Physical Chemistry of Surfaces

2019-20/Spring

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PHYSICAL CHEMISTRY OF SURFACES

1

Requirements
3 homeworks

Participation at 67 % of the contact hours
Completed homeworks
Optional test in the last week (threshold: 51 %)

References

- Compendium
- Thommes et al: IUPAC recommendation
- Rouquerol, J., Rouquerol, J., Sing, K: Adsorption by powders & porous solids - Academic 1999

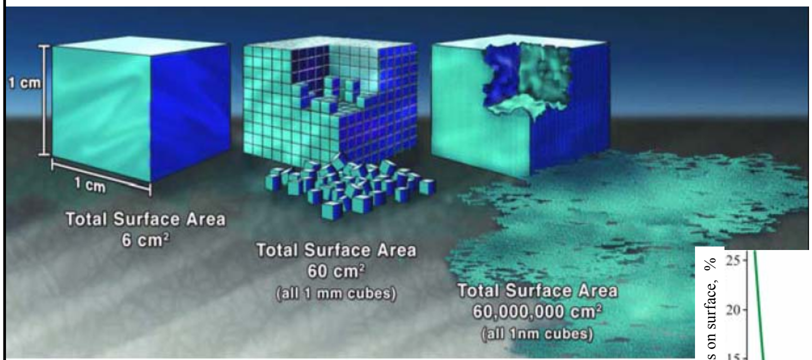
Teaching assistent:

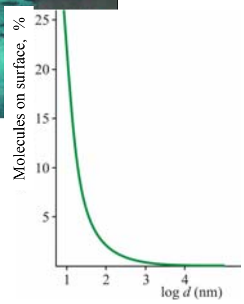
shereen.farah@mail.bme.hu

2

Particle size vs. surface

1 cube   1000 cubes 10^{21} cubes

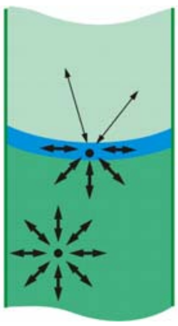




Surface/volume

„God created space,
and the devil created surface" Wolfgang Pauli

Why is surface position distinguished?



$$\gamma = \left(\frac{\partial G}{\partial A_S}\right)_{p,T}$$

Surface tension

intensive property,
work/surface area; force/route

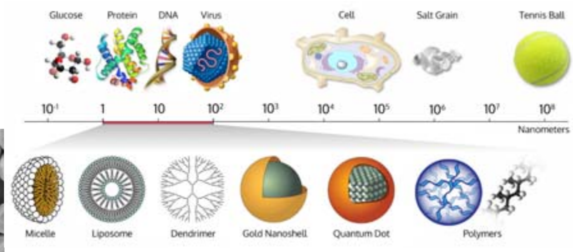
	$\gamma^{293\,K}$ mJ/m² or mN/m	interaction
He(l)	0,308 $^{2,5\,K}$	dispersion
n-hexane	18	dispersion
water	72	H-bridge
Hg(l)	472	metallic bond
$BaSO_4$	10^3	ionic bond

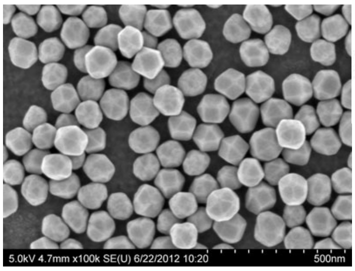
4

High surface area materials Examples1

Small particles

Nanoparticles (particles between 1 and 100 nm in size)



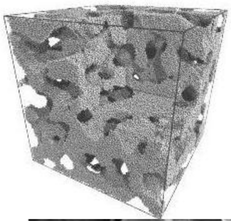
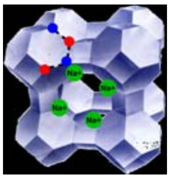
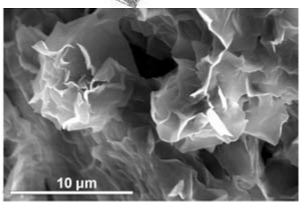


