Adsorption at the gas-solid interface.
Adsorption from solutions.

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Surfaces and Interfaces

- Definition of the interfacial region
- Types of interfaces: surface vs interface
- Surface tension
- Contact angle, wetting, and spreading
- Adsorption
- Biological interfaces
Adsorption on solid interfaces

- Solid interfaces
- Physisorption and chemisorption
- Adsorption isotherms (of types I, II, and IV)
- Practical importance
  - adsorption from gases and liquids
  - chromatography
Solid surfaces

- **Solids keep their shape** → surface tension of solids can be decreased only by adsorption. Surface tension depends on the structure and the solid’s “history” as well.

- **A solid surface has a structure.** Solid surface is *never homogeneous* at a molecular level even in the case of a single crystal.

- **An atom on the surface has less neighbors compared to the bulk.** The loss of coordination increases the surface energy.

![Hard sphere representation of surface features of a single crystal](image)
Crystal planes and Miller indices

- A crystal has a **periodic arrangement** of atoms, ions, or molecules → lattices
- Lattice planes are planes whose intersections with the lattice are **periodic**
- A crystal can be cut so that one face of the crystal makes up the surface of interest
- **Miller indices** are a notation system of the planes of a lattice
Physisorption and chemisorption

Qualitative properties of the adsorption are the strength and type of the binding to the surface. According to these properties the adsorption can be:

- physisorption (with van der Waals interactions)
- chemisorption (with chemical – covalent – bonds).

<table>
<thead>
<tr>
<th>Physisorption</th>
<th>Chemisorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>small [–] adsorption enthalpy Δ(H)</td>
<td>large [-] ads. enthalpy Δ(H) (kJ/mol)</td>
</tr>
<tr>
<td>acts at large distance</td>
<td>acts at small distance</td>
</tr>
<tr>
<td>several adsorbed layers</td>
<td>only one adsorbed layer</td>
</tr>
<tr>
<td>non-specific</td>
<td>generally specific</td>
</tr>
<tr>
<td>molecular structure unchanged</td>
<td>molecular structure changes</td>
</tr>
</tbody>
</table>

\[ ΔG = ΔH - T ΔS \]

Entropy generally decreases (ΔS<0), as the degree of freedom of the gas decreases as well, thus the sign of free enthalpy (\(G\)) depends on the sign and magnitude of enthalpy (\(H\)).
Enthalpy changes following G/S adsorption

Physical chemistry: free enthalpy of the system decreases during spontaneous changes at constant pressure and temperature ($\Delta G < 0$)

$$\Delta G = \Delta H - T \Delta S < 0$$

**Physisorption**: chemical structure of the adsorbate does not change, but its degrees of freedom decrease

- $\Delta S < 0$
- $T \Delta S < 0$

**Chemisorption**: chemical structure of the adsorbate changes, its degrees of freedom decrease

- If the adsorbate does not dissociate
  - $\Delta S < 0$
  - $|\Delta H| > |T \Delta S|$
  - $\Delta H < 0$, $\Delta H$ always exothermic
- If the adsorbate does dissociate
  - $\Delta S < 0$
  - $\Delta H$ depends on $\Delta S$
  - if $\Delta S < 0$
  - if $\Delta S \geq 0$
Adsorption at the gas-solid interface

A solid surface in contact with gas usually attracts an adsorbed layer of gas molecules

\[ \Delta G = \Delta H - T \Delta S < 0 \]

Even a gas like nitrogen, which is nonpolar and not very reactive, will adsorb to a surface under certain conditions. When adsorption occurs this is spontaneous which means that the free energy change, \( \Delta G \) is negative.

Adsorption isotherms: the amount of gas adsorbed as a function of the equilibrium gas pressure. Classification of adsorption isotherms is based on their shapes.

Adsorbed amount is shown as volume, mass or moles of molecules adsorbed per unit area, or as \( \theta \), coverage of surface vs. relative pressure \( p/p_0 \) (\( p \): actual pressure, \( p_0 \): saturation vapor pressure)

Strong interaction type I or Langmuir, type II or BET, type IV or capillary condensation
Sorption isotherm types

LANGMUIR

B.E.T.

