EPFL
École polytechnique fédérale de Lausanne

Institute of Materials - Institute of Bioengineering

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SuNMIL
Supramolecular NanoMaterials and Interfaces Laboratory

Adsorption at Interfaces
Lesson 7

MSE 304

Francesco Stellacci

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Key Topics in the Previous Class

Reading for this Class

Challenges in Defining an Interface

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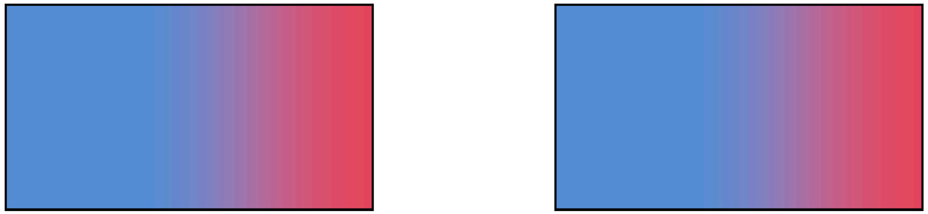
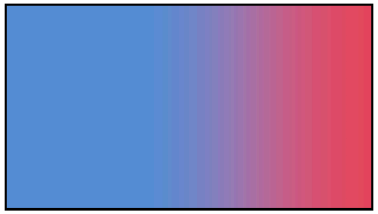


Gibbs Definition



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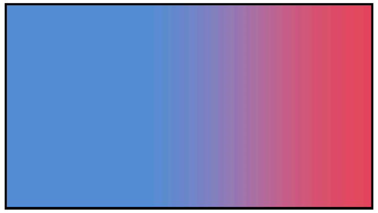
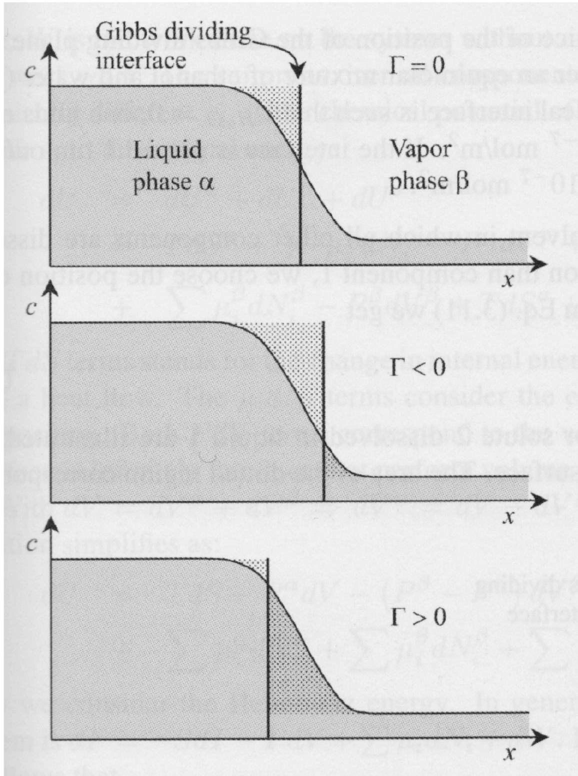
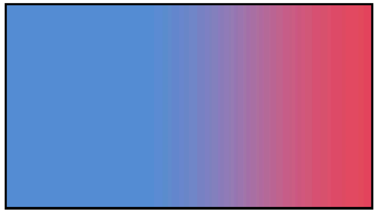




Gibbs Isotherm



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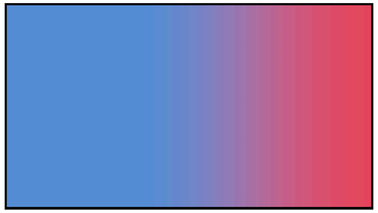

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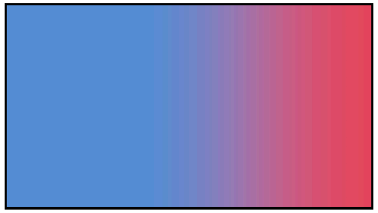

