Závislost Gibbsovy funkce na složení

$$\mathrm{d}G = \left(\frac{\partial G}{\partial T}\right)_{p,n} \mathrm{d}T + \left(\frac{\partial G}{\partial p}\right)_{T,n} \mathrm{d}p + \left(\frac{\partial G}{\partial n}\right)_{T,p} \mathrm{d}n$$

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{T,p}$$

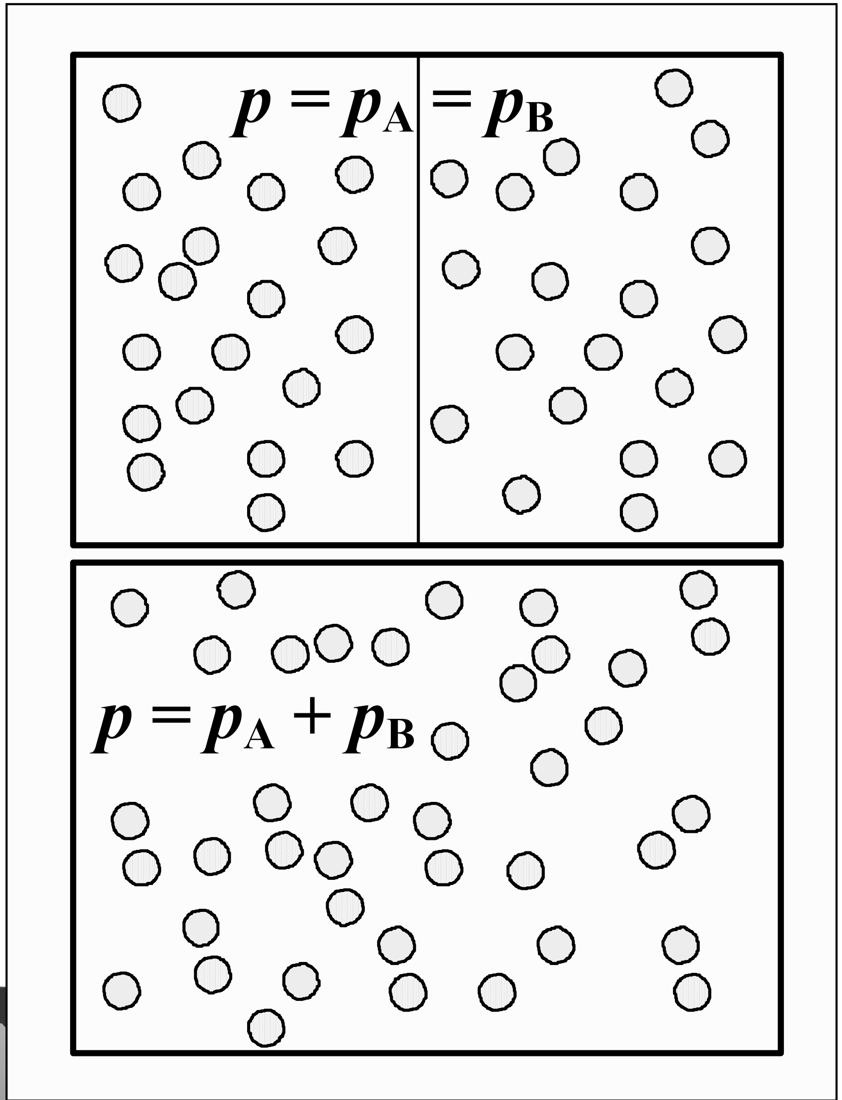
$$\mu_{\mathrm{A}} = \left(\frac{\partial G_{\mathrm{A}}}{\partial n_{\mathrm{A}}}\right)_{T,p} = \left(\frac{\partial\, n_{\mathrm{A}} \bar{G}_{\mathrm{A}}}{\partial n_{\mathrm{A}}}\right)_{T,p} = \bar{G}_{\mathrm{A}}$$

$$\mathbf{d}G_{\mathbf{A}} = V_{\mathbf{A}}\, \mathbf{d}p - S_{\mathbf{A}}\, \mathbf{d}T + \mu_{\mathbf{A}}\, \mathbf{d}n_{\mathbf{A}}$$

