Celková změna entropie

Proces

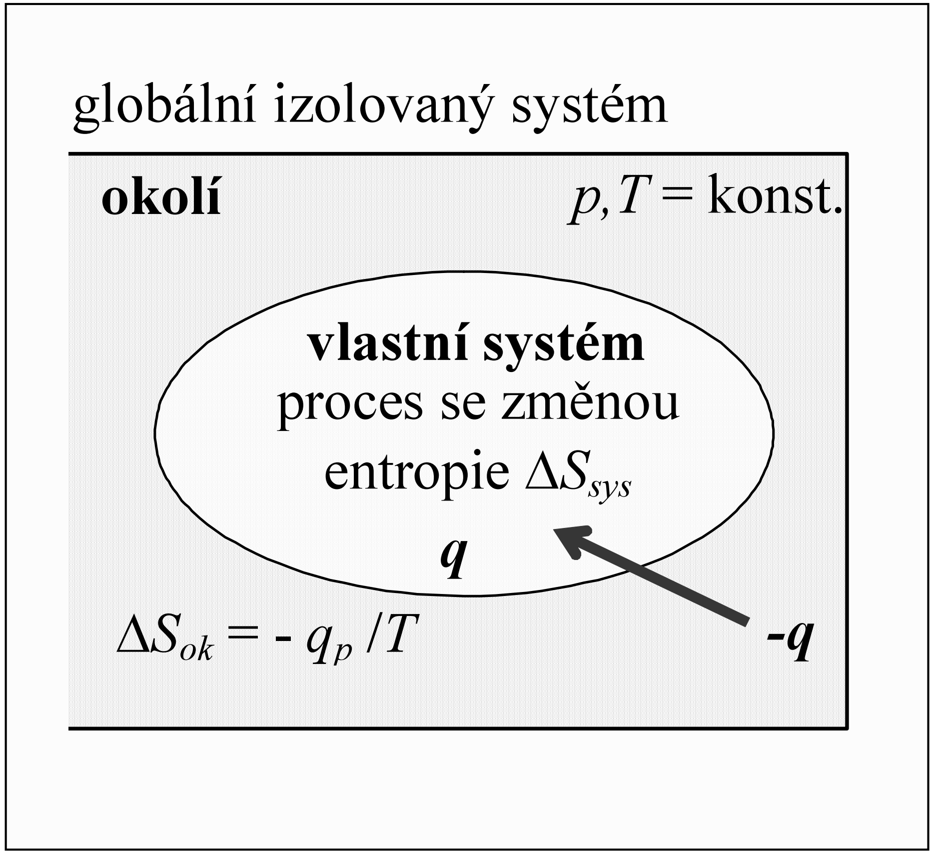
$dS_{celk} > 0$

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

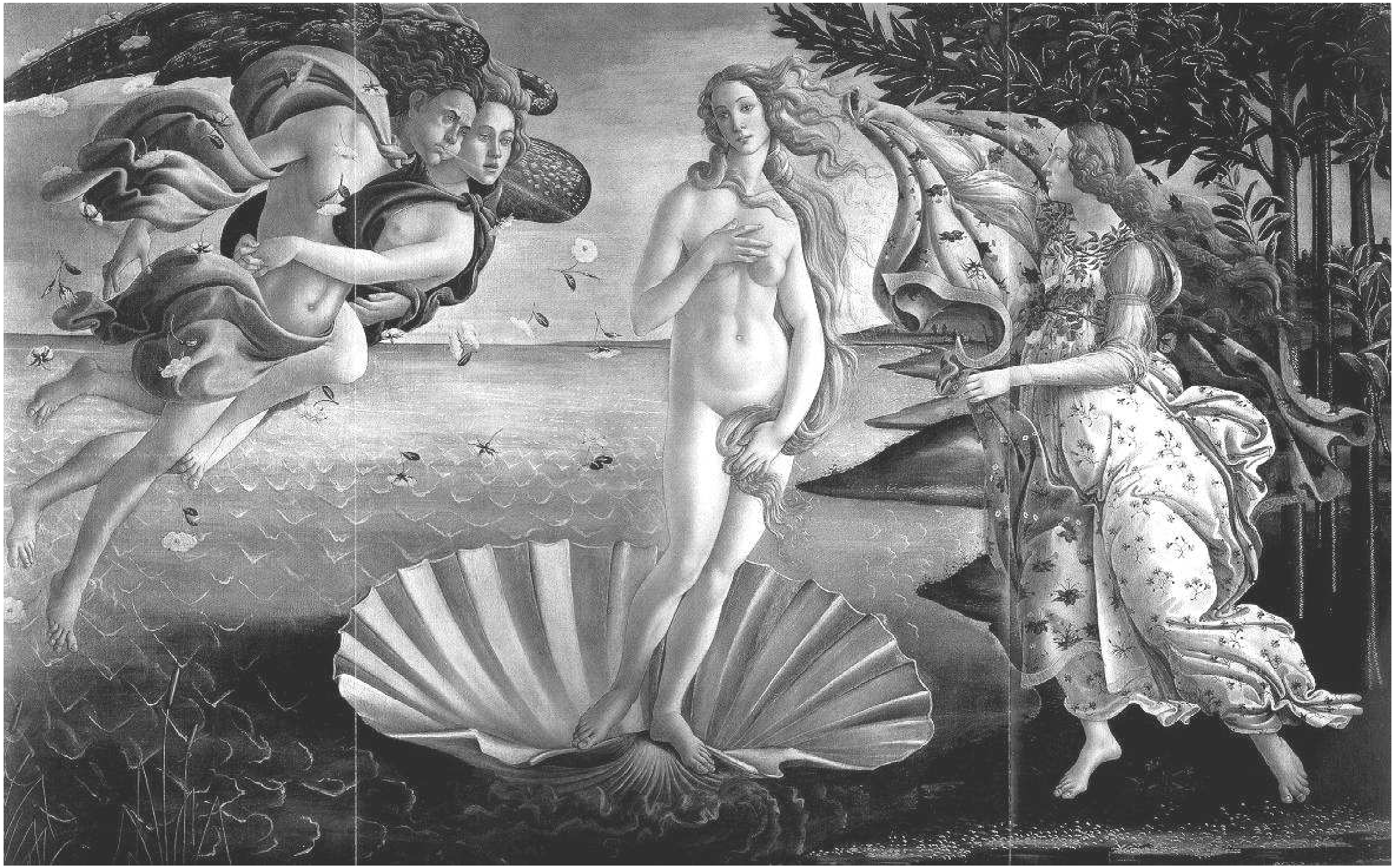
$dS_{sys} + dS_{ok} > 0$

Rovnováha

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



Vznik uspořádaných stavů



Dokonale uspořádaný a nádherný hmotný objekt (uprostřed) může v přírodě vznikat z nepořádku a chaosu (vlevo a vpravo). To rozpoznal už Sandro Botticelli ve svém obraze *Zrození Venuše*.

Sandro Botticelli (Alessandro di Moriano Filipepi, 1444/5-1510), *Zrození Venuše* (kolem roku 1485), tempera na plátně, rozměry 172,5x278,5 cm, uloženo v Galleria degli Uffizi, Florencie, Itálie.

