

# Teoretične fizikalno-kemijske osnove za oblikovanje kozmetičnih izdelkov

Odon Planinšek

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## Fazno pravilo

**Fazo** definiramo kot homogeno fizikalno različno in mehansko ločljivo količino sistema. Primeri so plini, čista topila (taline), trdne snovi in raztopine.

**Komponenta(C)**: Snov(i), ki so nujne, da obstaja faza!

**Prostostna stopnja(F)**: minimalno število variabel, ki jih moramo navesti, če želimo sistem definirati (npr. eno fazo, dve ali več faz)

**Ravnotežje** je stanje mirovanja sistema

T(temperatura)  
P(tlak)  
x( sestava) } Konst.



2

## Fazno pravilo

**Primer:** NaCl in voda

Topnost NaCl pri 30°C v vodi je 36,1 g v 100 g vode

**Število faz** enako 3-trdni NaCl, vodna raztopina in para

**Komponenti** sta dve: NaCl in H<sub>2</sub>O

Število komponent je najmanjše število snovi (sestavlin) s katerimi lahko opišemo sestavo posamezne faze.

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## Fazno pravilo

$$P+F=C-2$$

P-faza

F-prostostna stopnja

C-komponenta

Ločujemo

-enokomponentne sisteme

-dvokomponentne sisteme

-večkomponentne sisteme

F=0 nonvariantni sistem, vse je določeno

F=1 monovariantni sistem

F=2 divariantni sistem

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# Fazno pravilo

$$P+F=C+2$$

**Primer:**

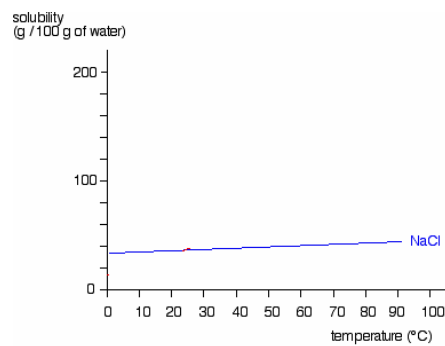
Enokomponentni sistem (voda), tri faze (para, tekoča voda, led)

$$F=1+2-3=0$$

**Primer:**

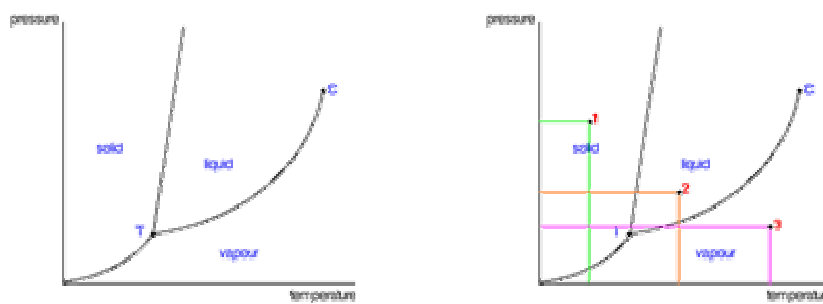
Dvokomponentni sistem (NaCl, voda), tri faze (trdno, tekoče, plinasto)

$$F=2+2-3=1$$



5

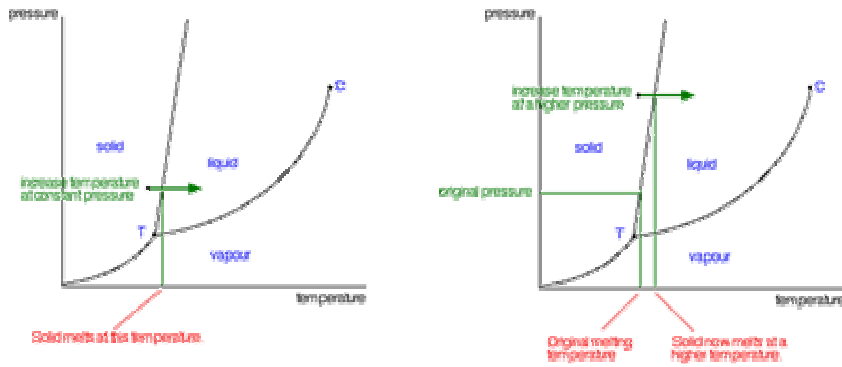
# Fazni diagrami čistih snovi



Fazni diagram snovi

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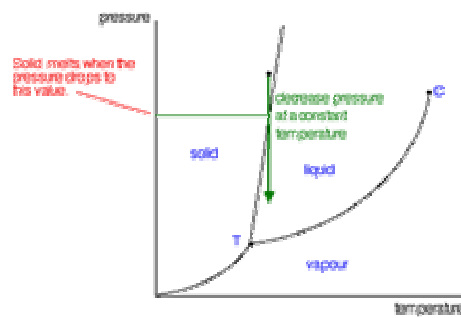
## Fazni diagrami čistih snovi



Prehod trdna snov-tekočina s spremembo temperature

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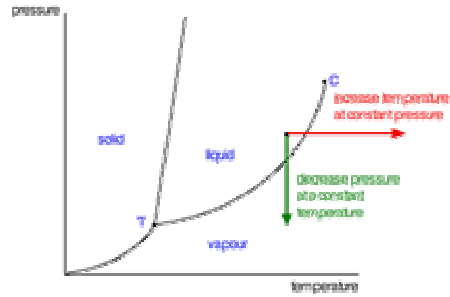
## Fazni diagrami čistih snovi