Adsorption at Interfaces

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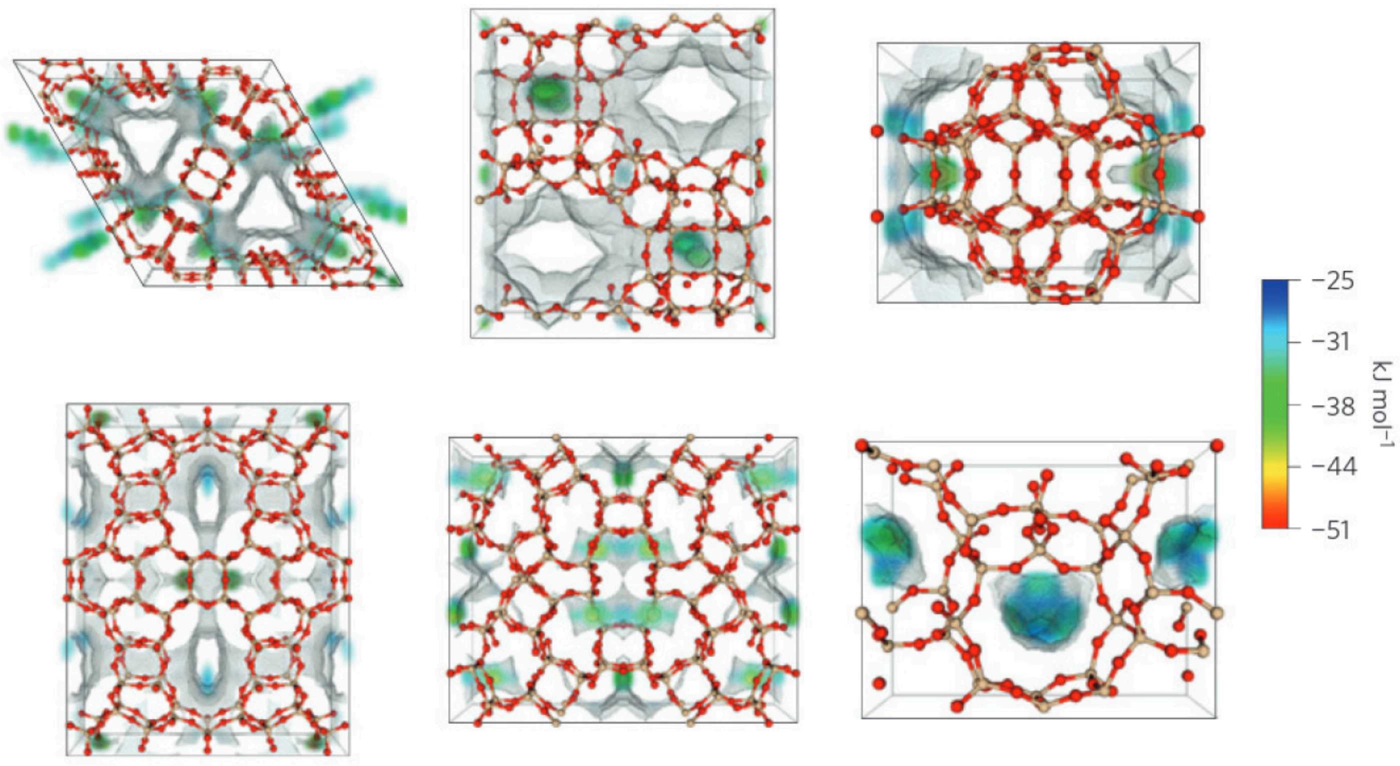
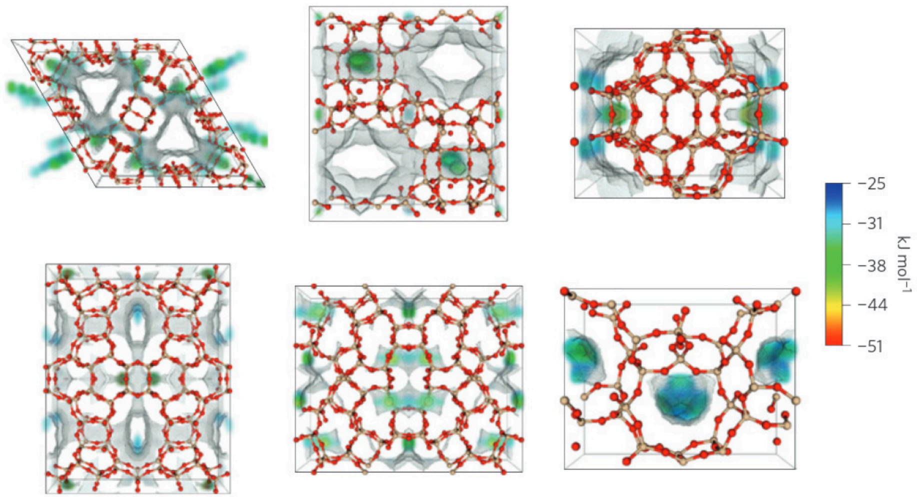


Adsorption at Interfaces

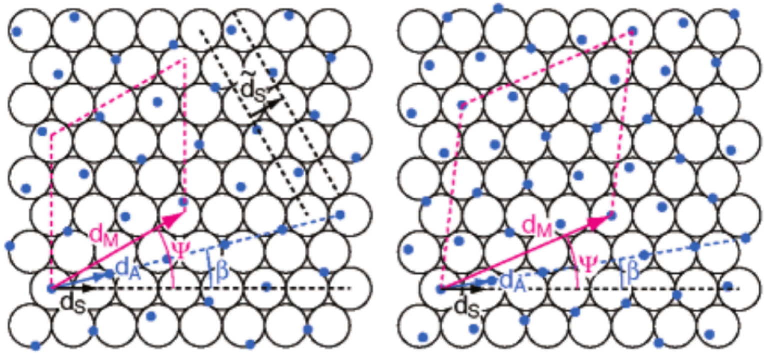
- Adsorption is crucial for catalysis, and storage of gases!
- Phenomenology of adsorption
- Langmuir adsorption interface: one species and competitive
- Different kinds of adsorption isotherms: FFG (correlated), BET (multilayer)



