Homework 3

Deadline of submission: 8 April

You use the same dataset.

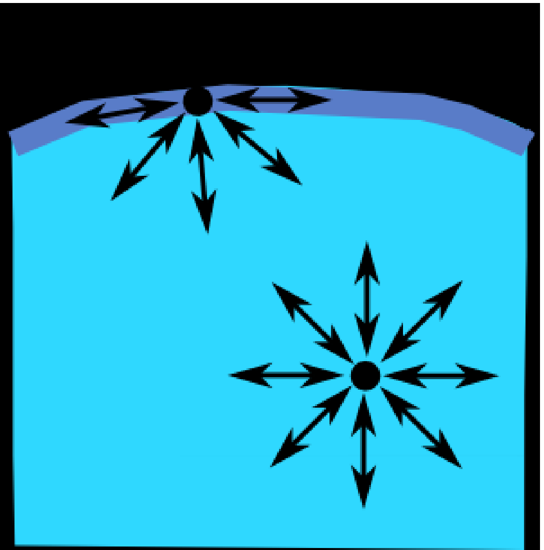
1. As it was shown in the last week material (#6) the limits of the Kelvin equation define the limits of the pore size marking the mesopore range.
2. From the Kelvin equation calculate the relative pressure values corresponding to the narrowest and widest mesopores. The surface tension of liquid nitrogen is 8.94 mN/m. You can calculate the molar volume of nitrogen from the density of liquid nitrogen given in homework 1. (0.808 g/cm^3). The contact angle is 0.
3. Using your isotherm data, calculate te pore volume corresponding to the mesopore range, supposing that all the gas adsorbed is in liquid form.

Adsorption at S/L interface

S+L

Applications/use:

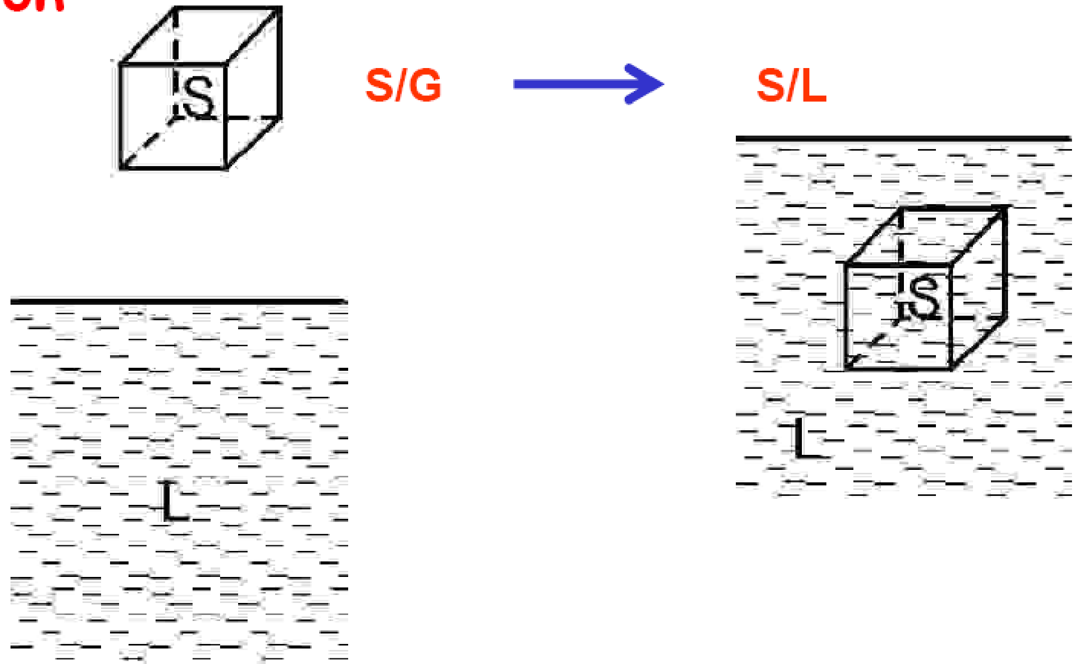
- solvent purification, e.g. with molecular sieves
- water treatment
- decolorisation
- dyeing
- washing
- separation techniques (liquid chromatography)
- surface characterisation



TEXT: Physical chemisty of surfaces Part 2

PURE (SINGLE COMPONENT) LIQUID:

immersion



S/G → S/L

heat of immersion: $q_w = h_{S/L} - h_S$

orientation on the surface

Multicomponent liquid phase

Players:

dissolved material	(B)
solvent	(A)
surface site	(S)

Interactions: A – A; B – B; A – S; B - S

Mechanism:

- wetting
- sorption
- mixing
- exchange

1) non-electrolytes or weak electrolytes

dispersive/hydrophobic/H-bond/van der Waals interactions

competition

Mechanism of S/L adsorption

$\beta A^L + B^s \longleftrightarrow \beta A^s + B^L$ **exchange**

$\beta = \frac{a_{m,B}}{a_{m,A}}$ **Cross sectional area of B and A**

2) electrolytes

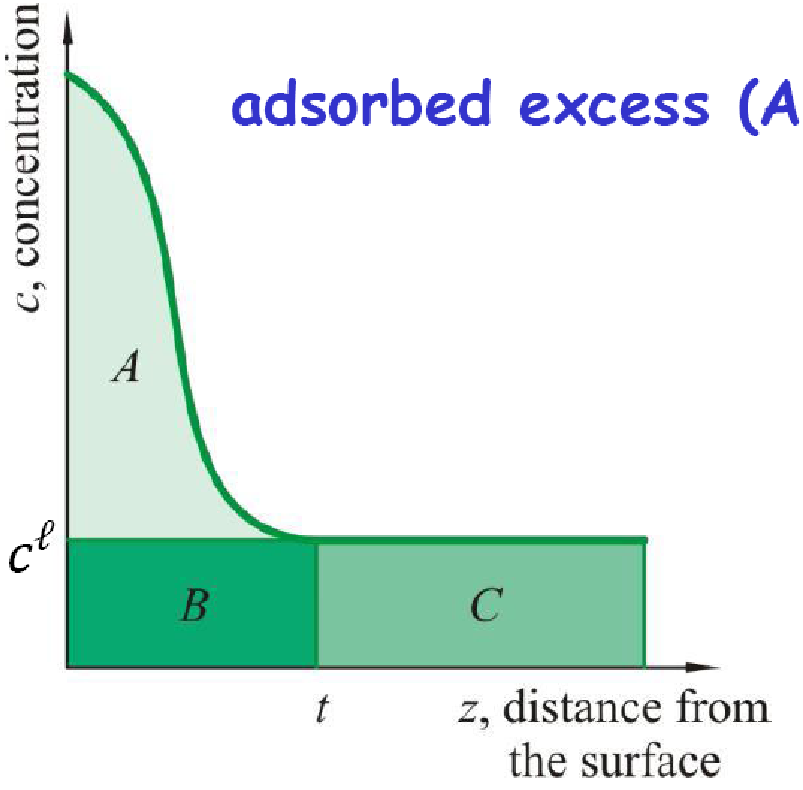
electrostatic interactions
(attraction, repulsion)

Quantitative description of the adsorption

$$S_A = \frac{\text{surface area}}{\text{mass of solid}}$$

adsorbed amount (A+B)

adsorbed excess (A)



$$n = A_s \int_0^t c\,dz + c^\ell V^\ell \quad (A+B+C)$$

$$n^\sigma = n - c^\ell V^\ell - c^\ell V^s \quad (A)$$

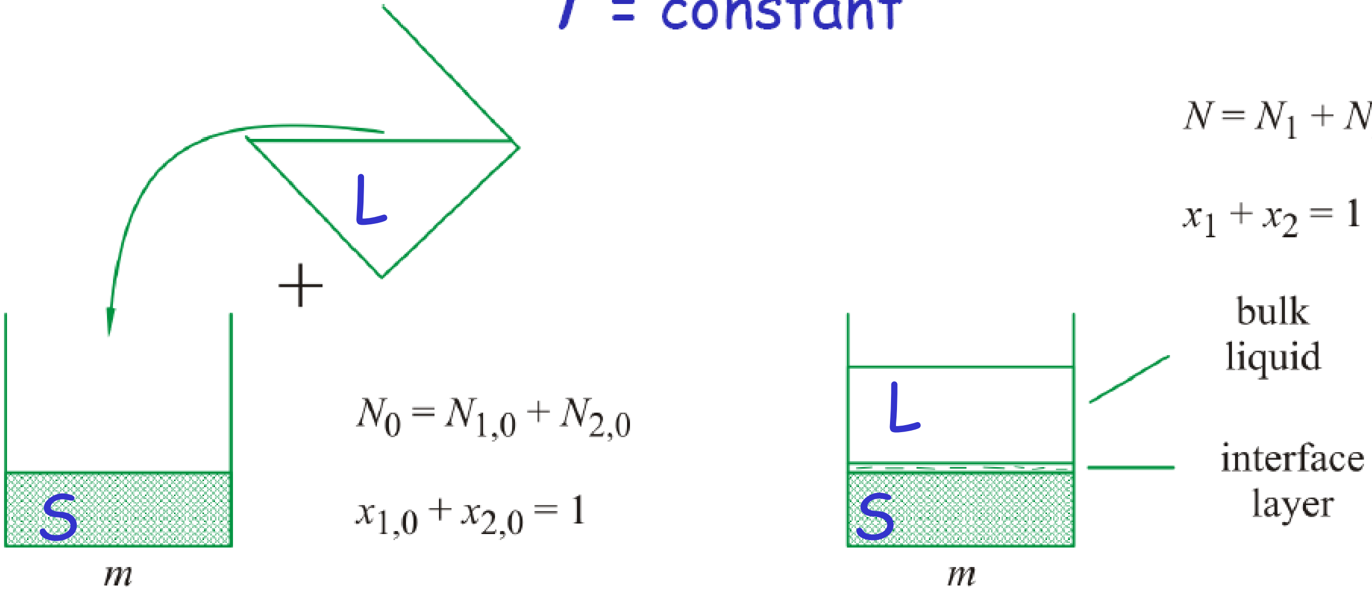
$$n^s = n^\sigma + c^\ell V^s \quad (A+B)$$

$$n^s \approx n^\sigma$$

only if c^ℓ is low
(ONLY for dilute solutions)

