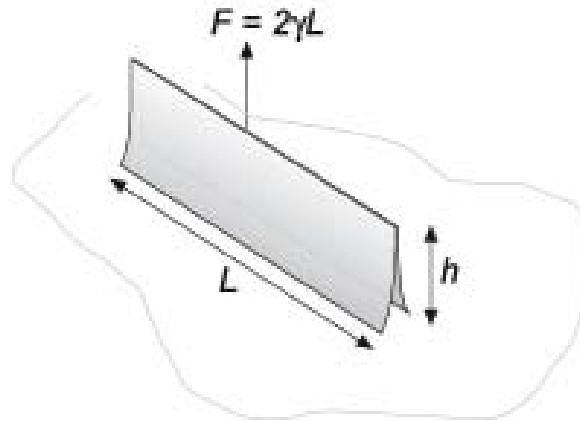


# Capillaire Verschijnselen en Adsorptie



# Oppervlaktespanning: experiment

Naald optrekken uit vloeistof



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

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

$$\gamma_{H_2O} = 75 \text{ mN/m}$$

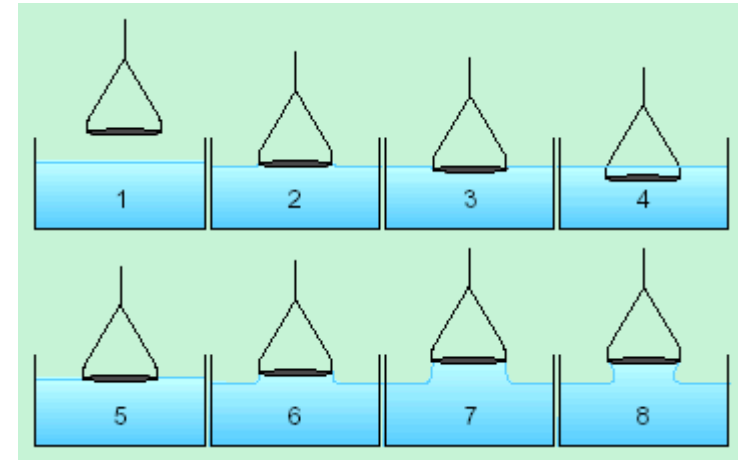
$$L = 5 \text{ cm}$$

$$F = 2 \times 5 \cdot 10^{-2} \times 75 \cdot 10^{-3} \text{ N} = 7.5 \text{ mN}$$

