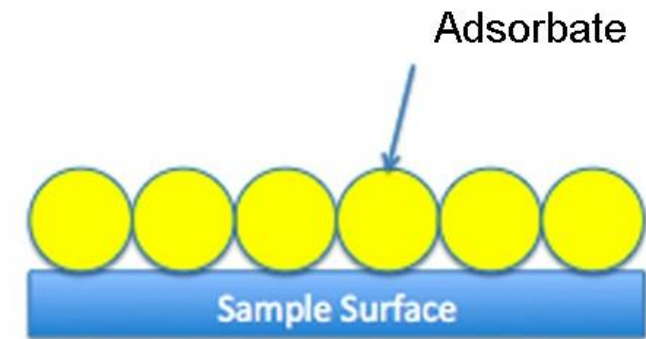
$$\frac{x}{m} = kP^{1/n}$$

x – mass of the gas adsorbed at equilibrium.

m – mass of the adsorbent

k and n are constants depending on adsorbent-adsorbate pair.

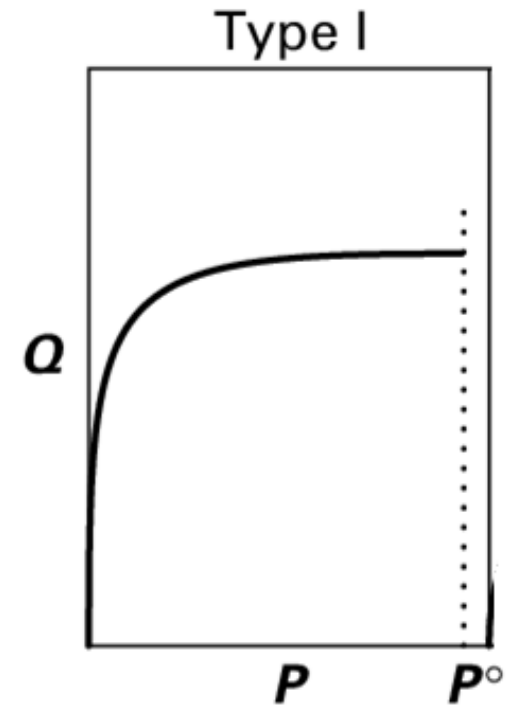- *Explain the Type I adsorption isotherm.*

Adsorbate

Sample Surface

- at low P – the extent of adsorption is proportional to P

$$\frac{x}{m} \propto P^1$$

- Beyond saturation pressure P_s, extent of reaction is independent of P

$$\frac{x}{m} \propto P^0$$

- Experimental value shows deviation from linearity.

- Freundich isotherm is only approximate and suitable only at moderate pressures.
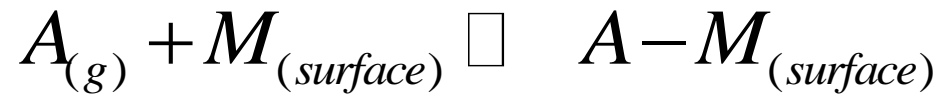


Type I

LANGMUIR ADSORPTION ISOTHERM

- Adsorption cannot proceed beyond monolayer coverage.

- All adsorption sites are equivalent.

- The adsorbed molecules have no lateral interaction with other adsorbed

  molecules.

- *A kinetic equilibrium is established between the condensation and*

  evaporation of gas molecules.