CAPILLARY CONDENS.

monolayer complete

hysteresis loop

monolayer complete

hysteresis loop

Relative pressure $p/p^\circ$
Sorption isotherms

Type I: Langmuir isotherm
Type II: BET isotherm
Type IV: Capillary condensation

Strong interactions → steep initial curve segment

The adsorbed amount can be:

- the number of adsorbed moles on a unit of adsorbent, $\Gamma$ (mol/g, mol/m$^3$, or mol/m$^2$)
- surface coverage $\theta$ (without unit or %)
- specific adsorbed gas volume (m$^3$/g or m$^3$/m$^2$)
- mass adsorbed per unit of adsorbent (g/g or g/m$^2$)

$p/p_0$ is the relative pressure (ratio between the actual pressure and the vapor saturation pressure)
Further reading

- Even a gas like nitrogen, which is nonpolar and not very reactive, will adsorb to a surface under certain conditions. When adsorption occurs this is spontaneous which means that the free energy change ($\Delta G$) is negative. In most cases there is also a decrease in entropy ($\Delta S$), because the gas loses degrees of freedom. Hence, to ensure that $\Delta G$ is negative, the enthalpy change ($\Delta H$) must be negative and large enough to compensate the term of entropy.

- **Physisorption** involves only the forces of molecular interaction, it is very similar to the condensation of a vapor to form a liquid. The enthalpy of the physical adsorption is roughly the same ($\approx 20 \text{ kJ/mol}$) as the enthalpy of condensation (or it is usually not greater than few times) and in many ways the adsorbed materials behave like a two-dimensional liquid. Physical adsorption can be reversed by simple reducing the gas pressure and usually without raising of the temperature.

- In **chemisorption**, a chemical bond is formed. The enthalpies of the adsorption are much greater (>80 kJ/mol) than for physical adsorption. The adsorbed atoms are localized at particular sites on the solid surface and only one layer of adsorbate may be chemisorbed. Physical adsorption on top of a chemisorbed layer is possible if the conditions are appropriate.

- Gas adsorption measurement methods
  - **Volumetric method** → during adsorption the change in volume of a gas is measured
  - **Gravimetric method** → a microbalance is used to measure the gas adsorbed
Langmuir type I isotherm (for gas)

\[ \Theta = \frac{\Gamma}{\Gamma_{\text{max}}} = \frac{b \, p}{1 + b \, p} \]

The equivalent linearized form:

\[ \frac{p}{\Gamma} = \frac{p}{\Gamma_{\text{max}}} + \frac{1}{b \, \Gamma_{\text{max}}} \]

- \( \Gamma_{\text{max}} \): amount required for complete monolayer coverage or monolayer capacity (mol/g or mol/m\(^2\))
- \( p \): pressure (Pa)
- \( b \): sorption or isotherm constant defined as: \( b = \frac{k_a}{k_d} \)

**Assumptions:**

- only a monolayer is formed
- the surface is uniform,
- adsorbed molecules do not interact with neighboring adsorbed molecules,
- adsorption-desorption is in dynamic equilibrium with \( k_a \) association and \( k_d \) dissociation rate constants respectively.

Irving Langmuir, Nobel prize in 1932
Freundlich type I isotherm (for gas)

\[ \Gamma = k \rho^{1/n} \]

\( \Gamma \) : surface excess \((\text{mol m}^{-2})\)
\( n > 1 \) : isotherm constant (without unit)
\( k \) : isotherm constant \((\text{mol m}^{-2} \text{ Pa}^{-1/n})\)
\( \rho \) : pressure \((\text{Pa})\)

Assumptions:
- Binding strength decreases with increasing surface coverage
- There is no \( \Gamma_{\max} \) but \( \Gamma \) keeps increasing
- Not based on theoretical considerations but on experimental data
- Mostly used for L/S adsorption
BET isotherm, type II (for gas)

\[ \Theta = \frac{\Gamma}{\Gamma_{\text{max}}} = \frac{Zp}{(p_0 - p)[1+(Z-1)\left(\frac{p}{p_0}\right)]} \]

Net adsorption enthalpy: \( Z \approx e^{\frac{(H_1-H_v)}{RT}} \)

- \( H_1 \): adsorption enthalpy of the first layer (J).
- \( H_v \): evaporation enthalpy of the adsorbate (J).

Assumptions:
- multilayer adsorption of gas
- the Langmuir equation is applied to each layer
- adsorption and desorption can only occur at exposed surfaces
- at equilibrium, the distribution of adsorbate between the different layers is constant
Authors of the BET isotherm

Stephen Brunauer
1903 — 1986

Paul Hugh Emmett
1900 — 1985

Edward Teller
1908 — 2003
Capillary condensation, type IV (for vapor)

Condensation occurs when the actual vapor pressure exceeds the equilibrium vapor pressure within capillaries of porous solids.