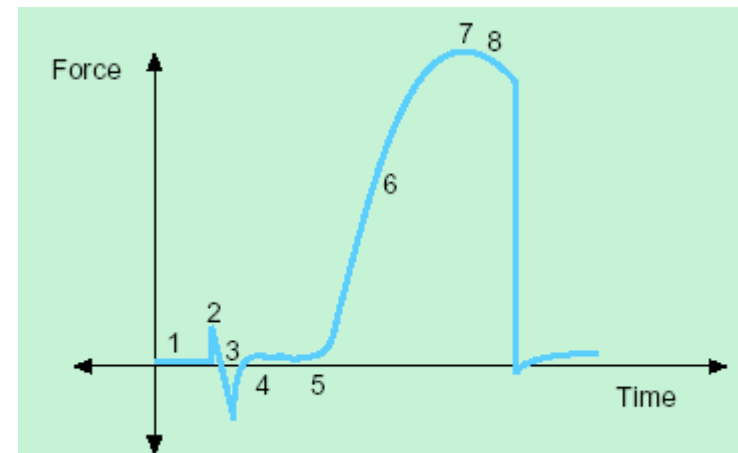
# Oppervlaktespanning: experiment

## Meetmethoden

- Wilhelmy plaatje



- Du Noüy ring



# Oppervlaktespanning: moleculair

- molecuul in volume

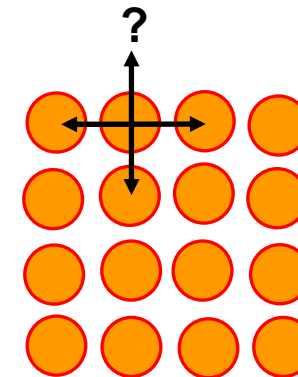
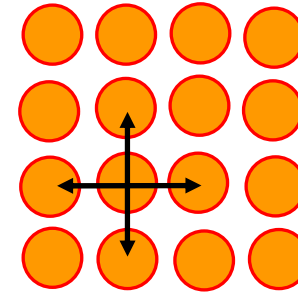
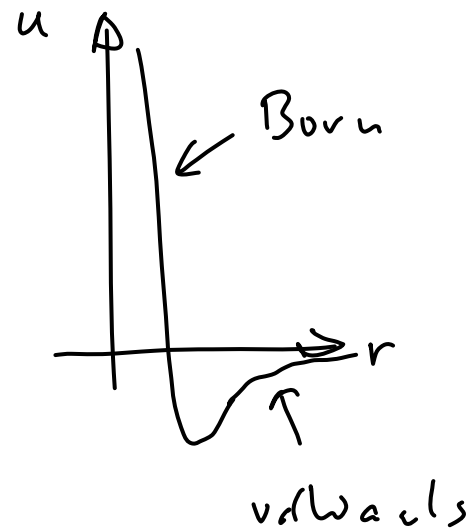
$$u_{\text{bulk}} = \frac{z}{2} W_{AA}$$

- 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: moleculair

Voorbeeld voor tetrachloormethaan

paar interactie energie ( $z = 6$ )

$$w_{AA} = -\frac{\Delta_{\text{vap}} H^{\circ}}{N_{\text{Av}} z/2} = -\frac{29.7 \text{ kJ/mol}}{3 \times 6.022 \cdot 10^{23} / \text{mol}} = -1.644 \cdot 10^{-20} \text{ J}$$

ongeveer  $-4 k_B T$

Oppervlak per molecule (veronderstel kubusjes)

$$d = \sqrt[3]{\frac{M}{\rho N_{\text{Av}}}} = \sqrt[3]{\frac{154 \cdot 10^{-3}}{1.6 \cdot 10^3 \times 6.0 \cdot 10^{23}}} = 0.54 \text{ nm} \rightarrow \sigma = d^2 = 0.3 \text{ nm}^2$$

oppervlaktespanning

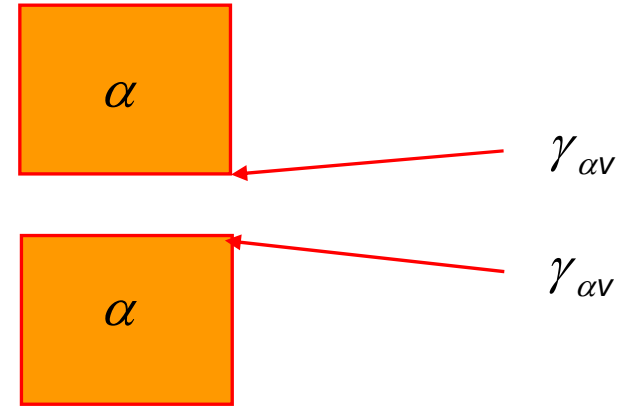
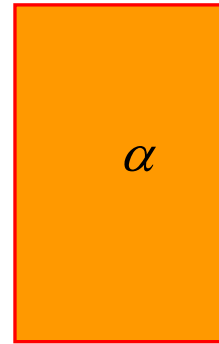
$$\gamma = \frac{z_s - z}{2\sigma} w_{AA} = \frac{5 - 6}{2 \times 0.3 \cdot 10^{-18}} \times -1.644 \cdot 10^{-20} \text{ J/m}^2 = 27.4 \text{ mJ/m}^2$$

getabuleerd:  
26.4 mJ/m<sup>2</sup>

# Oppervlaktespanning: adhesie en cohesie

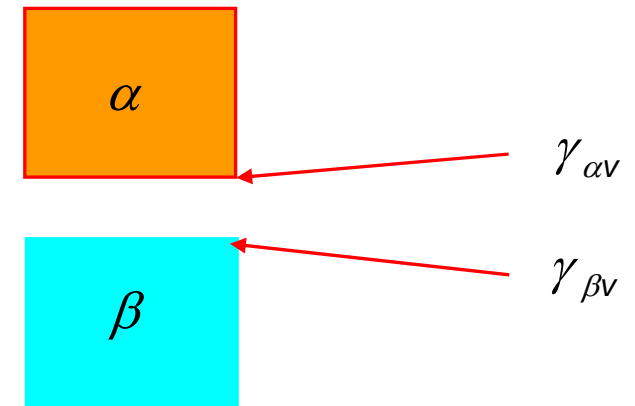
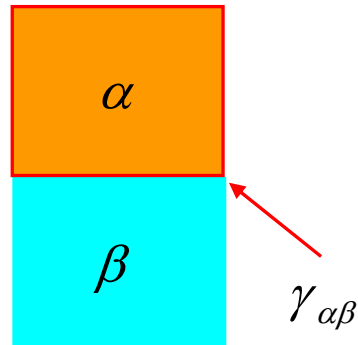
- Cohesie-arbeid

