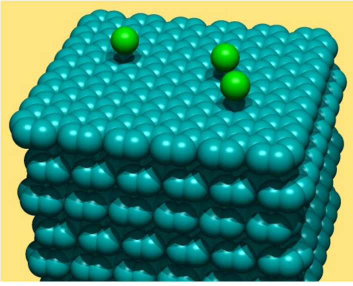
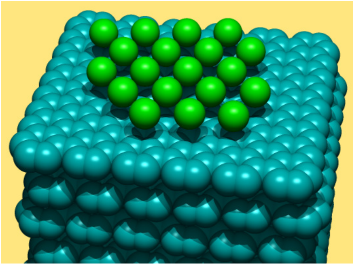
Adsorption



↑ Ar on graphite →

- adsorption: on surface (interface)
- absorption: inside (bulk)
- sorption: both
- molecular adsorption
  (g) → (s), (l) → (s)/(l), . . .
- ion adsorption
  Paneth-Fajans rule
- exchange ion adsorption,
  counterions in aluminosilicates



Physical adsorption and chemisorption

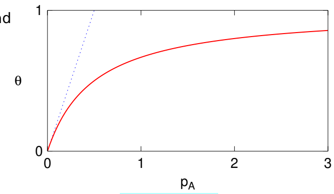
	physical adsorption	**chemisorption**
forces	physical (weak: van der Waals, H-bonds)	covalent bonds
specificity	non-specific (easy to liquefy – easily adsorbed)	specific
adsorption heat	-20 to $-40\,\mathrm{kJ\,mol^{-1}}$ (≈ condensation heat)	-40 to $-400\,\mathrm{kJ\,mol^{-1}}$ (≈ reaction heat)
number of layers	several layers possible (as condensation)	one layer
activation energy	0	> 0
rate	high (seconds)	slow at low T, fast at high T
amount adsorbed	large below T_c, small above T_c	small; usually given by kinetics
reversibility	easy (vacuum, temperature)	not so easy (vacuum + higher T)

Langmuir adsorption isotherm

- Good for chemisorption, adsorption in small cavities (zeolites); limited for physical adsorption ($p \ll p^s$)
- Independent (noninteracting) adsorption centers of one kind
- Max 1 molecule/center (one layer)

Known: Activity of the adsorbate: $a_A = \frac{p_A}{p^{st}}$, or from solution: $a_A = \frac{c_A(\circledcirc)}{c^{st}}$

Equilibrium constant of adsorption K_{ad}



Adsorption equilibrium:

$$L + A \rightarrow LA$$

$$[LA] + [L] = c_{L0}, \qquad \frac{[LA]}{a_A[L]} = K_{ad}$$

Coverage (saturation):

$$\boxed{\theta} = \frac{\text{adsorbed amount}}{\text{maximum amount (monolayer)}} = \frac{[LA]}{c_{L0}} = \boxed{\frac{K_{ad}a_A}{1 + K_{ad}a_A}}$$

Gas: $\boxed{\theta = \frac{bp_A}{1 + bp_A}}, \quad b = \frac{K_{ad}}{p^{st}}$

Options

- Dissociative adsorption

$$2\,L + A_2 \rightarrow 2\,LA$$

$$\theta = \frac{bp_A^{1/2}}{1 + bp_A^{1/2}}$$

- Competitive adsorption (2 compounds):

$$L + A \rightarrow LA$$

$$L + B \rightarrow LB$$

$$\theta_A = \frac{b_A p_A}{1 + b_A p_A + b_B p_B}$$

Heterogeneous catalysis

A catalyst in solid phase, large specific surface area.
The rate-determining process may be:

- diffusion (in solution: k drops if we increase the viscosity)
- chemisorption (T-dependent)
- surface diffusion

Example – chemisorption determines the rate, A → B
Independent active centers L, adsorption equilibrium

$$A + L \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} LA \xrightarrow{k_2} B + L$$

If not $k_2 \ll k_{-1}$, follow the Michaelis–Menten kinetics

for $k_2 \ll k_{-1}$ use pre-equilibrium, $K_{ad} = k_1/k_{-1}$

$$-\frac{dc_A}{d\tau} = \frac{dc_B}{d\tau} = k_2 c_{L0}\theta = k_2 c_{L0}\frac{K_{ad}c_A}{1 + K_{ad}c_A} \overset{\text{gas}}{\propto} \frac{bp_A}{1 + bp_A}$$

- small c_A: $-\frac{dc_A}{d\tau} = k_2 K_{ad} c_{L0} c_A \overset{\text{gas}}{\propto} p_A$ (**1st order**)
- large c_A: $-\frac{dc_A}{d\tau} = k_2 c_{L0} \overset{\text{gas}}{=} \text{const}$ (saturated catalyst – **0th order**)

E.g., decomposition of phosphane (phosphine, PH_3) on tungsten (W).

