Niet-ideale Mengsels

Ideaal versus niet-ideaal gedrag

- Ideaal gedrag
  - Gas $pV = nRT$ $p = \sum_j p_j$
  - Menging $\Delta_{\text{mix}} G = nRT\left(x_A \ln x_A + x_B \ln x_B\right)$
  - Evenwicht $K = \dfrac{x_{\text{NH}_3}^2}{x_{\text{N}_2} x_{\text{H}_2}^3}$ $p_j = x_j p_j^*$

Entropie domineert

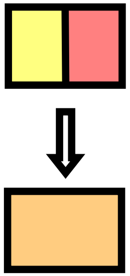
- Niet-ideaal gedrag
  - Viriaal ontwikkeling $p = \dfrac{RT}{V_m}\left(1 + \dfrac{B_2}{V_m} + \dfrac{B_3}{V_m^2} + \cdots\right)$
  - Activiteitscoëfficiënten $K = \dfrac{a\left(\text{Ag}^+\right) a\left(\text{Cl}^-\right)}{a\left(\text{AgCl}\right)}$

Moleculaire interacties

$\Downarrow$

Enthalpische bijdrage

Mengsels van Gassen



Toestandsvergelijking één-component gas

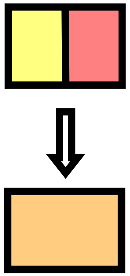
- $$V = n\left\{\frac{RT}{p} + B(T)\right\}$$

Uitbreiding naar twee componenten

- $$V = n_A\left\{\frac{RT}{p} + B_A(T)\right\} + n_B\left\{\frac{RT}{p} + B_B(T)\right\} + \frac{2n_A n_B}{n_A + n_B}\delta_{AB}$$

$$\delta_{AB} = B_{AB} - \tfrac{1}{2}\left(B_A + B_B\right) \approx 0$$

Mengsels van Gassen



Gibbs energie

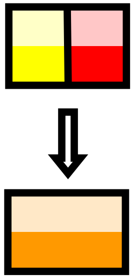
- $$G = \sum_j n_j \mu_j$$

Chemische potentiaal

- $$\mu_j = \mu_j^{\ominus} + RT \ln \frac{f_j}{p^{\ominus}} \quad \Rightarrow \quad = \mu_j^{\ominus} + RT \ln \frac{p_j}{p^{\ominus}} + pB_j$$

Fugaciteit

Eenvoudige oplossingen



Gibbs energie

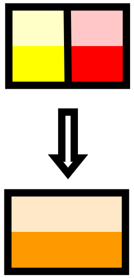
- $$G = \sum_j n_j \mu_j$$

Chemische potentiaal

Activiteit

$$\boxed{\mu_j = \mu_j^{\ominus} + RT \ln a_j} \Rightarrow = \mu_j^{\ominus} + RT \ln x_j + RT \ln \gamma_j$$

Eenvoudige oplossingen



Activiteit van oplosmiddel

- Afwijkingen van Raoult's vergelijking

$$\mu_A = \mu_A^* + RT \ln \frac{p_A}{p_A^*}$$

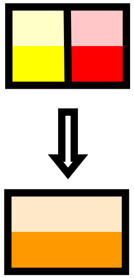
- Dampspanning

$$\frac{p_A}{p_A^*} = a_A$$

- Activiteitscoëfficiënt

$$\gamma_A = \frac{a_A}{x_A} \rightarrow 1 \text{ als } \boxed{x_A \rightarrow 1}$$

Eenvoudige oplossingen



Activiteit van opgeloste stof

- Voor verdunde oplossingen

$$\mu_B = \mu_B^{\ominus} + h_{AB} + RT\ln x_B$$

- Verandering “standaardtoestand”

$$\boxed{\mu_B^{\ominus} + h_{AB} \rightarrow \mu_B^{\varnothing}}$$

- Hogere concentraties

$$\mu_B = \mu_B^{\varnothing} + RT\ln a_B \quad \text{en} \quad \gamma_B = \frac{a_B}{x_B} \rightarrow 1 \;\; \text{als} \;\; \boxed{x_B \rightarrow 0}$$