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



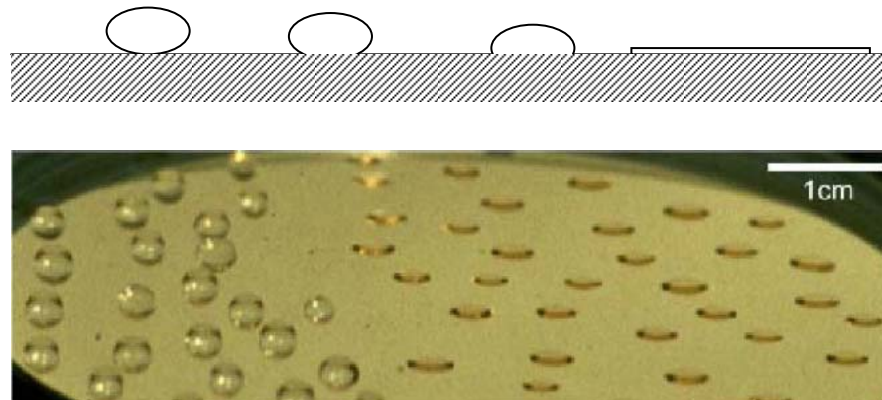
- Adhesie-arbeid

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



# Wet van Young: experiment

Bevochtiging

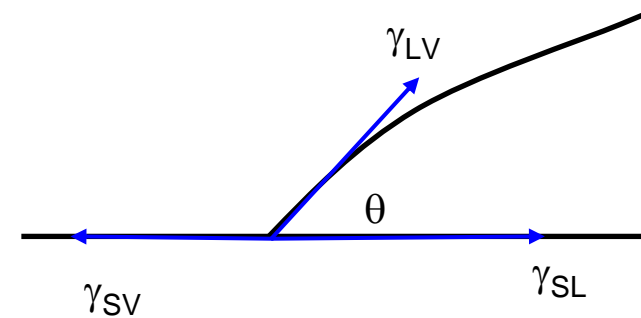


# Wet van Young: krachtenbalans

Wet van Dupré  
voor vloeistofoppervlakken



Thomas Young (1773 – 1829)



- Krachtenbalans

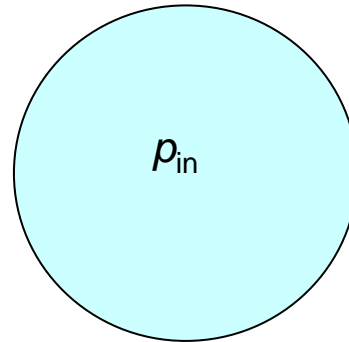
$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$$

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



# Wet van Laplace: druppeltjes

Druppel vloeistof in damp (mist)



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

- Krachtenbalans

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

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

$$\frac{dW_s}{da} = \frac{d(4\pi a^2 \gamma)}{da}$$

$$\gamma_{H_2O} = 75 \text{ mN/m}$$

$$a = 1 \mu\text{m}$$

$$\Delta p = \frac{2 \times 75 \text{ } 10^{-3}}{10^{-6}} \quad p_{atm} = 150 \text{ kPa}$$