Experimental

T = constant



$$N_0 = N_{1,0} + N_{2,0}$$

$$x_{1,0} + x_{2,0} = 1$$

$$N = N_1 + N_2$$

$$x_1 + x_2 = 1$$

$$N^s = N_1^s + N_2^s$$

$$x_1^s + x_2^s = 1$$

$$n_i = \frac{N_i}{m}$$

Material balance for component 1:

$$n_0 x_{1,0} = n_1^s + \left(n_0 - n^s\right) x_1$$

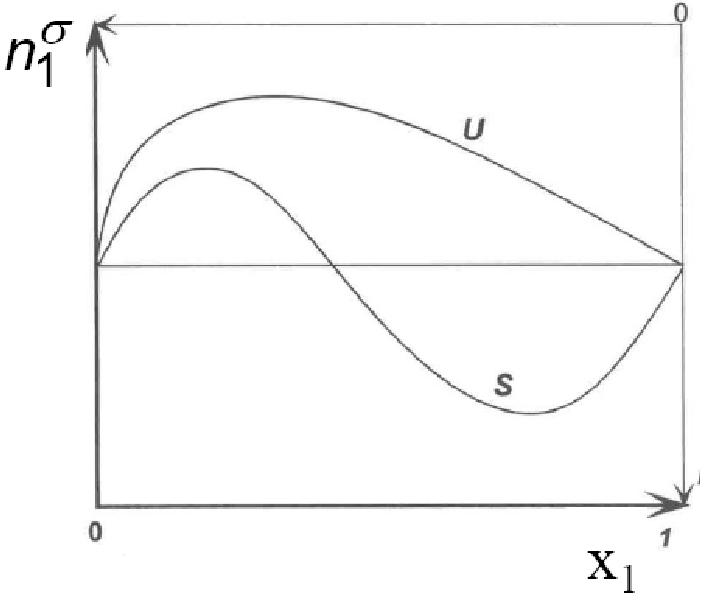
$$n_0 \left(x_{1,0} - x_1\right) = n_1^s - n^s x_1$$

$$n_1^\sigma \equiv n_1^s - n^s x_1 = n_0 \left(x_{1,0} - x_1\right)$$ **Adsorbed excess**

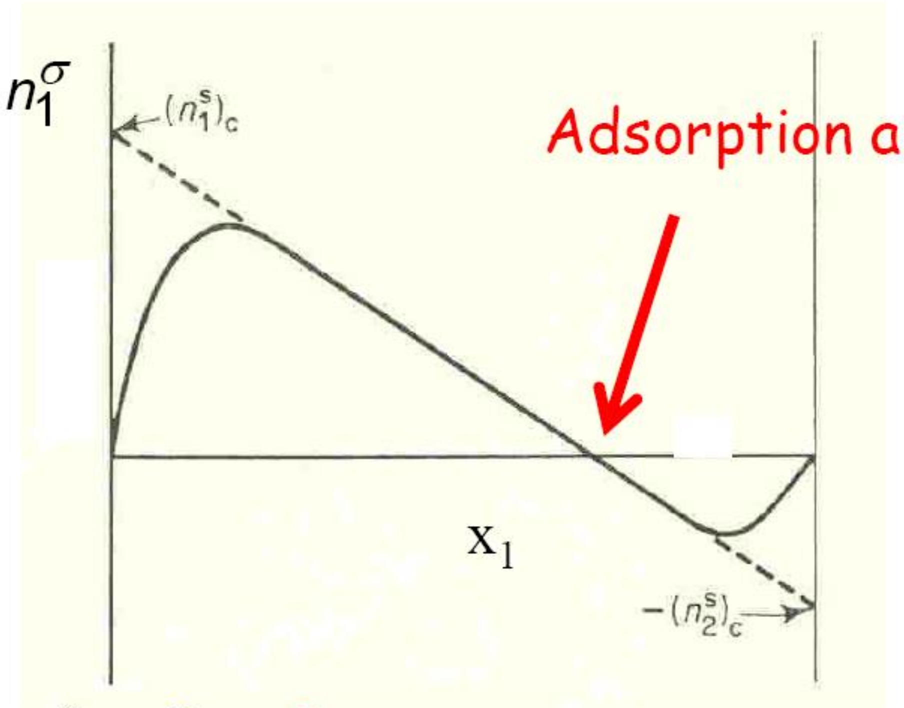
*COMPLETELY MISCIBLE LIQUIDS
(non-electrolytes or weak electrolytes)

$$n_0\left(x_{1,0}-x_1\right)=n_1^s-n^s x_1 \equiv n_1^\sigma\left(x_1\right) \qquad \mathrm{T = constant}$$

excess isotherm



Analysis of the isotherms having a linear section



Adsorption azeotrope point

$$n_0\left(x_{1,0}-x_1\right) = n_1^s - n^s x_1 \equiv n_1^\sigma\left(x_1\right) \qquad y = a + bx$$

Condition: monomolecular coverage

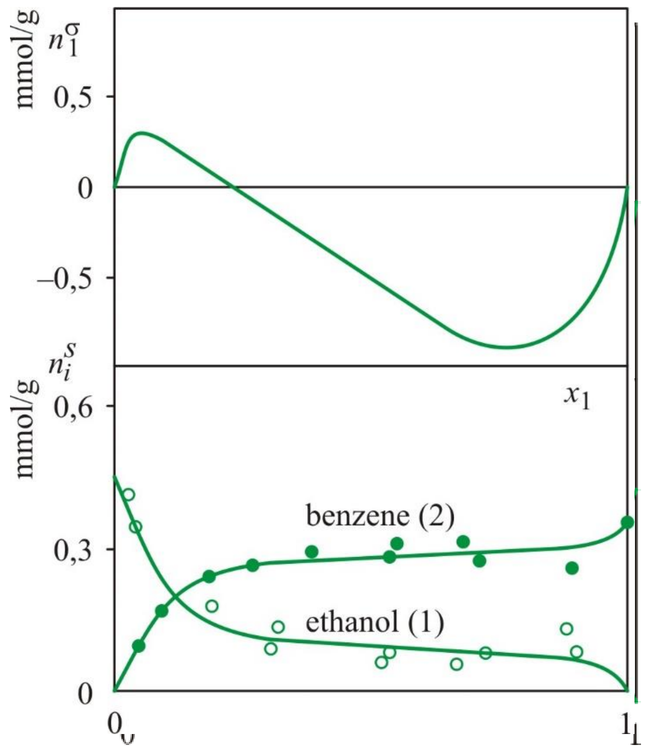
$$A_s = n_1^s a_{s,1} + n_2^s a_{s,2}$$

Alternative way of surface area determination

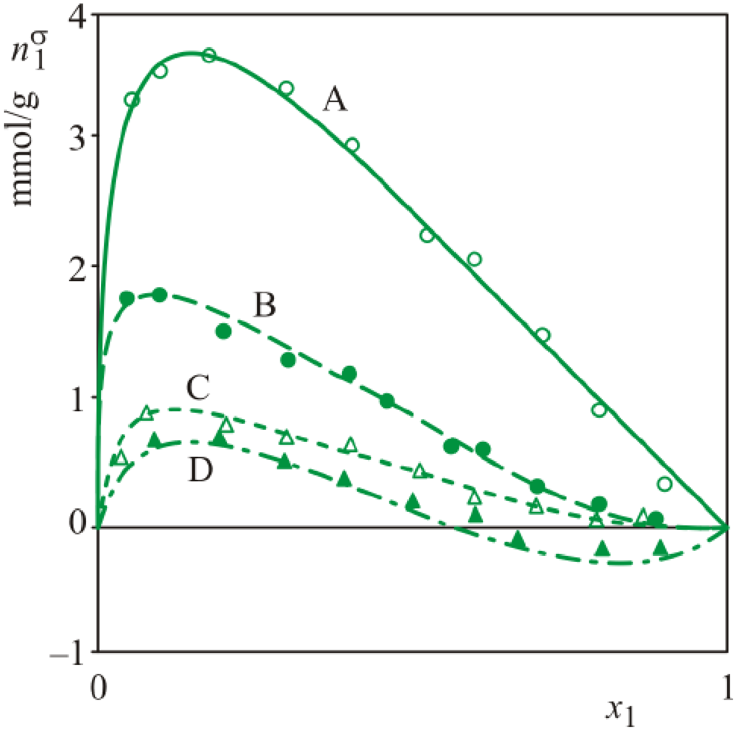
Molar cross sectional area of pure liquids

liquid	cross sectional area, m^2/mmol
methanol	94
ethanol	120
butanol	172
benzene	180
cyclohexane	208
heptane	256
toluene	206

