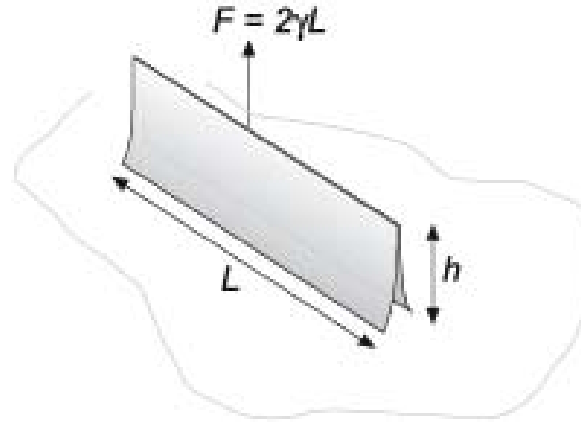


Capillaire Verschijnselen en Adsorptie

Oppervlaktespanning: experiment

Naald optrekken uit vloeistof



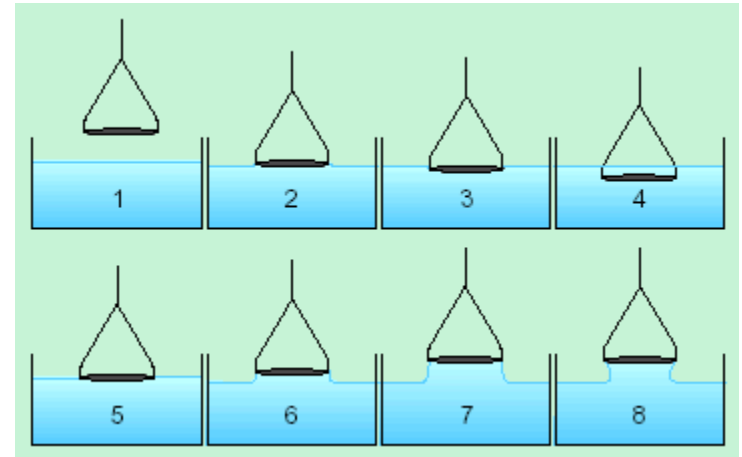
vergroting vloeistof-oppervlak kost arbeid $dW = \gamma dA$

- Hier: $dW = \gamma dA = 2\gamma L dh$ dus $F = \frac{dW}{dh} = 2\gamma L$

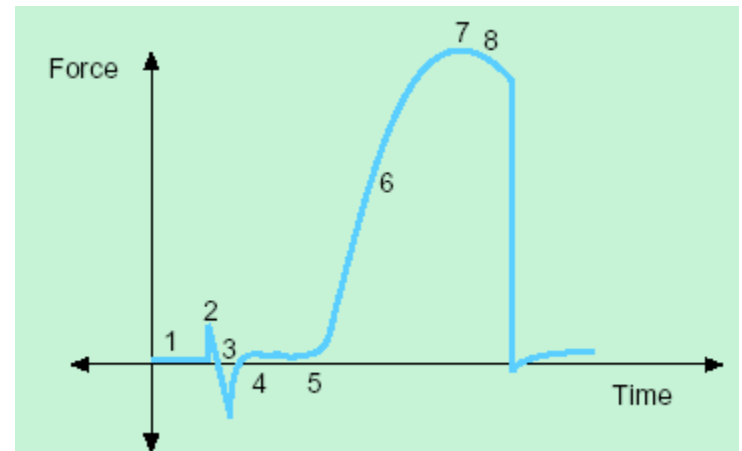
Oppervlaktespanning: experiment

Meetmethoden

- Wilhelmy plaatje



- Du Noüy ring



Oppervlaktespanning: moleculair

- molecuul in volume

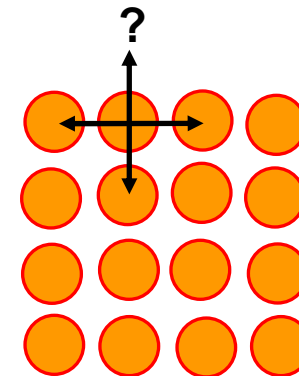
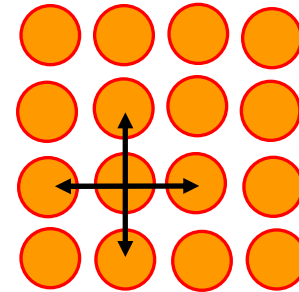
$$u_{\text{bulk}} = \frac{z}{2} W_{AA}$$