Relatie viriaalcoëfficiënten in osmotische druk

Reguliere oplossingen

Max Margules (1856 – 1920)

- Mengenthalpie

$$\Delta_{\text{mix}} H = \tfrac{1}{2} n x_A x_B h_{AB}$$

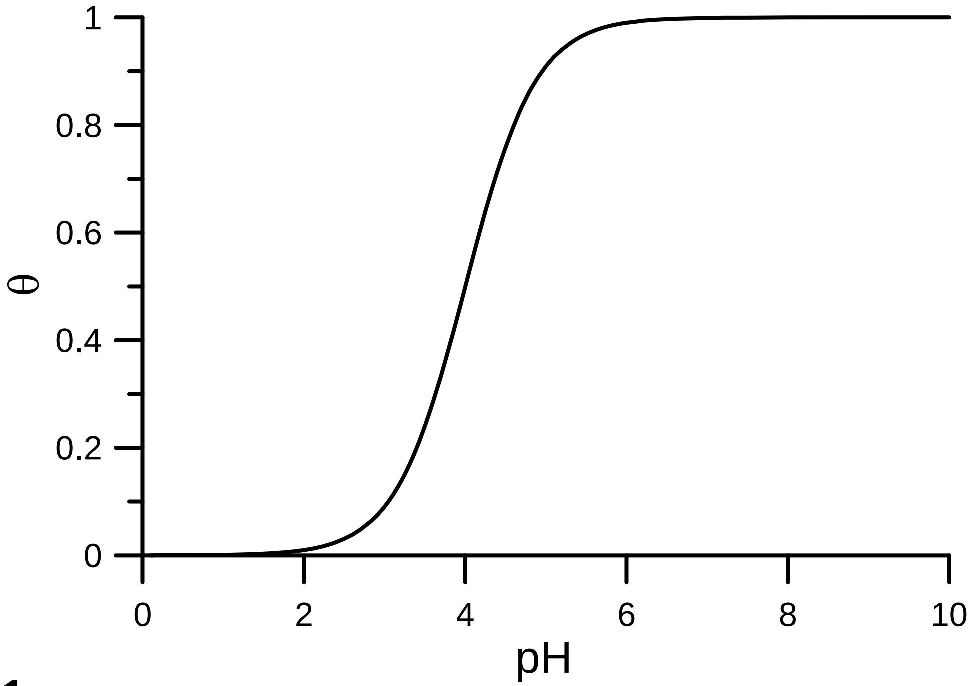
- Geeft aanleiding tot activiteitscoëfficiënten

$$\ln \gamma_j = \frac{h_{AB}}{RT}\left(1 - x_j\right)^2$$

- Modificatie Wet van Raoult

$$p_j = x_j p_j \exp\left[\frac{h_{AB}}{RT}\left(1 - x_j\right)^2\right]$$

Elektrolyten



Dissociatie (zuur, zout)

- $AH \leftrightarrow A^- + H^+$
- Dissociatiegraad

$$\vartheta = \frac{\left[A^-\right]}{\left[AH\right]+\left[A^-\right]} = \frac{1}{1+10^{-pH+pK}}$$

- Sterkte
  - Waarde pK

Elektrolyten

Elektroneutraliteit

- Oplossing MX $\rightarrow$ M^+ + X^-

- Gibbs energie

$$G = \mu^{\ominus}_{M^+} + RT\ln x_{M^+} + \mu^{\ominus}_{X^-} + RT\ln x_{X^-} + \boxed{RT\ln \gamma_{M^+}\gamma_{X^-}}$$

- Gemiddelde activiteitscoëfficiënt $\gamma_{\pm} = \sqrt{\gamma_{M^+}\gamma_{X^-}}$