Gibbsova funkce

$$\mathrm{d}q_{\mathrm{p,sys}} = \mathrm{d}H_{\mathrm{sys}}$$

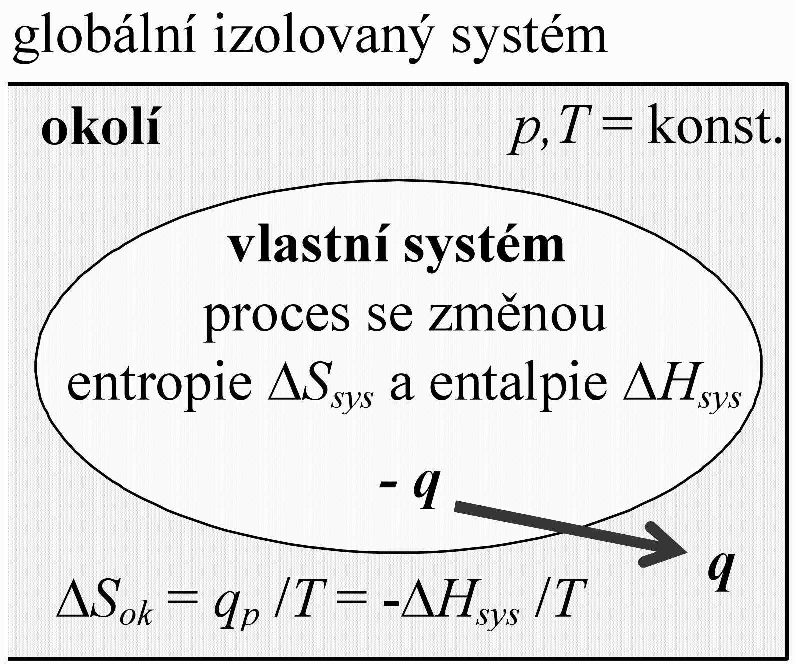
$$\mathrm{d}q_{\mathrm{p,ok}} = -\,\mathrm{d}q_{\mathrm{p,sys}} = -\,\mathrm{d}H_{\mathrm{sys}}$$

$$\mathrm{d}S_{\mathrm{celk}} = \mathrm{d}S_{\mathrm{sys}} + \mathrm{d}S_{\mathrm{ok}}$$

$$\mathrm{d}S_{\mathrm{ok}} = \frac{\mathrm{d}q_{\mathrm{ok}}}{T_{\mathrm{ok}}}$$

$$\mathrm{d}S_{\mathrm{celk}} = \mathrm{d}S_{\mathrm{sys}} + \frac{\mathrm{d}q_{\mathrm{ok}}}{T_{\mathrm{ok}}}$$

$$\mathrm{d}S_{\mathrm{celk}} = \mathrm{d}S_{\mathrm{sys}} - \frac{\mathrm{d}H_{\mathrm{sys}}}{T_{\mathrm{ok}}}$$



Gibbsova funkce

$T\,dS_{celk} = T\,dS - dH > 0$

$-T\,dS_{celk} = dH - T\,dS$

$dG = dH - T\,dS$

$dG < 0$

Termodynamická rovnováha

$dG = 0$

Gibbsova funkce

$G = H - TS$

$dG = dH - T\,dS - S\,dT$ (p = konst.)

$dG = dH - T\,dS$ (T = konst.)

$\boldsymbol{-T\,dS_{celk} = dG}$

$\boldsymbol{dS_{celk} = -\,dG/T}$

Aby

$\boldsymbol{dS_{celk} > 0}$

musí být

$\boldsymbol{dG < 0}$

J. W. Gibbs

„One of the principal objects of theoretical research in any department of knowledge is to find the point of view from which the subject appears in its greatest simplicity.“

Jedním z hlavních předmětů teoretického výzkumu v každém oboru vědění je nalezení pohledu, ze kterého se předmět jeví jako nejednodušší.

Gibbsova funkce

$$\boldsymbol{G = H - TS}$$

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

$$\mathrm{d}H = \mathrm{d}U + p\,\mathrm{d}V + V\,\mathrm{d}p$$

$$\mathrm{d}U = \mathrm{d}q + \mathrm{d}w$$

$$\mathrm{d}w = -\,p\,\mathrm{d}V$$

$$\mathrm{d}q = T\,\mathrm{d}S$$

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V$$

Gibbsova funkce

$\mathrm{d}H = \mathrm{d}U + p\,\mathrm{d}V + V\,\mathrm{d}p = T\,\mathrm{d}S - p\,\mathrm{d}V + p\,\mathrm{d}V + V\,\mathrm{d}p = T\,\mathrm{d}S + V\,\mathrm{d}p$

$\mathrm{d}G = \mathrm{d}H - T\,\mathrm{d}S - S\,\mathrm{d}T = T\,\mathrm{d}S + V\,\mathrm{d}p - T\,\mathrm{d}S - S\,\mathrm{d}T = V\,\mathrm{d}p - S\,\mathrm{d}T$