Chemisorption and Physisorption

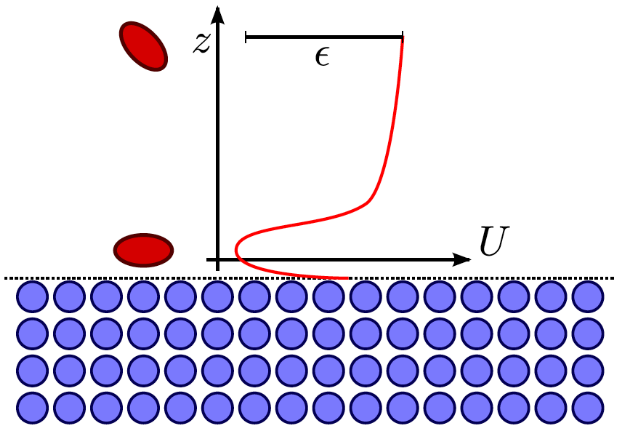
- Real surfaces are often covered in molecules, often with complex/regular arrangements
  - Adsorption lowers the surface energy
- Conventional classification as a function of the adsorption enthalpy
  - **physisorption**: reversible, weak binding ($<$ 40 kcal/mol), mobile species
  - **chemisorption**: irreversible, strong binding ($>$ 40kcal/mol), immobile species

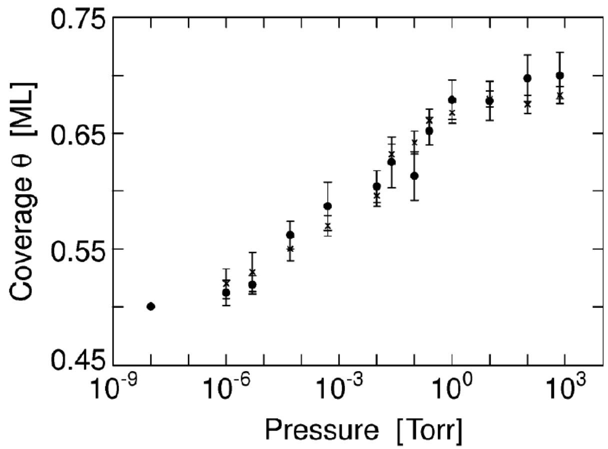
Monolayers



Key Definitions in Adsorption

- An adsorbate molecule often resides in specific adsorption sites (not necessarily one per surface unit cell).
- **Coverage** θ measures the number of occupied sites *n* relative to the maximum possible number *N*
- Adsorption energy ϵ: stabilization relative to the gas-phase molecule. **Residence time**: $\tau \sim \tau_0 e^{\epsilon/k_B T}$
- Experimental measure: **adsorption isotherm**





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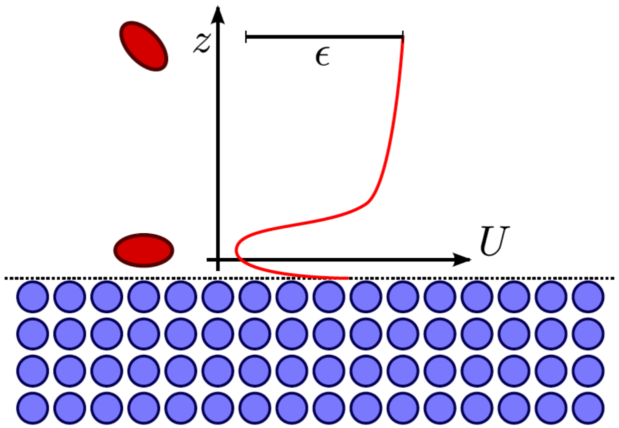
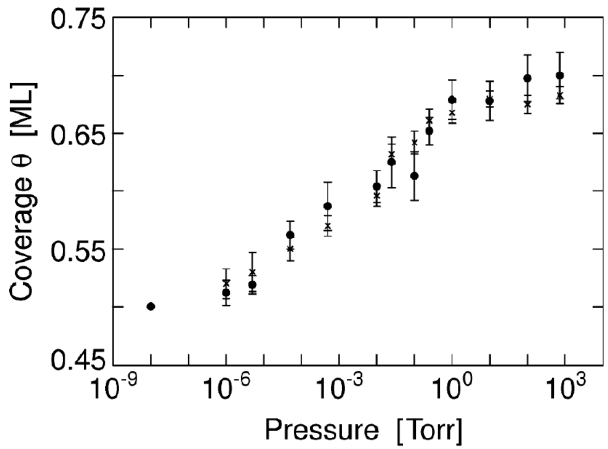
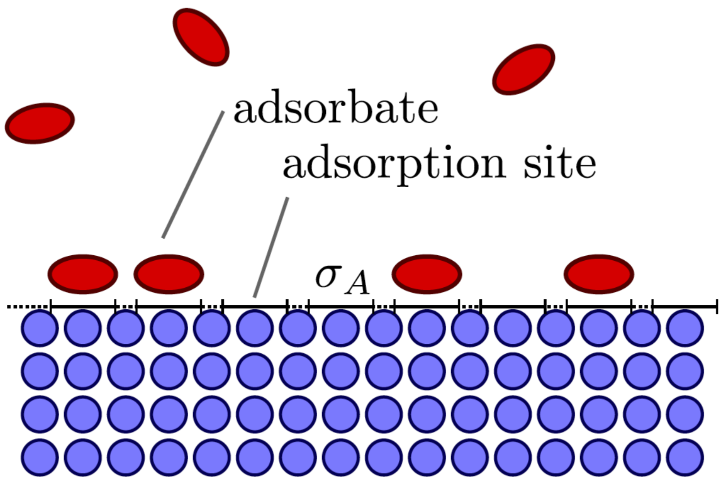