Prehod trdna snov-tekočina s spremembo tlaka

8

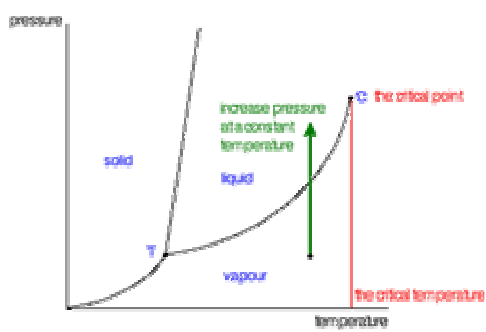
## Fazni diagrami čistih snovi



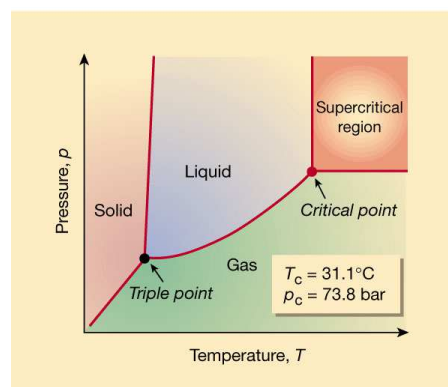
Prehod trdna snov tekočina-para

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## Fazni diagrami čistih snovi



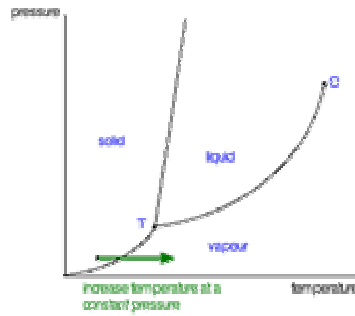
Kritična točka



Fazni diagram CO<sub>2</sub>-superkritični fluid

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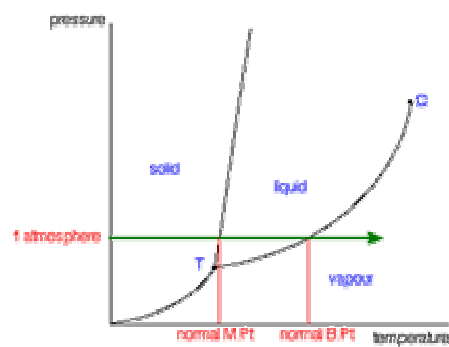
## Fazni diagrami čistih snovi



Prehod trdna snov para in trojna točka  
Liofilizacija <http://www.youtube.com/watch?v=ORI8PrCrLVs>

11

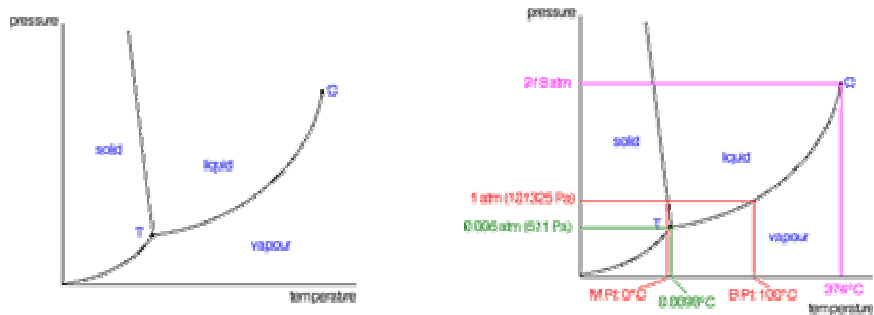
## Fazni diagrami čistih snovi



Fazni prehodi pri normalnem tlaku

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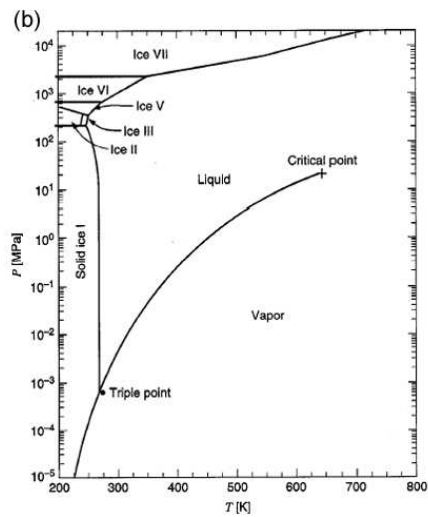
## Fazni diagram vode



Gostota ledu je manjša od gostote tekoče vode

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## Fazni diagram vode



<http://www.lsbu.ac.uk/water/sitemap.html>

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## Fazni diagram vode

It is commonly thought that ice skating is possible because of pressure melting; the pressure applied by the skate melts the ice below it, and the water film allows the blade to glide. That fact alone, however, cannot explain the slipperiness of ice; the answer involves not only frictional melting but also surface melting, which describes the natural state of the free surface of ice as being covered by a thin liquid film of water.

### The current theory

**So what is going on?** The problem seems to have been solved in the late 1990s by a chemist, Gabor Somorjai, and a physicist, Michel Van Hove, of the Lawrence Berkeley National Laboratory in California, who studied the slipperiness of ice on an atomic scale.

**According to them,** the ice itself is intrinsically slippery. You don't need to melt the ice to skate on it because the ice has a 'quasi-fluid layer' that coats the surface and provides a permanent lubricant. When pressure is applied, the molecules in the layer compact into underlying interstices, or spaces in the ice structure, and create a smooth surface for easy gliding.

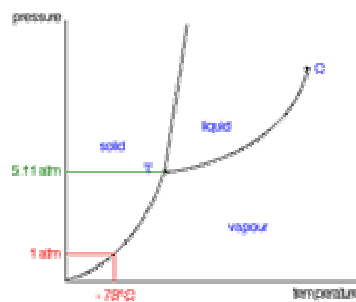
**The 'quasi-fluid layer'** is not actually liquid water but ice molecules vibrating very rapidly. The ice molecules have an unusually high degree of vibrational motion, several times that of the molecules deeper in the bulk of the ice. But importantly it is only in one direction, up and down. If the atoms moved from side to side, the 'quasi-fluid layer' would literally become liquid (which is what happens above 0°C).