$\mathrm{d}G = V\,\mathrm{d}p - S\,\mathrm{d}T$

$$\mathrm{d}G = \left(\frac{\partial G}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial G}{\partial p}\right)_T \mathrm{d}p$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

Závislost Gibbsovy funkce na teplotě

$$dG = -S\,dT$$

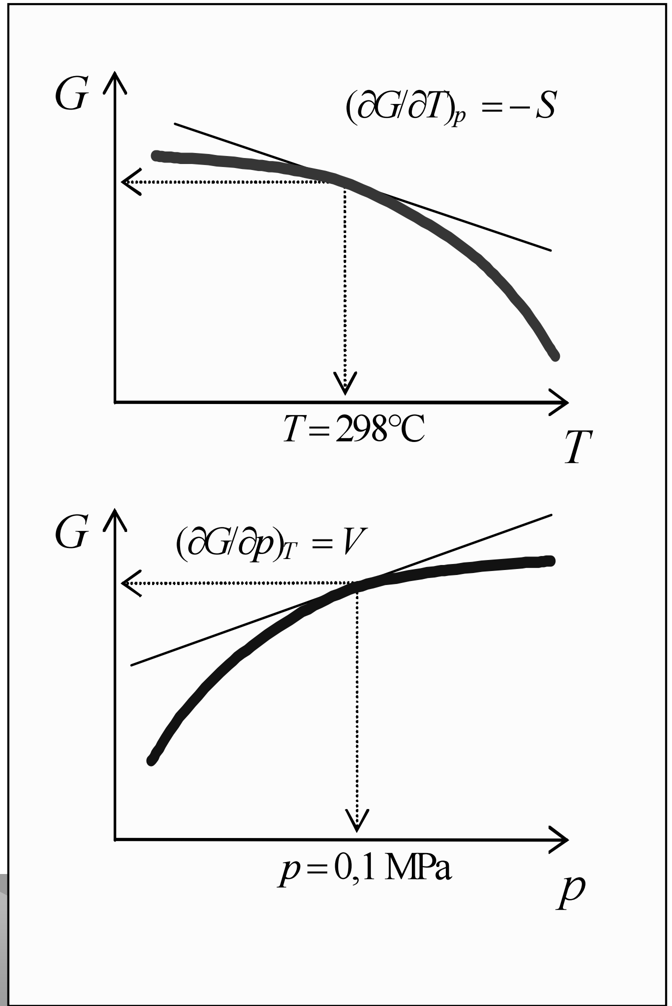
$$G_2 = G_1 - S\,(T_2 - T_1)$$

$$\Delta G_{2,\,\beta-\alpha} = \Delta G_{1,\,\beta-\alpha} - \Delta S_{\beta-\alpha}\,(T_2 - T_1)$$

$$\int_{G_1}^{G_2} dG = \int_{T_1}^{T_2} -S\,dT$$

$$G_2 - G_1 = \Delta G = \int_{T_1}^{T_2} -S\,dT$$

$$G_2 = G_1 + \Delta G = G_1 + \int_{T_1}^{T_2} -S\,dT$$



Gibbsova-Helmholtzova funkce

$$S = \frac{H - G}{T} \qquad \left(\frac{\partial G}{\partial T}\right)_p = -S$$

$$T\left(\frac{\partial}{\partial T}\frac{G}{T}\right)_p = -\frac{H}{T}$$

$$\left(\frac{\partial G}{\partial T}\right)_p = \frac{G - H}{T} \qquad \left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T} = -\frac{H}{T}$$

$$\left(\frac{\partial}{\partial T}\frac{G}{T}\right)_p = -\frac{H}{T^2}$$

$$\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T} = T\left(\frac{\partial}{\partial T}\frac{G}{T}\right)_p$$

$$\left(\frac{\partial \Delta S_{\mathrm{celk}}}{\partial T}\right)_p = \frac{\Delta H}{T^2}$$

$$T\left(\frac{\partial}{\partial T}\frac{G}{T}\right)_p = T\left(\frac{\left(\frac{\partial G}{\partial T}\right)_p T - G}{T^2}\right)_p = \left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T}$$