Langmuir Isotherm – Initial Hypotheses

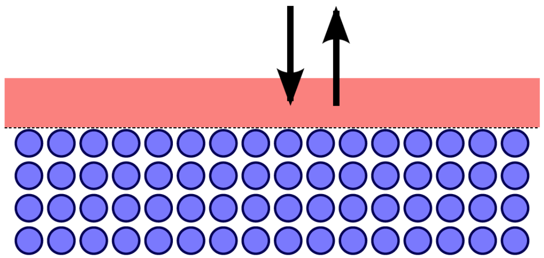
- A simple model for adsorption that leads to the **Langmuir adsorption isotherm**:
  - The surface is covered by *equivalent* adsorption sites, with area σ_A
  - The adsorption energy ϵ is *independent* on the site and on the occupation of nearby adsorption sites
  - The *sticking coefficient* (probability on binding upon a collision with the surface) on an empty site is one



Langmuir Isotherm – Equilibrium Derivation

- Equilibrium between adsorption rate K_{AD} and desorption rate K_{DE}
  - **Desorption rate** proportional to the fraction of occupied sites and the rate for one site
  - **Adsorption rate** proportional to the fraction of empty sites and the collision rate (assuming *sticking coefficient* is one)

$$K_{\mathrm{AD}} = (1-\theta)Pk_{\mathrm{AD}} \qquad K_{\mathrm{DE}} = \theta k_{\mathrm{DE}}$$

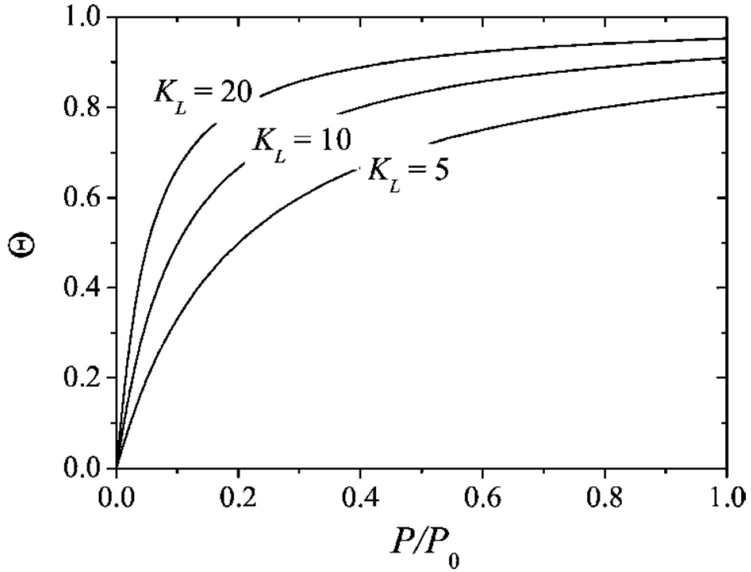


Langmuir Isotherm

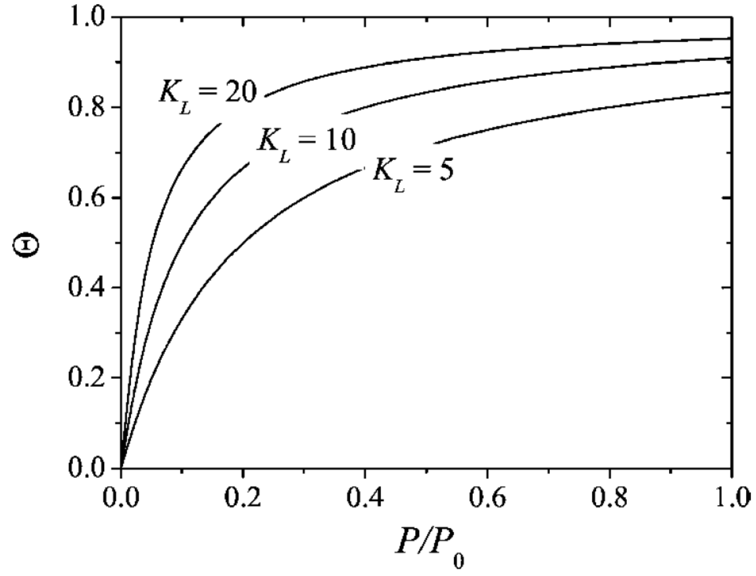
$$\theta = \frac{Pk_L}{Pk_L + 1},$$

$$\boxed{\frac{\theta}{1-\theta} = \frac{P}{P_0}} = k_L P = \frac{k_{AD}}{k_{DE}} P,$$