Drsanje <http://thermabladehockey.com/>

Taljenje ledu pri povišanem tlaku <http://www.youtube.com/watch?v=2mimXPID2QU>

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## Fazni diagram CO<sub>2</sub>

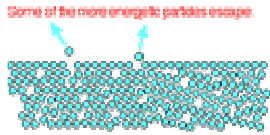


Suhi led

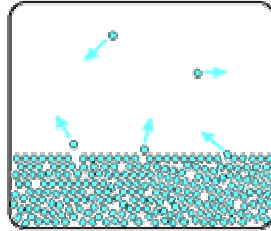
16



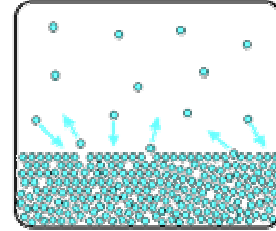
## Nasičen parni tlak



Izhlepanje v odprti posodi



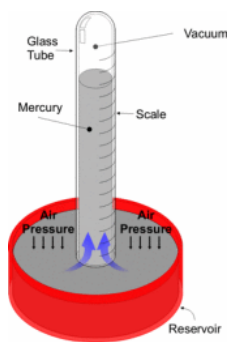
Izhlepanje v zaprti posodi



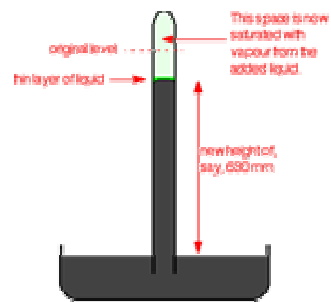
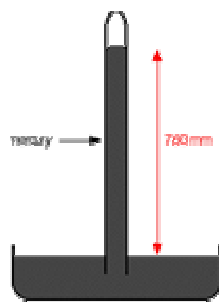
Ravnotežje

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## Merjenje nasičenega parnega tlaka



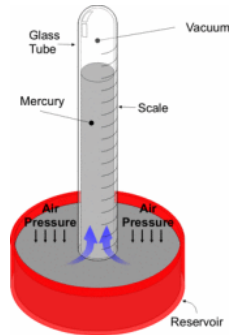
Dvig Hg v cevi



Tlak pare topila v zaprtem delu cevi

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## Merjenje nasičenega parnega tlaka

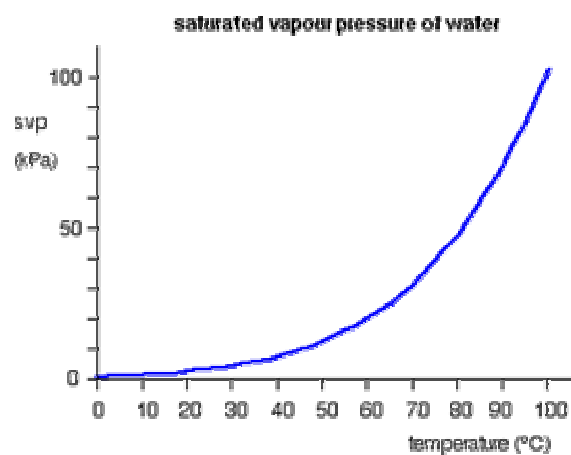


Elementary mercury occurs naturally and is present in the atmosphere. **The vapour pressure of Hg is 0.001201 mmHg at 20 °C**, and the solubility of Hg in water is about 20 mg dm<sup>-3</sup>.

*Pure & Appl. Chem.*, Vol. 70, No. 8, pp. 1585-1615, 1998  
**THE DETERMINATION OF MERCURY SPECIES IN ENVIRONMENTAL AND BIOLOGICAL SAMPLES**  
MASATOSHI MORITA, JUN YOSHINAGA AND JOHN S. EDMONDST

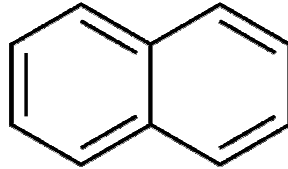
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## Vpliv temperature na parni tlak



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## Nasičen parni tlak in trdne snovi



Naftalen (tališče 78°C)

SUBLIMACIJA

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## Raultov zakon in raztopine z nehlapnim topljencem

Dvokomponentni sistem

$$p = x_{topilo} \cdot P_{topilo}^0$$

$p$  = parni tlak raztopine

$P_{topilo}^0$  = parni tlak čistega topila pri določeni temperaturi

$x_{topilo}$  = molski delež topila

$$x_{topilo} = \frac{\text{moli topila}}{\text{moli raztopine}}$$

Primer

Raztopina vsebuje 10 molov vode in 0,1 mol sladkorja skupaj 10,1 mol raztopine

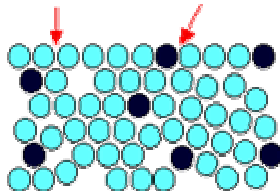
$$x_{voda} = \frac{10}{10,1} = 0,99$$

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## Omejitve Raultovega zakona

In an ideal solution, the forces between the solvent molecules ...

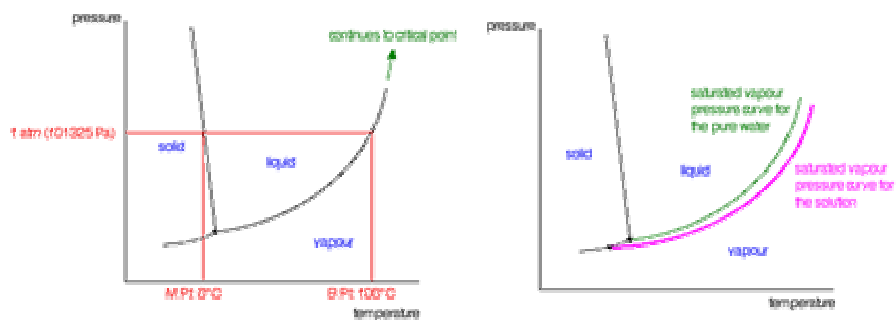
... are exactly the same as those between solvent and solute.



