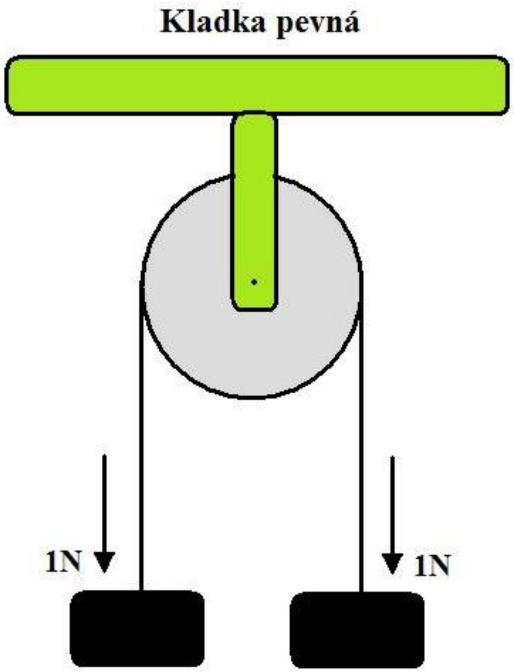
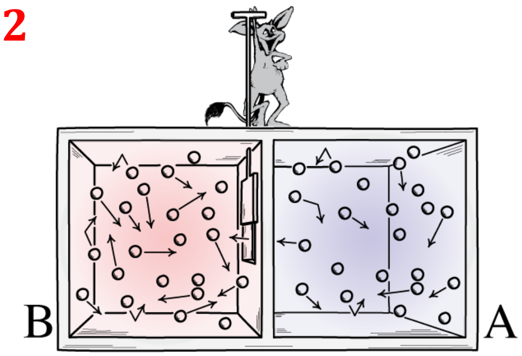


rovnováha

$$dU = dG = \cdots = \ldots + F_1\,ds_1 + F_2 ds_2 = 0$$

$$ds_1 = \underbrace{-ds_2 \Rightarrow F_1 ds - F_2 ds}_{F_1 = F_2} = 0$$



Objemová práce – rovnováha tlaku

$$dF = -SdT - p_A dV_A - p_B dV_B = 0$$

$$dV_A = -dV_B \Rightarrow p_A dV - p_B dV = 0 \Rightarrow p_A = p_B$$

Rovnováha teplot

$$dU = T_1 dS_1 - T_2 dS_2 - pdV = 0$$

celková $dS = 0 \Rightarrow T_1 dS - T_2 dS = 0 \Rightarrow T_1 = T_2$

Rovnováha – chemické potenciály

- Vnitřní energie $dU = 0$
- Enthalpie $dH = 0$
- Gibbsova energie $dG = 0$
- Helmholtzova energie $dF = 0$