Heterogeneous catalysis

Reaction in (g) or (less typically) in (l):

$$A + B \rightarrow P$$

Langmuir–Hinshelwood mechanism: both A and B are adsorbed and then react

$$-\frac{dc_P}{d\tau} = k\theta_A\theta_B = k\frac{b_A p_A b_B p_B}{(1 + b_A p_A + b_B p_B)^2}$$

Most common type for heat-activated reactions on a solid catalyst, e.g.:

$$CO + 2\,H_2 \overset{ZnO}{\rightarrow} CH_3OH$$

Complex rate/temperature dependence.

Elye–Rideal mechanism: A is adsorbed, then directly reacts with B in (g)

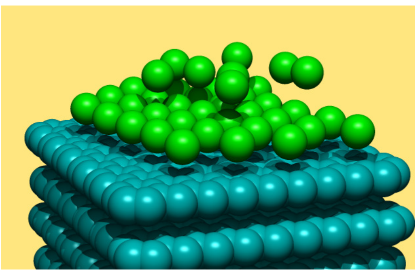
$$-\frac{dc_P}{d\tau} = k\theta_A p_B = k\frac{b_A p_A p_B}{1 + b_A p_A}$$

E.g., H + H → H_2 on dust grains in the interstelar space

BET Isotherm

Stephen **B**runauer
Paul Hugh **E**mmet
Edward **T**eller*

Usage: determining the specific surface area of adsorbent



- independent adsorption centers of the same kind
  simple but problematic assumption
- several layers
- 1st layer as in the Langmuir isotherm
- additional layers bound in the same way as in a liquid

Known: Activity of the adsorbate: a_A
Equilibrium constants of adsorption: K_{ad} (1st layer), K (more layers)

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* also known as "the father of the hydrogen bomb"

BET Isotherm

Adsorption center = L, molecule = A, complexes LA, LA_2, . . .

Balance: $\sum_{n=0}^{\infty}[LA_n] = c_{L0}$, coverage: $\theta = \frac{1}{c_{L0}}\sum_{n=0}^{\infty} n[LA_n] \in (0, \infty)$

$$\begin{array}{rcl} L + A \rightarrow LA & \quad & [LA] = K_{ad}a_A[L] \\ LA + A \rightarrow LA_2 & & [LA_2] = Ka_A[LA] \\ LA_2 + A \rightarrow LA_3 & & [LA_3] = Ka_A[LA_2] \\ \vdots & & \vdots \end{array}$$

$$c_{L0} - [L] = K_{ad}a_A[L] + Ka_A(c_{L0} - [L])$$

$$\Rightarrow \quad [L] = \frac{c_{L0}(1 - Ka_A)}{1 - Ka_A - K_{ad}a_A}$$

$$\theta = \frac{1}{c_{L0}}K_{ad}a_A[L]\left[1 + 2Ka_A + 3(Ka_A)^2 + \cdots\right] = \frac{K_{ad}a_A[L]}{(1 - Ka_A)^2}$$

$$S_1 = 1 + x + x^2 + x^3 + \cdots = 1 + xS_1 \quad \Rightarrow \quad S_1 = 1/(1-x)$$

$$S_2 = 1 + 2x + 3x^2 + \cdots = S_1 + xS_2 \quad \Rightarrow \quad S_2 = 1/(1-x)^2 \text{ or } S_2 = dS_1/dx$$

BET Isotherm II

$$\theta = \frac{K_{ad}a_A}{(1-Ka_A)[1+(K_{ad}-K)a_A]}$$

K describes the adsorption to 2nd, 3rd, ... layers = condensation.
From the equlibrium at the saturated vapor pressure p^s:

$$LA_n(l) + A(g) \to LA_{n+1}(l) \quad \Rightarrow \quad K = \frac{a(l)}{a(l)a_A} = \frac{p^{st}}{p^s}$$

Let us replace $a_A = \frac{p}{p^{st}}$ and let us define $C = \frac{K_{ad}}{K}$. The common form of BET is:

$$\theta = \frac{Cp/p^s}{(1-p/p^s)[1+(C-1)p/p^s]}$$

For C it holds:

$$C = \frac{K_{ad}}{K} = \exp\left[-\frac{\Delta_{ad,1}G_m^\ominus - \Delta_{ad,n}G_m^\ominus}{RT}\right] \approx \exp\left[-\frac{\Delta_{ad,1}H_m^\ominus - \Delta_{ad,n}H_m^\ominus}{RT}\right]$$

where $\Delta_{ad,n} = -\Delta_{vap}$

$C \gg 1$: forces adsorbent–adsorbate are much stronger than adsorbate–adsorbate e.g., very hydrofilic surface
$C \approx 1$: similar forces, bad adsorbent
$C \ll 1$: poor adsorption (hydrophobic surface)