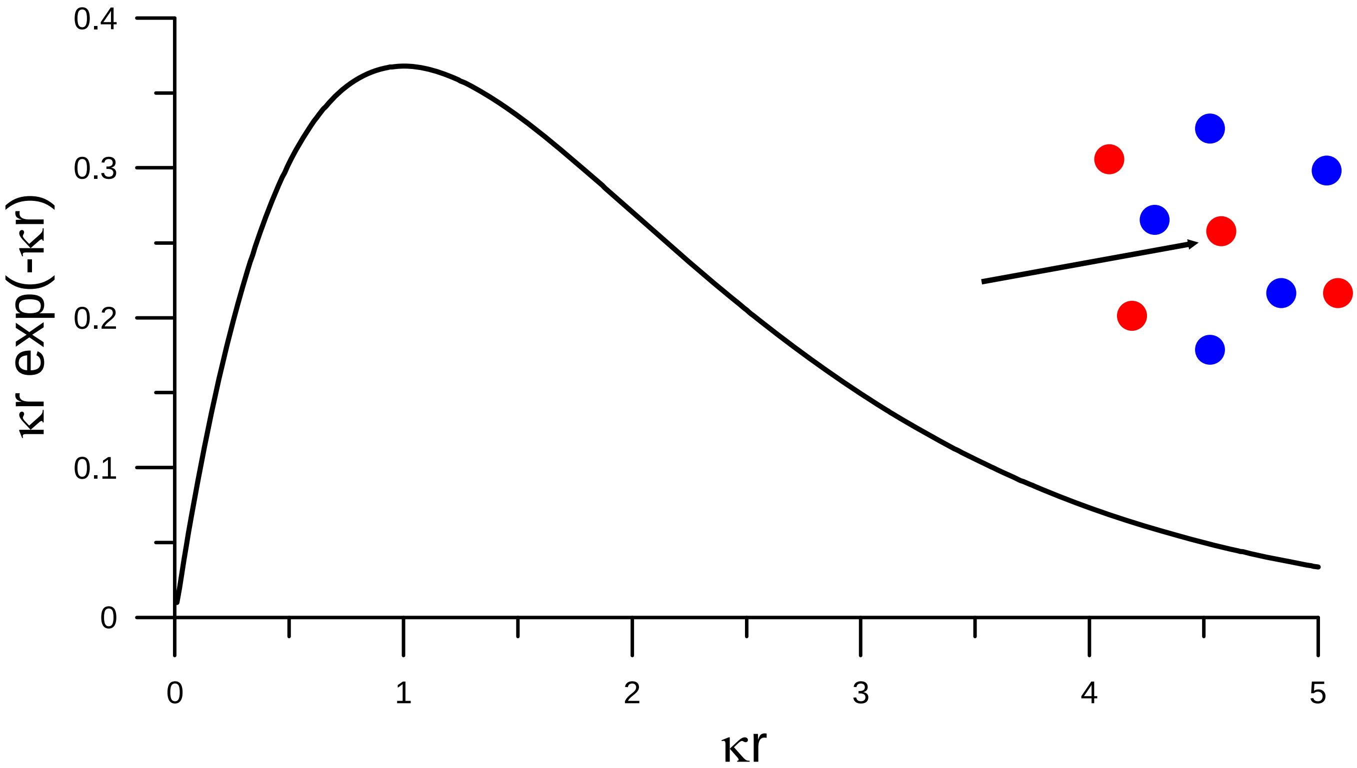
Elektrolyten

Debye – Hückel theorie

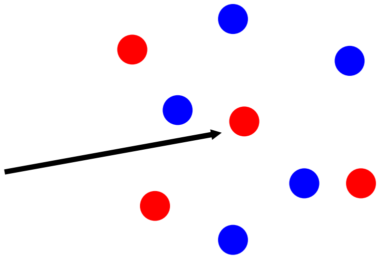
- Idee: ladingswolk om ionen

Peter Debye (1884 – 1966)

Erich Hückel (1896 – 1980)



