Surface-related phenomena

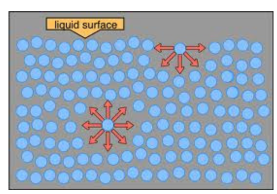
Lectures in Physical Chemistry 7

Tamás Turányi
Institute of Chemistry, ELTE

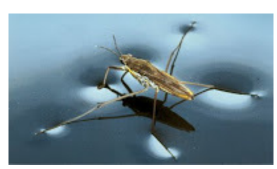
Surface tension

In a liquid those molecules have the lowest energy, which are surrounded by other molecules in all sides.

molecules close to the surface have an excess energy
⇒ surface energy

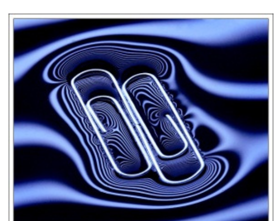


work is needed to increase the surface of a liquid
⇒ increasing the surface energy



change of surface energy ΔE is proportional to the change of the area of the surface ΔA :

$$\Delta E = \gamma \, \Delta A$$



DEF coefficient γ is called the surface tension

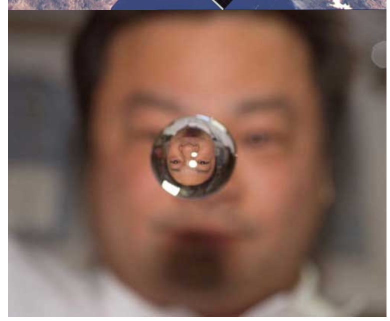
Unit: J/m^2 or N/m

Surface tension 2

Surface tension depends on the quality of the two phases of the boundary and temperature.

The surface of liquids tend to be minimized

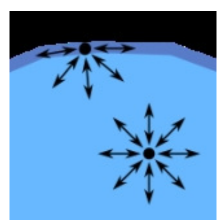
⇒ at zero gravity
liquid droplets have spherical shape.



drop of water aboard the ISS

Vapour pressure of curved surfaces

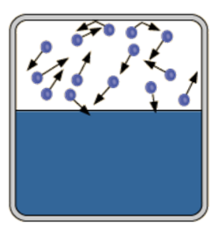
convex curved surfaces (∩) : each surface molecule has (on average) less neighbours compared to a flat surface.



⇒ these molecules are less anchored by the neighbours
⇒ can fly away more easiliy due to the thermic movements

Vapour pressure depends on the curvature of the surface:
Compared to a flat surface,
higher vapour pressure belongs to the convex (∩) surface and
lower vapour pressure belongs to the concave (∪) surface.

Vapour pressure *p* of a curved surface (**Kelvin equation**):



$$\ln \frac{p}{p^*} = \pm \frac{2\gamma V_m}{RTr}$$

p^*	vapour pressure of the planar surface
γ	liquid–vapour surface tension
V_m	molar volume of the liquid
r	curvature radius of the liquid
sign +:	convex (∩) surface
sign –:	concave (∪) surface

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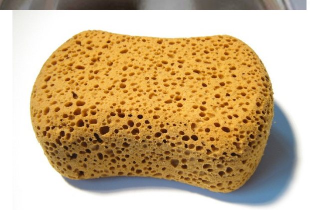
Vapour pressure of curved surfaces – strange consequences

In a closed system the smaller droplets evaporate onto larger droplets

Water droplets on the inside wall of a mineral water bottle evaporate to the bulk of the water, having flat surface.

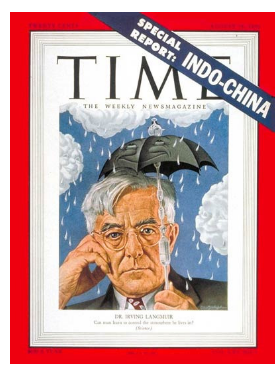


Water evaporates slowly from a sponge because of the concave water surfaces in the holes.

Emergence of rain droplets

If air becomes saturated (compared to a flat water surface), then small (highly curved) water droplets can be formed. However, these evaporate immediately, due to their hign vapour pressure.

formation of rain droplets: water molecules are adsorbing onto the surface of small dust particles („condensation nuclei"). A new layer of H_2O particles are adsorbed. The curvature decreases = lower vapour pressure = more deposition



„Langmuir, the rainmaker" on the cover of Time magazin 28 August, 1950

making rain: a failure

Project Cirrus (1946-1952)

Langmuir (Nobel prize in Chemistry, 1932) and his group seeded rainclouds with AgI crystals from airplanes and induced rain.