**Zsigmondy:** If surface of liquid is **concave** (radius \( r < 0 \)), the Kelvin equation shows that the equilibrium vapor pressure \( p_r \), may be significantly lower than \( p_\infty \). Thus condensation may occur at \( p_r/p_0 < 1 \), a phenomenon known as **capillary condensation**.

**Conditions:** porous solids, non-spherical pores, relative pressure is high, liquid wets the surface.

\[
\ln \left( \frac{p_r}{p_\infty} \right) = \left( \frac{\gamma V_L}{RT} \right) \left( \frac{1}{r'} + \frac{1}{r''} \right)
\]

The Kelvin equation

- \( r' \) : radius of curvature of the capillary itself (m)
- \( r'' \) : radius of curvature of the surface liquid layer (m)

as here \( r'' = r' \)
Capillary condensation, type IV (for vapor)

Underground storage water, water budget → The smaller capillaries store the higher amount of water

Pore size distribution can be calculated from $r \sim \frac{p_r}{p_0}$
Adsorption from solutions

Non-electrolyte adsorption
From dilute solution
Empirical rules

Component adsorption
Excess isotherms

Adsorption of strong electrolytes
Equivalent or molecular adsorption
Ion exchange or non-equivalent adsorption

Neutral surface
Non-neutral surface

Polar surface
Apolar surface
Electrical double layers
Adsorption at low solute concentration

For low solution concentrations adsorption isotherms generally have a form similar to the type I isotherms

\[ \Gamma \rightarrow a, \quad \Gamma_{\text{max}} \rightarrow a_{\text{max}}, \quad p \rightarrow c \]

**Figure 6.11.** Adsorption isotherms for fatty acids; (a) from aqueous solutions on to charcoal and (b) from toluene solutions on to silica gel

**Empirical rules**

"Similar likes similar": Every system seeks to achieve a minimum of free energy.

\[ a = \frac{V (c_0 - c)}{m} \]

- \( V \): volume (dm\(^3\))
- \( c \): equilibrium concentration (mol/dm\(^3\))
- \( c_0 \): initial concentration (mol/dm\(^3\))
- \( m \): mass of the adsorbent (g)
Adsorption isotherms from dilute solutions

Type I (Langmuir)
- active sites are rare
- specific binding (1 layer)
- equilibrium

\[ \Theta = \frac{a}{a_{\text{max}}} = \frac{b \cdot c}{1 + b \cdot c} \]

Type I (Freundlich)
- „classic” isotherm
- bond strength diminishes with saturation of the active sites
- there is no real saturation

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

Figure 6: Adsorption isotherm data and the Freundlich adjusted model
Analysis of Langmuir isotherms

\[ \Theta = \frac{a}{a_{\text{max}}} = \frac{bc}{1+bc} \]

Determination of the specific surface and the area occupied by 1 molecule from \( a_{\text{max}} \)
Component adsorption, adsorption of binary mixtures on solid surfaces

CCl₄ (top) and CHCl₃ (bottom) mixture onto activated charcoal

Excess isotherms:
- U shaped
- S shaped

Apparent excess adsorption

Ratio of hydrophobic/hydrophilic area:
60% / 40%

Benzene from solution in methanol on to charcoal

Ratio of hydrophobic/hydrophilic area:
60% / 40%
Chromatography

What is chromatography?

Chromatography is a separation method. The components to be separated are distributed between two phases: a stationary phase bed and a mobile phase which percolates through the stationary bed. The equilibration between the mobile and stationary phase may be based on adsorption, partition, size exclusion, ion exchange or special affinity. The smaller the affinity a molecule has for the stationary phase, the shorter the time spent in a column.

Basic expression for adsorption chromatography:

\[ \Gamma_1 = \Gamma_{\text{max}} \frac{b_1 p_1}{1 + b_1 p_1 + b_2 p_2} \]

selectivity \[ b_1 \gg b_2 \]
Types of Chromatography

- **Adsorption chromatography**: Solute adsorbed on surface of stationary phase.

- **Partition chromatography**: Solute dissolved in liquid phase coated on surface of solid support.

- **Molecular exclusion chromatography**: Large molecules are excluded, small molecules penetrate pores of particles.