- molecuul aan oppervlak

$$u_{\text{surf}} = \frac{z_s}{2} W_{AA}$$

- Oppervlakte-energie overschot

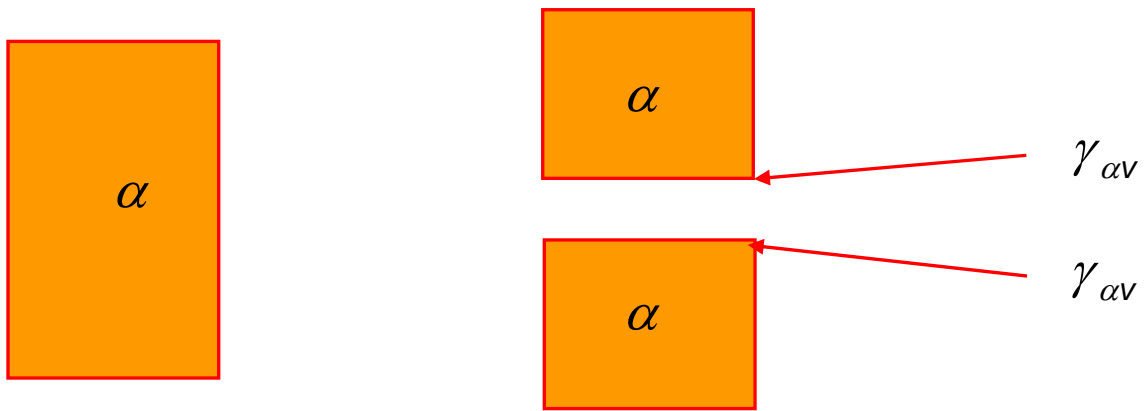
$$\gamma = \frac{u_{\text{excess}}}{\sigma} = \frac{z_s - z}{2\sigma} W_{AA}$$