- they were sued for the demages
- the experiments were taken over by the US Air Force. ASAF wanted sure success: they initiated rain only when the weather forecast predicted heavy rain.

making rain with success

Olimpic Games in Beijing, 2008

Using 1110 missiles, rainclouds approaching Beijing were seeded with AgI crystals. Rain was falling far from Beijing and not on the opening ceremony.

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Hailstones

Small hailstones are formed in the presence of many condensation nuclei:
Many small dust particles are covered with water and each start to grow with water adsorption. They compete for the water and each hailstone will be small with less than 1 mm diameter.

Large hailstones are formed in the presence of few condensation nuclei:
Few small dust particles start to grow with water adsorption. These collect all available water from the air. Large hailstones are formed with up to 5 cm diameter.
Significant agricultural damage.

Hail prevention in SW Hungary since 1991
Small burners are located in 141 villages.
The solution to be burnt is 8 g/dm^3
silver iodide – acetone solution.
The solution is sprayed to a chimney.
After the cooling of the flue gas,
AgI crystals are formed.
1 g AgI → 10^{15} small AgI crystal
consumption: 0.8 – 1.0 liter solution/hour

avoided hail demage 8 billion HUF annually
1 Ft prevention cost ⇒ 30 Ft decrease in demage

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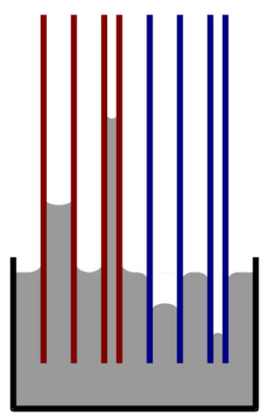
Capillary rise

Calculation of Capillary rise
(can be derived from the Kelvin equation)

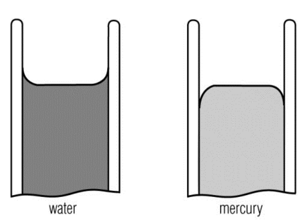
$$h = \pm \frac{2\gamma}{r\rho g}$$

+	capillary level elevation (∪ surface)
–	capillary level depression (∩ surface)
γ	liquid–vapour surface tension [J m^{-2}]
r	curvature radius of the liquid [m]
ρ	density of the liquid [kg m^{-3}]
g	gravity constant [9.81 m s^{-2}]



if the surface of the liquid is concave (∪)
⇒ „wets the wall” (*e.g.* water on a glass wall)
⇒ the level of liquid rizes in the capillary

if the surface of the liquid is convex (∩)
⇒ „does not wet the wall” (*e.g.* Hg on a glass wall)
⇒ the level of liquid decreases in the capillary

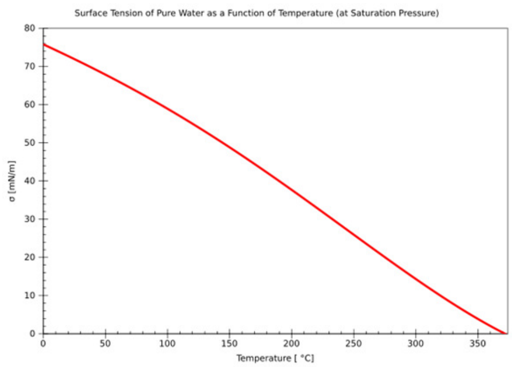


Temperature dependence of the surface tension

Eötvös rule: temperature dependence of the surface tension

$$\gamma V_m^{2/3} = k_E (T_k' - T)$$

γ surface tension
$V_m^{2/3}$ "molar surface"
k_E Eötvös constant, identical for most liquids: $k = 2.1 \times 10^{-7}$ [J K^{-1} mol$^{-2/3}$]
T_k' almost the critical temperature (lower by about 6 K)
critical temperature of water: T_c= 647 K (374 °C)



Eötvös Loránd
(1848 –1919)
Hungarian physicist

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Adsorption

DEF adsorption: moving particles of a phase are attached to the surface of the other phase

DEF absorption: moving particles of a phase are fixed inside the other phase
Examples: light absorption; absorption of H_2 in palládium

DEF physisorption: ('physical adsorption')
van der Waals interaction between the adsorbed particles and the surface.
Example: adsorption of acetone on the surface of medical carbon