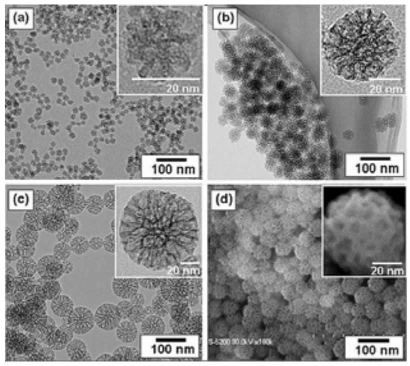
5

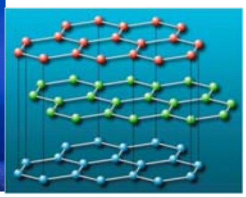
High surface area materials Examples2

6

Examples3



7

High surface area materials

- small/nano particles
- porous materials

High is relative
Low surface exhibit the same feature, but
the extent is limited

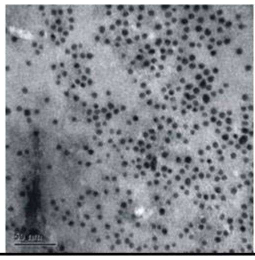
8

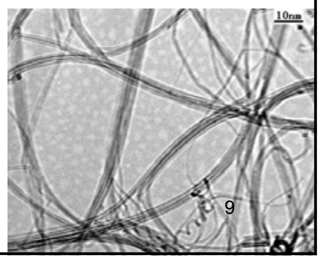
Particles, sizes and distributions

Characterisation of particles
- size
  - range
  - distribution
- shape (morphology)

aspect ratio: shortest/longest dimension

In case of nanoparticles:
d/l may be as high $1{,}5 \cdot 10^3$





9

Relevance of particle size (distribution)

Key factor in several pratical applications

Flow/storage behaviour
Sievability
Rheological properties (viscosity)
Adhesion (aggregation)
Sedimentation

Dusting

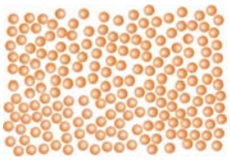
Activity/reaction rate (e.g., efficiency of a catalyst)
Solubility , rate of absorption (e.g., drug uptake)
Rate of burning (fuel)
Rate and measure of gas uptake
Water uptake (hydration)
Sensitivity to humidity

Penetration during breathing (lung)
… etc.

10

The size of the particles in the same batch might be different

Monodisperse: set of particles of identical size (narrow size distribution)



Bi…

Polydisperse: set of particles of different size (wide size distribution)

dispersity index: PDI

11

Calculation of the average size:

size of particles: x_i

number of particles with size x_i: ϕ_i

i) each particle is equal: average by number $$\overline{x_N} = \frac{\sum x_i \phi_i}{\sum \phi_i}$$

ii) particles have different weight (W_i) and we need the average by weight

$$\overline{x_W} = \frac{\sum x_i W_i}{\sum W_i} \qquad PDI = \frac{\overline{x_W}}{\overline{x_N}}$$

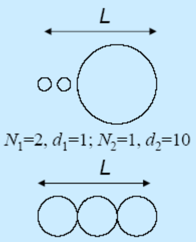
iii) particles have different volume (V_i) and we need the average by volume

$$\overline{x_V} = \frac{\sum x_i V_i}{\sum V_i} \qquad PDI = \frac{\overline{x_V}}{\overline{x_N}}$$

$PDI = 1$ if the system is monodisperse

12

Example:



$$\bar{d}_N = \frac{L}{N} = \frac{\sum L_i}{\sum N_i} = \frac{\sum d_i N_i}{\sum N_i} = \frac{1\times 2 + 10\times 1}{2+1} = \frac{12}{3} = 4$$

The diameter of the average ball is 4;
i.e., 3 average ball give the same chain length as our 3 balls of real size

Let's have a sackful of these balls, all made of the same material. Let's separate them by size and weigh the small and large balls (W_i). The average diameter by weight is:

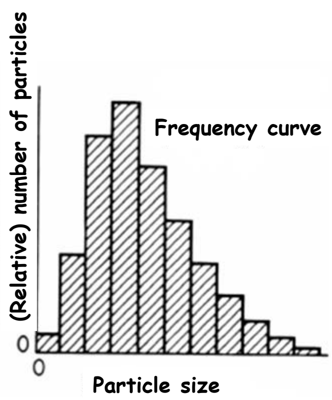
$$\bar{x} = \frac{\sum x_i \phi_i}{\sum \phi_i}$$

$$\overline{d_W} = \frac{\sum d_i W_i}{\sum W_i} = \frac{\sum d_i d_i^3 N_i}{\sum d_i^3 N_i} = \frac{1^4 \cdot 2 + 10^4 \cdot 1}{1^3 \cdot 2 + 10^3 \cdot 1} = \frac{10002}{1002} = 9{,}98$$

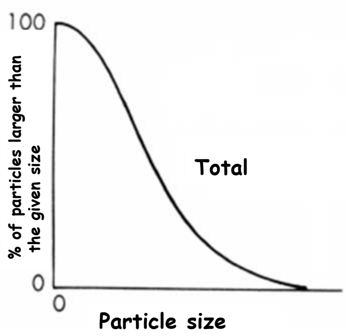
$$V_{sphere} = \frac{4\pi r^3}{3} \qquad PDI = \frac{\overline{d_W}}{\overline{d_N}} \approx 2.5$$

13

Size distribution



Differencial



Integral

14

Methods and sizes

Sieve	25 μm-125 mm
wet sieve	10 μm -100 μm
Sedimentation (H_2O)	above 1 μm
Centrifugation	below 5 μm
Optical microscopy	200 nm – 150 μm
Ultramicroscopy	10 nm – 1 μm
Electronmicroscopy (scanning – SEM, transmission - TEM)	1 nm - 1 μm
Light scattering	1 nm – a few μm

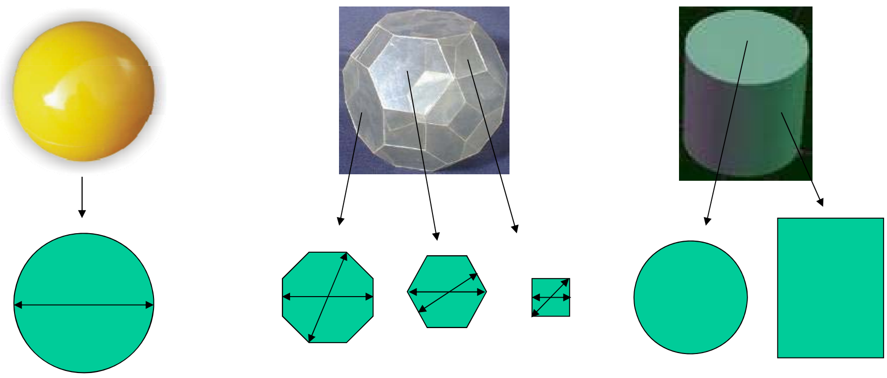
The various experimental methods are sensitive to different characteristics of the particles – may provide different results

WHEN REPORT SIZE AND DISTRIBUTION, NAME THE METHOD AS WELL

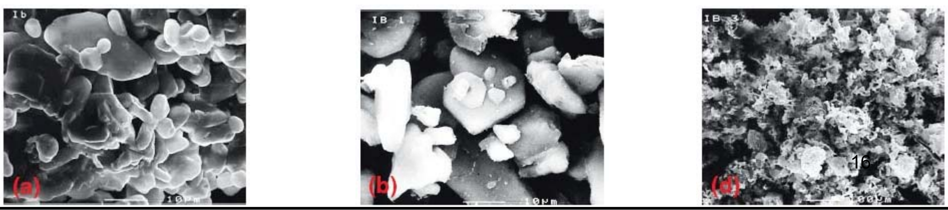
15

PARTICLE SIZE

but which one?