Elektrolyten



- Ionsterkte

$$I = \frac{1}{2}\sum_j m_j z_j^2$$

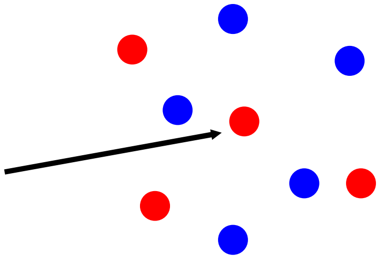
Molaliteit

- Debye afschermlengte

$$\kappa^{-1} \approx 3\sqrt{\frac{m^{\ominus}}{I}}\ \text{nm}$$

κ^{-1}/nm	[NaCl]/M
960	10^{-7}
30.4	10^{-4}
9.6	10^{-3}
0.3	1

Elektrolyten



- Gemiddelde activiteitscoëfficiënten

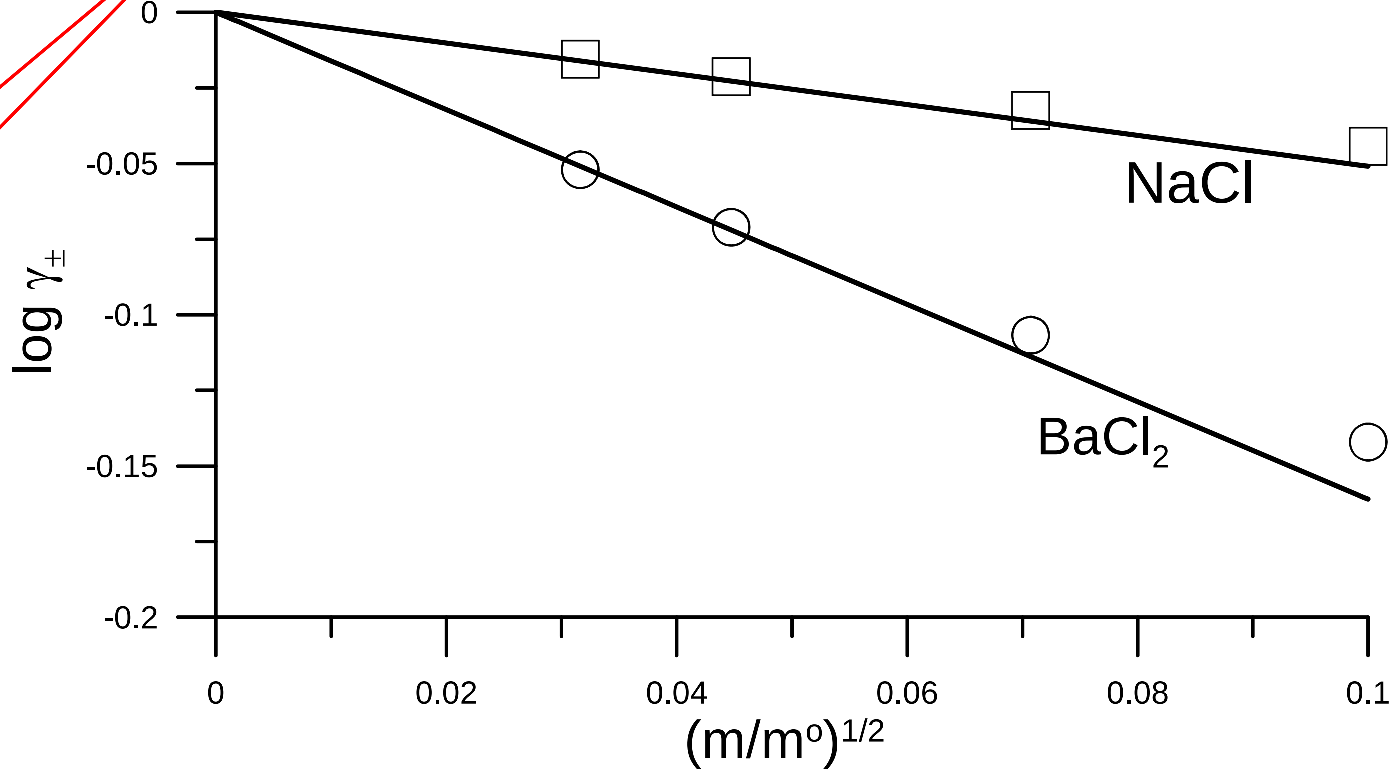
$$\log \gamma_{\pm} = -A\left|z_+ z_-\right|\sqrt{\frac{I}{m^o}}$$