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

# Wet van Laplace: experimenteel

Oppervlaktespanning meten met een luchtbelletje

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

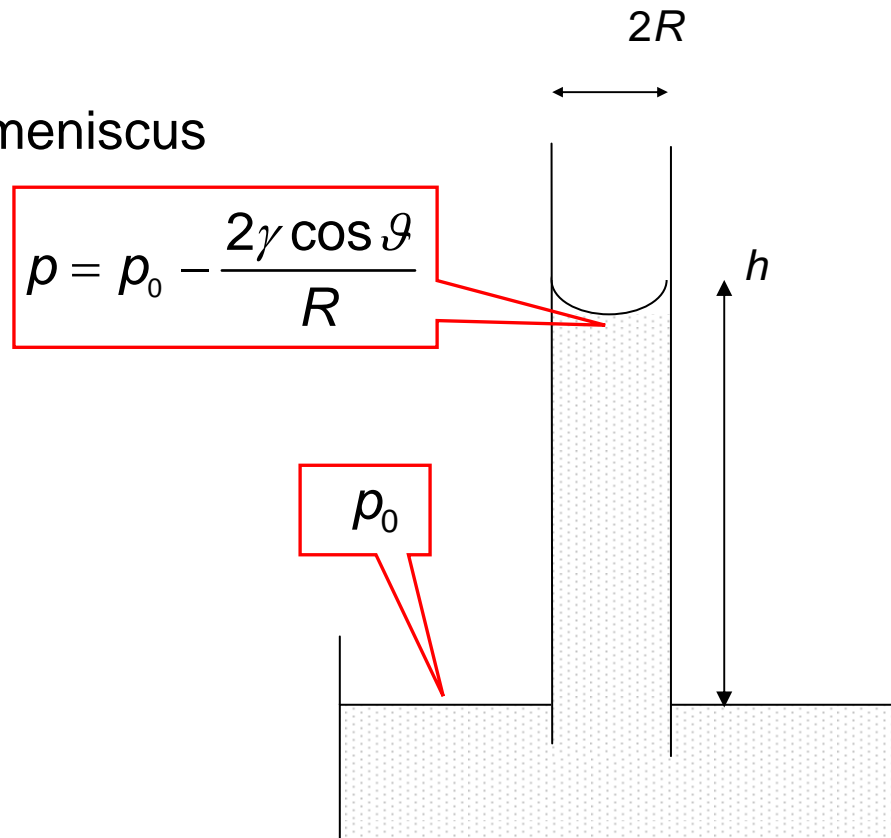


# Wet van Laplace: capillaire opstijging

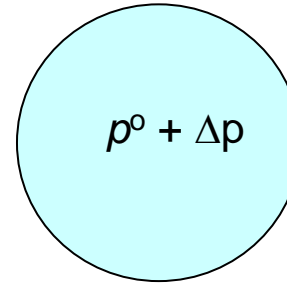
## Capillaire opstijging

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

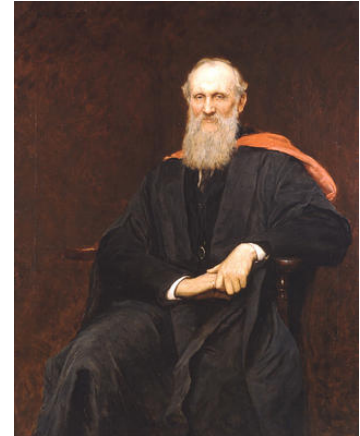
$$h = \frac{2\gamma \cos \theta}{\rho g R}$$



# Wet van Kelvin



$p^{\circ}$



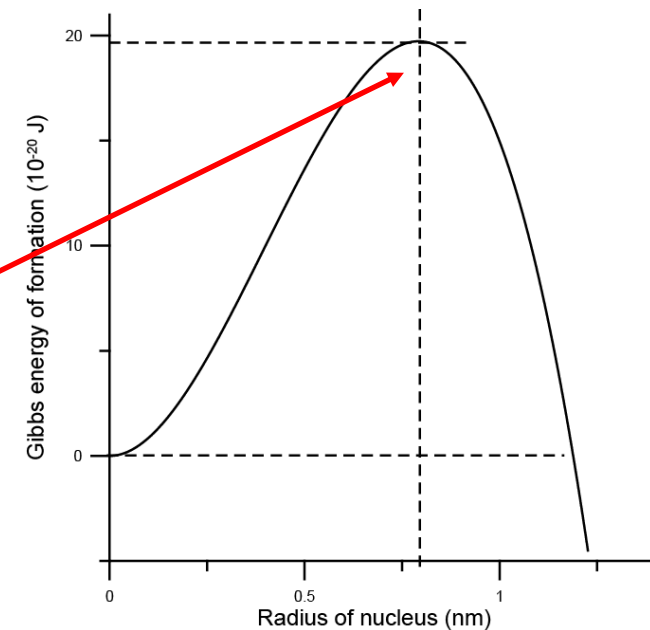
Lord Kelvin (1824 – 1907)

- Gibbs vormingsenergie van druppel

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

- Kelvin relatie: instabiel evenwicht

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



# Wet van Kelvin: nucleatie

## Homogeen

- Kristallisatie
- Koken (verdampen)
- ...

