Lecture 3.
Sorption Equilibrium

- Pure Gas Adsorption
  - Linear isotherm
  - Freundlich isotherm
  - Langmuir isotherm
  - Other adsorption isotherms
  - BET isotherm
- Gas Mixtures and Extended Isotherms
- Liquid Adsorption
- Ion–Exchange Equilibria
Adsorption Equilibrium

- Dynamic equilibrium in adsorption: solute distribution between fluid and solid surface
  - [concentration (if the fluid is a liquid) or partial pressure (if the fluid is a gas) of the adsorbate in the fluid] vs. [solute loading on the adsorbent (mass, moles, or volume of adsorbate per unit mass or surface area)]

- Adsorption isotherm: equilibrium data at a constant temperature
  - A limit on the extent to which a solute is adsorbed from a specific fluid mixture on a given adsorbent for one set of conditions
Classification of Adsorption Isotherms (1)

- **Type I isotherm**
  - Typical of adsorbents with a predominantly microporous structure
  - Corresponds to unimolecular adsorption
  - Maximum limit in the amount adsorbed
  - Gases at temperatures above their critical temperature
  - Example: nitrogen on carbon at 77K and ammonia on charcoal at 273K

Standard classification developed by IUPAC
Classification of Adsorption Isotherms (2)

• Type II isotherm
  - Physical adsorption of gases by non-porous solids
  - Corresponds to multimolecular BET adsorption (monolayer coverage followed by multilayering at high relative pressures)
  - Gases at temperatures below their critical temperature and pressures below, but approaching, the saturation pressure
  - The heat of adsorption for the first adsorbed layer is greater than that for the succeeding layers
  - Example: carbons with mixed micro- and meso-porosity

• Type III isotherm
  - Convex and undesirable (extent of adsorption is low except at high P)
  - Characteristic of weak adsorbate–adsorbent interactions
  - Corresponds to multimolecular adsorption
  - The heat of adsorption of the first adsorbed layer is less than that of succeeding layers
  - Example: adsorption of iodine vapor on silica gel
Classification of Adsorption Isotherms (3)

• Type IV isotherm
  - The maximum extent of adsorption occurs before the saturation pressure is reached
  - A hysteresis loop, which is commonly associated with the presence of mesoporosity
  - Capillary condensation gives rise to a hysteresis loop

• Type V isotherm
  - Convex to the relative pressure axis
  - Characteristic of weak adsorbate–adsorbent interactions at low relative pressures
  - Microporous or mesoporous solids
  - Hysteresis in multimolecular adsorption regions
  - Capillary condensation version of Type III
Classification of Adsorption Isotherms (4)

- Type VI isotherm
  - Complete formation of monomolecular layers before progression to a subsequent layer
  - Adsorption on extremely homogeneous, non-porous surfaces where the monolayer capacity corresponds to the step height
  - Example: adsorption of krypton on carbon black at 90 K
Classification of Adsorption Isotherms (5)

• Hysteresis loop
  - Occurs due to capillary condensation (gas adsorption in the pores at a low density → after a sufficient amount of gas has been supplied, it spontaneously condenses into a liquid–like state inside the pores)
  - Change of geometry during adsorption and desorption process

![Graph showing various hysteresis loops](image)

- Channels with uniform sizes and shapes
- Channels with a pore mouth smaller than pore body (ink-bottle-shaped pores)
- Solids with a very wide distribution of pore size
- Limited amounts of mesopores limited by micropores
Pure-Gas Adsorption

- Linear isotherm: a form of Henry’s law
  
  \[ q = kp \]

  \( q \): equilibrium loading
  \( k \): empirical, temperature-dependent constant for the component
  \( p \): partial pressure of the species

- As temperature increases, the amount adsorbed decreases because of Le Chatelier’s principle for an exothermic process
**Isosteric Heat of Adsorption**

- **Clausius–Clapeyron equation**

  \[
  \frac{d \ln p}{dT} = -\frac{\Delta H_{\text{ads}}}{RT^2} \quad \frac{d \log p}{d(1/T)} = -\frac{\Delta H_{\text{ads}}}{2.303RT}
  \]

  [Adsorption of NH$_3$ on charcoal]

  $-\Delta H_{\text{ads}}$ is initially 7,300 cal/mol $\rightarrow$ 6,100 cal/mol at 100 cm$^3$/g