That means that it takes the same amount of energy for solvent molecules to break away from the surface in either case.

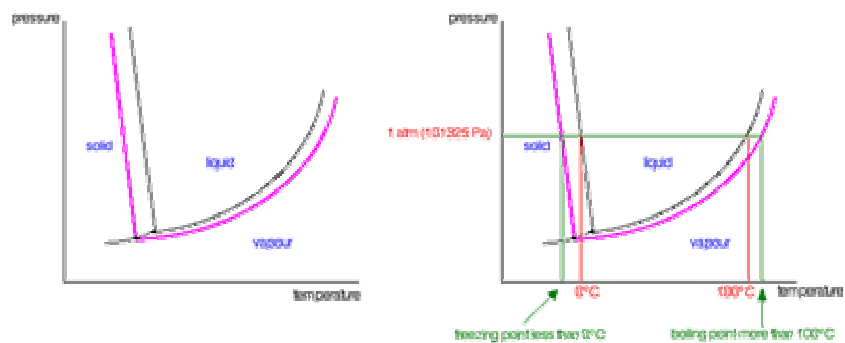
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## Raultov zakon, tališče in vrelišče



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## Raultov zakon, tališče in vrelišče



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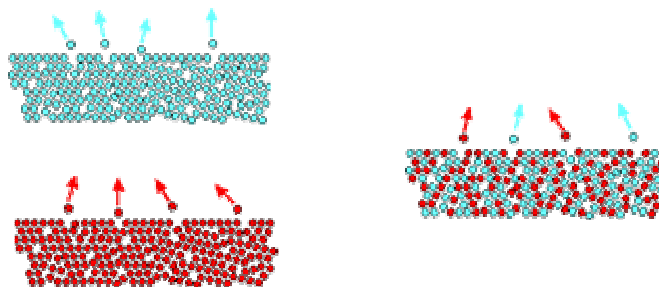
## Raultov zakon in idealne zmesi tekočin

Dvokomponentni sistem

Heptan - heksan

Benzen – metilbenzen

Propan-1-ol – propan-2-ol



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## Raultov zakon in idealne zmesi tekočin

$$p_A = x_A \cdot P_A^0$$

$$p_B = x_B \cdot P_B^0$$

$p_A, p_B$  = parcialni parni komponente A in B

$P_{A,B}^0$  = parni tlak čistega topila A ali B pri določeni temperaturi

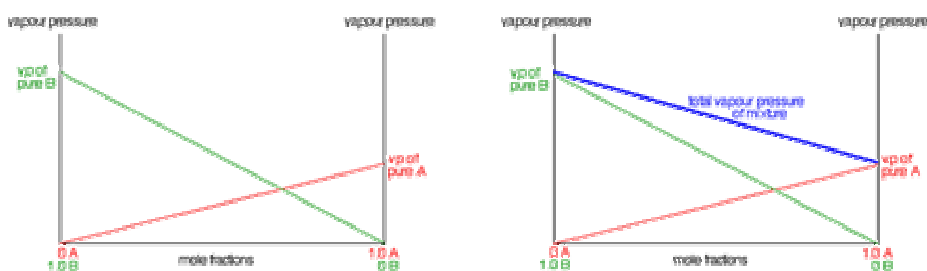
$X_{A,B}$  = molski delež topila

$$x_{A,B} = \frac{\text{moli } A, B}{\text{moli raztopine}}$$

$$\text{Celokupni parni tlak} = p_A + p_B$$

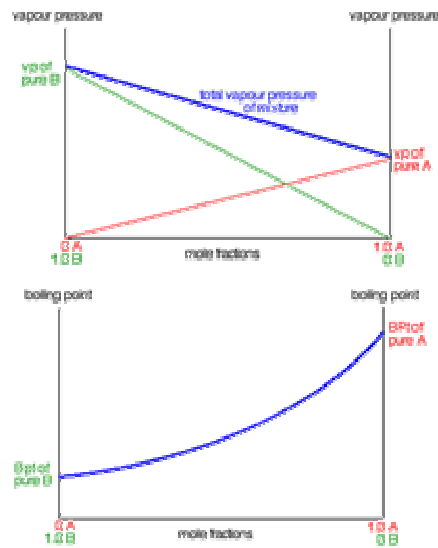
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## Raultov zakon in idealne zmesi tekočin



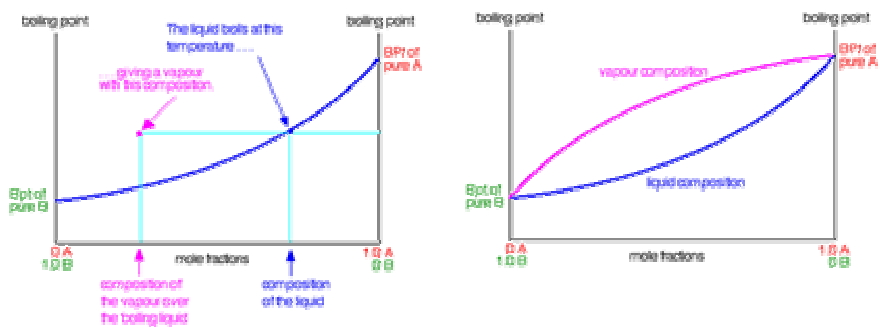
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## Povezava med vreliščem in parnim tlakom