## Heterogeen

- Regen / mist
- CO<sub>2</sub> in frisdrank
- ...

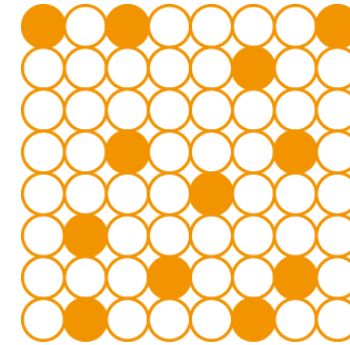


# Adsorptie

- gelokaliseerd

– Oppervlaktebedekking

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

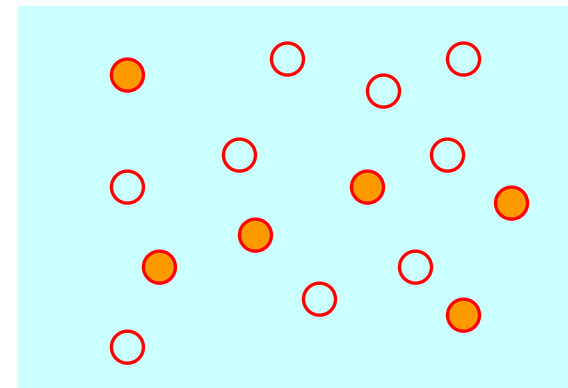


$$A = N\sigma$$

- niet-gelokaliseerd

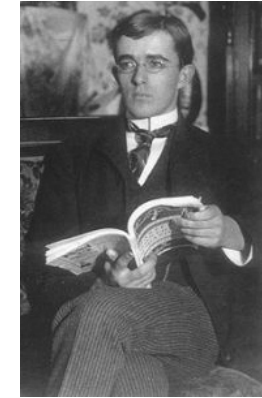
– Adsorptie

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



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

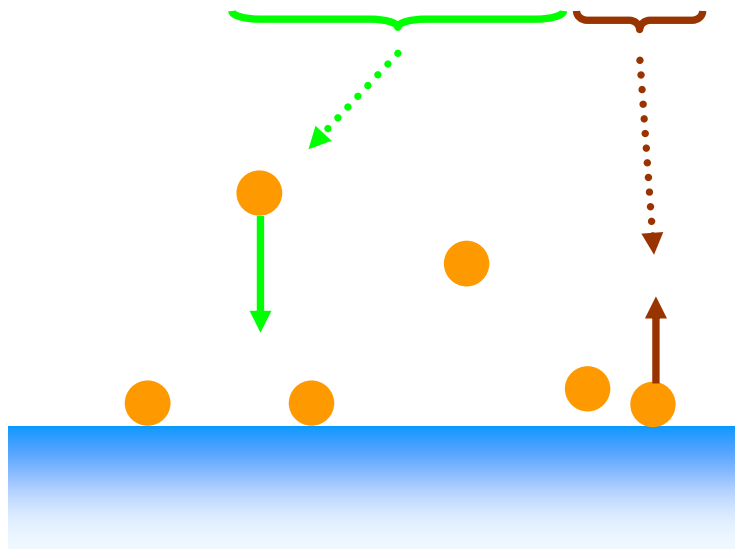
# Langmuir adsorptie-isotherm



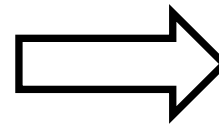
Irvin Langmuir  
(1881 – 1957)