Závislost Gibbsovy funkce na složení

Plyny oddělené

Plyny smísené



Závislost Gibbsovy funkce na složení

$$G_2 = G_1 + nRT \ln\frac{p_2}{p_1} \qquad \overline{G}_\mathrm{A} = \overline{G}_\mathrm{A}^\circ + RT \ln\frac{p}{p^\circ}$$

$$G_\mathrm{A} = n_\mathrm{A}\overline{G}_\mathrm{A} = n_\mathrm{A}\left(\overline{G}_\mathrm{A}^\circ + RT \ln\frac{p}{p^\circ}\right) = n_\mathrm{A}\overline{G}_\mathrm{A}^\circ + n_\mathrm{A}RT \ln\frac{p}{p^\circ}$$

$$G_\mathrm{A} = n_\mathrm{A}\overline{G}_\mathrm{A}^\circ + n_\mathrm{A}RT \ln\frac{p}{p^\circ} \qquad G_\mathrm{B} = n_\mathrm{B}\overline{G}_\mathrm{B}^\circ + n_\mathrm{B}RT \ln\frac{p}{p^\circ}$$

$$G_\mathrm{A,\,sm} = n_\mathrm{A}\overline{G}_\mathrm{A}^\circ + n_\mathrm{A}RT \ln\frac{p_\mathrm{A}}{p^\circ} \qquad G_\mathrm{B,\,sm} = n_\mathrm{B}\overline{G}_\mathrm{B}^\circ + n_\mathrm{B}RT \ln\frac{p_\mathrm{B}}{p^\circ}$$

Chemický potenciál

$$\Delta G_{\mathrm{A,\,mís}} = G_{\mathrm{A,\,sm}} - G_{\mathrm{A}} = n_{\mathrm{A}}\bar{G}_{\mathrm{A}}^{\circ} + n_{\mathrm{A}}RT\ln\frac{p_{\mathrm{A}}}{p^{\circ}} - n_{\mathrm{A}}\bar{G}_{\mathrm{A}}^{\circ} - n_{\mathrm{A}}RT\ln\frac{p}{p^{\circ}}$$

$$\Delta G_{\mathrm{A,\,mís}} = n_{\mathrm{A}}RT\ln\frac{p_{\mathrm{A}}}{p^{\circ}} - n_{\mathrm{A}}RT\ln\frac{p}{p^{\circ}} = n_{\mathrm{A}}RT\ln\frac{p_{\mathrm{A}}}{p^{\circ}}\frac{p^{\circ}}{p} = n_{\mathrm{A}}RT\ln\frac{p_{\mathrm{A}}}{p}$$

$$\Delta\bar{G}_{\mathrm{A,\,mís}} = RT\ln\frac{p_{\mathrm{A}}}{p} \qquad \bar{G}_{\mathrm{A}} = \bar{G}_{\mathrm{A}}^{\circ} + \Delta\bar{G}_{\mathrm{A,\,mís}} = \bar{G}_{\mathrm{A}}^{\circ} + RT\ln\frac{p_{\mathrm{A}}}{p}$$

John Dalton $p_{\mathrm{A}} = X_{\mathrm{A}}\, p$

$$X_{\mathrm{A}} = \frac{p_{\mathrm{A}}}{p} \qquad X_{\mathrm{A}} = \frac{n_{\mathrm{A}}}{n} \qquad \bar{G}_{\mathrm{A}} = \bar{G}_{\mathrm{A}}^{\circ} + RT\ln X_{\mathrm{A}}$$

$$\mu_{\mathrm{A}} = \left(\frac{\partial G_{\mathrm{A}}}{\partial n_{\mathrm{A}}}\right)_{T,p} = \left(\frac{\partial\, n_{\mathrm{A}}\bar{G}_{\mathrm{A}}}{\partial n_{\mathrm{A}}}\right)_{T,p} = \bar{G}_{\mathrm{A}}$$

$\bar{G} = \bar{G}^\circ + RT \ln \frac{p}{p^\circ}$

Závislost chemického potenciálu na složení

$\mu_A = \mu_A^\circ + RT \ln X_A$

$G_{\check{c}ist\acute{e}} = n_A \mu_A^\circ + n_B \mu_B^\circ$

$G_{sm\check{e}s} = n_A \mu_A + n_B \mu_B = n_A (\mu_A^\circ + RT \ln X_A) + n_B (\mu_B^\circ + RT \ln X_B)$