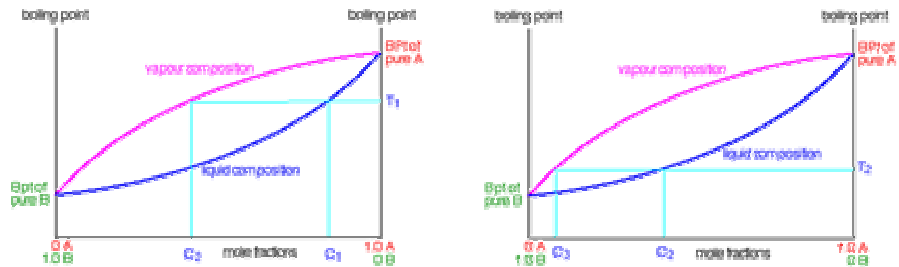
29

## Povezava med vreliščem in parnim tlakom



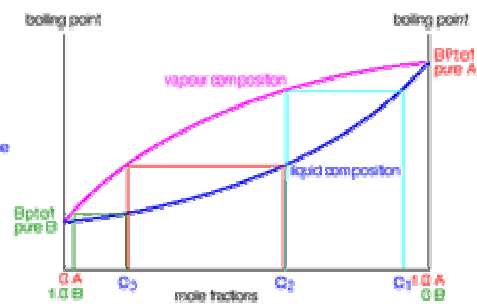
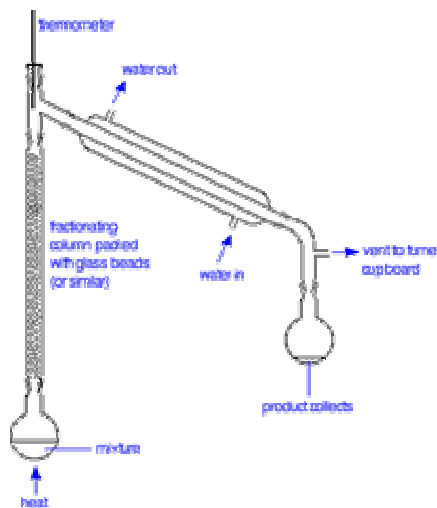
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## Povezava med vreliščem in parnim tlakom



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## Frakcionirana destilacija v laboratoriju



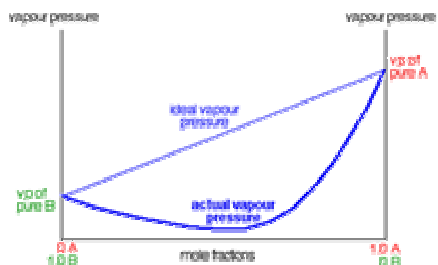
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## Neidealne zmesi tekočin

Negativen odklon od Raultovega zakona



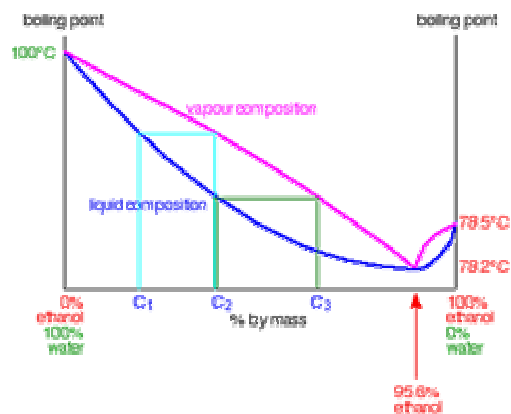
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## Neidealne zmesi tekočin -fazni diagram zmesi etanol-voda



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## Neidealne zmesi tekočin -fazni diagram zmesi etanol-voda



Kaj se zgodi če destiliramo zmes, ki vsebuje več kot 96,5% etanola

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## GOSTOTA

$$\rho = \frac{m}{V},$$

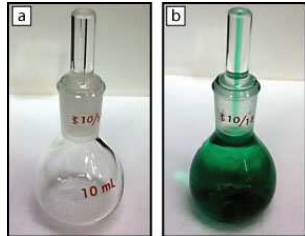
### Gostota vode

Temp (°C)	Density (kg/m <sup>3</sup> )
100	958.4
80	971.8
60	983.2
40	992.2
30	995.6502
25	997.0479
22	997.7735
20	998.2071
15	999.1026
10	999.7026
4	999.9720
0	999.8395
-10	998.117
-20	993.547
-30	983.854

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# Določanje gostote tekočin

Piknometrično določanje gostote tekočin



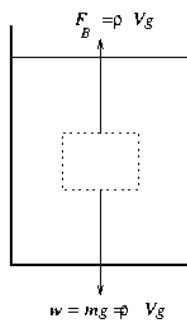
Določanje gostote tekočin na osnovi Arhimedovega zakona



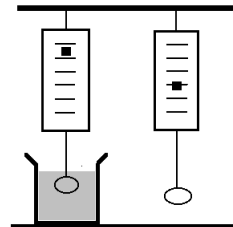
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# Določanje gostote trdnih snovi

Določanje gostote tekočin na osnovi Arhimedovega zakona



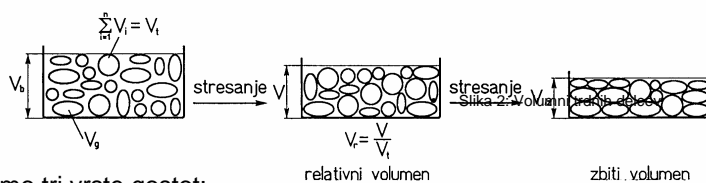
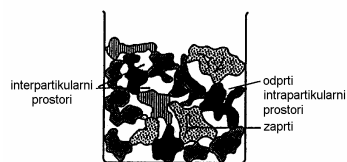
Archimedes' Principle



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# Določanje gostote trdnih snovi

Vrste praznih prostorov v delcih in med njimi



Ločimo tri vrste gostot:

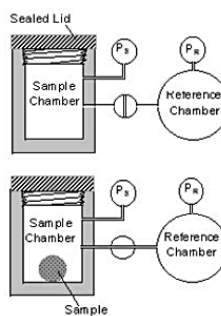
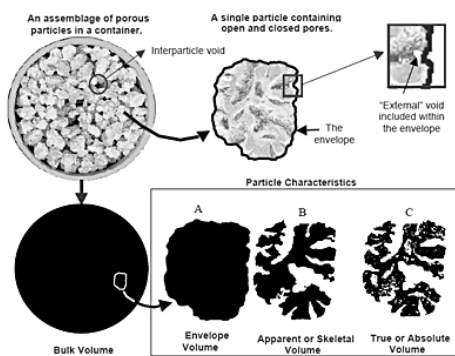
Prava gostota izljuje vse intrapartikularne ter interpartikularne prostore.