The isotherm simultaneously characterizes the solid surface and the binary liquid



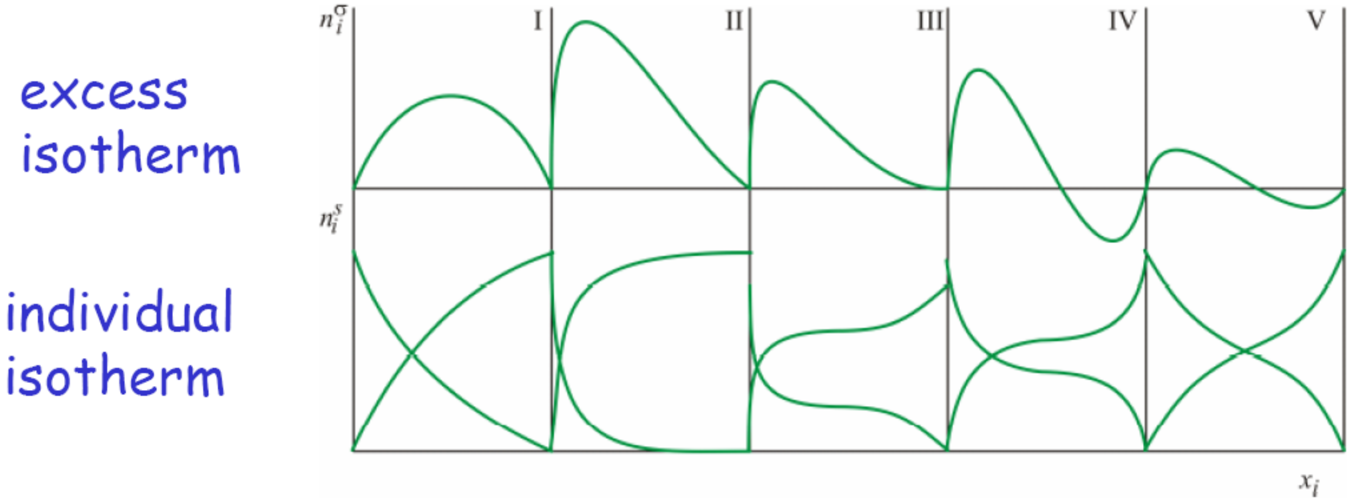
ethyl alcohol (1) - benzene (2) on activated carbon



A: methanol - benzene
B: ethanol - benzene
C: n-propanol - benzene
D: i-propanol - benzene
on palygorskite

$$x_1^s = \frac{n_1^s}{n^s} = \frac{n_1^\sigma}{n^s} + x_1$$

The individual isotherm (the total adsorbed amount of each component) can be calculated?



$$x_1^s = \frac{n_1^s}{n^s} = \frac{n_1^\sigma}{n^s} + x_1 \qquad n_i^s = n_i^\sigma + n^s x_i$$

*DILUTE NON-ELECTROLYTES OR WEAK ELECTROLYTES

$$n_i^s = n_i^\sigma + n^s x_i$$

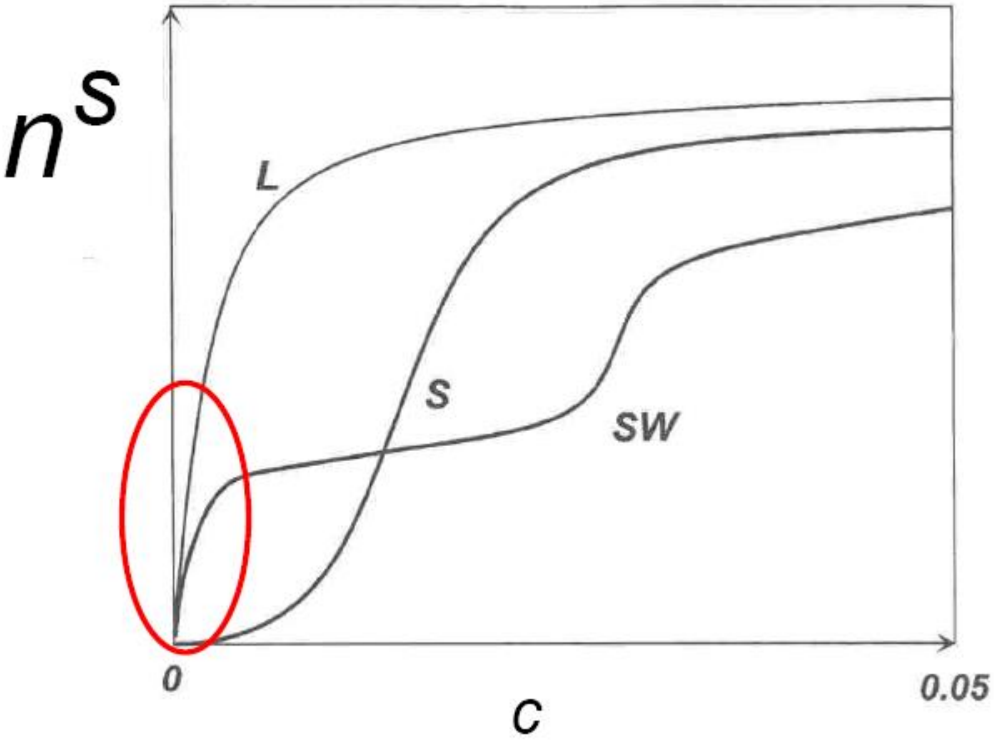
$$x_i \to 0 \qquad n^\sigma \approx n^s$$

Experimental:

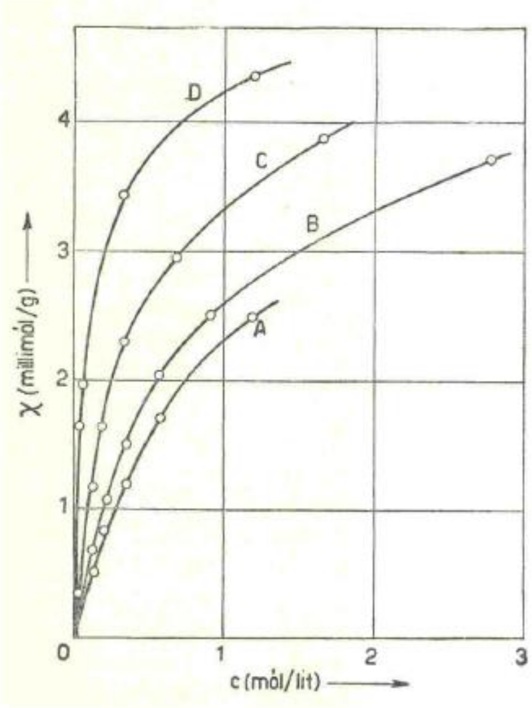
$$n^s = \frac{c_0 V_0 - c_e V_e}{m} = \frac{(c_0 - c_e)V}{m}$$

Swelling?