- **Affinity chromatography**: One kind of molecule in complex mixture becomes attached to molecule that is covalently bound to stationary phase; all other molecules simply wash through.
Adsorption chromatography utilizes a mobile liquid or gaseous phase that is adsorbed onto the surface of a stationary solid phase. The equilibration between the mobile and stationary phase accounts for the separation of different solutes.

Partition Chromatography is based on a thin film formed on the surface of a solid support by a liquid stationary phase. Solute equilibrates between the mobile phase and the stationary liquid.

Ion Exchange Chromatography: the matrix (the stationary solid phase) bears permanent charges. Solute ions of the opposite charge in the mobile liquid phase are attracted to the resin by electrostatic forces.

Size exclusion chromatography also known as gel permeation or gel filtration: there is no attractive interaction between the stationary phase and solute. The liquid or gaseous phase passes through a porous gel which separates the molecules according to their size and/or shape. The pores are normally small and exclude the larger solute molecules, but allows smaller molecules to enter the gel, causing them to flow through a larger volume. Larger molecules pass through the column at a faster rate than the smaller ones.

Affinity Chromatography: the most selective type of chromatography employed. It utilizes the specific interaction between one kind of solute molecule and a second molecule that is immobilized on a stationary phase. For example, the immobilized molecule may be an antibody to some specific protein. When solute containing a mixture of proteins are passed by this molecule, only the specific protein is reacted to this antibody, binding it to the stationary phase. This protein is later extracted by changing the ionic strength or pH.
Retention

The retention is a **measure of the speed** at which a substance moves in a chromatographic system. In continuous development systems like HPLC or GC, where the compounds are eluted with the eluent, the retention is usually measured as the **retention time** $R_t$ or $t_R$, the time between injection and detection. In interrupted development systems like TLC the retention is measured as the **retention factor** $R_f$, the run length of the compound divided by the run length of the eluent front.

Purification, separation (industry, biotechnology, gas mask)

The smaller the affinity a molecule has for the stationary phase, the shorter the time spent in a column.
Thin layer chromatography (TLC)

Solvent = mobile phase
Layer = stationary phase

\[ R_f = \frac{\text{distance moved by compound}}{\text{distance moved by solvent}} \]

C chamber for development e.g. beacher with a lid or a closed jar
after ~5 min
after ~10 min
after drying

\[
\begin{align*}
\text{S1: } & R_f = \frac{34 \text{ mm}}{60 \text{ mm}} = 0.57 \\
\text{S2: } & R_f = \frac{22 \text{ mm}}{60 \text{ mm}} = 0.37 \\
\text{P: } & R_f = \frac{54 \text{ mm}}{60 \text{ mm}} = 0.90
\end{align*}
\]
**Reading:** Proteins Purification and Characterization

http://www.biochem.arizona.edu/classes/bioc462/462a/NOTES/Protein_Properties/protein_purification.htm

Nelson & Cox, *Lehninger Principles of Biochemistry*
Size Exclusion chromatography

Note how the small red spheres pass into the channels in the beads, whereas the large blue spheres do not. Thus, the small spheres have a longer "distance" to transverse than the large spheres to get to bottom of column, which means that a larger volume of solvent must pass through the column before the red spheres are eluted.
Ion Exchange Chromatography

- Ion exchange resins have charged groups covalently attached to the stationary phase (adsorbent, matrix).
- Analytes bind to the matrix by electrostatic interactions.
- Strength of these interactions depends on:
  - net charge on the analyte (a function of buffer pH and the nature of the ionizable groups)
  - salt concentration of the buffer (high salt concentrations reduce the interaction and can be used to elute the analytes by competing with its electrically charged groups for binding to the charged groups on the matrix).

The higher the net charge on the analyte at the pH of the environment on the column, the more tightly it binds to an oppositely charged matrix, and the higher the salt concentration required to elute it from the column.

The further the buffer pH is from the isoelectric point (pl) of an analyte, the greater its net charge and the more tightly it will bind to an ion exchanger of opposite charge.

By proper choice of eluting buffer (often a gradient with increasing salt concentration, or changing the pH), specific proteins can be eluted from the column and separated from other proteins in the mixture.
A more specific adsorbent in which a ligand specifically recognized by the analyte is covalently attached to the column material.

When a mixture is passed through the column, only those that bind specifically to the ligand adsorb, while the others pass through the column.

The analyte is eluted with a buffer containing the free ligand, which competes with the column ligand to bind to the protein, and the analyte washes off (with bound ligand). Non-specific release agents (pH, electrolyte, urea, etc.) can also be used to elute the analyte.