Granularna gostota vključuje intrapartikularne prostore

Nasipna gostota vključuje intrapartikularne in interpartikularne prostore.

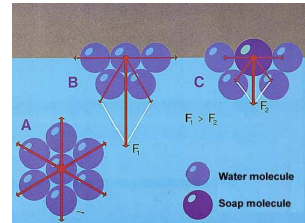
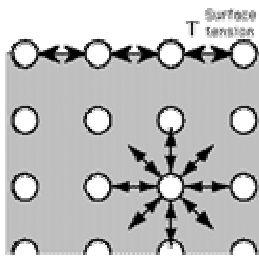
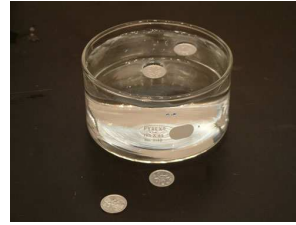
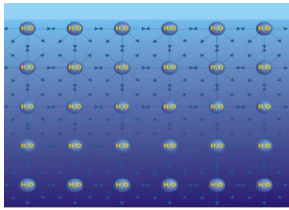
# Določanje gostote trdnih snovi

Določanje gostote trdnih snovi s pomočjo plina



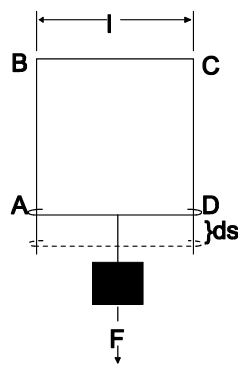
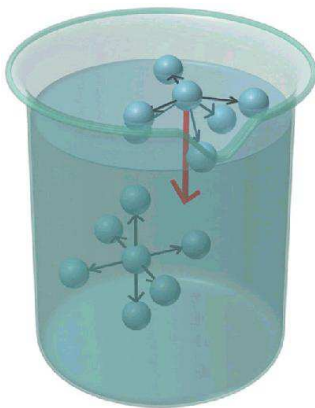
■  $PV = nRT$

## POVRŠINSKA NAPETOST TEKOČIN



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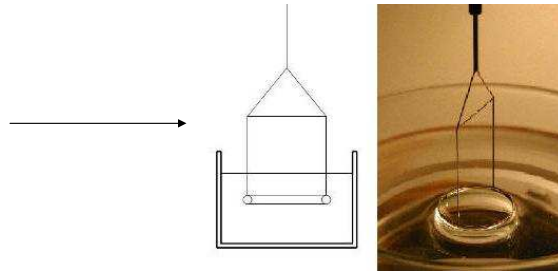
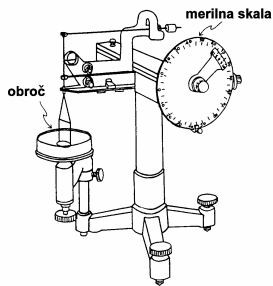
## Površinska napetost tekočin



$$\gamma = \frac{W}{\Delta A} = \frac{Fds}{2lds} = \frac{F}{2l}$$

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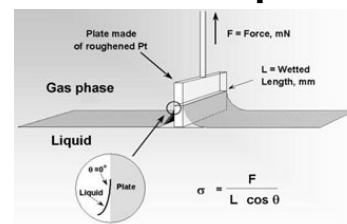
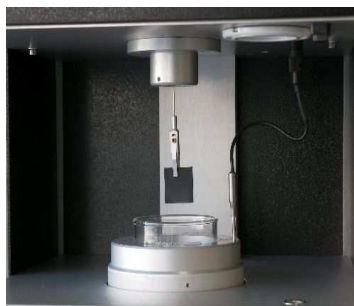
## Tenziometrični način določanja površinske napetosti



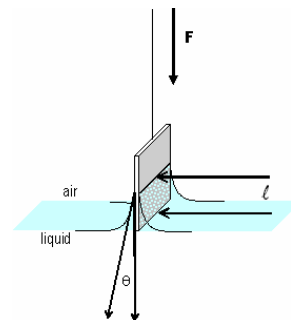
$$F = 4\pi r_0 \gamma$$

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## Tenziometrični način določanja površinske napetosti



$$\sigma = \frac{F}{2l \cdot \cos \theta}$$



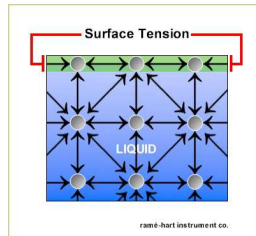
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# Površine in medfaze

Prekinitev (meja) med fazami:

**Tekoče/plin (zrak)** -površinska napetost

**Tekoče/tekoče** -medfazna napetost



**Trdno/plin (zrak)** -površinska energija

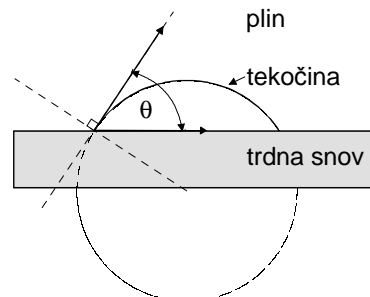
**Trdno/tekoče** -medfazna energija, medfazna napetost

**Trdno/trdno** -medfazna energija

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# Močenje

- Močenje vrednotimo z merjenjem stične kota.
- Kapljico tekočine kanemo na gladko trdno površino.