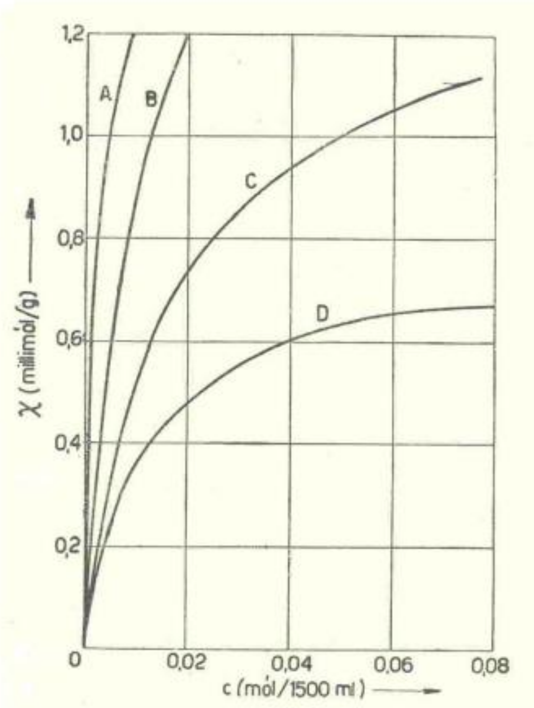
CLASSIFICATION



A: formic acid
B: acetic acid
C: propionic acid
D: butyric acid



From water on activated carbon



From toluene on silica

Oriented adsorption

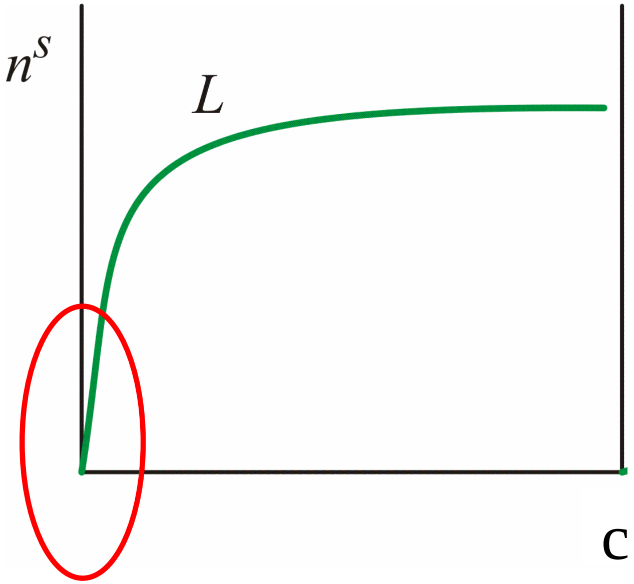
Models

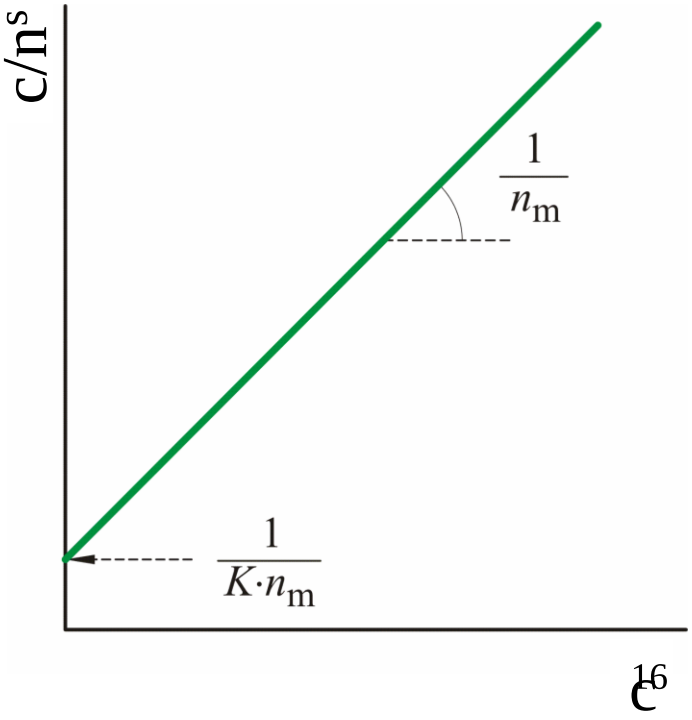
1. Langmuir

$$n^s = n_m^s \frac{Kc}{1+Kc}$$

Henry c→0

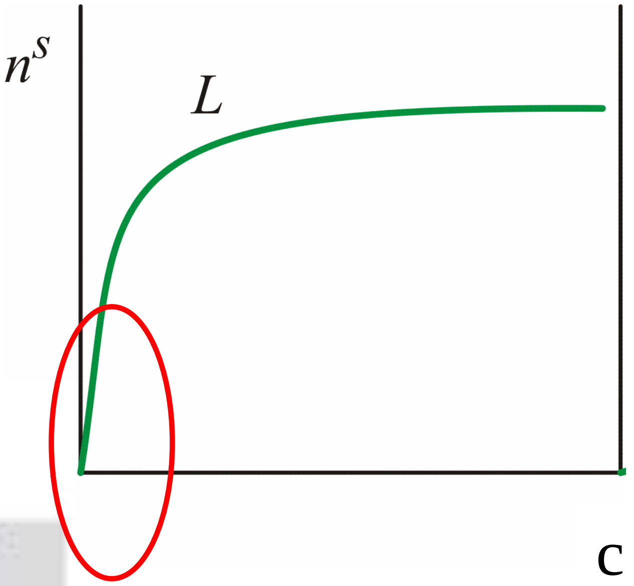
$$\frac{c}{n} = \frac{1}{Kn_m} + \frac{c}{n_m}$$

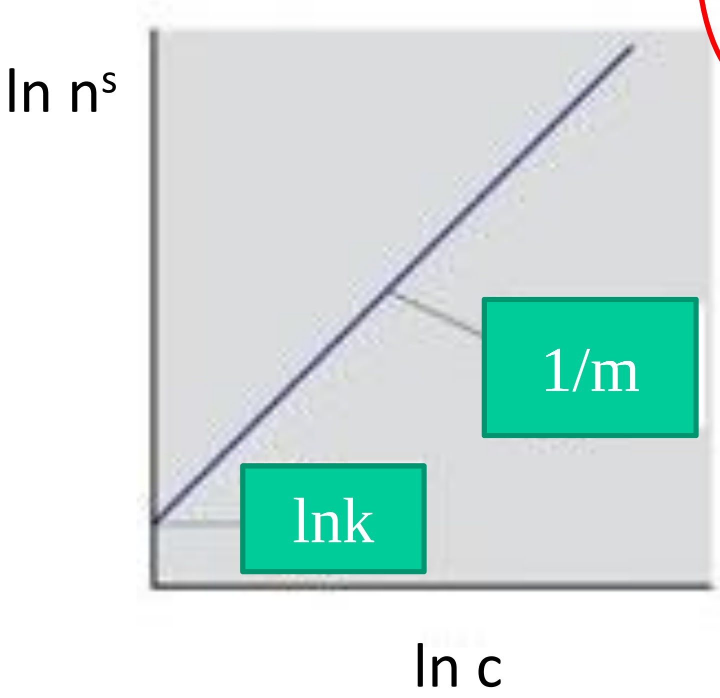




2. Freundlich

$$n^s = kc^{1/m} \quad m>1$$





3. Complex models: surface heterogeneity

- bi-Langmuir

$$n^s = \frac{a_1 c_e}{1 + b_1 c_e} + \frac{a_2 c_e}{1 + b_2 c_e}$$

-adsorption sites on the solid with two different energies

or

- the adsorptive has two kinds of binding sites
  - e.g. - chiral molecules
    - proteins

- **competitive Langmuir**

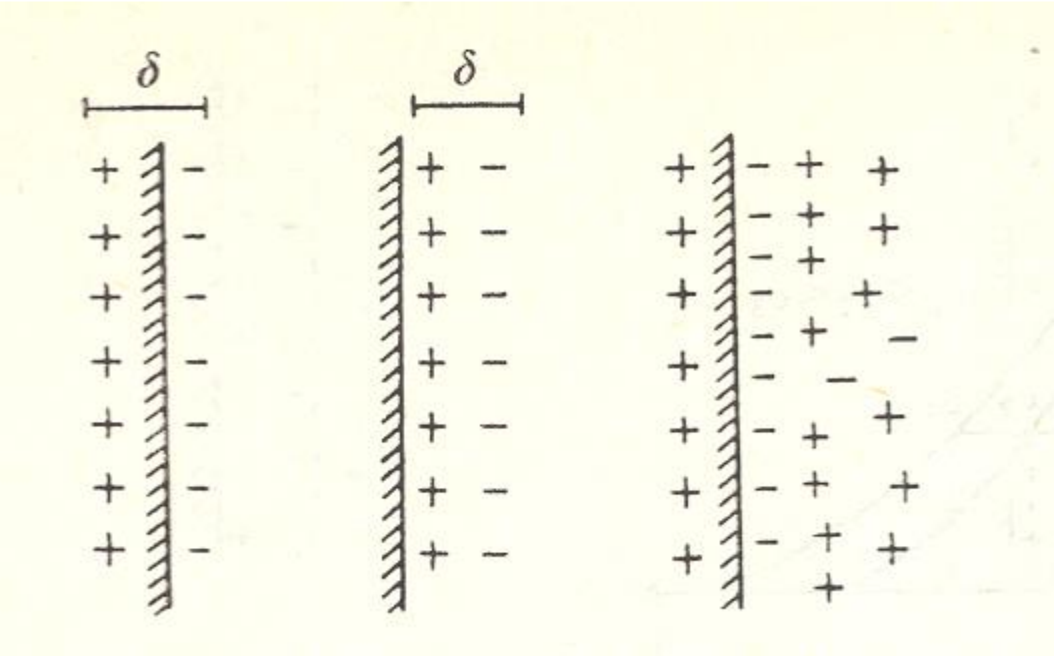
$$n_i^s = n_{m,i}^s \frac{K_i c_{i,e}}{1 + \sum K_i c_{i,e}}$$