$\Delta G_{m\acute{i}s} = G_{sm\check{e}s} - G_{\check{c}ist\acute{e}} = n_A RT \ln X_A + n_B RT \ln X_B = n RT (X_A \ln X_A + X_B \ln X_B)$

$$\bar{G} = \bar{G}^\circ + RT \ln \frac{p}{p^\circ} \qquad \mu = \mu^\circ + RT \ln \frac{p}{p^\circ}$$

$$\mu = \mu^\circ + RT \ln \frac{p}{p^\circ} + RT \ln \frac{p_A}{p} = \mu^\circ + RT \ln \frac{p}{p^\circ} + RT \ln X_A$$

Kapalné roztoky

$$\mu_A^*(l) = \mu_A(g) = \mu_A^\circ(g) + RT \ln \frac{p_A^*}{p^\circ}$$

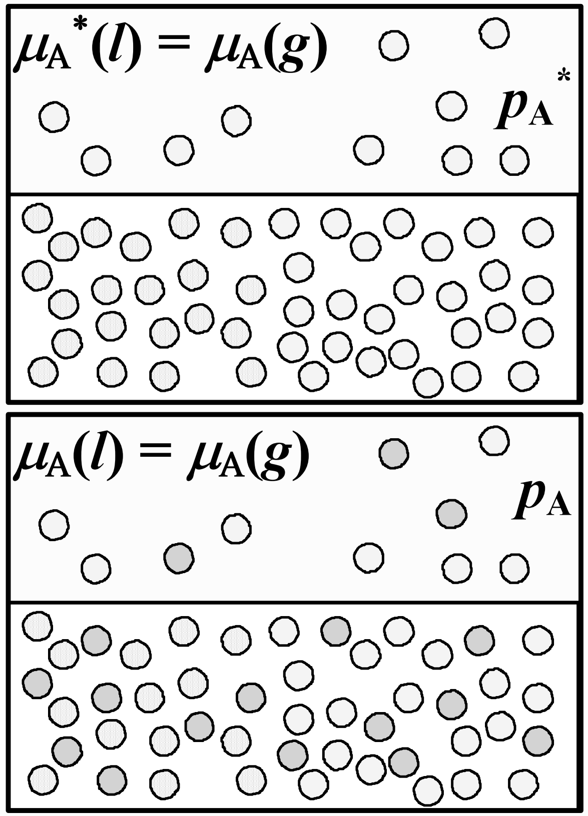
$$\mu_A(l) = \mu_A(g) = \mu^\circ_A(g) + RT \ln \frac{p_A}{p^\circ}$$

$$\mu_A^\circ(g) = \mu_A^*(l) - RT \ln \frac{p_A^*}{p^\circ}$$

$$\mu_A(l) = \mu_A^*(l) - RT \ln \frac{p_A^*}{p^\circ} + RT \ln \frac{p_A}{p^\circ}$$

$$\mu_A(l) = \mu_A^*(l) + RT \ln \frac{p_A}{p^\circ} \frac{p^\circ}{p_A^*}$$

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



François Marie Raoult

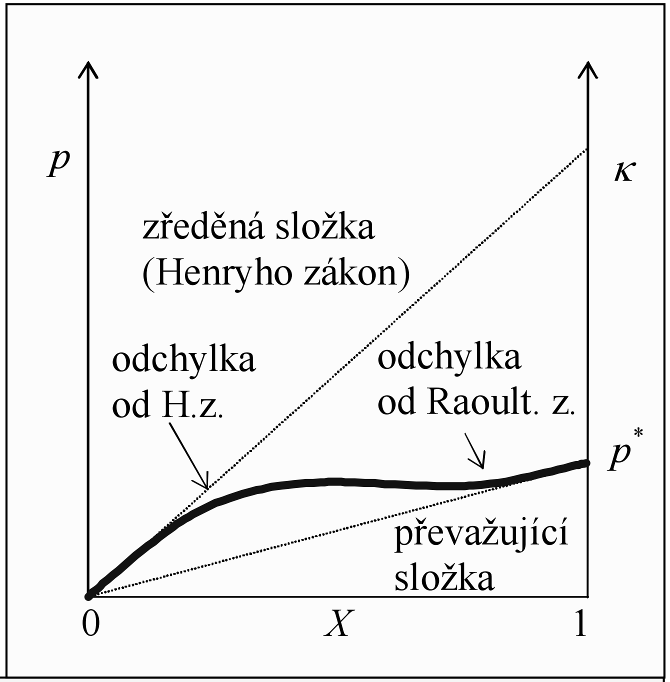
$$p_A = X_A \, p_A^*$$

$$\mu_A(l) = \mu_A^*(l) + RT \ln X_A$$

Zředěné kapalné roztoky

William Henry

$$\boldsymbol{p_B = \kappa_B X_B}$$



$$\mu_B(l) = \mu_B{}^*(l) + RT \ln \frac{p_B}{p_B{}^*} = \mu_B{}^*(l) + RT \ln \frac{\varkappa_B X_B}{p_B{}^*}$$