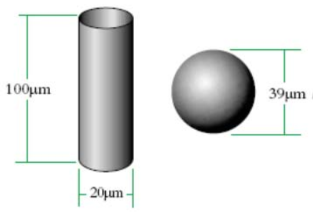


Ibuprofen crystals (SEM)



16

Equivalent sphere (here: by volume)



Size of cylinder		Aspect Ratio	Equivalent Sperical Diameter
Height	Diam.		
20	20	1:1	22.9
40	20	2:1	28.8
100	20	5:1	39.1
200	20	10:1	49.3
400	20	20:1	62.1
10	20	0.5:1	18.2
4	20	0.2:1	13.4
2	20	0.1:1	10.6

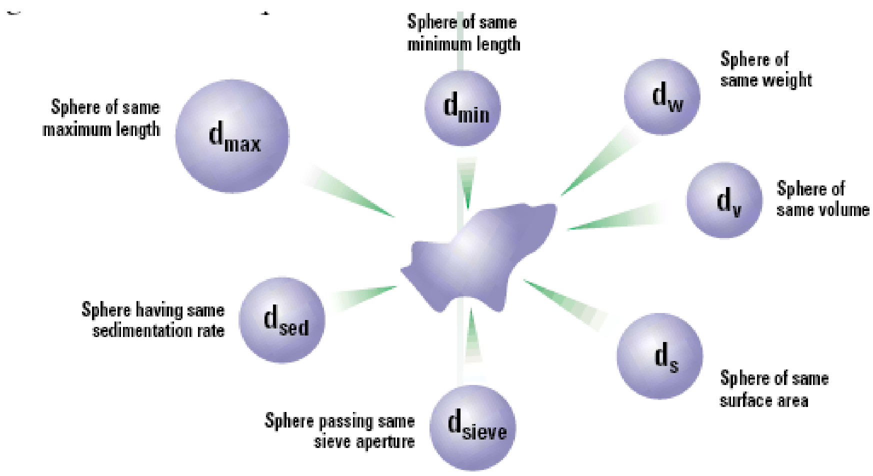
- A single characteristic size (r or d)
- Easy calculation:

$$V = \frac{1}{6}\pi d^3 \qquad S = \pi d^2 \qquad m = \frac{\rho}{6}\pi d^3$$

- Simple and easy to use

17

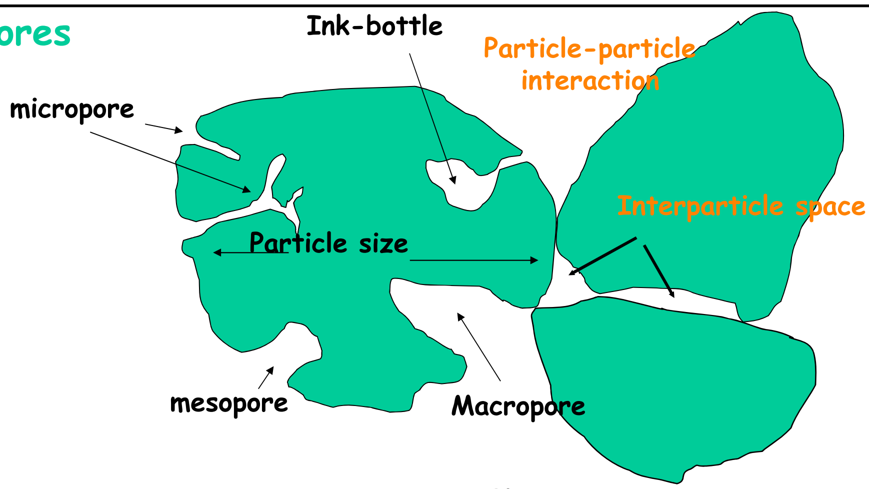
The size of the equivalent sphere also depends on the method