Freundlich isotherm

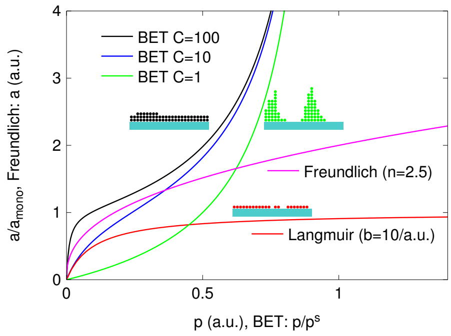
Freundlich isotherm

- empirical
- heterogeneous surfaces
- fails close to $p_A = p^s$

$$a = k\,p^{1/n}$$

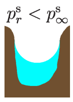
a = amount adsorbed
k = constant (decreasing with increasing T)
n = constant, $n > 1$ ($n \approx 1$ for high T)

Isotherms compared

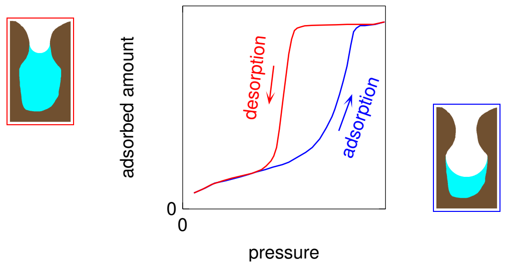


Capillary condensation and hysteresis

It follows from the Kelvin equation that there is a lower saturated pressure above the meniscus in hydrophilic/lyofilic pores (contact angle < 90°). Therefore, the pores get filled already at $p < p^s$, hence the amount adsorbed (a) increases.



Complex pore shape (cavities, bottle-like), open cylinders (curvatures for adsorption/desorption differ) ⇒ hysteresis (different shape for adsorption/desorption)



Example

The adsorption of ethylene on activated carbon at 273 K, expressed as the mass of ethylene per mass of charcoal (a) in dependence on pressure (p), is shown in the table below. Determine the constants of the Langmuir isotherm and the specific surface area of the adsorbent. One molecule of ethylene covers 19 Å^2 = 0.19 nm^2.

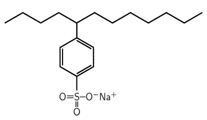
p/MPa	0.1	0.2	0.28	0.41	0.98	1.39	1.93	2.75	3.01	3.51
a	0.089	0.127	0.144	0.163	0.189	0.198	0.206	0.208	0.209	0.210

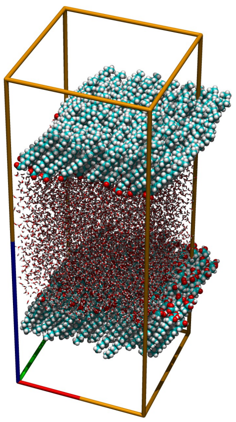
$a_{max} = 0.219$, $b = 6.84$ MPa^{-1}, $A_{spec} = 900$ m^2 g^{-1}

Surfactants

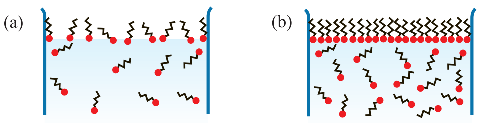
surface active (acting) agent

- adsorbed at the solvent surface
- decreases the surface tension





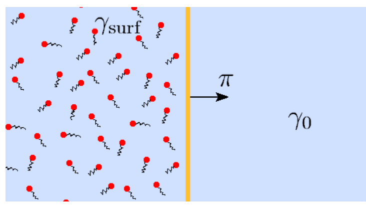
- usually a hydrophilic "head" (-COOH, -SO$_3$H) and a hydrophobic "tail" (aliphatic: 0.205 nm^2/molecule)



- longer molecules are not dissolved, but can compose films at a surface

Surface pressure

Experiment. Throw matches to water, touch the surface with soap or other detergent.

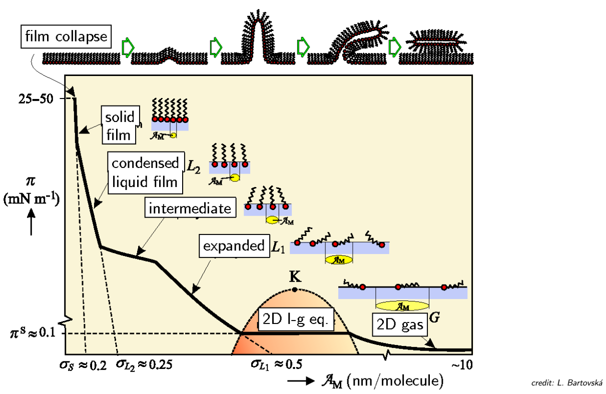


Lowering surface (Gibbs) energy ⇒ increase the surface covered by a surfactant ⇒ surface pressure