DEF chemisorption: ('chemical adsorption') chemical bond between the adsorbed particles and the surface. (*e.g.* covalent bond of the adsorbing molecule or of the atoms/radicals after dissociation)
Example: adsorption of CO on Pt surface; H_2 gas → bound H-atoms on the surface

DEF active site: site on the surface that is able bind a particle

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Langmuir adsorption isotherm

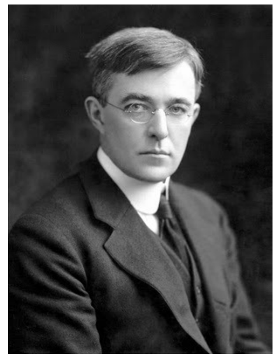
DEF θ fractional coverage: the ratio of the occupied active sites (N_o) and the total number of active sites (N) $\theta = N_o / N$

DEF adsorption isotherm: at constant temperature fractional coverage θ is given as a function of partial pressure p of the adsorbing gas

It is not related to the „isotherms of gases"!

Langmuir adsorption isotherm:
the simplest adsorption isotherm

Conditions:
- adsorption in a single layer
- each active site of the surface is equivalent
- ability of a particle to bind is independent of weather the nearby sites are occupied



Irving Langmuir [ˈlæŋmjʊr]
(1881 –1957)
USA physicist and chemist
Nobel prize, 1932

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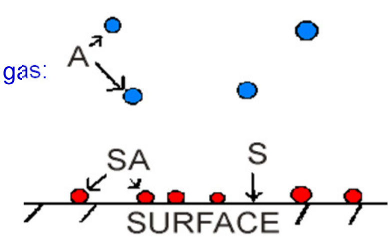
Langmuir adsorption isotherm 2

rate of adsorption
is proportional to the number of the available active sites $(1 - \theta)N$ and the partial pressure of the gas:
$v_a = d\theta / dt = k_a (1 - \theta) N p$

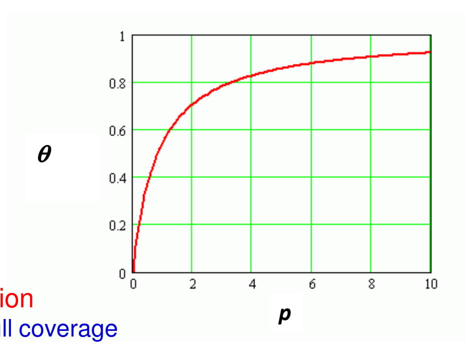


rate of desorption
is proportional to the number of adsorbed particles:
$v_d = d\theta / dt = k_d \theta N$

In equilibrium $v_a = v_d$

$\Rightarrow$ Langmuir isotherm:

$$\theta = \frac{Kp}{1 + Kp}; \quad K = \frac{k_a}{k_d}$$



K is the equilibrium constant of adsorption
if p=0 then $\theta = 0$; increasing pressure the full coverage $\theta = 1$ is approximated, where all active sites are occupied.

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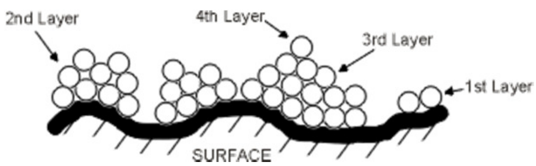
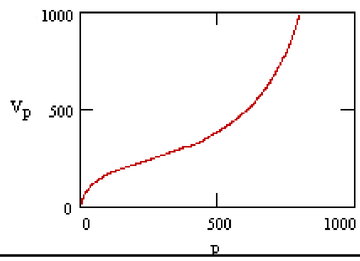
BET adsorption isotherm

Brunauer-Emmett-Teller isotherm

the initial monolayer may adsorb further particles: adsorption in multilayers





Teller, Emmett and Brunauer (~1960)

Edward Teller
(1908 – 2003)
Hungarian-USA physicist

Paul Hugh Emmett
(1900 – 1985)
USA chemical engineer

Stephen Brunauer
(1903 – 1986)
Hungarian-USA physicist and chemist

Internet resources

NEFELA Hail Prevention Union of Southern Hungary
http://www.nefela.hu/

Irving Langmuir and Project Cirrus
http://aviationtrivia.blogspot.hu/2010/08/irving-langmuir-and-project-cirrus.html

How Beijing used rockets to keep opening ceremony dry
http://www.independent.co.uk/sport/olympics/how-beijing-used-rockets-to-keep-opening-ceremony-dry-890294.html

Stephen Brunauer
http://it.wikipedia.org/wiki/Stephen_Brunauer

THE END

of topic

surface phenomena

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