WHEN REPORT SIZE AND DISTRIBUTION,
ADD THE METHOD AS WELL

18

Pores



Closed/open/one end open
Shape: cylindrical
slit
ink-bottle

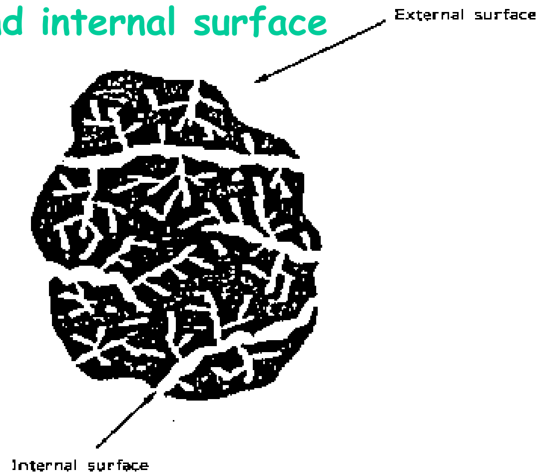
Size:

IUPAC-classification (1984):

- *micropore* d < 2 nm
- *mesopore* 2 nm < d < 50 nm
- *macropore* d > 50 nm
- supermacropore d > 500 nm

19

External and internal surface



Porosity

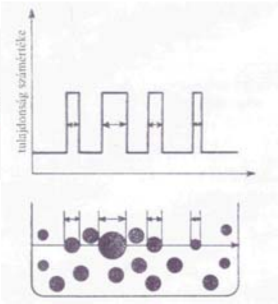
$$\varepsilon = \frac{V_{pores}}{V_{pores} + V_{solid}} = \frac{\rho_{matrix} - \rho_{apparent}}{\rho_{matrix}}$$