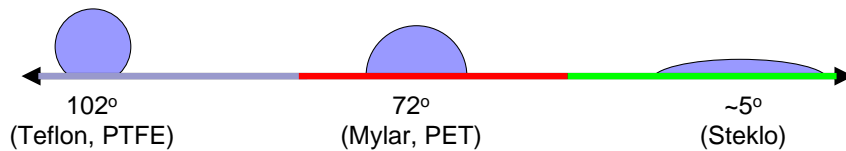


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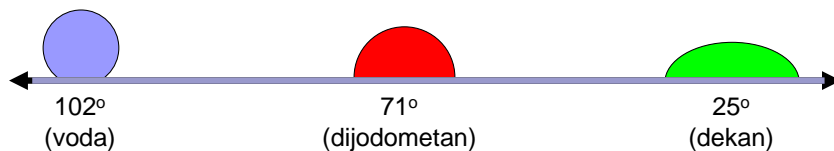


## Močljivost kvantificiramo z merjenjem stičnega kota

Površinska napetost vode ( $\gamma_{LV} = 72.8 \text{ mN/m}$ )-najpogosteje uporabljena tekočina za vrednotenje močljivosti trdnih površin.



Močljivost površine lahko vrednotimo z različnimi tekočinami (npr. na teflonu).



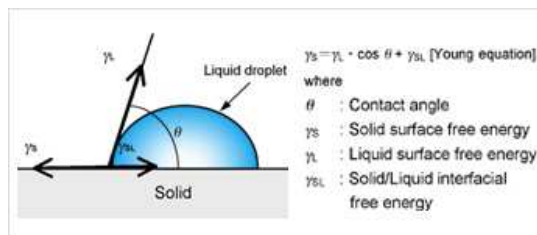
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### Površinska napetost (energija):

$\gamma_{lv}$  - liquid/vapor

$\gamma_{ls}$  - liquid/solid

$\gamma_{sv}$  - solid/vapor



$$\gamma_{sv} = \gamma_{ls} + \gamma_{lv} \cos \theta$$

Youngova enačba

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**Slabo močenje**      **Dobro močenje**      **Popolno močenje**

$\theta > 90^\circ$        $90^\circ > \theta > 0^\circ$        $\theta \rightarrow 0^\circ$

$\cos \theta < 0$        $\cos \theta > 0$        $\cos \theta = 0$

$$\cos \theta = \frac{\gamma_{sv} - \gamma_s}{\gamma_w}$$

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POVRŠINSKA IN MEDFAZNA NAPETOST



**Površinske napetosti kapljev in medfazne napetosti kapljev, ki se ne mešajo z vodo.**

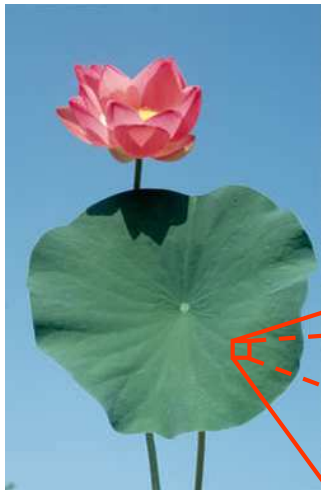
kapljevina	pov. napetost $\gamma$ [mN/m]	kapljevina	medfazna napetost kapljev in z vodo $\gamma$ [mN/m]
voda	72,8	tekoči parafin	45,0
glicerol	63,4	benzol	35,0
benzen	28,9	kloroform	32,8
kloroform	27,1	olje	15,6
tetraklogljik	26,7	oktanol	8,5
ricinusovo olje	39,0		

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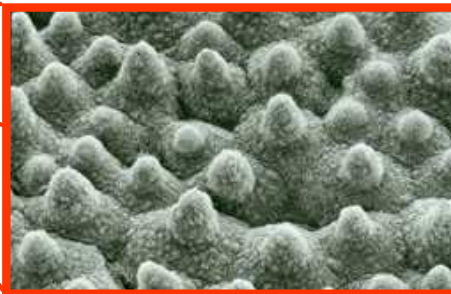
# Primer pomena močenja v naravi



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Listi lotusa so ekstremno  
hidrofobne in samočistilne  
površine



By Erika Eiser, Complex Fluids Group, UvAmsterdam

<http://www.youtube.com/watch?v=MFHcSrNRU5E>

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## Lotusov efekt



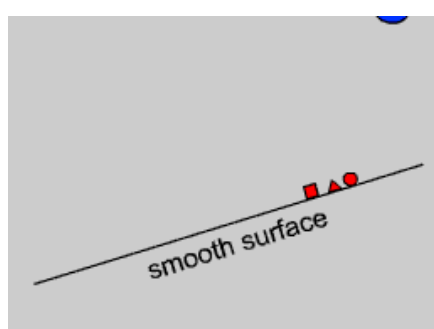
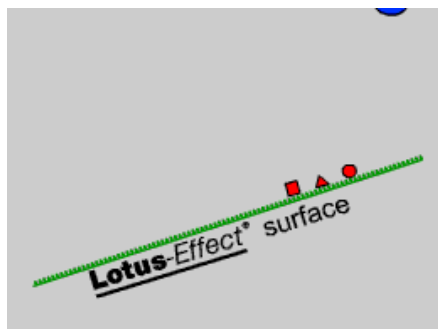
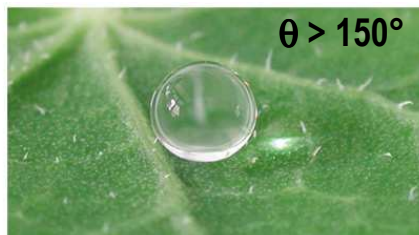
Viskozno vodotopno lepilo se skotali po lotusovem listu.



Barva se s površine spere.