$$\mu_B(l) = \mu_B{}^*(l) + RT \ln \frac{\varkappa_B}{p_B{}^*} + RT \ln X_B$$

$$\mu_B{}^+ = \mu_B{}^* + RT \ln \frac{\varkappa_B}{p_B{}^*} \qquad \mu_B(l) = \mu_B{}^+(l) + RT \ln X_B$$

Zředěné kapalné roztoky

$$X_B = \frac{n_B}{n_A + n_B}$$

$$X_B \approx \frac{n_B}{n_A}$$

$$X_B \approx k\frac{m_B}{m^{\circ}}$$

$$\mu_B = \mu_B^{+} + RT\ \ln X_B = \mu_B^{+} + RT\ \ln k\frac{m_B}{m^{\circ}} = \mu_B^{\prime} + RT\ \ln\frac{m_B}{m^{\circ}}$$

$\Delta X = \int_{X_1}^{X_2} f(X)\, \mathrm{d}X$

Pevné roztoky

$\mu_A(s) = \mu_A{}^*(s) + RT \ln X_A$

$G_A \mathrm{id} = n_A\, (\mu_A{}^\circ + RT \ln X_A)$

$\mu_B(s) = \mu_B{}^\circ(s) + RT \ln X_B$

$G_B{}^{\mathrm{id}} = n_B\, (\mu_B{}^\circ + RT \ln X_B)$

$G^{\mathrm{id}} = G_A{}^{\mathrm{id}} + G_B{}^{\mathrm{id}} = n_A\, (\mu_A{}^\circ + RT \ln X_A) + n_B\, (\mu_B{}^\circ + RT \ln X_B)$

Reálné roztoky

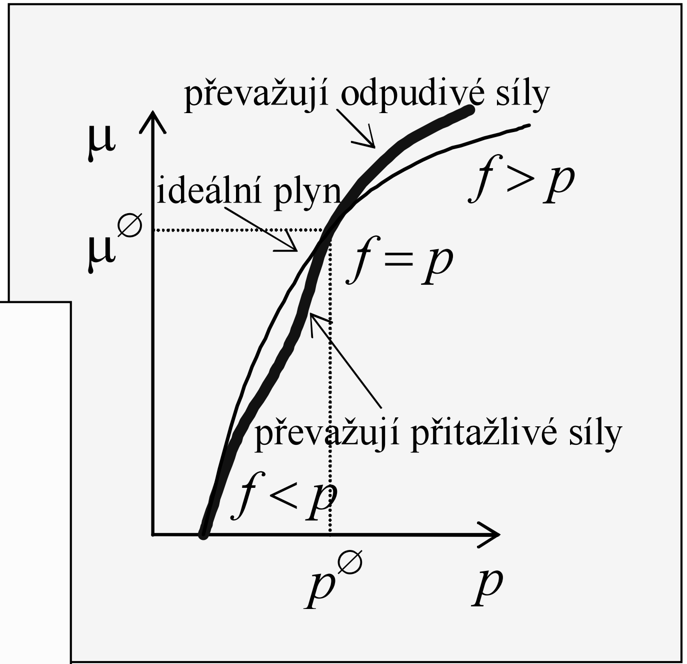
Ideální roztoky

A ↔ A ≡ B ↔ B ≡ … ≡ A ↔ B

Reálné plyny

fugacita

$f = \gamma p$ $\qquad f \rightarrow p$ a $\gamma \rightarrow 1$ při $p \rightarrow 0$