Competitive adsorption for the same sites

n_m and K from single component Langmuir parameters

* Ionic systems

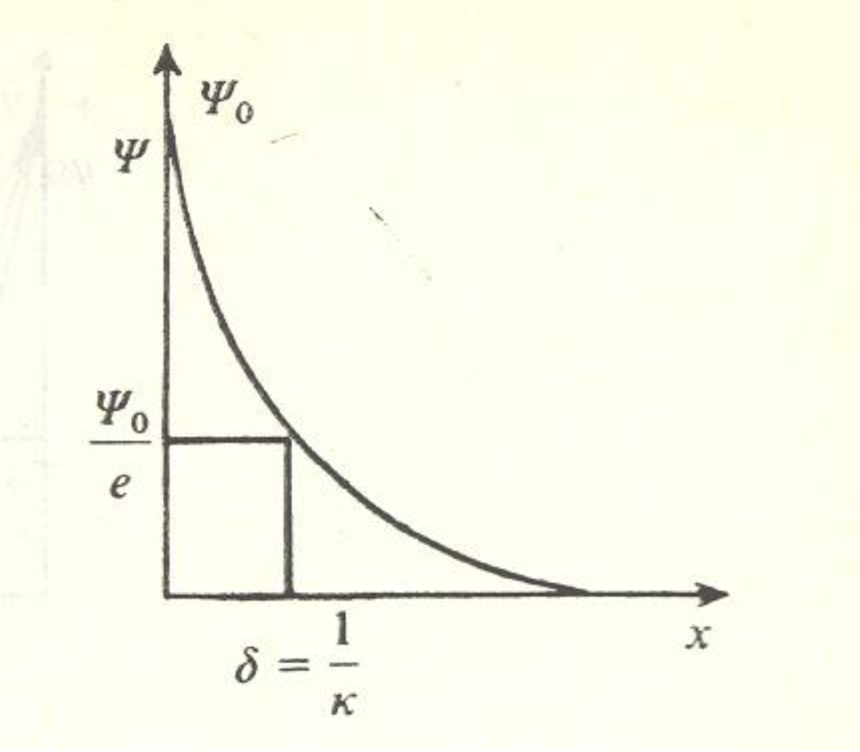
Electrostatic interactions: attraction
repulsion



The role of the counterion

Thickness of the electric double-layer δ

Brownian motion
Diffuse double-layer
Stern-layer



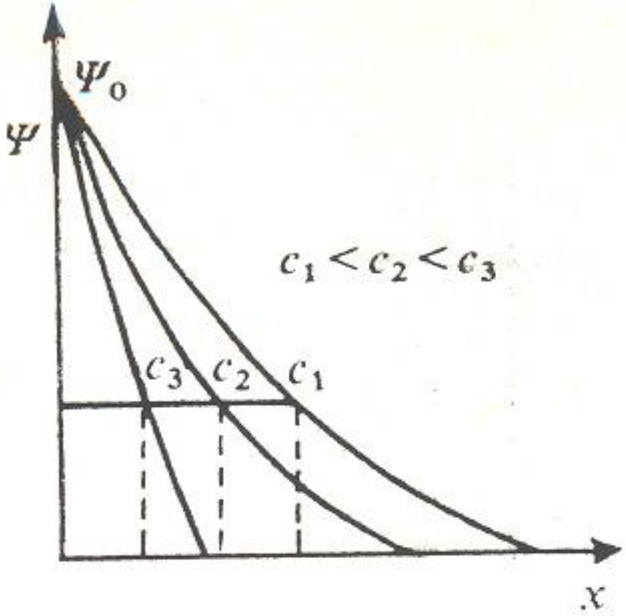
$$\Psi = \Psi_0 e^{-\kappa x}$$

$$\kappa = \text{konst} \cdot z\sqrt{c}$$

z the charge of the counterion (symmetric electrolites)

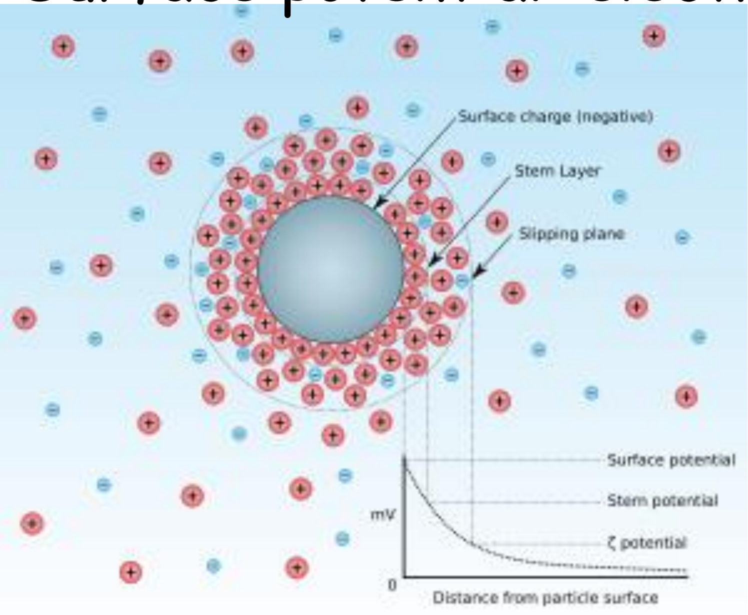
$1/\kappa$: fictive thickness

The thickness of the double-layer is influenced by the concentration of the ions



$$I = 0.5\sum_i z_i^2 c_i$$ ionic strength

Surface potential: electrokinetic potential or ***ζ - potential***



$$\zeta = \frac{q}{4\pi\varepsilon r}$$

q: surface charge density
ε: permittivity of the medium
r: radius of the spherical particle

Zeta potential [mV]	**Stability behavior of the colloid**
from 0 to ±5,	Rapid coagulation or flocculation
from ±10 to ±30	Incipient instability
from ±30 to ±40	Moderate stability
from ±40 to ±60	Good stability
more than ±61	Excellent stability

Dynamics of surface processes

TEXT: Physical chemisty of surfaces Part 3
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Interactions with the surface

- Difference in the binding energies of the different sites
- Occupied and unoccupied sites → Δc→ diffusion

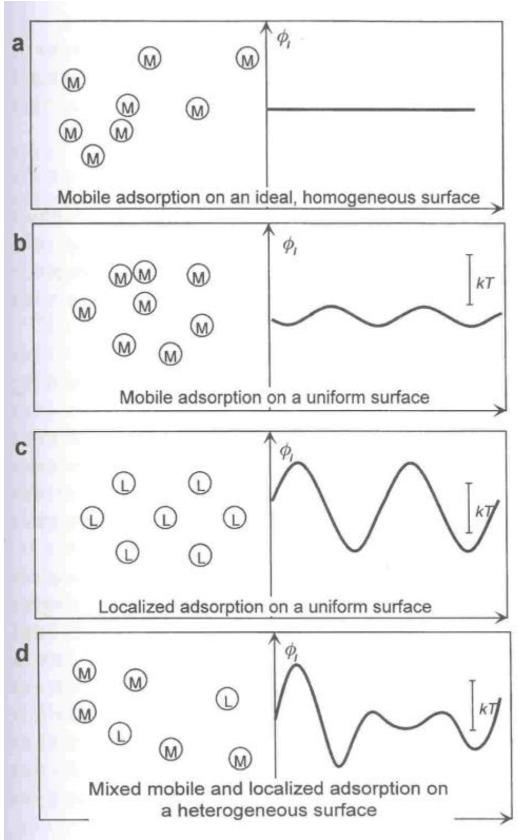
random

vibration energy > E_{ads}

$$D = D_0 e^{-\frac{E_{diff}}{RT}}$$

Affecting parameters?

Mobility on surface (surface diffusion)



Non-localized diffusion $E^{act} \le RT$

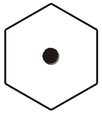
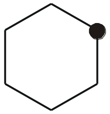
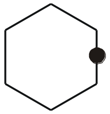
E.g.: H_2 on metal surface (generally as H)