minimum

- Entropie $dS = 0$ **maximum**

Chemická rovnováha

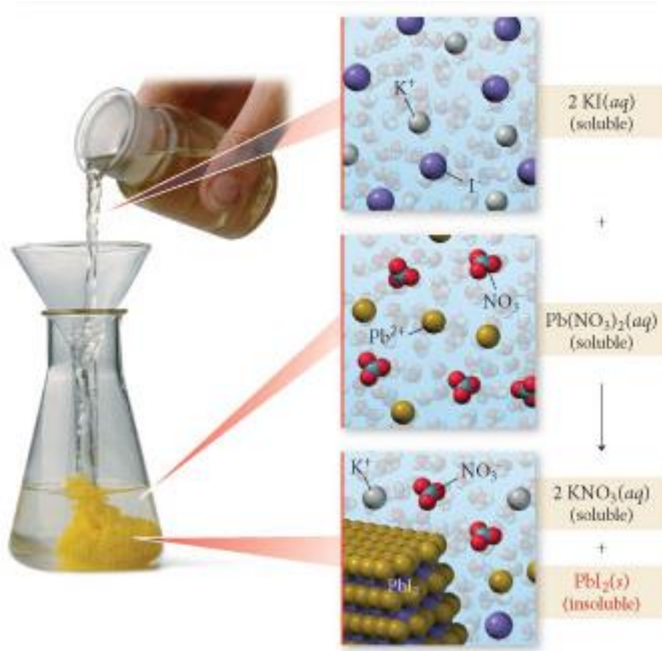
$$A \rightleftharpoons B$$

$$dG = -SdT + Vdp + \mu_A dn_A + \mu_B dn_B$$

$$-dn_A = dn_B \Rightarrow \mu_B dn_B - \mu_A dn_A = (\mu_B - \mu_A) dn_A = 0$$

$$\mu_A = \mu_B$$

- **Chemická rovnováha**
  - **Chemické reakce**
- **Fyzikálně chemická rovnováha**
  - **Osmóza**
  - **Fázové rovnováhy**
  - **Rozpouštění etc.**



Chemická rovnováha

$$A \rightleftharpoons B$$

$$dG = -TdS + Vdp + \mu_A dn_A + \mu_B dn_B$$

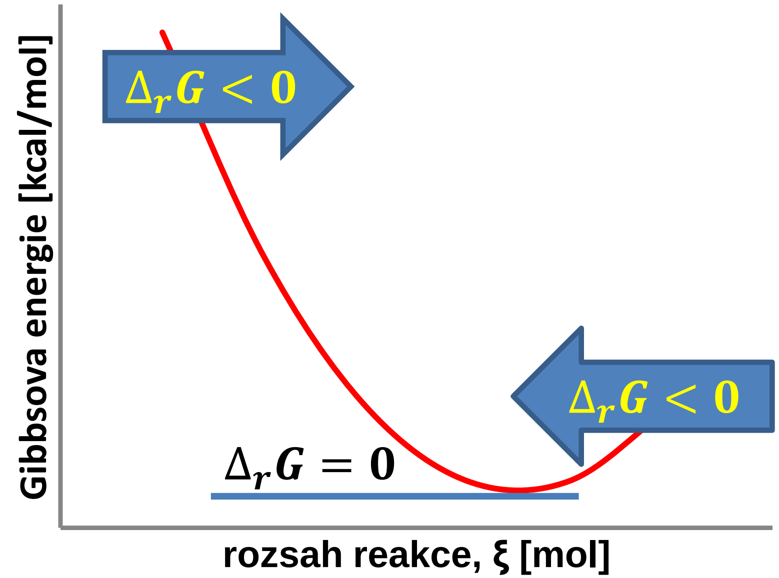
Rovnováha: $(\mu_B - \mu_A)dn_A = 0 \qquad \mu_A = \mu_B$

Reakční Gibbsova energie:

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{p,T} = \mu_B - \mu_A$$

$$\mu_i = \mu_i^{\ominus} + RT \ln a_i$$

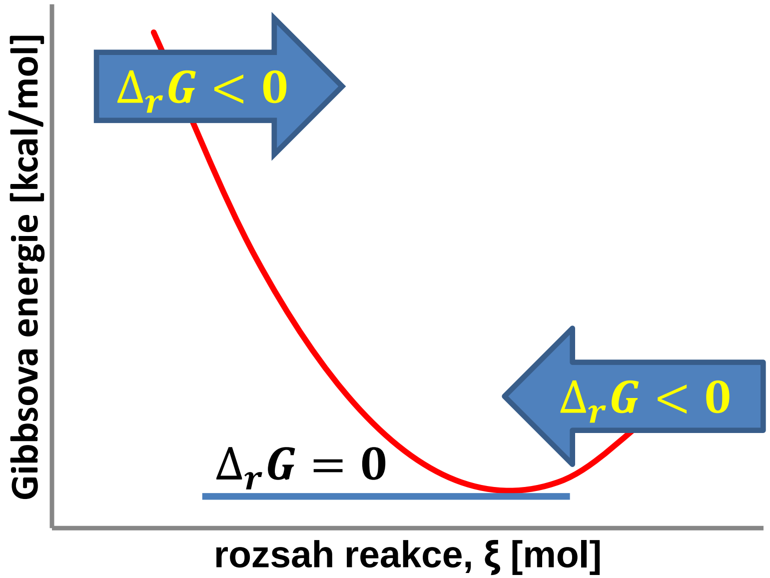
$$a_i = \gamma_{x,i} x_i$$



Chemická rovnováha

$$A \rightleftharpoons B$$

$$\Delta_r G = \mu_B - \mu_A = 0$$



Guldberg-Waagův zákon

$$\mu_i = \mu_i^\Theta + RT \ln a_i$$

$$\Delta_r G = \mu_B^\Theta - \mu_A^\Theta + RT \ln a_B - RT \ln a_A = \Delta_r G^\Theta + RT \ln \frac{a_B}{a_A} = 0$$

$$\Delta_r G^\Theta = -RT \ln \frac{a_B}{a_A} \Rightarrow \boxed{K = \frac{a_B}{a_A} = e^{-\frac{\Delta_r G^\Theta}{RT}}}$$

zředěný roztok

$$a_i = \gamma_{x,i} x_i = \gamma_{c,i} \frac{c_i}{c_i^\Theta} \qquad K = \frac{a_B}{a_A} = \frac{\gamma_B}{\gamma_A} \frac{c_B}{c_A} = K_\gamma K_c \cong K_c$$

Chemická rovnováha

Guldberg-Waagův zákon (obecně)

$$aA + bB \rightleftharpoons cC + dD$$

$$K = \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b} = K_\gamma \frac{c_C^c \cdot c_D^d}{c_A^a \cdot c_B^b} \cong \frac{c_C^c \cdot c_D^d}{c_A^a \cdot c_B^b}$$

$$H_2 + I_2 \rightleftharpoons 2HI$$

$$K = \frac{a_{HI}^2}{a_{H_2} \cdot a_{I_2}} \cong \frac{c_{HI}^2}{c_{H_2} \cdot c_{I_2}}$$

$$K = e^{-\frac{\Delta_r G^\ominus}{RT}}$$

$$\Delta_r G^\ominus = -RT \ln K$$

Chemická rovnováha

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}$$

$$K = \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b}$$ **poměr aktivit v rovnováze** → **rovnovážná konstanta**

$$Q_r = \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b}$$ **obecně mimo rovnováhu** → **reakční kvocient**

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{p,T} = \Delta_r G^{\ominus} + RT \ln Q_r$$ **Van´t Hoffova reakční izoterma**

stupeň konverze $$\alpha = \frac{n_i}{n_{i,0}}$$

Zreagované množstvíc

V původní reakční směsi

Chemická rovnováha

Závislost na teplotě

$$K = e^{-\frac{\Delta_r G^\ominus}{RT}} = e^{-\frac{\Delta_r H^\ominus - T\Delta_r S^\ominus}{RT}}$$

$$K = \boxed{e^{-\frac{\Delta_r H^\ominus}{RT}}} \boxed{\cdot\, e^{\frac{\Delta_r S^\ominus}{R}}}$$

vliv enthalpie (energie)

vliv entropie

$$G = H - TS$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta_r G = \Delta_r H - T\Delta_r S$$

$$\lim_{T\to\infty} K = e^{\frac{\Delta_r S^\ominus}{R}}$$

$$\lim_{T\to 0} K = \begin{cases} \infty & \Delta_r H^\ominus < 0 \\ 0 & \Delta_r H^\ominus > 0 \end{cases}$$

Chemická rovnováha

Závislost na teplotě

$$-RT\ln K = \Delta_r H^\ominus - T\Delta_r S^\ominus$$

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = -\frac{\Delta_r H^\ominus}{RT^2}$$

$$\left(\frac{\partial \ln K}{\partial \, {}^1/_T}\right)_p = -\frac{\Delta_r H^\ominus}{R}$$