Čistý

$$\mu_A = \mu_A{}^\circ + RT \ln \frac{f}{p^\circ} = \mu_A{}^\circ + RT \ln \frac{\gamma\, p}{p^\circ}$$

$$\mu_A = \mu_A{}^\circ + RT \ln \frac{p}{p^\circ} + RT \ln \gamma$$

Směs

$$\mu_A = \mu_A{}^\circ + RT \ln \frac{f_A}{p^\circ} = \mu_A{}^\circ + RT \ln \frac{\gamma_A\, p_A}{p^\circ}$$

$$\mu_A = \mu_A{}^\circ + RT \ln \frac{p_A}{p^\circ} + RT \ln \gamma_A$$

$$\mu_A = \mu_A{}^\circ + RT \ln X_A + RT \ln \gamma_A$$

Reálné kapalné roztoky

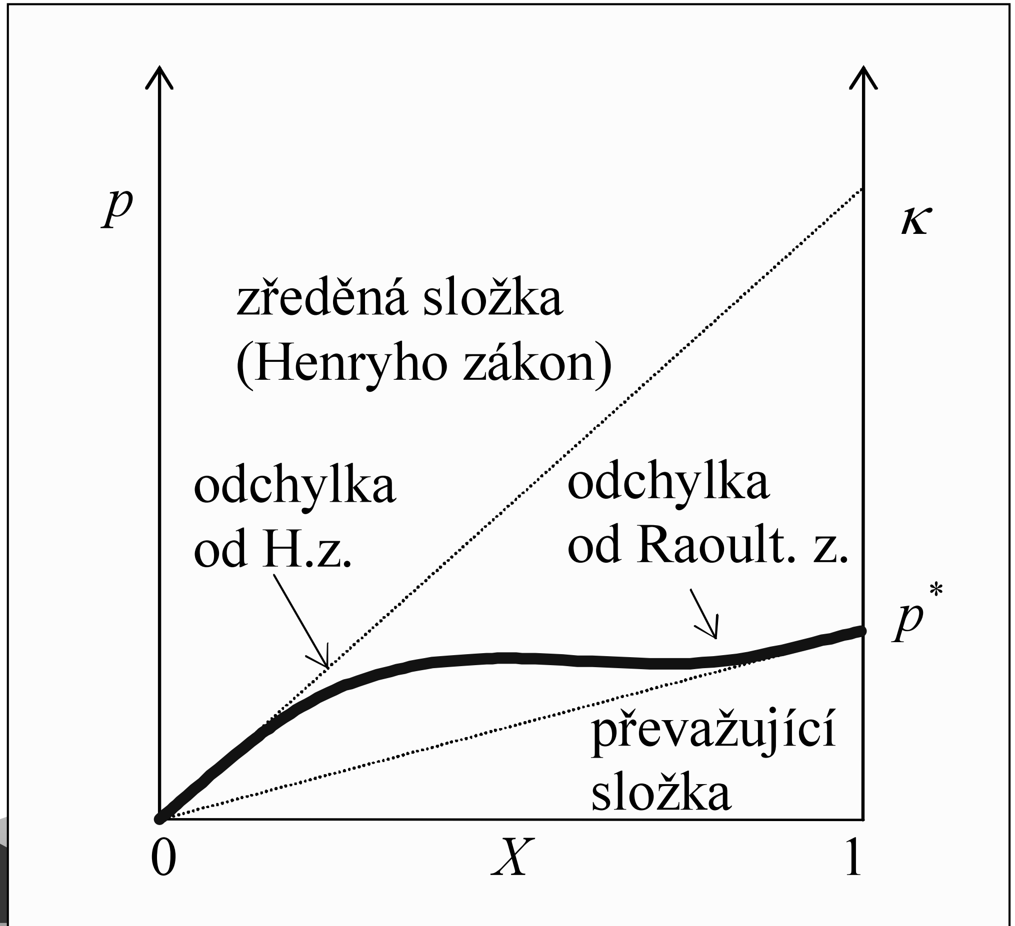
$$a_{\mathrm{A}} = \gamma_{\mathrm{A}} X_{\mathrm{A}}$$

$$\mu_{\mathrm{A}} = \mu_{\mathrm{A}}^* + RT \ln \gamma_{\mathrm{A}} X_{\mathrm{A}} = \mu_{\mathrm{A}}^* + RT \ln X_{\mathrm{A}} + RT \ln \gamma_{\mathrm{A}}$$