$$A_{(g)} + M_{(surface)} \rightleftharpoons A-M_{(surface)}$$
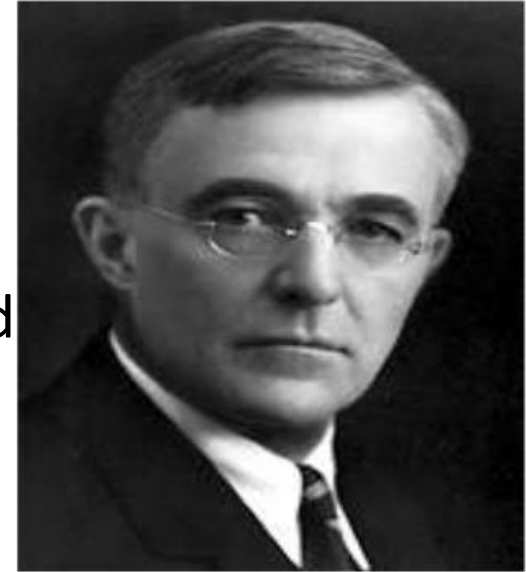
   $k_1 -$ *rate constant of condensation* $k_2 -$ *rate constant of evaporation*
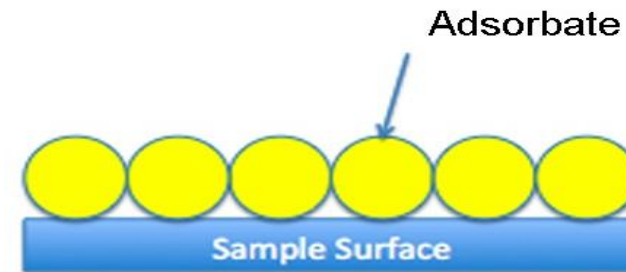
- *The rate of condensation is given by:*

   $$r_c = k_1 P(1-\theta)$$

Adsorbate

Sample Surface

Irving Langmuir

$\theta = $ fractional surface coverage

$$\theta = \frac{\text{number of adsorption sites occupied}}{\text{number of adsorption sites available}}$$

$$\theta = \frac{V}{V_m} = \frac{\text{volume of adsorbate adsorbed}}{\text{volume of monolayer coverage}}$$

- *The rate of evaporation is given by:*

$$r_e = k_2 \theta$$

At equilibrium: $r_c = r_e$

$$k_1 P(1-\theta) = k_2 \theta$$

$$\theta = \frac{k_1 P}{k_2 + k_1 P} \quad \Longrightarrow \quad \theta = \frac{\left(k_1/k_2\right)P}{1+\left(k_1/k_2\right)P} \quad \Longrightarrow \quad \boxed{\theta = \frac{bP}{1+bP}} \qquad \left(k_1/k_2\right) = b$$

$$\frac{x}{m} = k_3 \theta \quad \Longrightarrow \quad \boxed{\theta = \frac{1}{k_3} \times \frac{x}{m}}$$

$$\frac{1}{k_3} \times \frac{x}{m} = \frac{bP}{k_2 + bP} \quad \Longrightarrow \quad \frac{x}{m} = \frac{k_3 bP}{1+bP} \quad \Longrightarrow \quad \boxed{\frac{x}{m} = \frac{aP}{1+bP}} \qquad k_3 b = a$$

Langmuir adsorption isotherm

Verification of Langmuir adsorption isotherm

$$\frac{x}{m} = \frac{aP}{1+bP}$$

$$\frac{P}{\left(\dfrac{x}{m}\right)} = \frac{1}{a} + \left(\frac{b}{a}\right)P$$

$$\frac{P}{\left(\dfrac{x}{m}\right)} \ vs \ P$$

$$\text{intercept} = \frac{1}{a} \qquad slope = \left(\frac{b}{a}\right)$$

Langmuir adsorption isotherm at different conditions of P

At very low P:

- **The adsorption is very poor.**

$$\frac{x}{m} = \frac{aP}{1+bP}$$ ⟶ $$\frac{x}{m} = aP$$ ⟶ $$\frac{x}{m} \propto P$$ ⟶ $$\frac{x}{m} \propto P^1$$

At very high P:

$$\frac{x}{m} = \frac{b}{b} \times \frac{aP}{1+bP} = \left(\frac{a}{b}\right) \times \frac{bP}{1+bP}$$ ⟶ $$\frac{x}{m} = \left(\frac{a}{b}\right)\theta$$

At very high P, θ reaches a limiting value of 1 $$\frac{x}{m} = \left(\frac{a}{b}\right)$$ ⟶ $$\frac{x}{m} \propto P^0$$

At intermediate P: $\dfrac{x}{m} = kP^{1/n}$

Langmuir adsorption isotherm is a special case of Freundlich adsorption isotherm

<u>Limitations of Freundlich adsorption isotherm</u>

Deviation from isotherm at high P and low T

- Deviation from ideal behavior of gases.

- Interaction between adsorbed gas molecules.

- Formation of multilayers.

- Different types of attractive interactions between gas molecules and surfaces.