Oppervlaktespanning: adhesie en cohesie

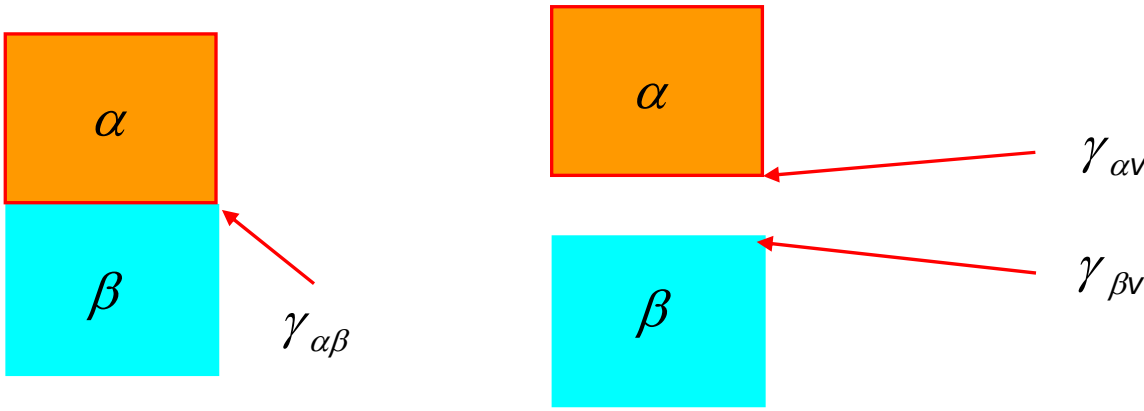
- Cohesie-arbeid

$$W = 2\gamma_{\alpha v}$$



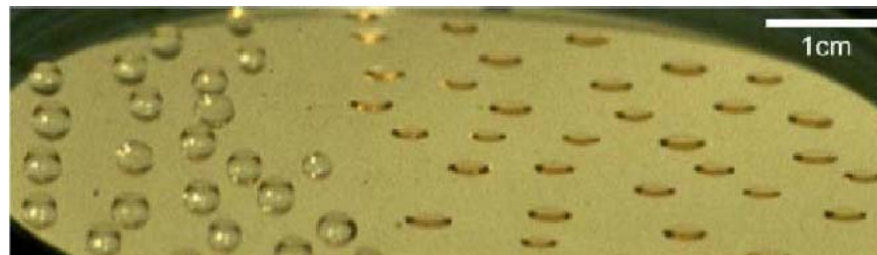
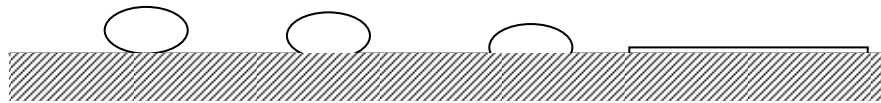
- Adhesie-arbeid

$$W = \gamma_{\alpha v} + \gamma_{\beta v} - \gamma_{\alpha\beta}$$



Wet van Young: experiment

Bevochtiging



Wet van Young: krachtenbalans



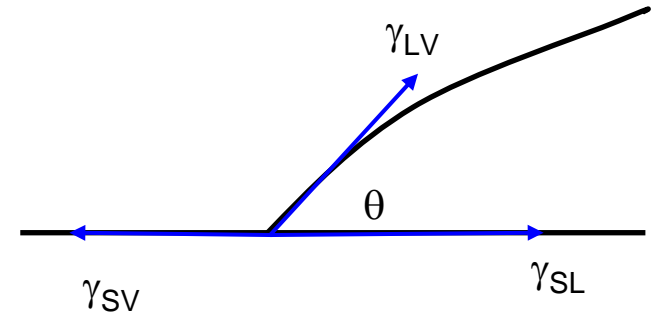
Thomas Young (1773 – 1829)

Wet van Dupré
voor vloeistofoppervlakken

- Krachtenbalans

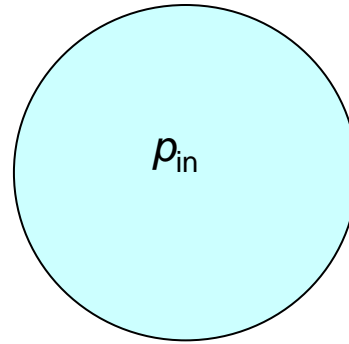
$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$$

- Bevochtiging $0 \leq \theta \leq 90^\circ$

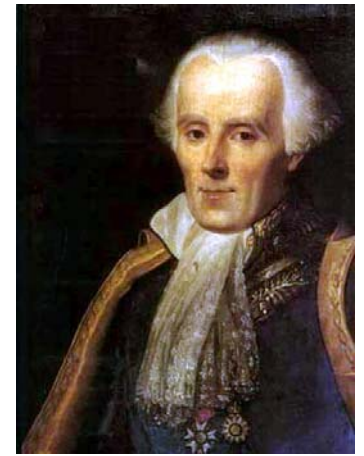


Wet van Laplace: druppeltjes

Druppel vloeistof in damp (mist)



p_{out}



Pierre-Simon, Marquis de Laplace
(1749 – 1827)