$a_{\mathrm{A}} \to X_{\mathrm{A}}$

$\gamma_{\mathrm{A}} \to 1$

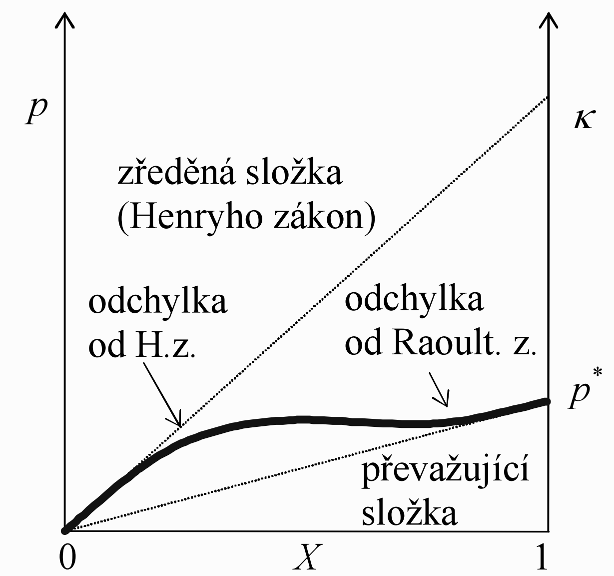
při $X_{\mathrm{A}} \to 1$



Reálné zředěné kapalné roztoky

$$\mu_B = \mu_B^\circ + RT \ln a_B$$

$a_B \rightarrow m_B$ a $\gamma_B \rightarrow 1$ při $m_B \rightarrow 0$



$$a_B = \gamma_B \frac{m_B}{m^\circ}$$

$$\mu_B = \mu_B^\circ + RT \ln a_B = \mu_B^\circ + RT \ln \gamma_B \frac{m_B}{m^\circ}$$

$$\mu_B = \mu_B^\circ + RT \ln \frac{m_B}{m^\circ} + RT \ln \gamma_B$$

Reálné pevné roztoky

$$G^{re} = G_A^{re} + G_B^{re} = n_A\,(\mu_A^{\circ} + RT \ln a_A) + n_B\,(\mu_B^{\circ} + RT \ln a_B)$$

$$G^{re} = n_A\,(\mu_A^{\circ} + RT \ln \gamma_A X_A) + n_B\,(\mu_B^{\circ} + RT \ln \gamma_B X_B)$$

$$\Delta G^{re\text{-}id} = n_A\,RT \ln \gamma_A + n_B\,RT \ln \gamma_B$$

$$\Delta G^{re\text{-}id} = RT\,(n_A \ln \gamma_A + n_B \ln \gamma_B)$$

$$\Delta \bar{G}^{re\text{-}id} = RT\,(X_A \ln \gamma_A + X_B \ln \gamma_B)$$

$$\Delta \bar{G}^{E} = \Delta \bar{G}^{re\text{-}id}$$

Vyjádření fugacitních a aktivitních koeficientů

Plyny

$pV = nRT$

$pV_m = RT$

Ideální

$$1 = \frac{pV_m}{RT}$$

Reálný – kompresní faktor

$$Z = \frac{pV}{RT}$$

Polynomy

$$Z = 1 + \frac{b}{V_m} + \frac{c}{V_m^2} + \ldots$$

$$Z = 1 + b\,p + c\,p^2 + \ldots$$

$$\ln\gamma = \int_0^p \left(\frac{Z-1}{p}\right) \mathrm{d}p$$

Kapalné roztoky

$\mu_i = \mu_{i\text{-}id} + RT \ln \gamma_\pm$

Debye-Hückel (roz.): do I = 0,1

$$\log \gamma_\pm = -\frac{A|z_+ z_-|(I/m^\circ)^{1/2}}{1 + B(I/m^\circ)^{1/2}}$$

Debye-Hückel

$\log \gamma_\pm = -|z^+ z^-| A (I/m^\circ)^{1/2}$

$I = \frac{1}{2} \sum z_i^2 m_i$

Güntelberg: do I = 0,1

$$\log \gamma_\pm = -\frac{A|z_+ z_-|(I/m^\circ)^{1/2}}{1 + (I/m^\circ)^{1/2}}$$

do I = 0,002

Davies: I = 0,5

$$\log \gamma_\pm = -A|z_+ z_-| \left(\frac{(I/m^\circ)^{1/2}}{1 + (I/m^\circ)^{1/2}} - 0{,}2(I/m^\circ)^{1/2} \right)$$