$$\pi = \gamma_0 - \gamma_{surf} > 0$$

Unit: N/m

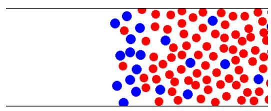
Films of surfactants



hexadecanol, palmitate: 2D crystal
phospholipides (less regular): 2D liquid film

Thermodynamics of adsorption

1 = solvent
2 = surfactant

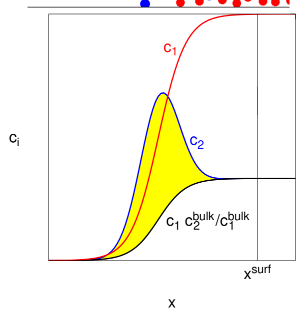


Surface excess:

$$\Gamma_{2,1} = \int_{-\infty}^{\infty}\left[c_2(x) - \frac{c_2^{bulk}}{c_1^{bulk}}c_1(x)\right]dx$$

$$= \frac{1}{\mathcal{A}}\left[n_2^{surf} - \frac{n_2^{bulk}}{n_1^{bulk}}n_1^{surf}\right]$$

$c_i(x)$ = concentration of compound i at x
c_i^{bulk} = concentration of i in the bulk
$n_i^{surf} = \mathcal{A}\int_{-\infty}^{x^{surf}} c_i(x)dx$ for x^{surf} far away



Gibbs adsorption isotherm

Gibbs–Duhem equation in the bulk at constant $[p, T]$:

$$\mathrm{d}G^{\text{bulk}} = \mu_1 \mathrm{d}n_1^{\text{bulk}} + \mu_2 \mathrm{d}n_2^{\text{bulk}} = \mathrm{d}(\mu_1 n_1^{\text{bulk}} + \mu_2 n_2^{\text{bulk}})$$

$$\Rightarrow \quad \mathrm{d}\mu_1 n_1^{\text{bulk}} + \mathrm{d}\mu_2 n_2^{\text{bulk}} = 0 \quad \Rightarrow \quad \mathrm{d}\mu_1 = -\mathrm{d}\mu_2 \frac{n_2^{\text{bulk}}}{n_1^{\text{bulk}}} \qquad (1)$$

Similarly for the surface (to x^{surf}):

$$\mathrm{d}G^{\text{surf}} = \mu_1 \mathrm{d}n_1^{\text{surf}} + \mu_2 \mathrm{d}n_2^{\text{surf}} + \gamma \mathrm{d}\mathcal{A} = \mathrm{d}(\mu_1 n_1^{\text{surf}} + \mu_2 n_2^{\text{surf}} + \gamma \mathcal{A})$$

$$\Rightarrow \mathrm{d}\mu_1 n_1^{\text{surf}} + \mathrm{d}\mu_2 n_2^{\text{surf}} + \mathrm{d}\gamma \mathcal{A} = 0 \qquad (2)$$

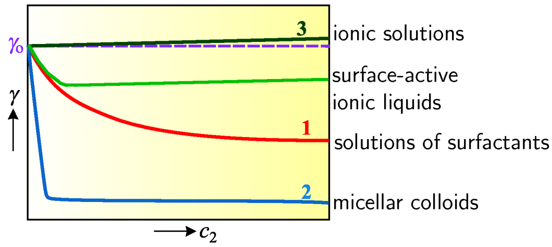
The chemical potentials are the same! On inserting (1) to (2):

$$-\mathrm{d}\mu_2 \frac{n_2^{\text{bulk}}}{n_1^{\text{bulk}}} n_1^{\text{surf}} + \mathrm{d}\mu_2 n_2^{\text{surf}} + \mathrm{d}\gamma \mathcal{A} = \mathrm{d}\mu_2 \overbrace{\left(n_2^{\text{surf}} - \frac{n_2^{\text{bulk}}}{n_1^{\text{bulk}}} n_1^{\text{surf}} \right)}^{\Gamma_{2,1}} + \mathrm{d}\gamma \mathcal{A} = 0$$

$$\boxed{\Gamma_{2,1} =} - \left(\frac{\partial \gamma}{\partial \mu_2} \right)_{p,T} \approx \boxed{-\frac{c_2}{RT} \left(\frac{\partial \gamma}{\partial c_2} \right)_{p,T}}$$

A surfactant (decreasing the surface energy) exhibits a positive surface excess

Concentration dependence of the surface tension



Atomic Layer Deposition (ALD)

A precursor adsorbed to a monomolecular layer. Example:

- vapor of $Al_2(CH_3)_6$ (trimethylaluminium dimer): disociative chemisorption
- remove vapor (vacuum, nitrogen)
- water vapor → Al_2O_3
- remove vapor