Kinetisch argument

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



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



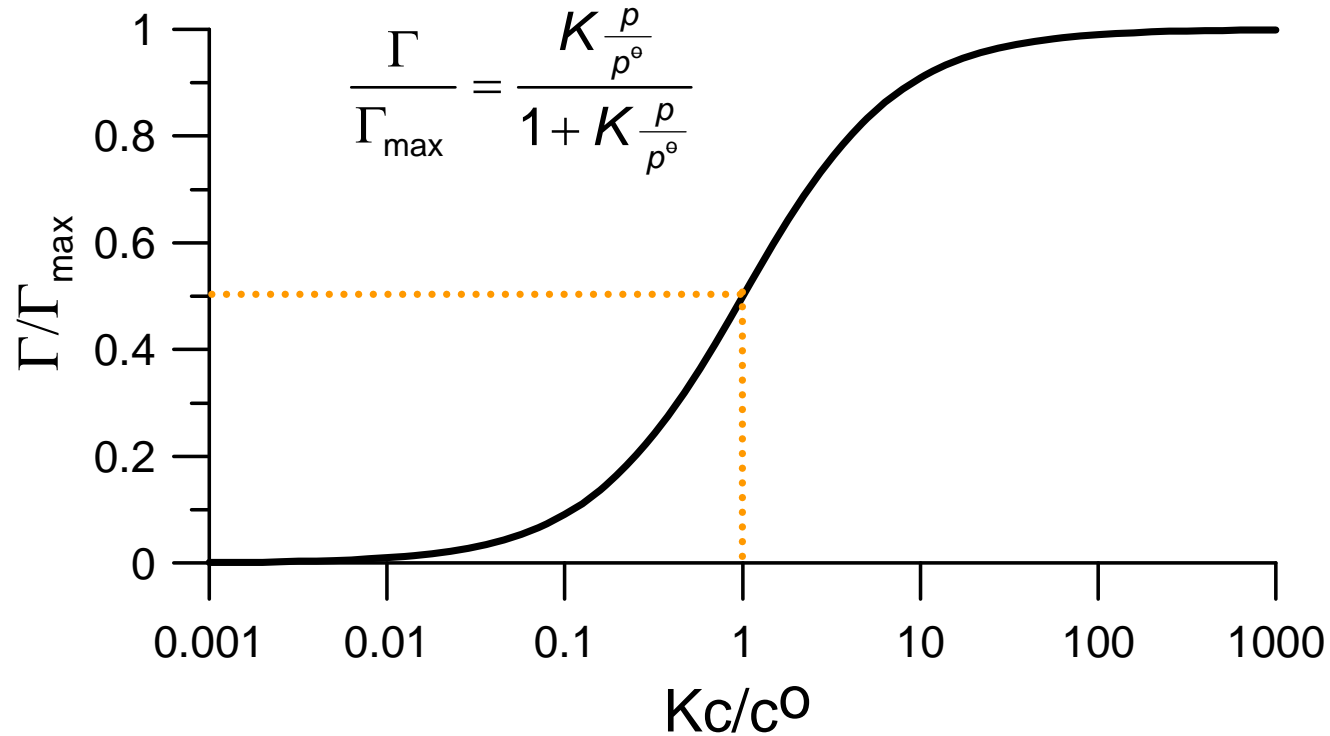
$$\frac{\Gamma}{\Gamma_{\max}} = \frac{K \frac{p}{p^\ominus}}{1 + K \frac{p}{p^\ominus}}$$