- Krachtenbalans

- naar buiten $4\pi a^2 p_{in}$

- naar binnen $4\pi a^2 p_{out} + 8\pi a\gamma$

- Laplace vergelijking $\Delta p = p_{in} - p_{out} = \frac{2\gamma}{a}$

Wet van Laplace: experimenteel

Oppervlaktespanning meten met een luchtbelletje

$$\gamma = \frac{a\Delta p}{2}$$



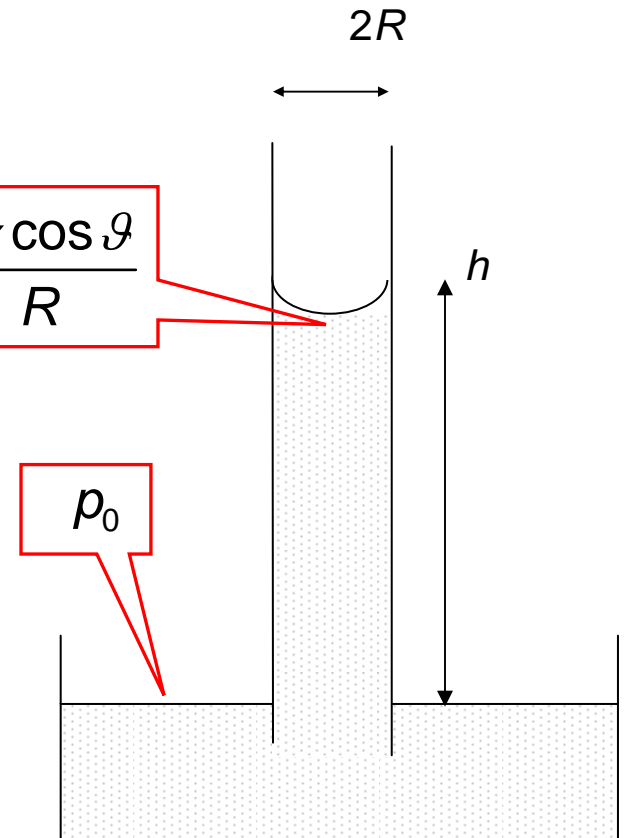
Wet van Laplace: capillaire opstijging

Capillaire opstijging

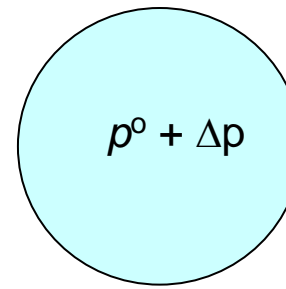
- Bevochtiging wand door vloeistof: meniscus
- Levert onderdruk over kromming
- compensatie door opstijging
- Krachtenbalans

$$h = \frac{2\gamma \cos \theta}{\rho g R}$$

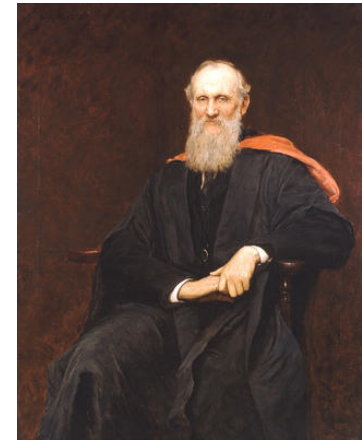
$$p = p_0 - \frac{2\gamma \cos \theta}{R}$$