$$k_L = \frac{1}{P_0} = \frac{k_{AD}}{k_{DE}} = \frac{\sigma_A \tau_0}{\sqrt{2\pi m k_B T}} e^{\epsilon / k_B T}$$



Langmuir Isotherm - Considerations



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Langmuir Isotherm – Competitive Adsorption

- What if we have multiple molecules in the gas phase? $\theta = \sum_i \theta_i$
- At equilibrium one must have mass balance for each specie separately

$$\theta_i k_{\mathrm{DE}}^i = K_{\mathrm{DE}}^i = K_{\mathrm{AD}}^i = (1-\theta)\, k_{\mathrm{AD}}^i P_i$$

$$\frac{\theta}{1-\theta} = \sum_i k_{\mathrm{L}}^i P_i \rightarrow \theta = \frac{\sum_i k_{\mathrm{L}}^i P_i}{1+\sum_i k_{\mathrm{L}}^i P_i} \rightarrow 1-\theta = \frac{1}{1+\sum_i k_{\mathrm{L}}^i P_i}$$

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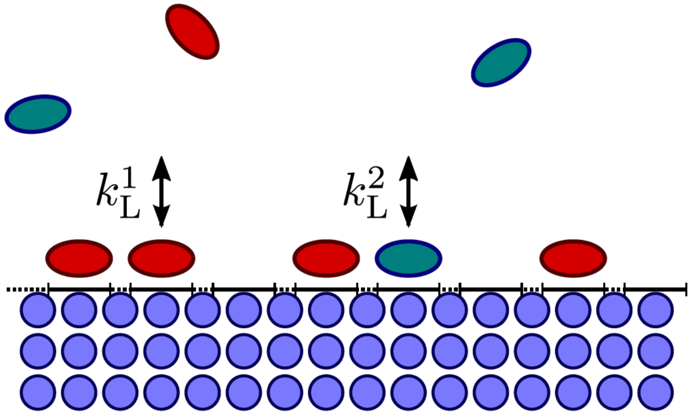

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$$\theta_i k^i_{\mathrm{DE}} = K^i_{\mathrm{DE}} = K^i_{\mathrm{AD}} = (1-\theta)\, k^i_{\mathrm{AD}} P_i$$

$$\frac{\theta}{1-\theta} = \sum_i k^i_{\mathrm{L}} P_i \rightarrow \theta = \frac{\sum_i k^i_{\mathrm{L}} P_i}{1+\sum_i k^i_{\mathrm{L}} P_i} \rightarrow 1-\theta = \frac{1}{1+\sum_i k^i_{\mathrm{L}} P_i}$$

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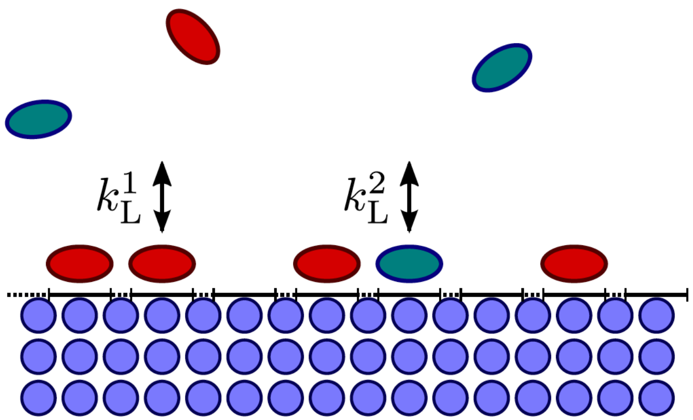

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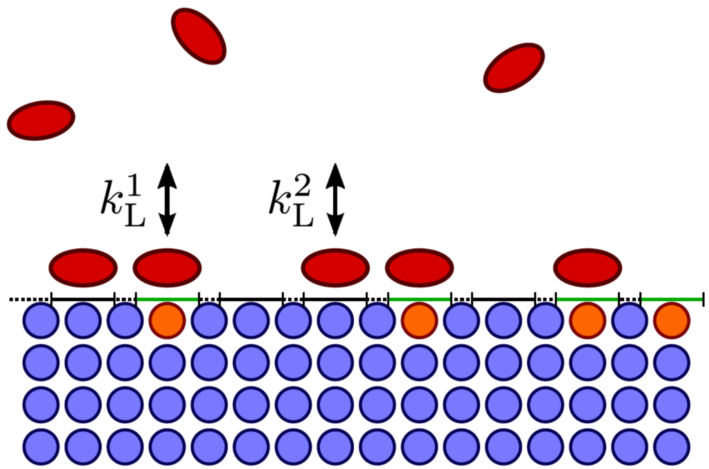
Langmuir Isotherm – Competitive Adsorption