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

Aanname: geen interactie tussen buren

# Langmuir adsorptie-isotherm

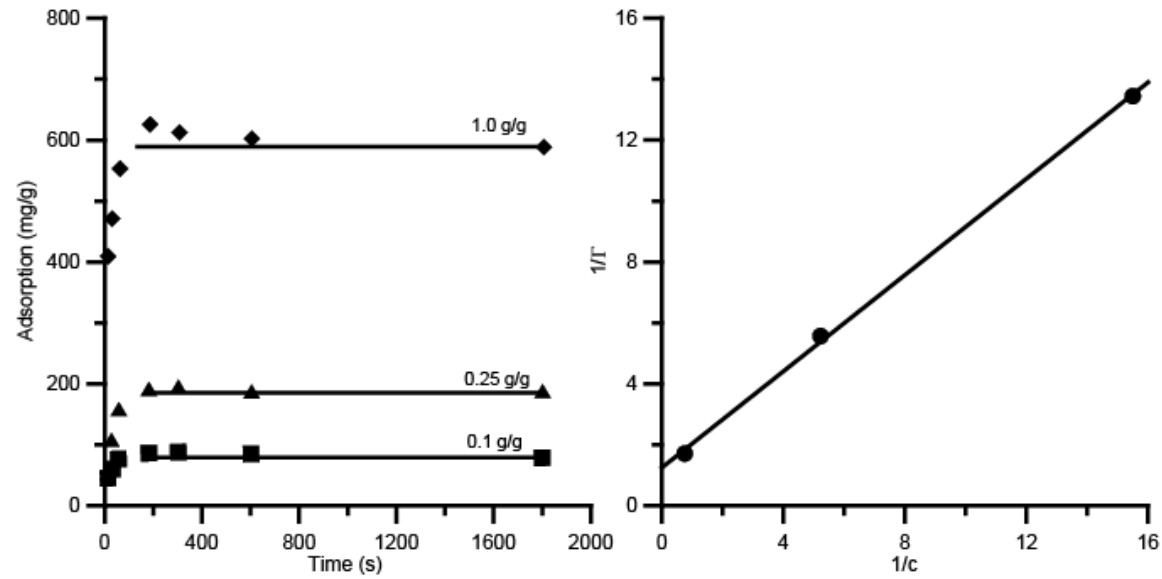
Kanonieke grafiek





# Langmuir adsorptie-isotherm

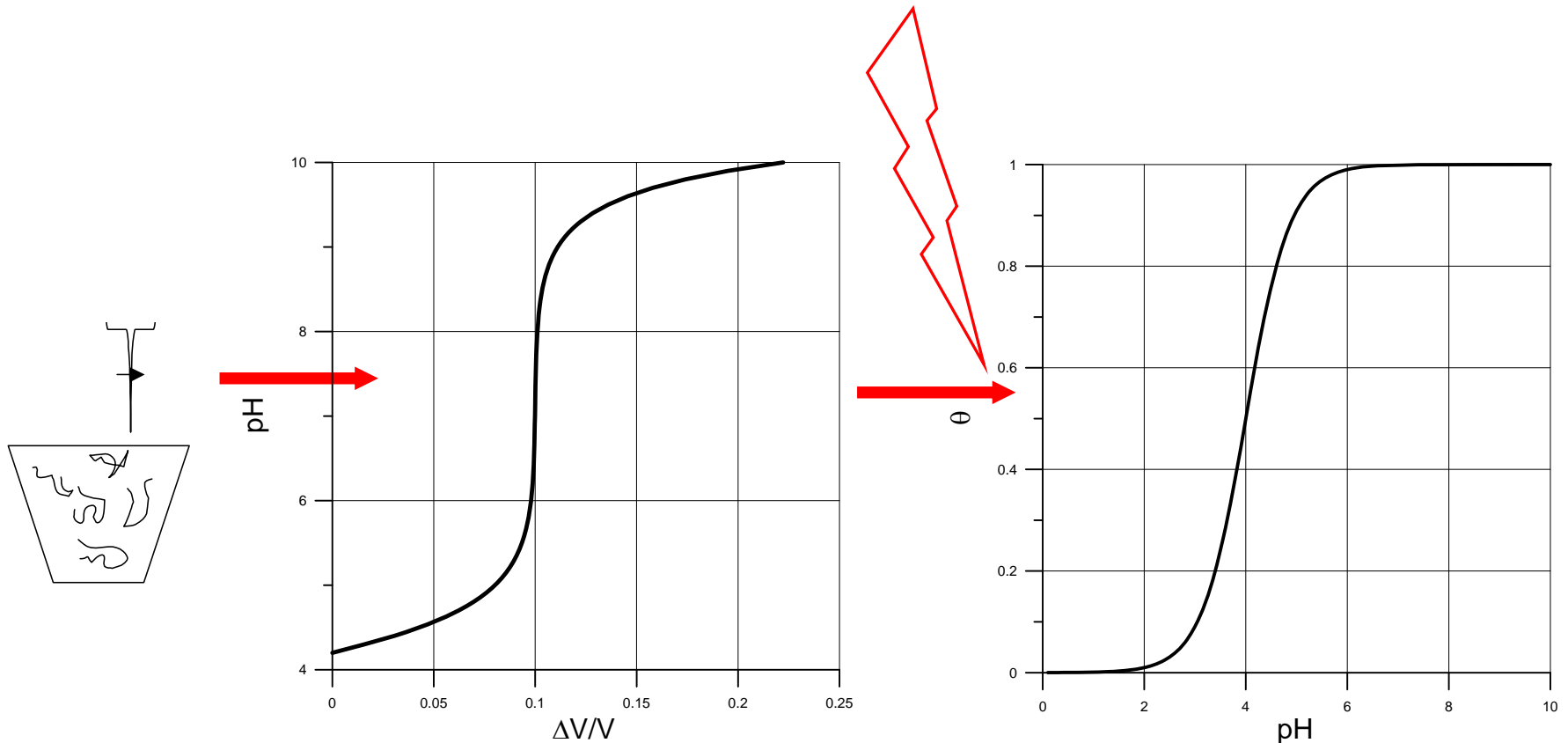
Analyse met Lineweaver-Burke-grafiek



# Potentiometrische titratie

Dissociatiegraad

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



# 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

# Reversibiliteit