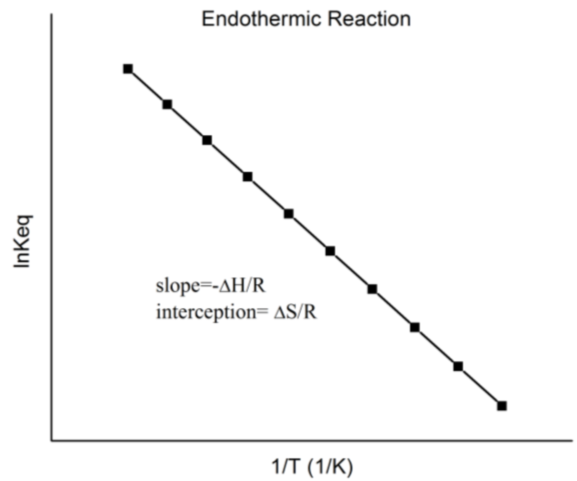
Van´t Hoffova rovnice (izobara)

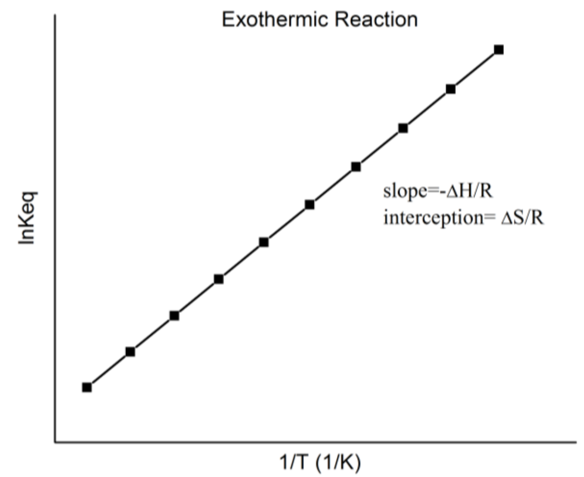
$$G = H - TS$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta_r G = \Delta_r H - T\Delta_r S$$

Van´t Hoffovovy grafy





Chemická rovnováha v plynné fázi

$$aA + bB \rightleftharpoons cC + dD$$

$$\mu_i = \mu_i^\ominus + RT\ln\left(\frac{p}{p^\ominus}\right)$$

$$p_A = x_A p$$

Závislost na tlaku

$$\Delta_r G = \Delta_r G^\ominus + RT\ln\frac{\left(\frac{p_C}{p^\ominus}\right)^c\left(\frac{p_D}{p^\ominus}\right)^d}{\left(\frac{p_A}{p^\ominus}\right)^a\left(\frac{p_B}{p^\ominus}\right)^b} = 0$$

$$K = \frac{\left(\frac{p_C}{p^\ominus}\right)^c\left(\frac{p_D}{p^\ominus}\right)^d}{\left(\frac{p_A}{p^\ominus}\right)^a\left(\frac{p_B}{p^\ominus}\right)^b} = \frac{p_C{}^c p_D{}^d}{p_A{}^a p_B{}^b}\cdot\left(\frac{1}{p^\ominus}\right)^{\Delta\nu} = \frac{x_C{}^c x_D{}^d}{x_A{}^a x_B{}^b}\cdot\left(\frac{p}{p^\ominus}\right)^{\Delta\nu} = K_x\left(\frac{p}{p^\ominus}\right)^{\Delta\nu}$$