Závislost Gibbsovy funkce na tlaku

dG = V dp (konst. T)

$pV = nRT$

$G_2 = G_1 + \Delta G = G_1 + V\,(p_2 - p_1)$

$$\int_{G_1}^{G_2} \mathrm{d}G = \int_{p_1}^{p_2} V \,\mathrm{d}p$$

$$G_2 - G_1 = \Delta G = \int_{p_1}^{p_2} V \,\mathrm{d}p$$

$$G_2 = G_1 + \Delta G = G_1 + \int_{p_1}^{p_2} V \,\mathrm{d}p$$

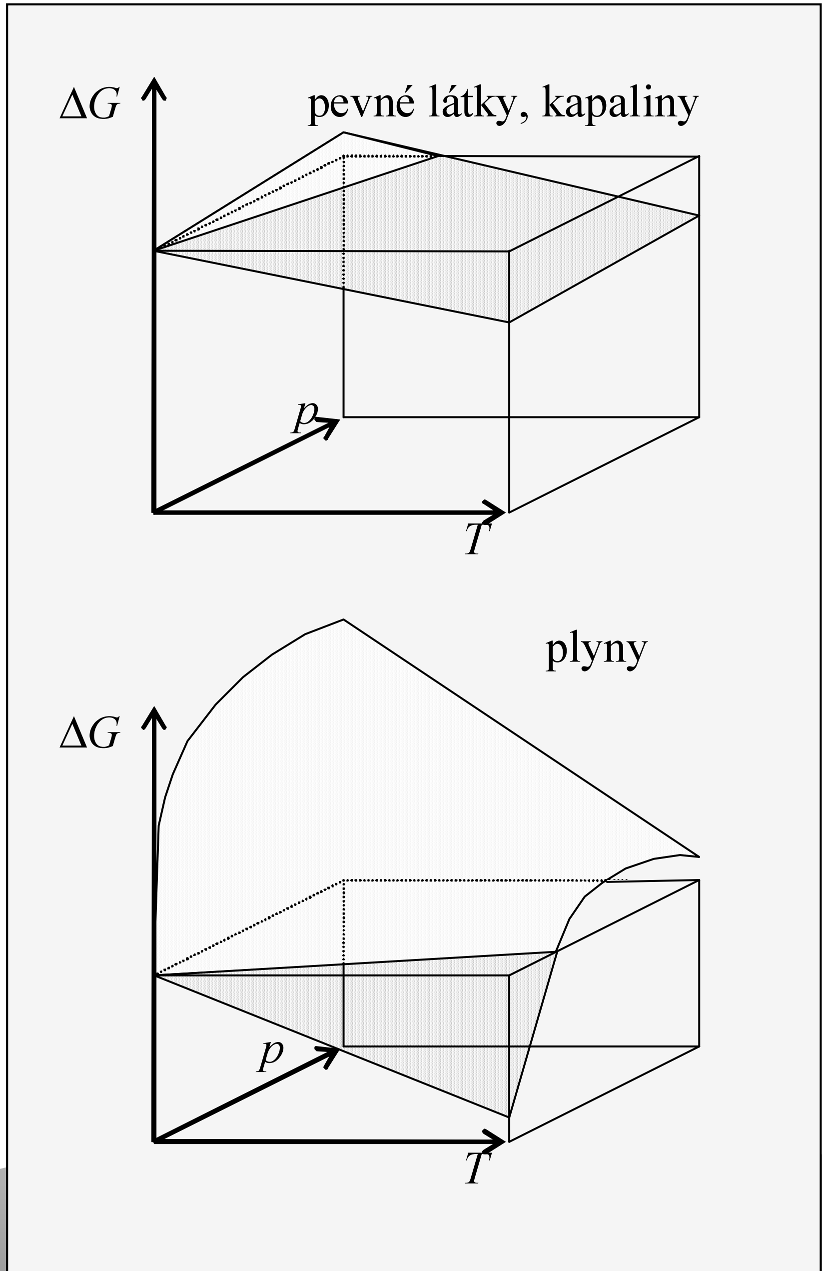
$$V = \frac{nRT}{p}$$

$$G_2 = G_1 + \int_{p_1}^{p_2} \frac{nRT}{p} \,\mathrm{d}p$$

$$G_2 = G_1 + nRT \int_{p_1}^{p_2} \mathrm{d}\ln p$$

$$G_2 = G_1 + nRT \ln\frac{p_2}{p_1}$$

Závislost Gibbsovy funkce na tlaku a teplotě



Závislost Gibbsovy funkce na složení

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

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

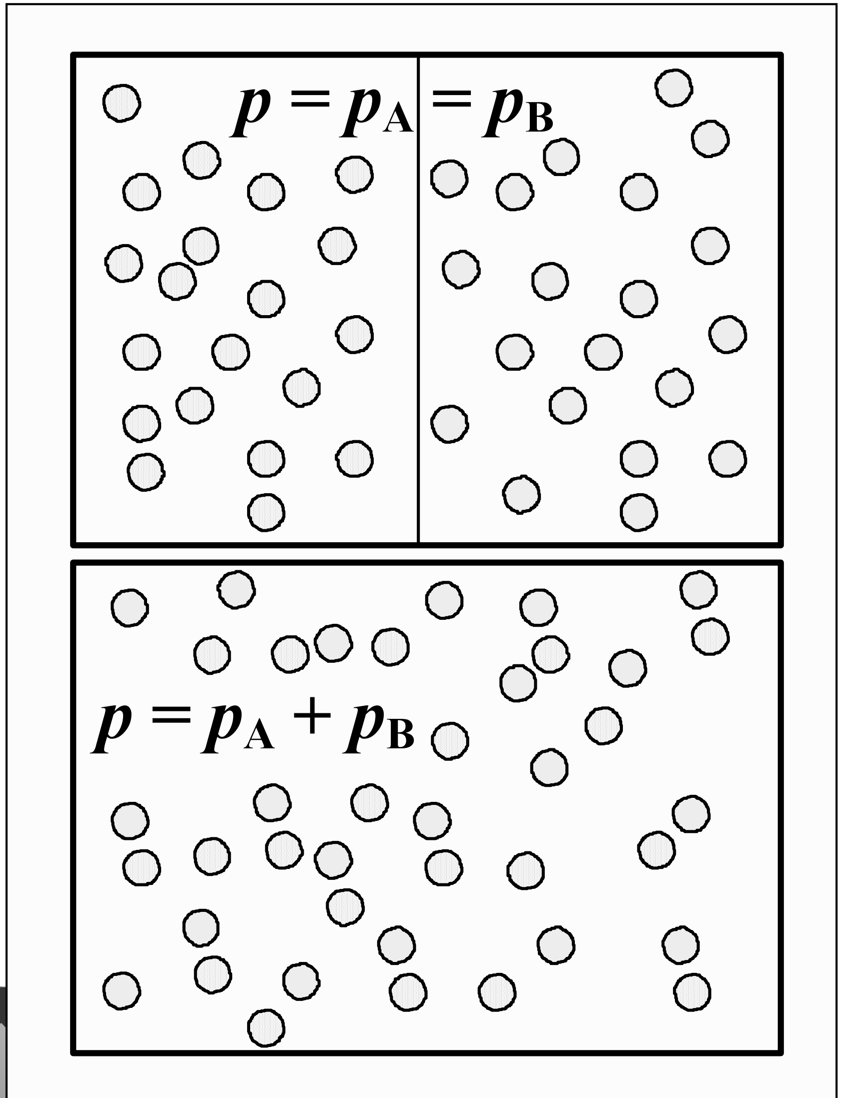
$$\mu_\mathrm{A} = \left(\frac{\partial G_\mathrm{A}}{\partial n_\mathrm{A}}\right)_{T,p} = \left(\frac{\partial\, n_\mathrm{A}\bar{G}_\mathrm{A}}{\partial n_\mathrm{A}}\right)_{T,p} = \bar{G}_\mathrm{A}$$

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

Závislost Gibbsovy funkce na složení

Plyny oddělené

Plyny smísené



Závislost Gibbsovy funkce na složení

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

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

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

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

Chemický potenciál

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

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

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

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

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

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