- Multiple adsorption sites, with fraction x_i and different adsorption energies ϵ_i
- Can treat as independent adsorption problems, but $\theta = \sum_i x_i\theta_i$

$$\theta_i x_i k_{\mathrm{DE}}^i = K_{\mathrm{DE}}^i = K_{\mathrm{AD}}^i = x_i\left(1-\theta_i\right)k_{\mathrm{AD}}^i P$$

$$\boxed{\theta_i = \frac{k_{\mathrm{L}}^i P}{1+k_{\mathrm{L}}^i P}, \qquad \theta = \sum_i \frac{x_i k_{\mathrm{L}}^i P}{1+k_{\mathrm{L}}^i P}}$$

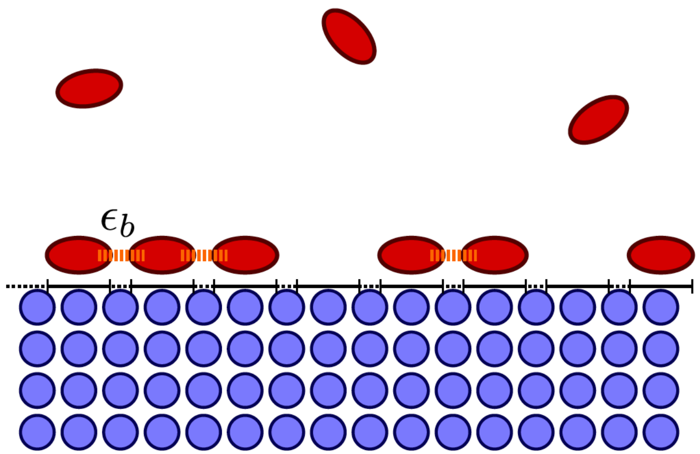


Collaborative Adsorption – FFG Isotherm

- Consider the possibility of bonding between molecules.
- The number of bonds per molecule at full coverage is n, and the energy per bond ϵ_b
- The probability of one neighbor being occupied is θ, so the mean energy of an adsorbed molecule becomes $\epsilon \leftarrow \epsilon + n\theta\epsilon_b$
- Isotherm is given by the (physical) solutions to the implicit equation

$$\boxed{\frac{\theta}{1-\theta} = k_L e^{\frac{n\epsilon_b\theta}{k_B T}} P}$$

$$k_L = \frac{1}{P_0} = \frac{k_{AD}}{k_{DE}} = \frac{\sigma_A \tau_0}{\sqrt{2\pi m k_B T}} e^{\epsilon/k_B T}$$



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Collaborative Adsorption – FFG Isotherm

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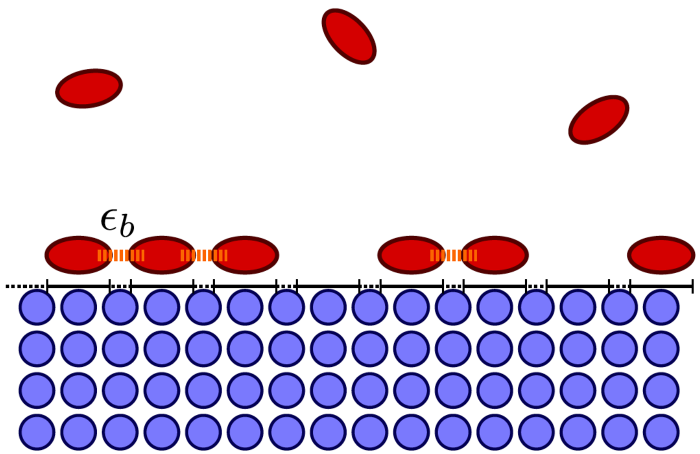