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

$$K = \frac{x_{HI}^2}{x_{H_2}\cdot x_{I_2}}$$

Nezávisí na tlaku

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

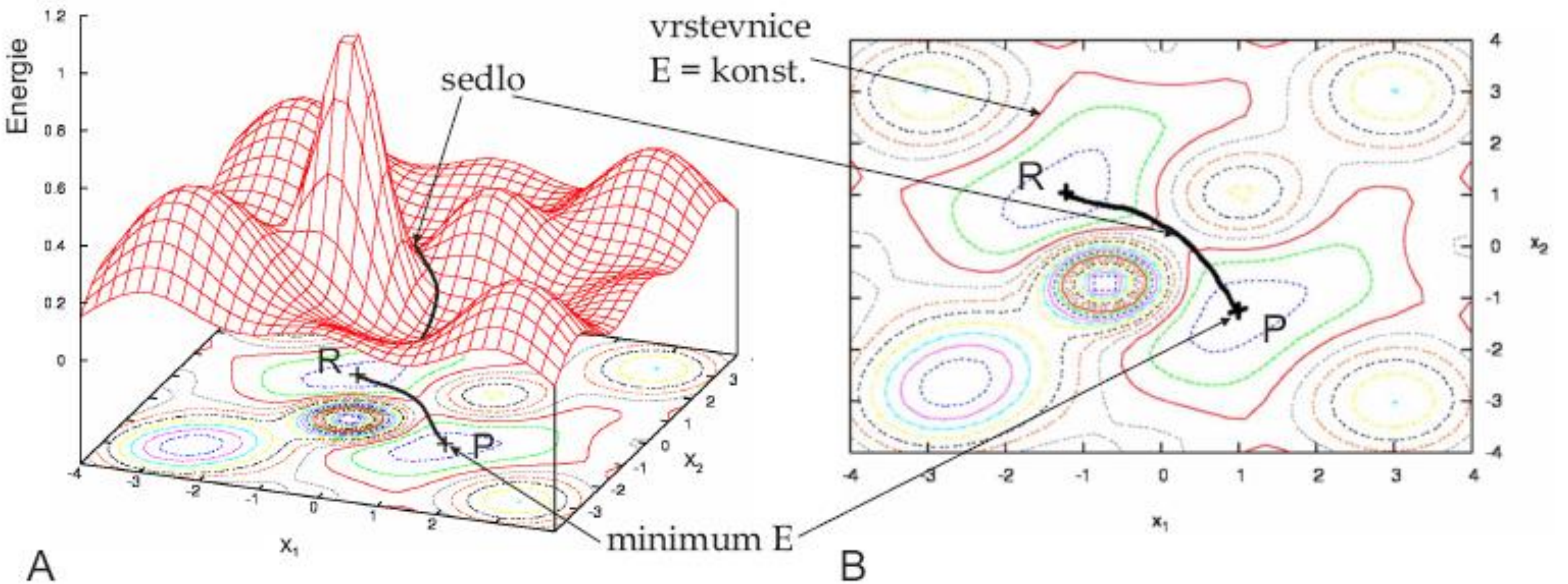
$$K = \frac{x_{NH_3}^2}{x_{N_2}\cdot x_{H_2}^3}\left(\frac{p}{p^\ominus}\right)^{-2}$$