Reálné pevné roztoky

$$\Delta \bar{G}^{E} = a + b X_B + c X_B^2 + d X_B^3$$

Symetrické

$$a = d = 0,\ b = -c = W$$

$$\Delta \bar{G}^{E} = W X_B - W X_B^2 = W X_B (1 - X_B) = W X_A X_B$$

$$\Delta \bar{G}^{E} = W X_A X_B \times 1 = W X_A X_B \times (X_A + X_B) = X_A W X_B^2 + X_B W X_A^2$$

$$\Delta \bar{G}^{E} = X_A RT \ln \gamma_A + X_B RT \ln \gamma_B$$

$$RT \ln \gamma_A = W X_B^2$$

$$RT \ln \gamma_B = W X_A^2$$

Reálné pevné roztoky

Nesymetrické

$$a = 0,\ b = W_B,\ c = W_A - 2\,W_B,\ d = W_A - W_B$$

$$\Delta\ \bar{G}^E = W_B\,X_B + (W_A - 2\,W_B)\,X_B^2 + (W_B - W_A)\,X_B^3$$

$$\Delta\ \bar{G}^E = X_A\,X_B\,(W_A\,X_B + W_B\,X_A)$$

$$\Delta\ \bar{G}^E = X_A\,RT \ln \gamma_A + X_B\,RT \ln \gamma_B$$

$$RT \ln \gamma_A = (2W_B - W_A)\,X_B^2 + 2(W_A - W_B)\,X_B^3$$

$$RT \ln \gamma_B = (2W_A - W_B)\,X_A^2 + 2(W_B - W_A)\,X_A^3$$

Souhrn

Entropie

$$dS = \frac{dq}{T}$$

- **pokud systém nevyměňuje s okolím teplo a práci, zůstává jeho energie konstantní (zachování energie)**
- **při všech samovolných procesech celková entropie systému roste**

$$dS_{celk} = dS_{sys} + dS_{ok} > 0$$

$$dS_{ok} = \frac{dq}{T}$$

$$dS_{celk} = dS_{sys} + dS_{ok} = dS_{sys} + \frac{dq_{ok}}{T}$$

$$dS_{celk} = dS_{sys} - \frac{dH_{sys}}{T} > 0$$

$$G = H - TS$$

$$dG = dH - T\,dS \quad (p, T = \text{konst.})$$

Energie

$dU = dq + dw$

$dw = p\,dV$

$dU = dq - p\,dV$

$dH = dq_p$

Souhrn

$$\frac{\mathrm{d}G}{T} = \frac{\mathrm{d}H}{T} - \mathrm{d}S$$

$$-\frac{\mathrm{d}G}{T} = \mathrm{d}S - \frac{\mathrm{d}H}{T}$$

$$\mathrm{d}S_{\mathrm{celk}} = -\frac{\mathrm{d}G}{T}$$

$$\frac{\mathrm{d}S_{\mathrm{celk}}}{\mathrm{d}T} = -\left(\frac{1}{\mathrm{d}T}\frac{G}{T}\right) = \frac{H}{T^2}$$

$\mathbf{d}\boldsymbol{G} < \mathbf{0}$

$\mathbf{d}\boldsymbol{G} = \boldsymbol{V}\,\mathbf{d}\boldsymbol{p} - \boldsymbol{S}\,\mathbf{d}\boldsymbol{T} + \boldsymbol{\mu}\,\mathbf{d}\boldsymbol{n}$

$\boldsymbol{\mu}_{\mathbf{A}} = \boldsymbol{\mu}_{\mathbf{A}}° + \boldsymbol{RT}\,\mathbf{ln}\,\boldsymbol{X}_{\mathbf{A}}$

Reálné

$\boldsymbol{\mu}_{\mathbf{A}} = \boldsymbol{\mu}_{\mathbf{A}}° + \boldsymbol{RT}\,\mathbf{ln}\,\boldsymbol{a}_{\mathbf{A}}$

$\boldsymbol{f}_{\mathbf{A}} = \boldsymbol{\gamma}_{\mathbf{A}}\,\boldsymbol{p}_{\mathbf{A}}$

$\boldsymbol{a}_{\mathbf{A}} = \boldsymbol{\gamma}_{\mathbf{A}}\,\boldsymbol{X}_{\mathbf{A}}$