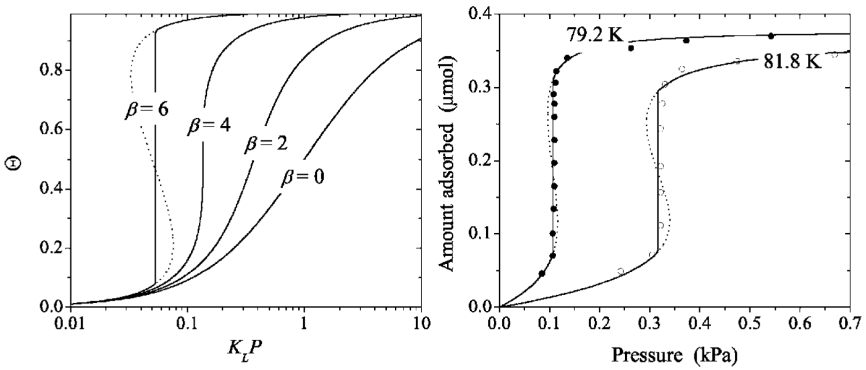
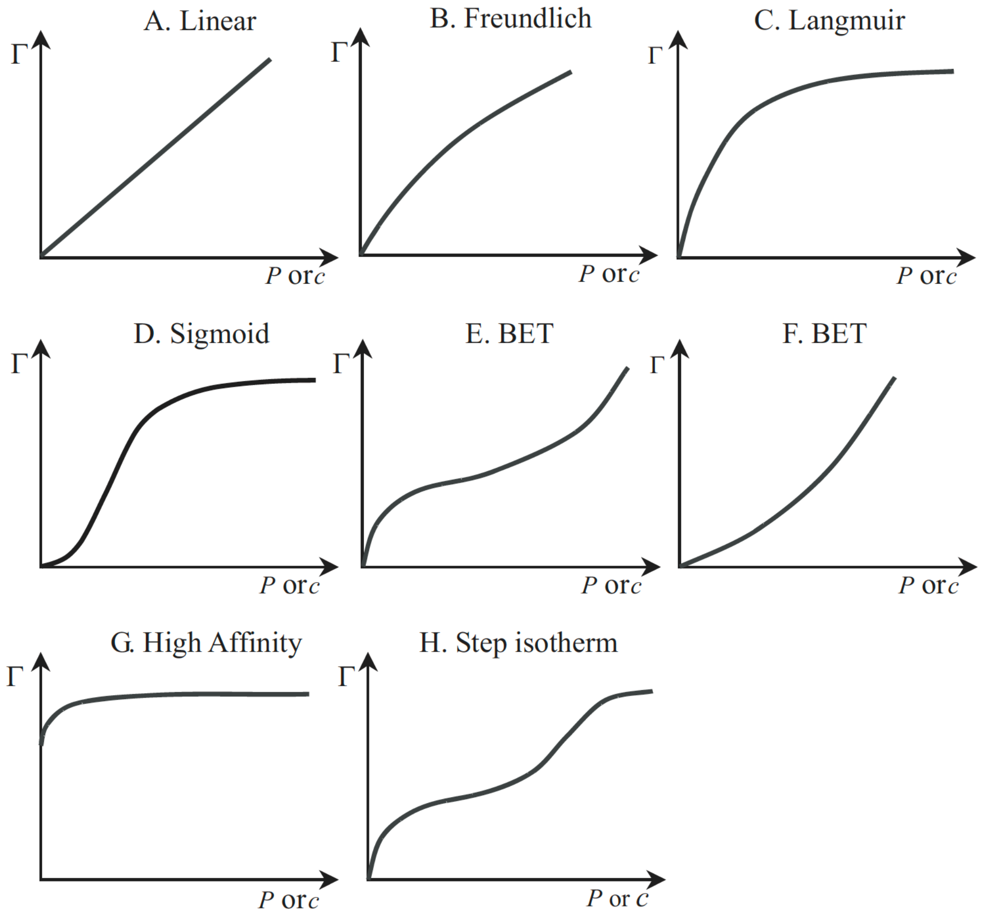


Figure 9.7: Left: Frumkin–Fowler–Guggenheim (FFG) adsorption isotherms (coverage θ versus the pressure in units of K_L^{-1}). The curves were calculated using Eq. (9.35) with $\beta = 0, 2, 4, 6$. For $\beta = 6$ the physically correct adsorption curve is plotted as a continuous curve while the one calculated with Eq. (9.35) is plotted as a dotted curve. Right: Adsorption isotherms for krypton adsorbing to the (0001) plane of graphite at two different temperatures. The dotted curves were fitted using Eq. (9.35) with $\beta = 4.5$. Experimental results were taken from Ref. [377].

Isotherms



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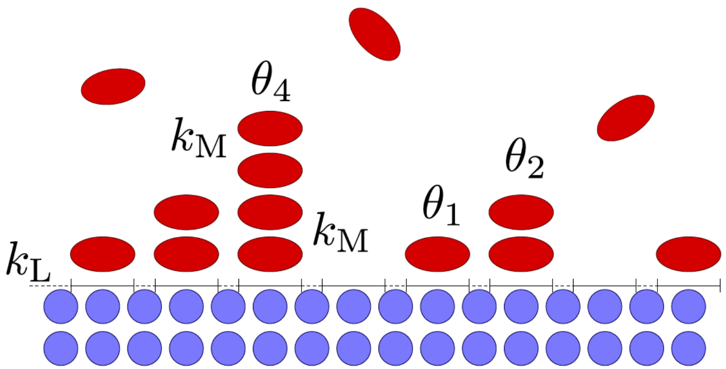
BET