Wet van Kelvin



p^0



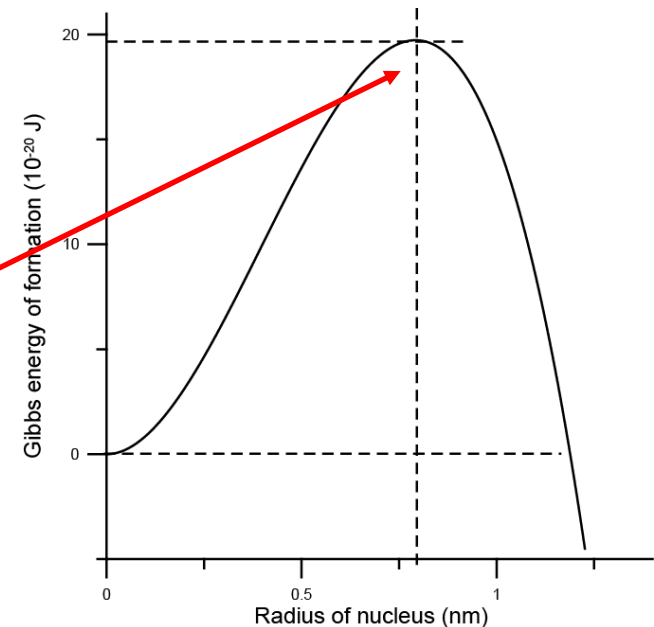
Lord Kelvin (1824 – 1907)

- Gibbs vormingsenergie van druppel

$$\Delta G = -\frac{4\pi a^3 / 3}{V_L} RT \ln \frac{p^0 + \Delta p}{p^0} + 4\pi a^2 \gamma$$

- Kelvin relatie: instabiel evenwicht

$$RT \ln \frac{p^0 + \Delta p}{p^0} = \frac{2\gamma V_L}{a}$$



Wet van Kelvin: nucleatie

Homogeen

- Kristallisatie
- Koken (verdampen)
- ...

Heterogeen

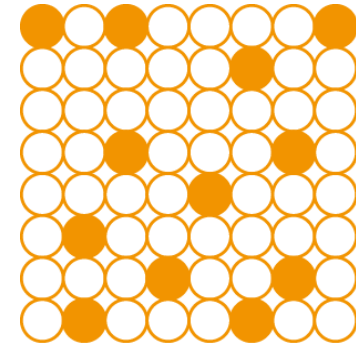
- Regen / mist
- CO₂ in frisdrank
- ...



Adsorptie

- gelokaliseerd

– Oppervlaktebedekking $\theta = \frac{M}{N}$

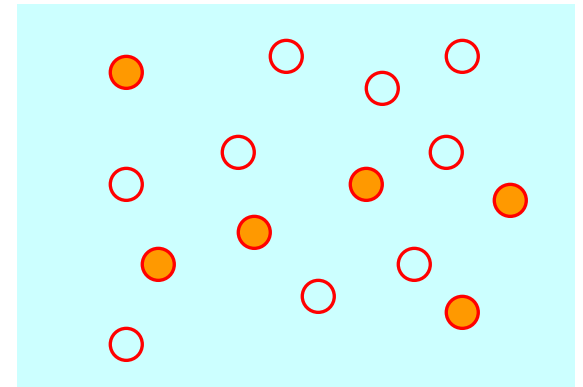


$$A = N\sigma$$

- niet-gelokaliseerd

– Adsorptie

$$\Gamma = \frac{M}{A}$$



- Maximale adsorptie $\Gamma_{\max} = \frac{N}{A}$

Langmuir adsorptie-isotherm

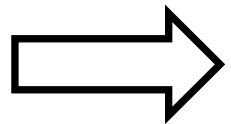


Irvin Langmuir
(1881 – 1957)