Localized adsorption $E^{act} > RT$

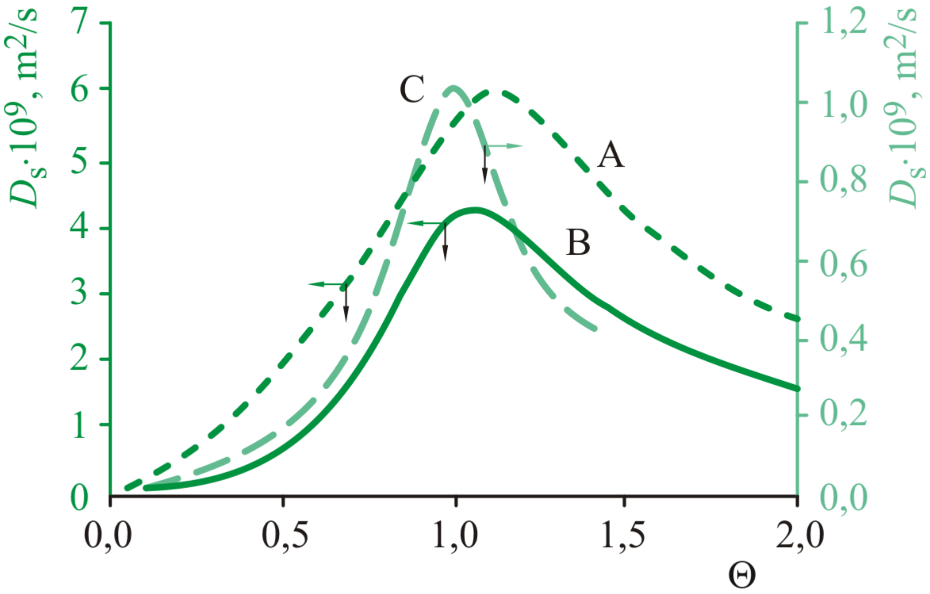
Activated diffusion

Low activation energy between high adsorption energy sites

$E_{ads} = E^{act}$ seldom typically $E^{act} = 0.1 \div 0.8 E_{ads}$

	E_{ads} J/mol
Ar/graphite	
	7315
	7145
	7145
Ar/KCl	
Cl —●— Cl	6646
K	6061
Cl	5308
Cl —●— K	5476

Further factors influencing surface mobility



A: argon/silica 89 K
B: argon/silica 77 K
C: N_2/amorphous carbon 77 K

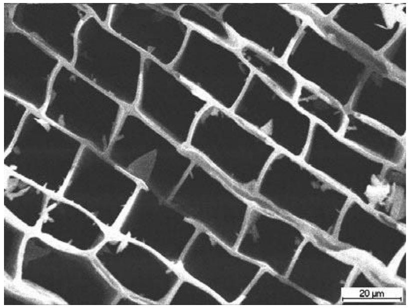
Properties of the chemicals
Temperature
Coverage

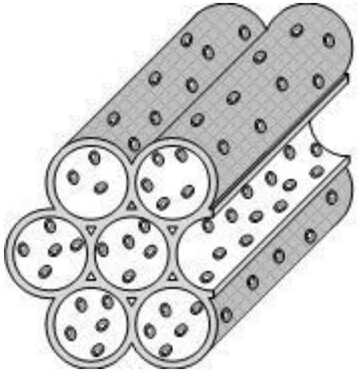
Low q θ: random walk for time τ ideig, 2D gas

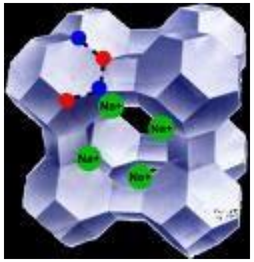
Θ increases → liquid like properties

~Activation energy follows the adsorption energy

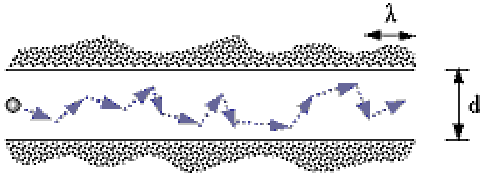
Mechanisms





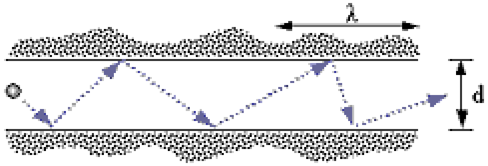


Molecular (Fick) diffusion (Brownian motion)



$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

Knudsen-diffusion



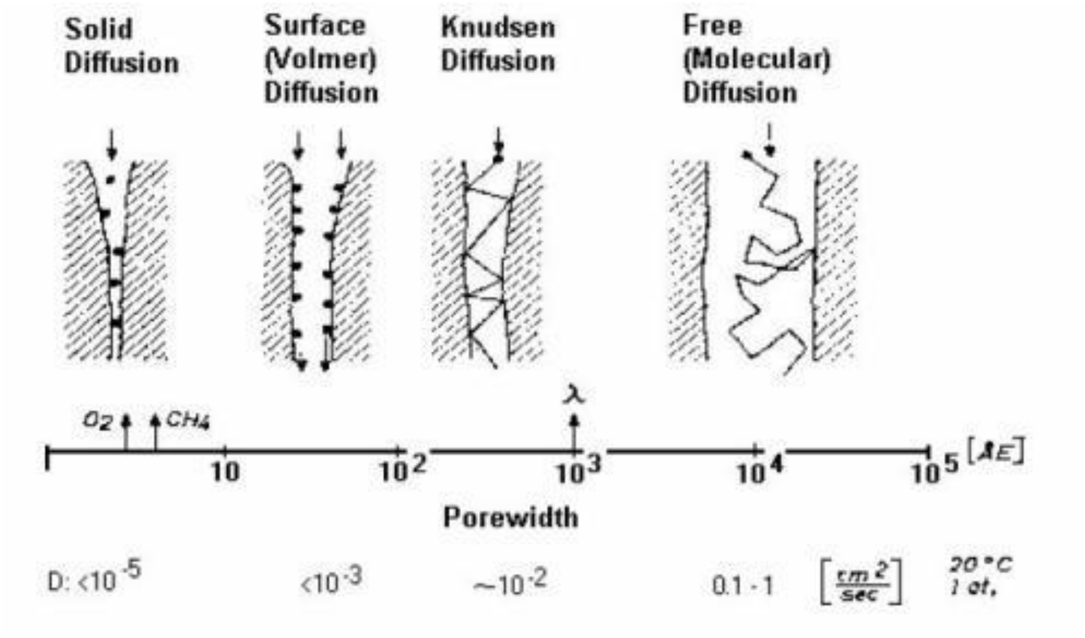
Knudsen number:

Kn=λ/d

Kn<< 1 viscous flow
Kn>> 1 Knudsen flow

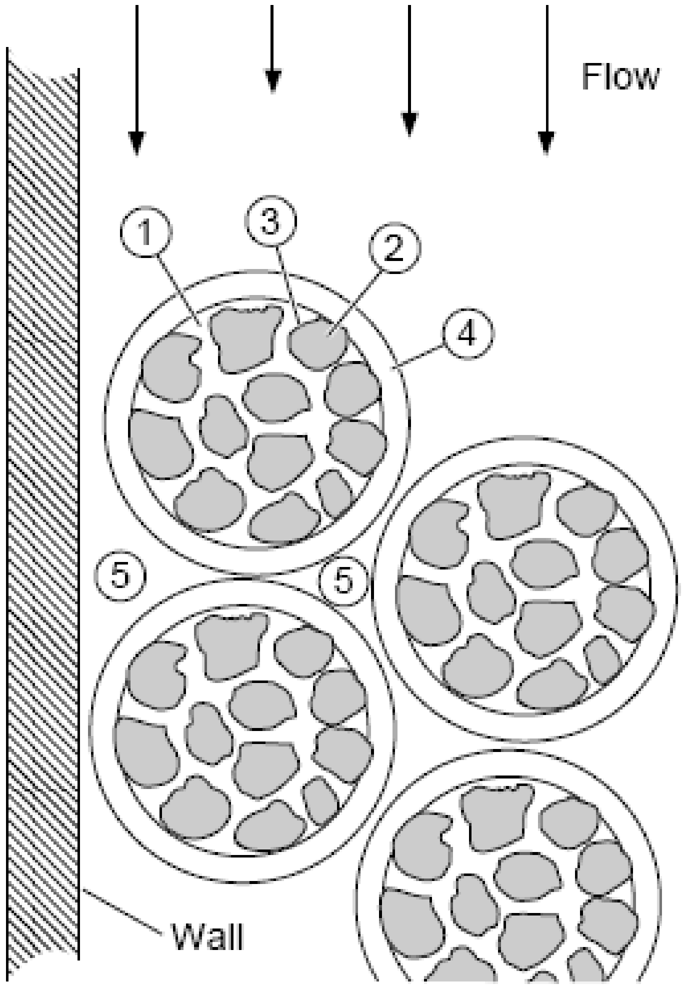
transport type	pore diameter (nm)
viscous flow	>20
molecular diffusion	>10
Knudsen diffusion	$2-100$
micropore (configurational) diffusion	<1.5

Activated diffusion (Volmer)



Diffusion	D, m^2/s
Fick	10^{-5} - 10^{-4}
Knudsen	10^{-6}
Volmer	10^{-7}

Transport mechanisms in porous materials



1 diffusion in pores
2 solid diffusion
3 reaction/soprion at phase boundary
4 free transport on the surface
5 mixing in the fluid phase