  Heat of vaporization of HN$_3$ at 30°C: 4,600 cal/mol
Freundlich Isotherm

- Freundlich isotherm: empirical and nonlinear in pressure (Type I)

\[ q = kp^{1/n} \]
- \( k \) and \( n \) are temperature-dependent constants
- \( n \) lies in the range of 1 to 5
- In general, with \( T \uparrow \), \( n \uparrow \) but \( k \downarrow \), approaching a value of 1 at high \( T \)
- Can be derived by assuming a heterogeneous surface with a nonuniform distribution of heat of adsorption

- Fitting of experimental data to the Freundlich equation
  - By a nonlinear curve fit
  - By plotting \( \log q \) vs. \( \log p \) for the linear form

\[ \log q = \log k + \left(\frac{1}{n}\right) \log p \]
Langmuir Isotherm (1)

• Basis of Langmuir equation
  - From mass-action kinetics, assuming chemisorption
  - The surface of adsorbent pores is homogeneous ($\Delta H_{\text{ads}} = \text{constant}$)
  - Negligible interaction forces between adsorbed molecules

$\theta$ : fraction of surface covered by adsorbed molecules
1 $-$ $\theta$ : fraction of bare surface

• Net rate of adsorption

$$\frac{dq}{dt} = k_a p (1 - \theta) - k_d \theta$$

$k_a$ : adsorption kinetic constant
$k_d$ : desorption kinetic constant

At equilibrium, $dq/dt = 0$

$$\theta = \frac{(k_a / k_d) p}{1 + (k_a / k_d) p} = \frac{Kp}{1 + Kp}$$

$K$ : adsorption–equilibrium constant

$\theta = \frac{q}{q_m}$

$q_m$ : maximum loading corresponding to complete surface coverage
Langmuir Isotherm (2)

Langmuir adsorption isotherm is restricted to a monomolecular layer

\[ q = \frac{Kq_m p}{1 + Kp} \]

At low pressures \((Kp \ll 1)\), \(q = Kq_m p\) (linear isotherm)

At high pressures \((Kp \gg 1)\), \(q = q_m\)

Although originally Langmuir adsorption isotherm is devised for chemisorption, it is widely applied to physical-adsorption data.

- Fitting of experimental data to the Langmuir equation
  - By a nonlinear curve fit
  - By plotting \(p/q\) vs. \(p\) for the linear form

\[ \frac{p}{q} = \frac{1}{q_m K} + \frac{p}{q_m} \]

- Theoretically, \(K\) should change rapidly with \(T\) but \(q_m\) should not
Other Adsorption Isotherms

• Toth isotherm

\[ q = \frac{mp}{(b + pt)^{1/t}} \]

- \( m, b, \) and \( t \) are constants for a given adsorbate–adsorbent and \( T \)
- Obeys Henry’s law at low \( P \) and reaches a maximum at high \( P \)
- Reduce to the Langmuir isotherm for \( t = 1 \)

• UNILAN isotherm

\[ q = \frac{n}{2s} \ln \left[ \frac{c + pe^s}{c + pe^{-s}} \right] \]

- \( n, s, \) and \( c \) are constants for a given adsorbate–adsorbent and \( T \)
- Based on a model of heterogeneous surfaces assuming a uniform distribution of adsorption energy
- Reduce to the Langmuir isotherm for \( s = 0 \)
**BET Isotherm (1)**

- **BET theory**: physical adsorption of gas molecules on a solid surface to form multilayer

- **Number of adsorbed molecules**
  \[ N = N_{\text{sites}} (\theta_1 + 2\theta_2 + 3\theta_3 + \cdots) \]

  - \( N_{\text{sites}} \): total number of sites
  - \( \theta_0 \): fraction of surface sites unoccupied
  - \( \theta_1 \): fraction of surface sites covered by a monolayer
  - \( \theta_2 \): fraction of surface sites covered by a bilayer

- **First layer**
  
  Rate of adsorption = \( Nk_{a,0}p\theta_0 \)
  
  Rate of desorption = \( Nk_{d,0}\theta_1 \)

  At equilibrium, \( k_{a,0}p\theta_0 = k_{d,0}\theta_1 \)
BET Isotherm (2)

• Second layer
  Rate of adsorption = $N k_{a,1} p \theta_1$
  Rate of desorption = $N k_{d,1} \theta_2$
  At equilibrium, $k_{a,1} p \theta_1 = k_{d,1} \theta_2$

• Third layer
  Rate of adsorption = $N k_{a,2} p \theta_2$
  Rate of desorption = $N k_{d,2} \theta_3$
  At equilibrium, $k_{a,2} p \theta_2 = k_{d,2} \theta_3$

Once a monolayer has been formed, all the rate constants involving adsorption and desorption from the physisorbed layers are assumed to be the same.