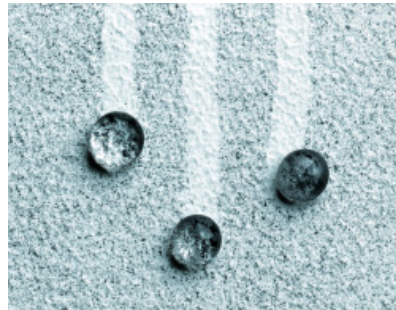
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## Samočistilni učinek



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## Uporaba nanotehnologije-samočistilni učinek.



Fasadna barva, ki se sama očisti  
bed dežjem zaradi "Lotus-effect®"

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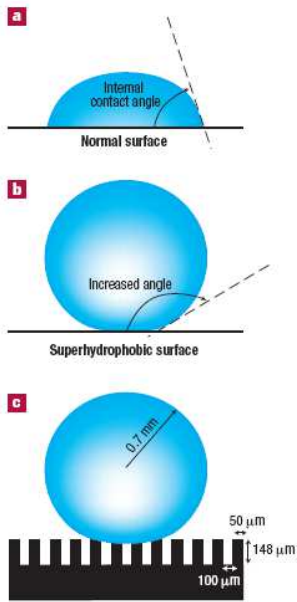
## Primer izdelave hidrofobne površine

### Samočistilni premaz za steklo



<http://www.youtube.com/watch?v=96iMj5NSyyY&NR=1>

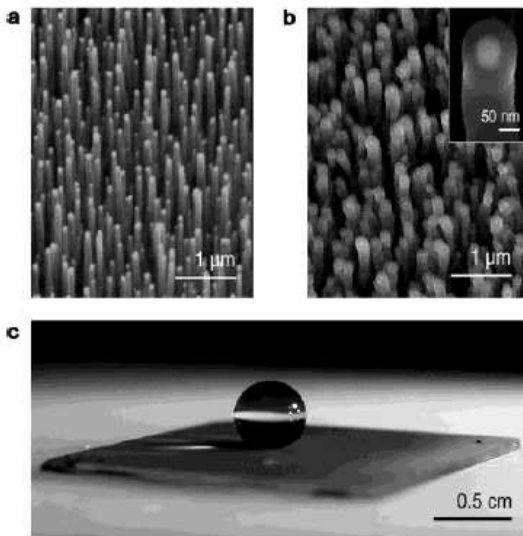
58



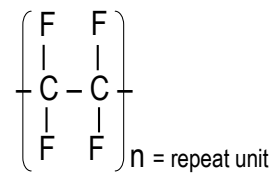
- Micro- or nanopatterning an already hydrophobic surface will make that surface even more hydrophobic ( $\theta > 150^\circ$ ).
- Some call such superhydrophobic surfaces also 'fakir surface'



David Quéré, nature materials, vol. 1, Sept. 2002



poly(tetrafluoroethylene)  
(PTFE) = non-wetting coating.



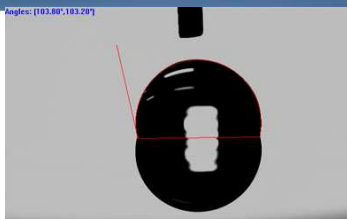
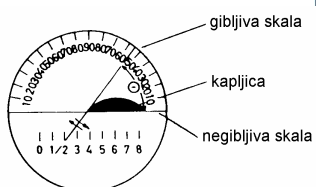
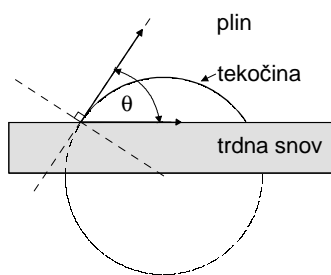
Kenneth K. S. Lau et al. Nano Letters 2004

# Metode določanja močenja



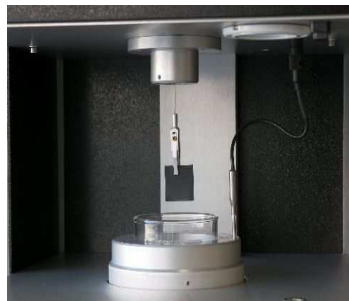
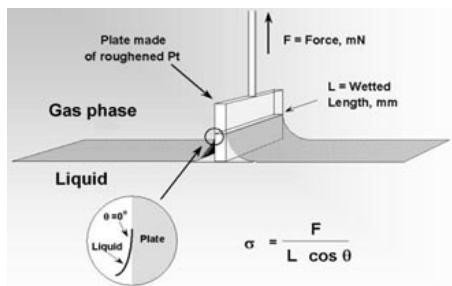
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## 1 Metoda sedeče kapljice (goniometrična metoda)



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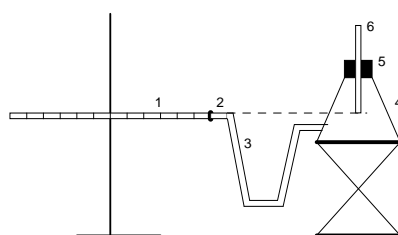
## 2 Wilhelmijska metoda s ploščico



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## 3 Washburnova metoda

Shema Washburnove naprave



1. Washburnova steklena cev napolnjena z vzorcem
2. steklena siga,
3. silikonska cev,
4. posoda s tekočino,
5. gumijasti zamašek
6. tanka cevka za zrak

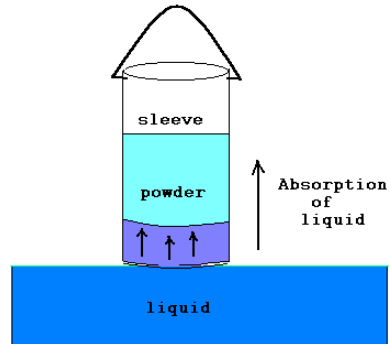
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### 3 Modificirana Washburnova metoda

$$l^2 = \frac{r\gamma \cos \theta}{2\eta} t$$

r=povprečni radij kapilar  
l=dolžina, ki jo prepotuje fronta tekočine v času t  
η=viskoznost tekočine  
γ=površinska napetost tekočine



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