CHEMISORPTION

TEXT: Physical chemisty of surfaces Part 3
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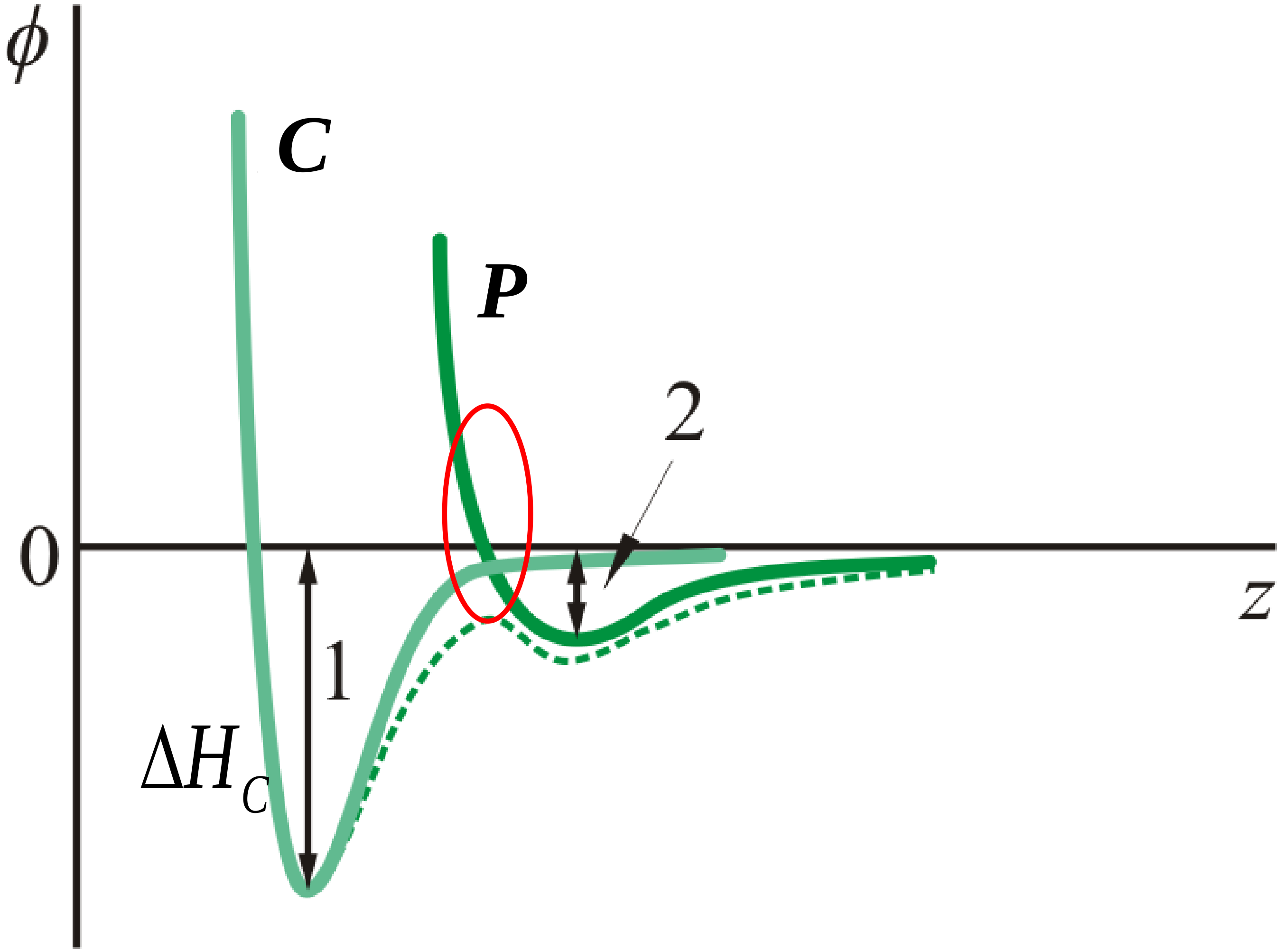
Physisorption vs Chemisorption

PHYSISORPTION	CHEMISORPTION
WEAK, LONG RANGE BONDING Van der Waals interactions	STRONG, SHORT RANGE BONDING Chemical bonding involved.
NOT SURFACE SPECIFIC Physisorption takes place between all molecules on any surface providing the temperature is low enough.	SURFACE SPECIFIC E.g. Chemisorption of hydrogen takes place on transition metals but not on gold or mercury.
ΔH_{ads} = 5 ….. 50 kJ mol-1	ΔH_{ads} = 50 ….. 500 kJ mol^{-1}
Non activated with equilibrium achieved relatively quickly. Increasing temperature always reduces surface coverage.	Can be activated, in which case equilibrium can be slow and increasing temperature can favour adsorption.
No surface reactions.	Surface reactions may take place: Dissociation, reconstruction, catalysis.
MULTILAYER ADSORPTION	MONOLAYER ADSORPTION

Electron transfer

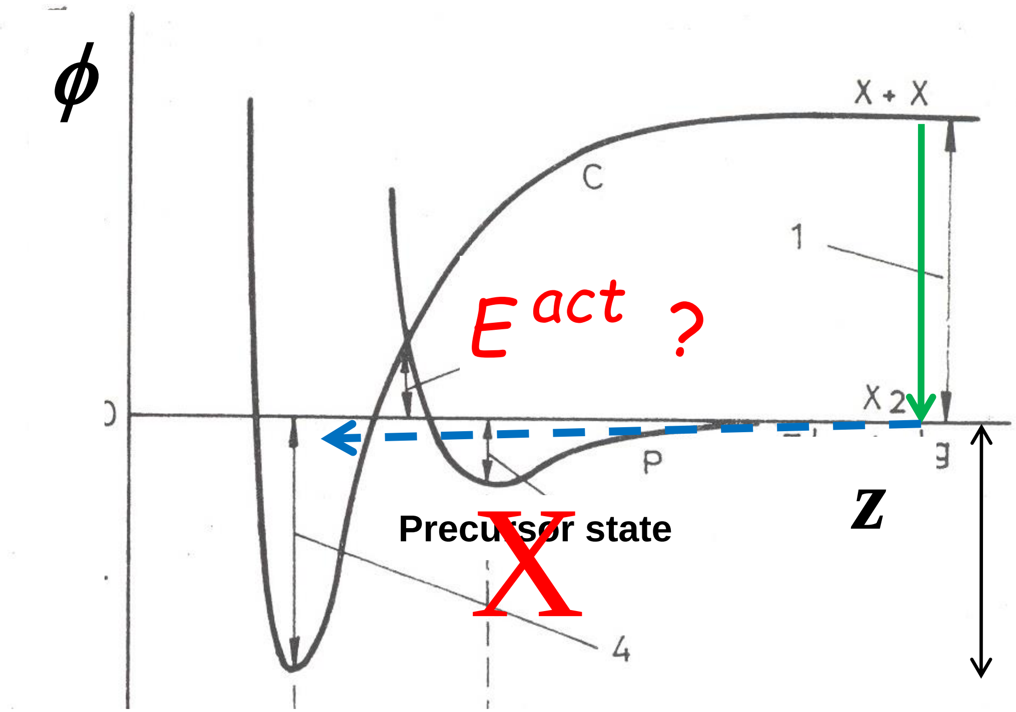
Chemisorption



1. Non-activated chemisorption

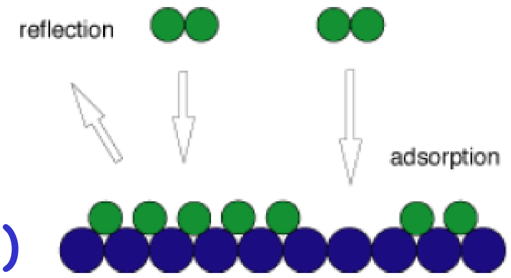
***molecular* O2/carbon; H2/carbon; Cl2/carbon; ethylene/silver**

$$E_d^{act} = -\Delta H_C$$



$H_2 \rightarrow H+H$ 435 kJ/mol

X_2



2(M-X)

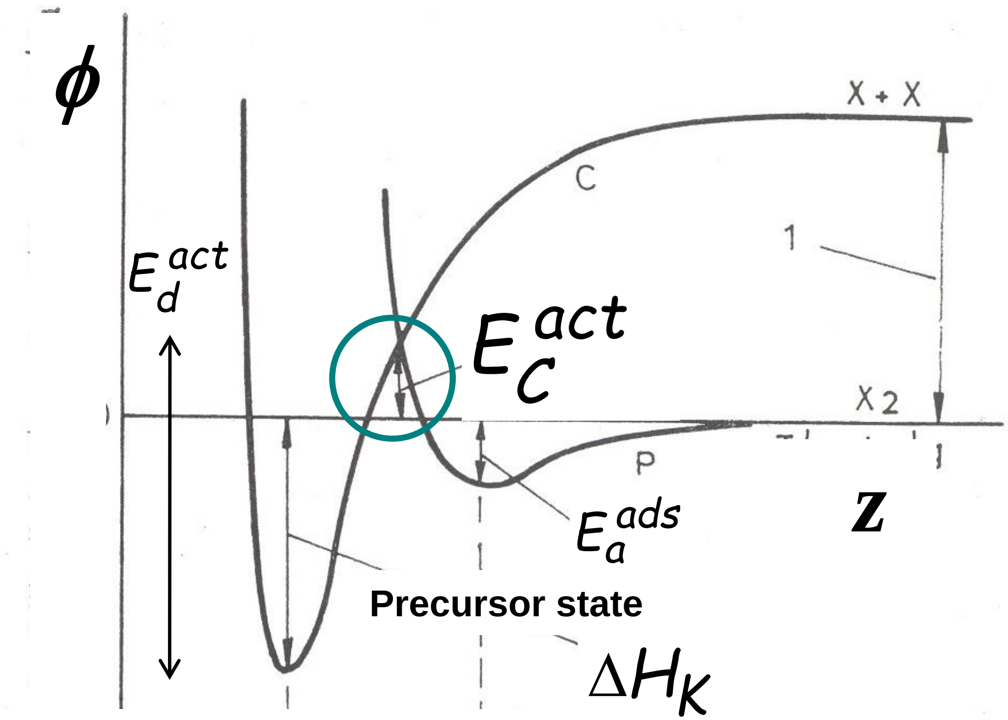
2. Dissociative chemisorption

H_2, Hlg_2,O_2 on metal surface

a. Direct

b. Through precursor state

b) Through a precursor state



H2→ 2H→2H/Cu; Co; ZnO

↓

20-40 kJ/mol

$$E_d^{act} = -\Delta H_C + E_C^{act}$$

chemi vs physi: rate is not necessarily helps to decide

$$k = Ae^{-\frac{E^{act}}{RT}}$$

Rate of desorption (1st order)