\[
\begin{align*}
  k_{a,0} p \theta_0 &= k_{d,0} \theta_1 \\
  &\quad \rightarrow \quad \theta_1 = \left(\frac{k_{a,0}}{k_{d,0}}\right) p \theta_0 = K_0 p \theta_0 \\
  k_{a,1} p \theta_1 &= k_{d,1} \theta_2 \\
  &\quad \rightarrow \quad \theta_2 = \left(\frac{k_{a,1}}{k_{d,1}}\right) p \theta_1 = \left(\frac{k_{a,0}}{k_{d,0}}\right) \left(\frac{k_{a,1}}{k_{d,1}}\right) p^2 \theta_0 \\
  &\quad = K_0 K_1 p^2 \theta_0 \\
  k_{a,2} p \theta_2 &= k_{d,2} \theta_3 \\
  &\quad \rightarrow \quad \theta_3 = \left(\frac{k_{a,2}}{k_{d,2}}\right) p \theta_2 = \left(\frac{k_{a,0}}{k_{d,0}}\right) \left(\frac{k_{a,1}}{k_{d,1}}\right)^2 p^3 \theta_0 \\
  &\quad = K_0 K_1^2 p^3 \theta_0
\end{align*}
\]
BET Isotherm (3)

Because $\theta_0 + \theta_1 + \theta_2 + \theta_3 + \cdots = 1$

\[
1 = \theta_0 + K_0 p \theta_0 + K_0 K_1 p^2 \theta_0 + K_0 K_1^2 p^3 \theta_0 + \cdots
\]

\[
= \theta_0 + K_0 p \theta_0 \left\{1 + K_1 p + K_1^2 p^2 + \cdots\right\}
\]

\[
= \left\{1 + \frac{K_0 p}{1 - K_1 p}\right\} \theta_0 = \left\{\frac{1 - K_1 p + K_0 p}{1 - K_1 p}\right\} \theta_0
\]

\[
\theta_0 = \frac{1 - K_1 p}{1 - (K_1 - K_0) p}
\]

- Number of adsorbed species

\[
N = N_{\text{sites}} K_0 p \theta_0 + 2 N_{\text{sites}} K_0 K_1 p^2 \theta_0 + \cdots
\]

\[
= N_{\text{sites}} K_0 p \theta_0 \left(1 + 2 K_1 p + 3 K_1^2 p^2 + \cdots\right)
\]

\[
= \frac{N_{\text{sites}} K_0 p \theta_0}{(1 - K_1 p)^2}
\]
BET Isotherm (4)

\[
N = \frac{N_{\text{sites}} K_0 p}{(1 - K_1 p)^2} \times \frac{1 - K_1 p}{1 - (K_1 - K_0) p}
\]

\[
= \frac{N_{\text{sites}} K_0 p}{(1 - K_1 p)\{1 - (K_1 - K_0) p\}}
\]

The ratio \(N/N_{\text{sites}}\) is equal to the ratio \(v/v_{\text{mon}}\)

- \(v\): total volume adsorbed
- \(v_{\text{mon}}\): volume adsorbed for complete monolayer coverage

\(K_1\) is the equilibrium constant for the reaction in which the reactant is a molecule physisorbed and the product is the molecule in the vapor.

\[
K = 1/P_0 \quad P_0: \text{vapor pressure of the liquid}
\]

\[
\frac{v}{v_{\text{mon}}} = \frac{K_0 P}{(1 - P/P_0)\{1 - (1 - K_0/K_1) P/P_0\}}
\]
Gas Mixtures and Extended Isotherms (1)

• One component can increase, decrease, or have no influence on adsorption of another, depending on interactions of adsorbed molecules.

• Data for binary and multi-component gas–solid adsorbent equilibria are scarce and less accurate than corresponding pure-gas data.

• Extended Langmuir isotherm
  - Neglect interactions
  - Assume the only effect is the reduction of the vacant surface area
  - For a binary gas mixture of A and B

\[
\begin{align*}
\theta_A & : \text{fraction of surface covered by A} \\
\theta_B & : \text{fraction of surface covered by B} \\
1 - \theta_A - \theta_B & : \text{fraction of vacant surface}
\end{align*}
\]

\[
(k_A)_a p_A (1 - \theta_A - \theta_B) = (k_A)_d \theta_A
\]

\[
(k_B)_a p_B (1 - \theta_A - \theta_B) = (k_B)_d \theta_B
\]

\[
\theta_i = \frac{q_i}{(q_i)_m}
\]