vliv tlaku

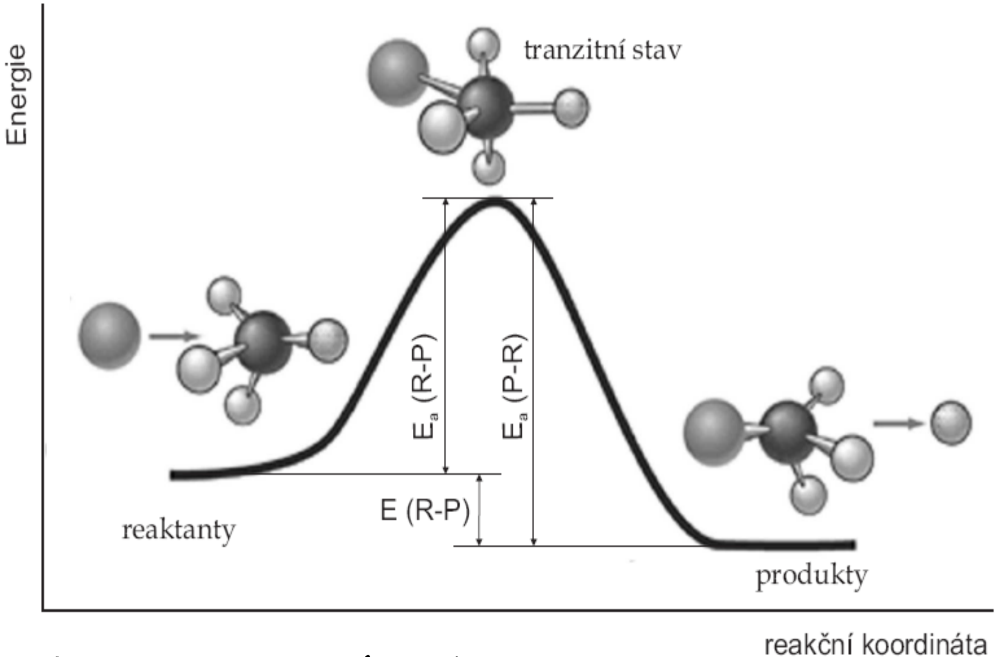
Atkins 22.3.2

Plocha potenciální energie (PES)

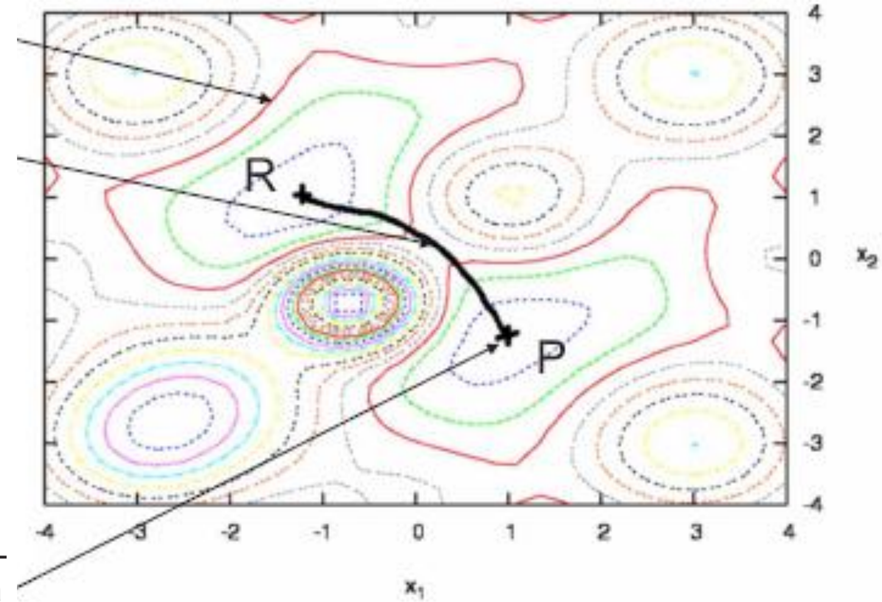
Obrázek 6.1: Panel A ukazuje plochu potenciální energie E závislou na dvou proměnných x_1 a x_2, vedlejší panel zobrazuje tutéž plochu ve formě mapy. Bod R představuje reaktanty a bod P produkty.

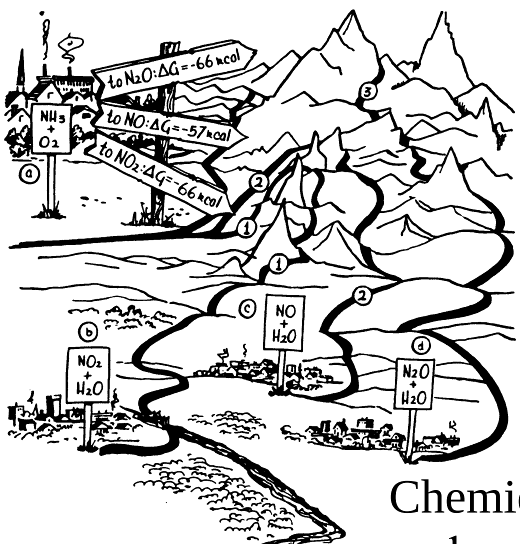


Plocha potenciální energie (PES)