$$k_d = Ae^{-\frac{E_d^{act}}{RT}} \qquad t_{1/2} = \frac{\ln 2}{k_d} = \frac{\ln 2}{A} e^{\frac{E_d^{act}}{RT}} = \tau_0 e^{\frac{E_d^{act}}{RT}}$$

Residence time

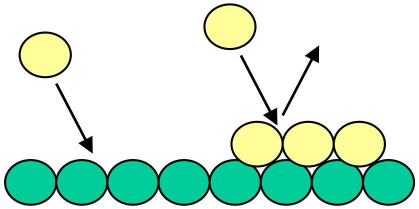
E_d^{act}, kJ/mol	$\tau_0 = \frac{\ln 2}{A}$, s
0,4	$6 \cdot 10^{-14}$
4,0	$2,7 \cdot 10^{-13}$
40	$1,6 \cdot 10^{-6}$
60	$9 \cdot 10^{-3}$
80	50
100	$3 \cdot 10^{5}$
120	$2 \cdot 10^{9}$

$\tau_0 = f(\Theta)$ ~ covered site

~ lateral interaction with the neighbour

Rate of the surface reactions

number of collisions: z



$$z = \frac{p}{\sqrt{2\pi mkT}}$$

10^{18} -10^{19} surface atom/m^2

Ambient pressure, 25 °C 3×10^{27} collisions/m^{2}s

on a single surface site → ~ 10^8 collisions/s

10^{-6} torr 4×10^{18} m^{-2}s^{-1} 1 collision/s

V_{ads}= frequency of collisions x sticking probability

sticking probability, S

dissipation of the energy of the particle colliding

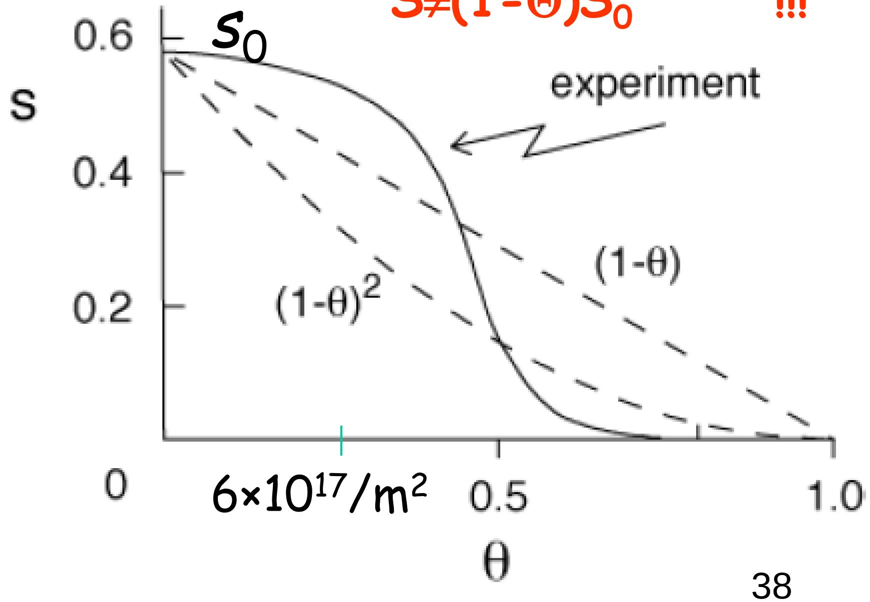
measured, from $p=f(t)$

$$S=\frac{v_{ads}}{\text{frequency of the surface collisions}}$$

from kinetic gas theory

$$z=\frac{p}{\sqrt{2\pi mkT}}$$

$S \neq (1-\Theta)S_0$!!!



S_0 depends on the potential function

RT

CO/trabónsient metal	0,1-1
N_2/rhenium	<0,01
O_2/silver	0,0001

Heterogeneous catalysis

homogeneous ↔ heterogeneous

Influences only the rate but not the equilibrium:

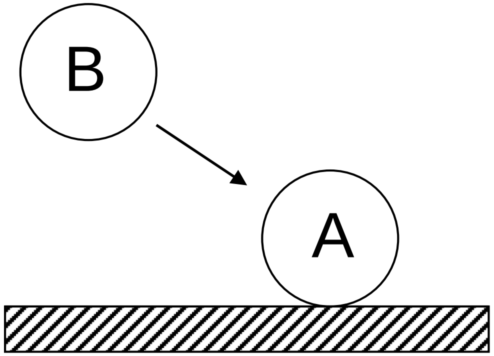
Reaction path with reduced activation energy

Important for industry

process	reagents	catalyst	product
Ammonia synth. (Haber-Bosch)	N_2+H_2	Al_2O_3 supported iron oxides	NH_3
Ethylene oxide synth.	C_2H_4+O_2	Al_2O_3 supported silver	C_2H_4O
Desulphurization of mineral oil	H_2+R_2S	Al_2O_3 supported Mo-Co	RH + H_2S
Polymerization of olephines (Ziegler-Natta)	propylene	$MgCl_2$ supported $TiCl_3$	polypropylene

Mechanism of the surface reactions

1. Eley-Rideal



$$\mathrm{A(g)+S(s)} \rightleftharpoons \mathrm{AS(s)}$$

$$\mathrm{AS(s)+B(g)} \rightarrow \mathrm{product}$$

$$v = kp_B \cdot \Theta_A$$

if $\Theta_A = f(p_A)$ Langmuir

$$v = \frac{kKp_Ap_B}{1+Kp_A}$$

1) low p_A: $Kp_A \ll 1$

2) high p_A: $Kp_A \gg 1$ $\quad v \approx kp_B$

Eley-Rideal mechanism, examples

reagent	catalyst	product
CO_2 + H_2(s)		H_2O + CO
C_2H_2 + H_2(s)	Fe or Ni	C_2H_4
2 NH_3+ ½ O_2(s)	Pt	N_2 + 3 H_2O
C_2H_4 + ½ O_2(s)		H_2COCH_2

2. Langmuir - Hinshelwood

adsorption to the surface
diffusion
reaction
desorption

$$A(g) + S(s) \rightleftharpoons AS(s)$$

$$B(g) + S(s) \rightleftharpoons BS(s)$$

$$AS(s) + BS(s) \rightarrow \text{product}(g)$$

$$\Theta_A + \Theta_B + \Theta_{free} = 1 \qquad v = k \cdot \Theta_A \cdot \Theta_B$$

Langmuir $\Theta_A = \dfrac{K_A p_A}{1 + K_A p_A + K_B p_B}$ $\quad \Theta_B = \dfrac{K_B p_B}{1 + K_A p_A + K_B p_B}$

$$v = \frac{k K_A p_A K_B p_B}{(1 + K_A p_A + K_B p_B)^2}$$

complex T-dependence

$$v=\frac{kK_Ap_AK_Bp_B}{\left(1+K_Ap_A+K_Bp_B\right)^2}$$

a) Both A and B adsorb weakly

$$v=kK_Ap_AK_Bp_B$$

b) B adsorbs weakly

$$v=\frac{kK_Ap_AK_Bp_B}{\left(1+K_Ap_A\right)^2}$$

c) A adsorbs very strongly

$$v=\frac{kK_Bp_B}{1+K_Ap_A}$$

Examples for Langmuir – Hinshelwood mechanism

reagents	catalyst	product
$2\,CO + O_2$	Pt	$2CO_2$
$CO + 2H_2$	ZnO	CH_3OH
$C_2H_4 + H_2$	Cu	C_2H_6
$N_2O + H_2$	Pt	$N_2 + H_2O$
$C_2H_4 + \frac{1}{2}O_2$	Pd	CH_3CHO
$CO + OH$	Pt	$CO_2 + H^+ + e^-$