0,509 bij 25 ^{o}C

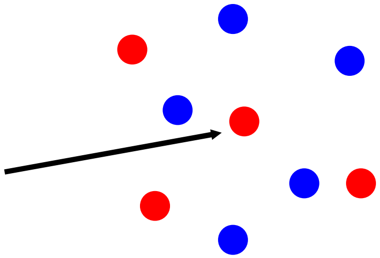
valenties

ionsterkte

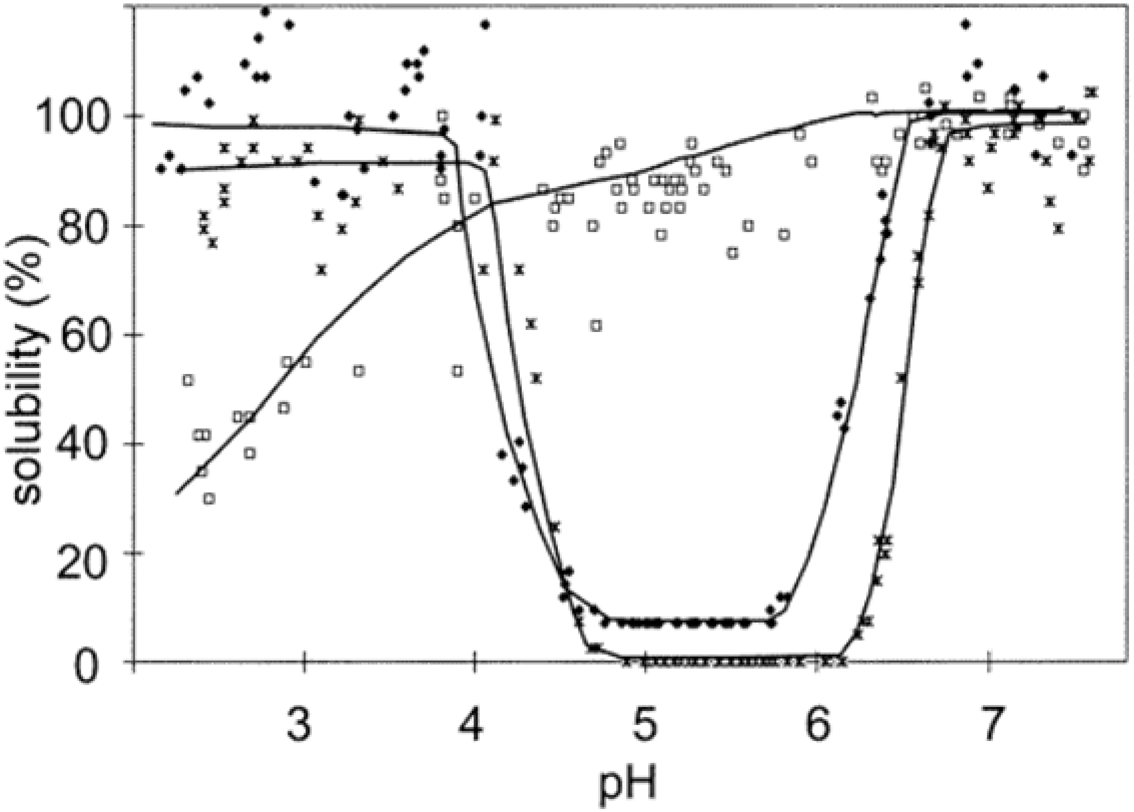
$$I = \frac{1}{2}\sum_j m_j z_j^2$$



Elektrolyten



- Effect op oplosbaarheid



pH-dependent solubility profiles of glycinin [*I* = 0.5 (□), 0.2 (◆), 0.03 (✷)] determined after incubation of 0.6 mg/mL samples for 16 h at 20 C.
(J. Agric. Food Chem., **48** (2000) 1985 -1990)