- Random adsorption on multiple layers. Langmuir constant for the first layer is k_L, other layers bind on the previous with $k_M = k_L e^{(\epsilon_M - \epsilon_1)/k_B T}$
- One must equate ad/desorption rate from the sites covered by *i* layers
- The sums of θ_i's are geometric series.
- Total coverage (number of molecules per number of *surface* sites)

$$\theta_1 = k_L P \left(1 - \sum_i \theta_i\right), \qquad \theta_i = \theta_{i-1} k_M P = \theta_1 \left[k_M P\right]^{i-1}$$



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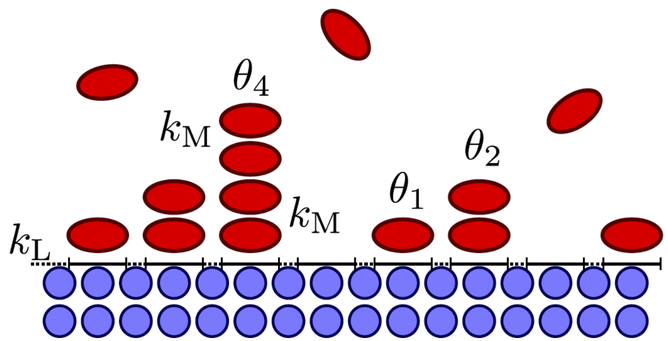
BET - Multilayers

$$\sum_{i=1}^{\infty} [k_M P]^{i-1} = \frac{1}{1 - k_M P}, \qquad \sum_{i=1}^{\infty} i\,[k_M P]^{i-1} = \frac{1}{(1 - k_M P)^2}$$

$$\theta = \theta_1 \sum_{i=1}^{\infty} i\,[k_M P]^{i-1} = \theta_1 \frac{1}{(1 - k_M P)^2} = \frac{k_L P\,(1 - k_M P)}{1 + k_L P - k_M P} \frac{1}{(1 - k_M P)^2}$$

$$\theta \approx \frac{1}{(1 - x_B)} \frac{x_B c_B}{1 + x_B\,(c_B - 1)}, \qquad x_B = k_M P,\; c_B = k_L / k_M$$

$$\boxed{\theta = \frac{k_L P}{1 + k_L P - k_M P} \frac{1}{1 - k_M P}}$$



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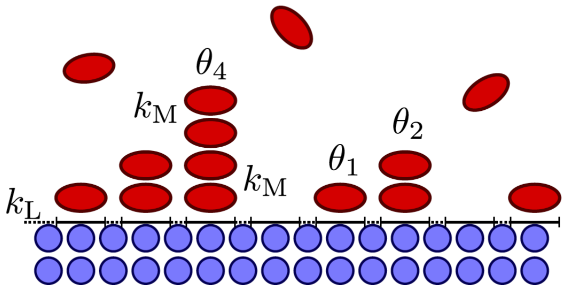

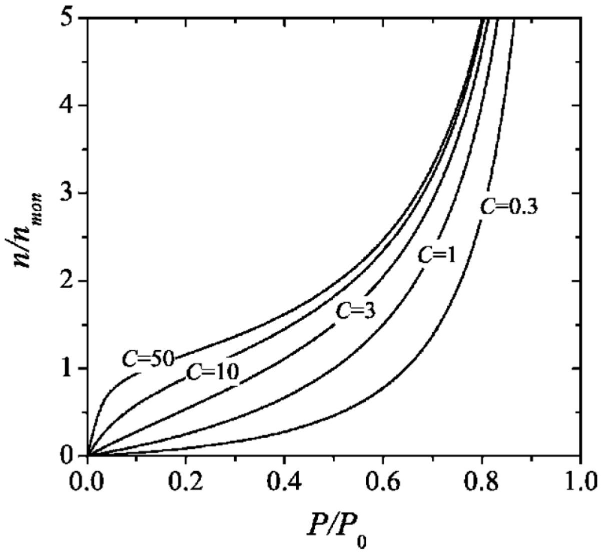

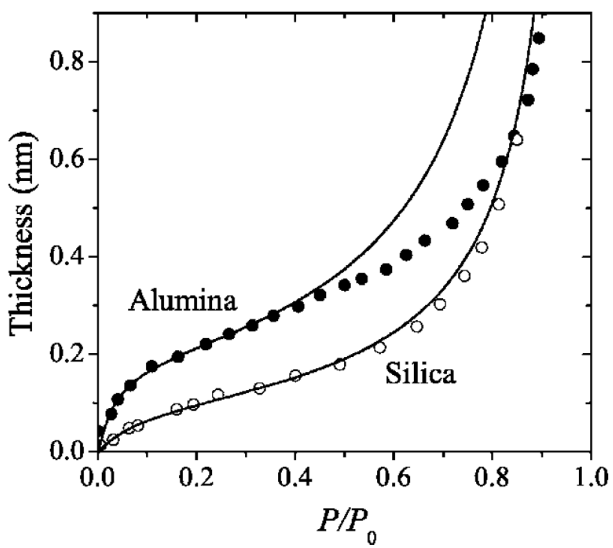

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Conclusions