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
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

Cubic crystal

Monoclinic crystal
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 $\Delta H$</td>
<td>large [-] ads. enthalpy $\Delta H$ (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>

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

Entropy generally decreases ($\Delta S < 0$), 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 ($H$).
Energetics of the adsorption

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
  - $\Delta S < 0$
  - $-T\Delta S > 0$
  - $\Delta H > 0$, always exothermic

- **Chemisorption**: chemical structure of the adsorbate changes, its degrees of freedom decrease
  - If the adsorbate does not dissociate → entropy decreases
    - $\Delta S < 0$
  - If the adsorbate does dissociate → entropy can increase or decrease
    - $\Delta S < 0$ or $\Delta S \geq 0$
    - $\Delta H$ depends on $\Delta S$
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

- Type I: Adsorption is complete at low pressures.
- Type II: Adsorption continues to increase with increasing pressure.
- Type III: Adsorption reaches a saturation point.
- Type IV: Adsorption isotherm with hysteresis, characteristic of capillary condensation.
- Type V: Adsorption isotherm with a sharp increase at low pressures, followed by a slower increase.
- Type VI: Adsorption isotherm with a plateau at high pressures.
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)
• 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 looses 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 (20kJ/mol) as the enthalpy of condensation (or it is usually not greater than few times) and in many ways the adsorbed materials, especially when many layers have been adsorbed, behaves like a two dimensional liquid. Reversibility: Physical adsorption can be reversed by simple reducing the gas pressure and usually without raising of the temperature.

• In chemisorption, on the other hand, a chemical bond is formed. Consequently the enthalpies of the adsorption are much greater (>80 kJ/mol) than for physical adsorption. Furthermore, 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
  1) Volumetric method → during adsorption the change in volume of a gas is measured
  2) Gravimetric method → a microbalance is used to measure the gas adsorbed
Langmuir type I isotherm (for gas)

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

The equivalent linearized form:

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

\( \Gamma_{\text{max}} \) is the amount required for complete monolayer coverage or monolayer capacity (mol/g or mol/m\(^2\)), and \( b \), the 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 (mol m\(^{-2}\))
- \( n > 1 \): isotherm constant (without unit)
- \( k \): isotherm constant (mol m\(^{-2}\) Pa\(^{-1/n}\))
- \( \rho \): pressure (Pa)

Assumptions:

- Binding strength decreases with increasing surface coverage
- There is no \( \Gamma_{\text{max}} \) 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)

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

\[
Z \approx e^{\frac{(E_1-E_v)}{RT}}
\]

Net adsorption enthalpy: \( Z \approx e^{\frac{(E_1-E_v)}{RT}} \)

\( E_1 \) and \( E_v \) are the enthalpies of adsorption of the first layer and the evaporation enthalpy of the adsorbate respectively.

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)

\[
\ln\left(\frac{p_r}{p_\infty}\right) = \left(\frac{\gamma V_L}{RT}\right)\left(\frac{1}{2r'}\right)
\]

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 $r \sim p_r/p_0$

successive adsorption + capillary condensation
simultaneous capillary desorption + evaporation

Adsorption–desorption hysteresis
(Advancing and receding contact angle hysteresis, surface roughness, microscopic chemical heterogeneity of solid surface, drop size effect, molecular reorientation, and penetration into the pores)
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

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

Emprical 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

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

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

\[ a = k \, c^{1/n} \]
Analysis of Langmuir isotherms

$$\Theta = \frac{a}{a_{\text{max}}} = \frac{b c}{1+b c}$$

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

Excess isotherms:
- U shaped
- S shaped

Apparent specific adsorbed surface excess

Mole fraction of component(1) $x_1$, azeotropic composition

Adsorption capacity from the intercepts

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

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

Benzene from solution in methanol on to charcoal

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

$$\Gamma_1 = \Gamma_{max} \frac{b_1 p_1}{1 + b_1 p_1 + b_2 p_2}$$

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
Summary

**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 use of a *resin* (the stationary solid phase) is used to *covalently attach* anions or cations onto it. 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*, this type of chromatography lacks an attractive interaction between the stationary phase and solute. The liquid or gaseous phase passes through a porous gel which separates the molecules according to its *size* and *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. This causes the larger molecules to pass through the column at a faster rate than the smaller ones.

**Affinity Chromatography** is 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

\[ R_f = \frac{\text{distance moved by compound}}{\text{distance moved by solvent}} \]
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*
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 resins have charged groups covalently attached to the stationary phase (adsorbent, matrix), either positive or negative. Obviously, if ionizable groups are weak acids or bases, the pH of the buffer determines the charge state of the matrix. Proteins bind to the matrix by electrostatic interactions. Strength of these interactions depends on net charge on the protein (a function of buffer pH and the nature of the ionizable groups on that protein, reflected in the pI of the protein), and salt concentration of the buffer (high salt concentrations reduce the interaction and can be used to elute the proteins by competing with the protein groups for binding to the charged groups on the matrix). The higher the net charge on the protein at the pH of the environment on the column, the more tightly it sticks to an oppositely charged matrix, and the higher the salt concentration required to elute it from the column.

The further the "working pH" is from the isoelectric point (pI) of a protein, the greater the net charge on the protein, and the more tightly it will stick 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.
Affinity Chromatography

a more specific adsorbent in which a **ligand specifically recognized by the protein of interest** is covalently attached to the column material.

When a mixture of proteins is passed through the column, only those few that bind strongly to the ligand stick, while the others pass through the column.

Protein of interest is eluted with a **buffer** containing the **free ligand**, which competes with the column ligand to bind to the protein, and protein washes off (with bound ligand).