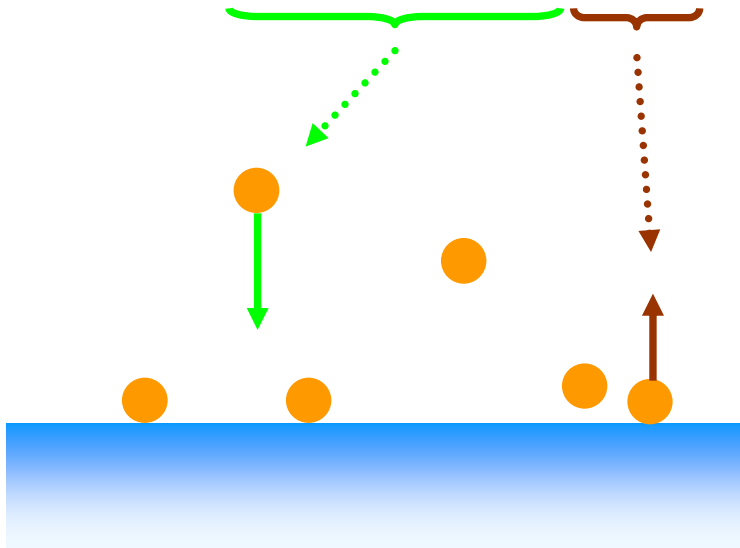
Kinetisch argument

$$\frac{d\Gamma}{dt} = k_a \frac{p}{p^\ominus} (\Gamma_{\max} - \Gamma) - k_d \Gamma$$

$$\frac{d\Gamma}{dt} = 0$$



$$\frac{\Gamma}{\Gamma_{\max}} = \frac{K \frac{p}{p^\ominus}}{1 + K \frac{p}{p^\ominus}}$$