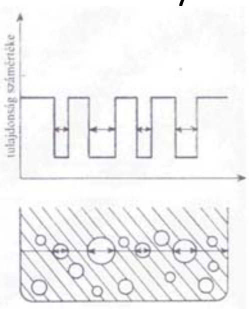
20

Fabrication of high surface area material

1. Dispersion (top down)

incoherent coherent systems

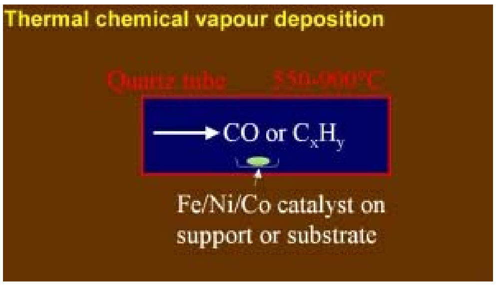




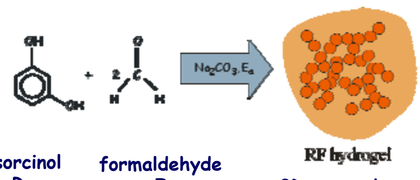
21

2. Synthesis (bottom up)

~ Vapour deposition



~ Sol/gel



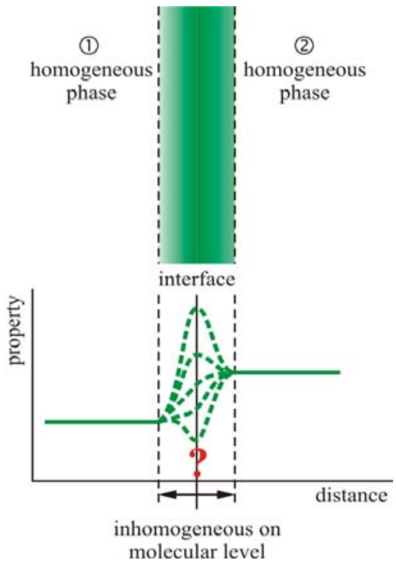
resorcinol
R

formaldehyde
F

3D network

22

Interface



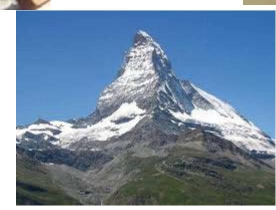
Separates and connects

23

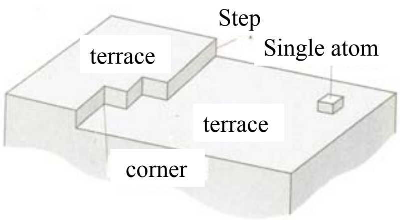
Classification of interfaces

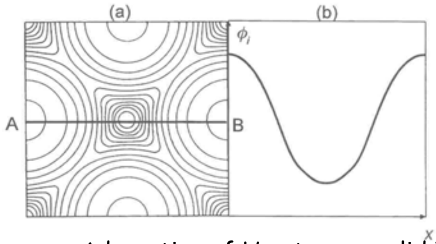
1. state of the connecting phases

(solid, liquid, gas/vapour): S/S; S/L; S/G; L/L; L/G



2. geometry: **planar, curved**



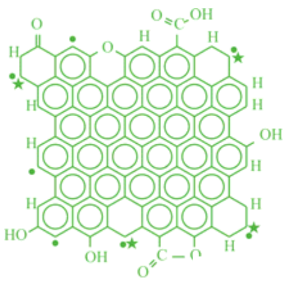


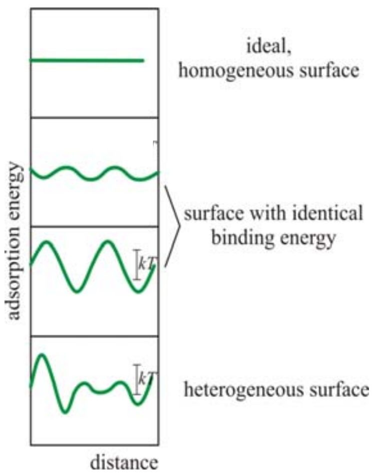
Adsorption of He atom on solid Xe (100) surface

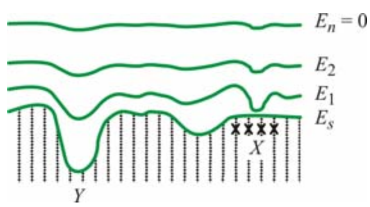
No flat surface on molecular/atomic level