\((q_i)_m : \text{maximum amount of adsorption of species } i \text{ for coverage of the entire surface}\)
Gas Mixtures and Extended Isotherms (2)

\[ q_A = \frac{(q_A)_m K_A p_A}{1 + K_A p_A + K_B p_B} \]
\[ q_B = \frac{(q_B)_m K_B p_B}{1 + K_A p_A + K_B p_B} \]

- For a mixture of \( j \) components

\[ q_i = \frac{(q_i)_m K_i p_i}{1 + \sum_j K_j p_j} \]

- Extended Langmuir–Freundlich equation

\[ q_i = \frac{(q_i)_0 k_i p_i^{1/n_i}}{1 + \sum_j k_j p_j^{1/n_j}} \]

Represents data for nonpolar, multicomponent mixtures in molecular sieves reasonably well

- Separation factor (selectivity)

\[ \alpha_{i,j} = \frac{q_i}{q_j} = \frac{p_i}{p_j} = \frac{(q_i)_m K_i}{(q_j)_m K_j} \]
Liquid Adsorption (1)

- Assumptions in a homogeneous binary liquid mixture adsorption
  - The composition change of the bulk liquid in contact with the porous solid is due entirely to adsorption of the solute.
  - Solvent adsorption does not occur.

- From a solute material balance

\[ q_1^e = \frac{n^0(x_1^0 - x_1)}{m} \]

Assuming negligible change in the total moles of liquid mixture.

- Isotherms in the dilute region
  - Solvent adsorption, if any, may be constant.
  - All changes in total amount adsorbed are due to solute.

\[ q = k c^{1/n} \]

\[ q = \frac{K q_m c}{1 + K c} \]
Liquid Adsorption (2)

- Isotherms over entire concentration range

- Composite isotherms or isotherms of concentration change
  - $q_1^e$: surface excess
  - When the solvent is not adsorbed, a composite curve without negative adsorption is obtained

- Origin of various types of composite isotherms

A: solute, B: solvent
Ion Exchange Equilibria (1)

- Ion exchange
  - One sorbate (a counterion) is exchanged for a solute ion, the process being governed by a reversible, stoichiometric, chemical-reaction equation
  - Selectivity of the ion exchanger for one counterion over another may be just as important as the ion-exchanger capacity
  - The law of mass action is used to obtain an equilibrium ratio

1. Case 1. The counterion initially in the ion exchanger is exchanged with a counterion from an acid or base solution

\[
\text{Na}^{+}_{(aq)} + \text{OH}^{-}_{(aq)} + \text{HR}_{(s)} \leftrightarrow \text{NaR}_{(s)} + \text{H}_2\text{O}_{(l)}
\]

Leaving no counterion

2. Case 2. The counterion being transferred from exchanger to fluid remains as an ion

\[
\text{A}^{n\pm}_{(1)} + n\text{BR}_{(s)} \leftrightarrow \text{AR}_{n(s)} + n\text{B}^{\pm}_{(1)}
\]

Molar selectivity coefficient for A displacing B

\[
K_{A,B} = \frac{q_{\text{AR}^n c_{B}^{n\pm}}}{q_{\text{BR}^n c_{A}^{n\pm}}}
\]
**Ion–Exchange Equilibria (2)**

- The total concentrations, C and Q, in equivalents of counterions in the solution and the resin, remain constant during exchange

\[
c_i = C \frac{x_i}{z_i}
\]

\[
q_i = Q \frac{y_i}{z_i}
\]

\(x_i\) and \(y_i\): equivalent fractions \((x_A + x_B = 1, y_A + y_B = 1)\)

\(z_i\): valence of counterion \(i\)

- For counterions A and B of equal charge

\[
K_{A,B} = \frac{y_A x_B}{y_B x_A} = \frac{y_A (1 - x_A)}{x_A (1 - y_A)}
\]

- For counterions A and B of unequal charge

\[
K_{A,B} = \left(\frac{C}{Q}\right)^{n-1} \frac{y_A (1 - x_A)^n}{x_A (1 - y_A)^n}
\]
Ion–Exchange Equilibria (3)

- Estimation of $K_{A,B}$
  
  $$K_{ij} = K_i / K_j$$

  $K_i$ and $K_j$: relative selectivities

- Isotherms for ion exchange of $\text{Cu}^{2+}$ and $\text{Na}^+$

- Separation factor, SP (ignoring the valence of the exchange ions)

  $$S_{A,B} = \frac{y_A (1 - x_A)}{x_A (1 - y_A)}$$

At low total-solution concentration, the resin is highly selective for $\text{Cu}^{2+}$, whereas at high total-solution concentration, the selectivity is reversed to slightly favor $\text{Na}^+$