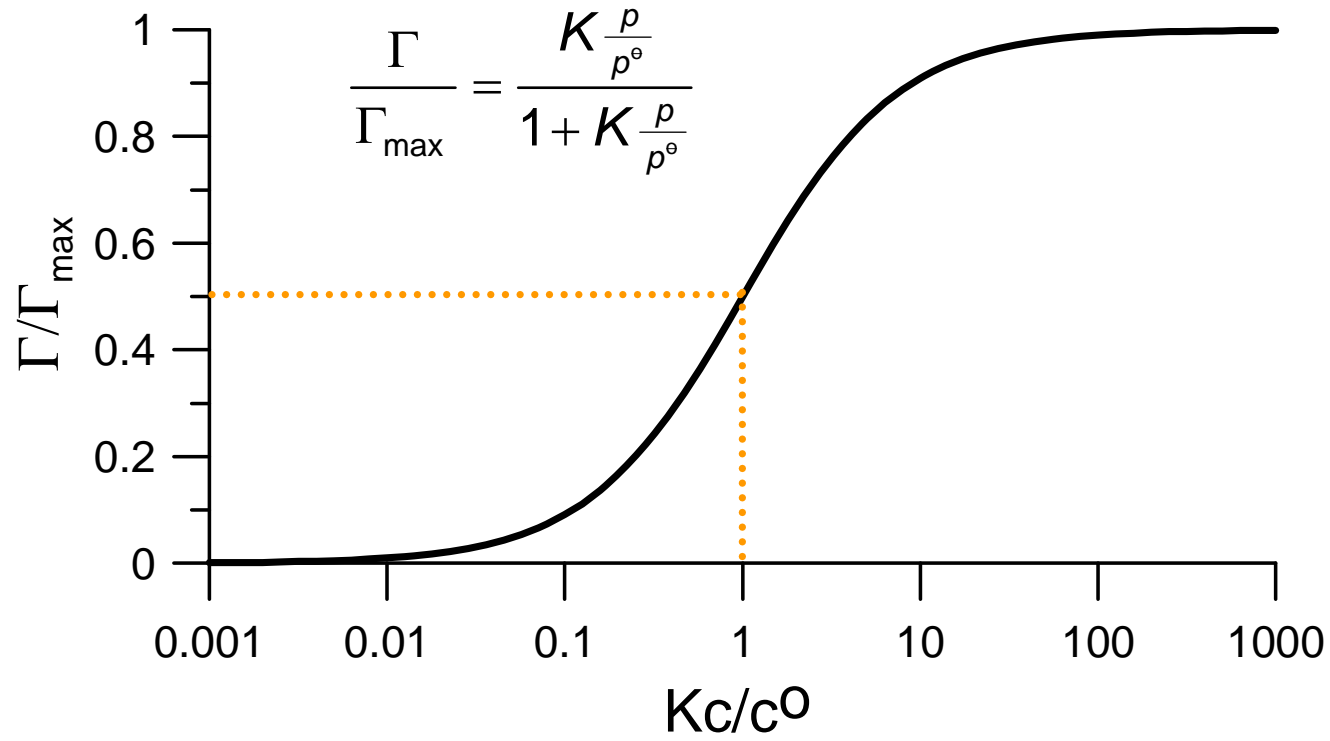


$$K = \exp\left(-\frac{\Delta_{\text{ads}} G}{RT}\right)$$

Aanname: geen interactie tussen buren

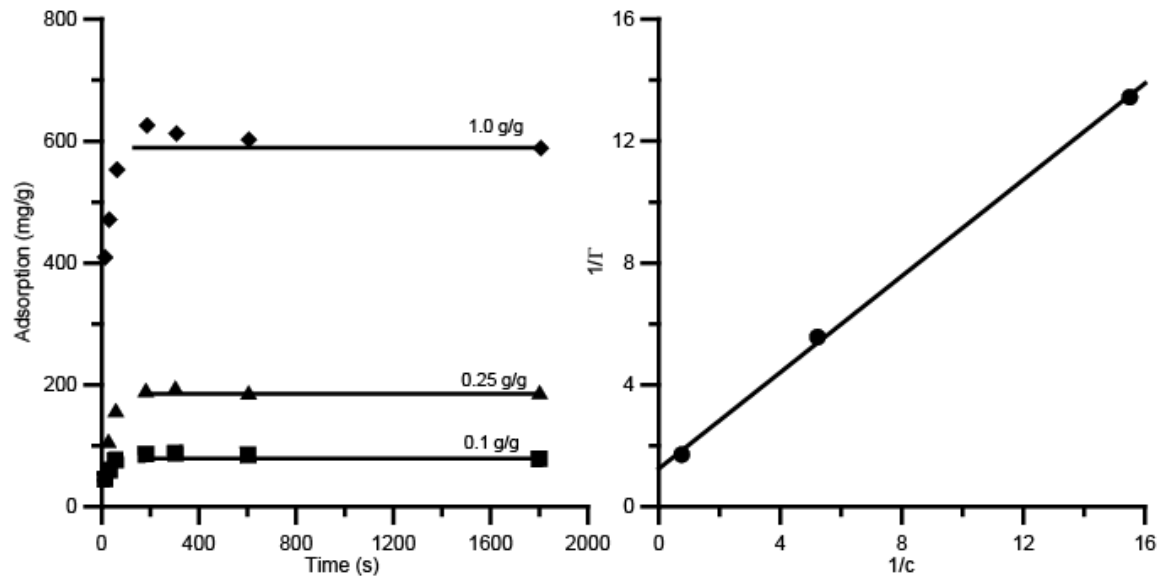
Langmuir adsorptie-isotherm

Kanonieke grafiek



Langmuir adsorptie-isotherm

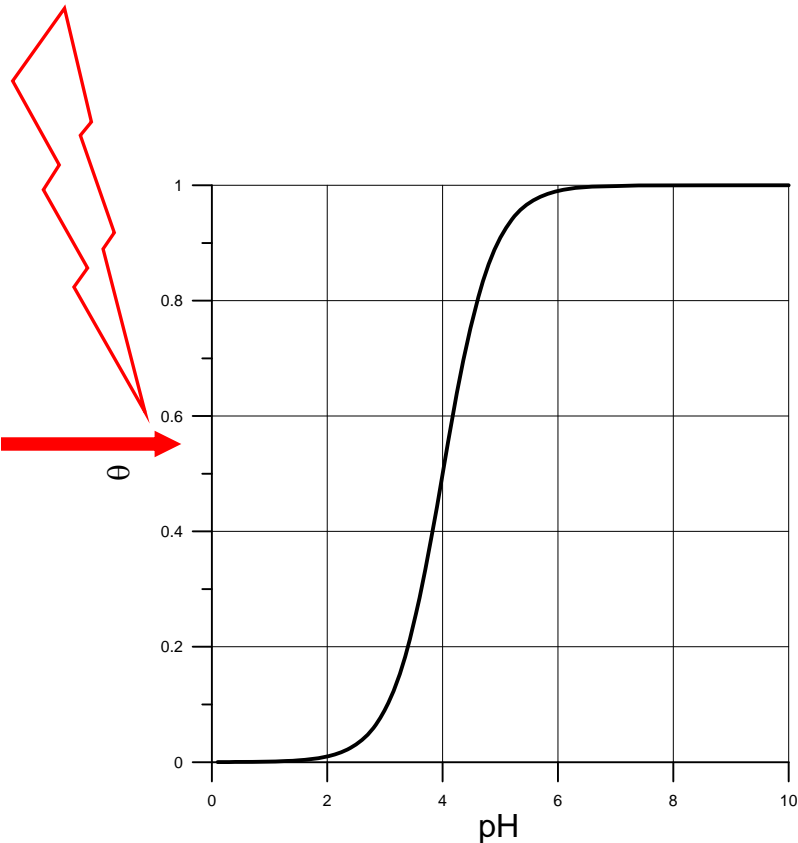
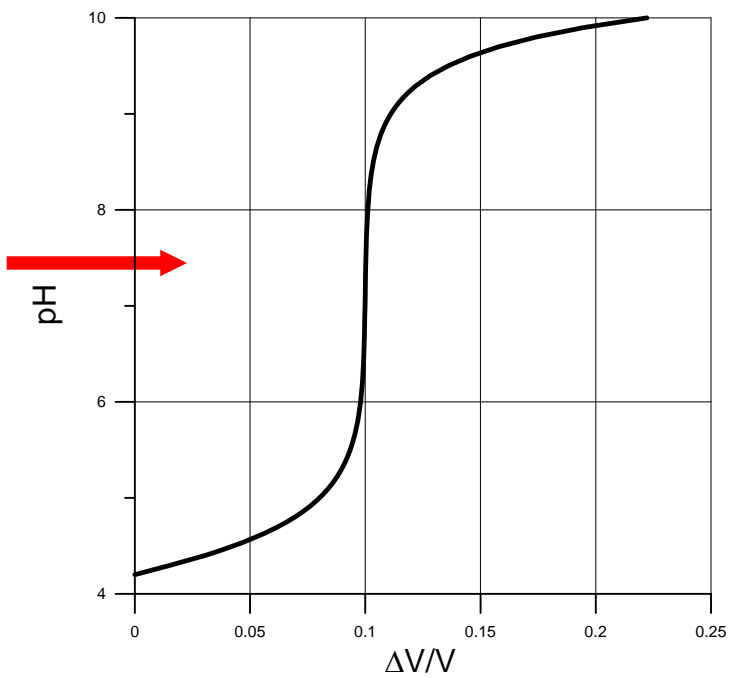
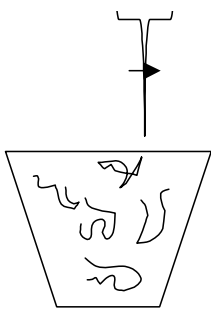
Analyse met Lineweaver-Burke-grafiek



Potentiometrische titratie

Dissociatiegraad

$$\theta = \frac{[A^-]}{[A^-] + [AH]} = \frac{\Delta V}{V} \frac{c_B}{c_A} + \left(1 + \frac{\Delta V}{V}\right) \left(10^{-pH} - 10^{-pK_w + pH}\right)$$



Potentiometrische titratie

Henderson-Hasselbalch vergelijking

$$\theta = \frac{1}{1 + 10^{-\text{pH} + \text{pK}}} \quad \text{of} \quad 10^{\text{pH} - \text{pK}} = \frac{\theta}{1 - \theta}$$

Andere adsorptie-isothermen:

- Brunauer-Emmett-Teller (BET) – isotherm
- Frumkin-Fowler-Guggenheim isotherm

Reversibilititeit