3. energetics

low and high energy
homogeneous or heterogeneous
→ energy distribution





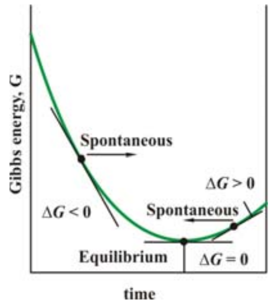


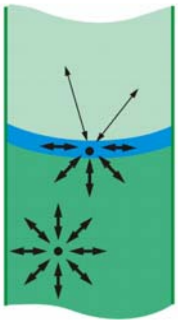
„active” site

26

The consequence of the excess surface energy

Spontaneous processes





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

mobility: fluid phase
solid phase

27

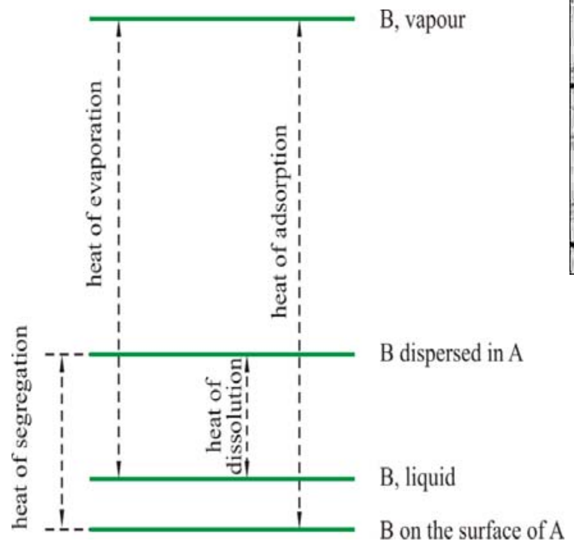
SPONTANEOUS PROCESSES REDUCING EXCESS SURFACE ENERGY

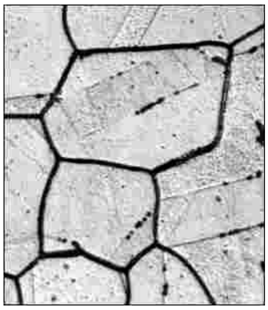
1. Surface (grain boundary) segregation

initial state

the doped atoms/impurities (O) congregate on the grain surface

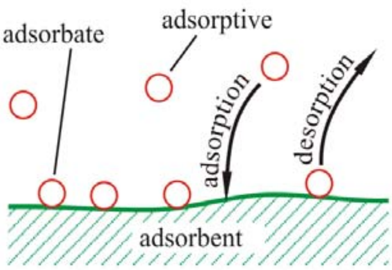
Alloy of A with impurity B





29

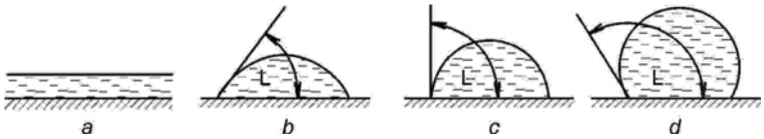
2. (Ad)sorption

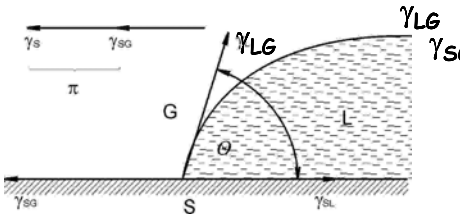


30

3. Contact wetting

S/G + a drop of liquid → S/L + L/G





$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos\theta$

YOUNG eq.

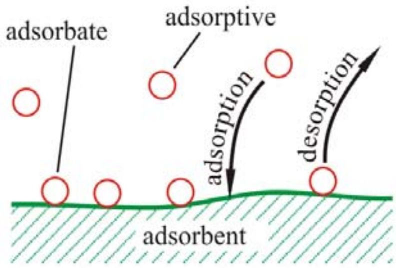
Complete wetting $\theta = 0°$

$\gamma_S - \gamma_{SG} = \pi$ spreading pressure

31

Adsorption: enrichment on the surface (binding on „active" sites)

Desorption: removal of the adsorbed species



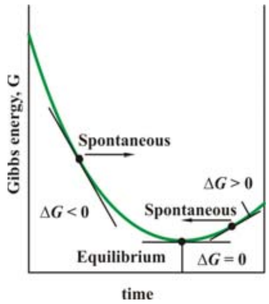
Equilibrium process

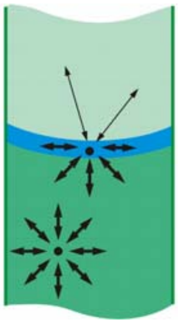
DYNAMIC EQUILIBRIUM

Adsorption is brought by the forces acting between the solid and the molecules of the gas. These forces are of two kinds: physical (physisorption) and chemical (chemisorption).

32

Spontaneous process





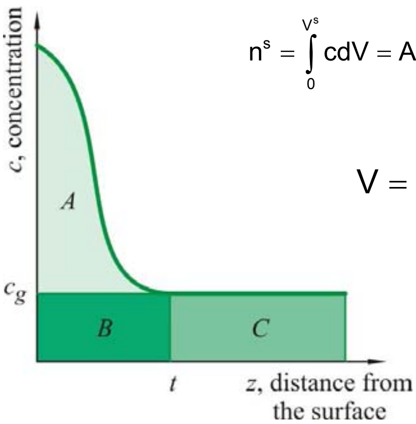
$\Delta G = \Delta H - T\Delta S$ exothermic

rate
mobility: fluid
solid

33

Quantitative description of the adsorption

$A_s = \dfrac{\text{surface area}}{\text{mass of solid}}$



$V^s = A_s t$

$$n^s = \int_0^{V^s} c\,dV = A_s \int_0^t c\,dz \qquad n = A_s \int_0^t c\,dz + c^g V^g$$

$n^s = n - c^g V^g$ adsorbed amount

$$V = V_{solid,0} + V^{g,0} = V_{solid} + V^s + V^g$$

$V^{g,0} = V^g + V^s$

$n^\sigma = n - c^g V^{g,0}$ adsorbed excess

$n^\sigma = n - c^g V^g - c^g V^s$

$n^s = n^\sigma + c^g V^s$

$n^s \approx n^\sigma$ if c^g is low

$V^s << V^g$

34