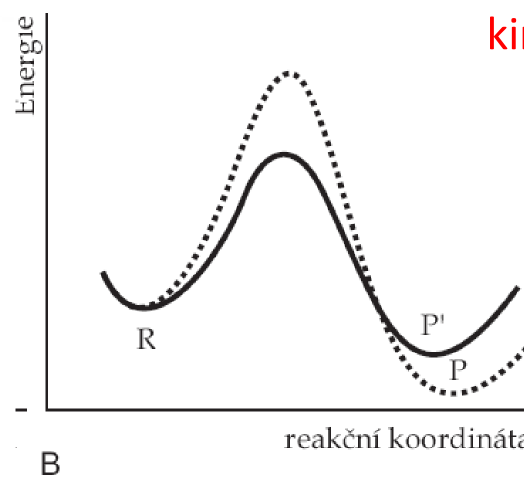


energeticky minimální reakční cesta





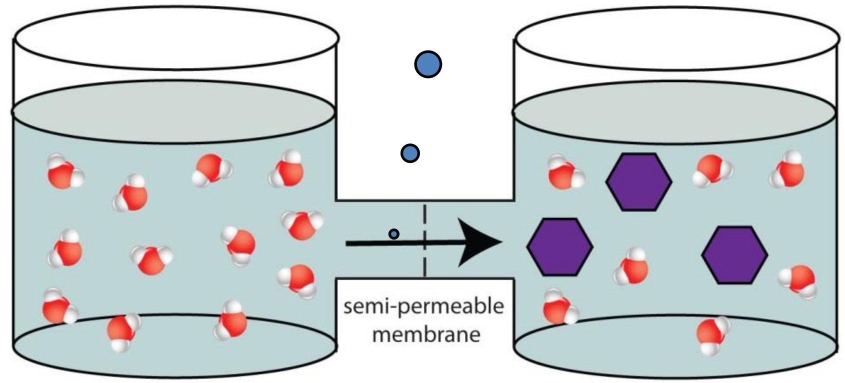
Chemie – turistika po hyperplochách



kineticky/termodynamicky řízený děj

Osmóza

Osmotický tok

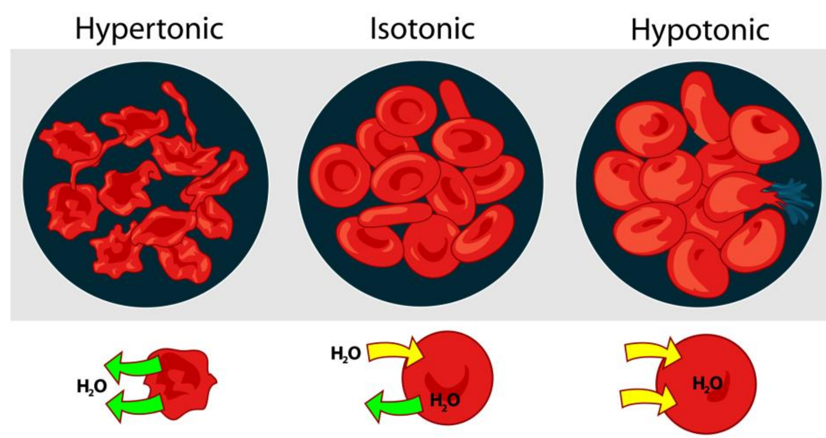


$$\mu_{l,p} = \mu_{l,x_i,p+\pi}$$

Osmotický tlak

$$\mu_{l,x_i,p+\pi} = \mu^{\theta}_{l,p+\pi} + RT \ln a_i$$

$$\mu^{\theta}_{l,p+\pi} = \mu^{\theta}_{l,p} + \int_{p}^{p+\pi} V\,dp = \mu^{\theta}_{l,p} + V\pi$$



$$\pi = -\frac{RT}{V} \ln a_i$$

Osmóza a reverzní osmóza