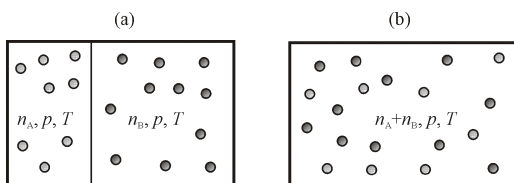
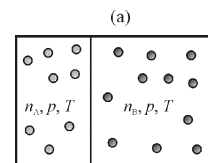


**PROMJENE TERMODINAMIČKIH
VELIČINA PRILIKOM MIJEŠANJA
PLINOVA I TEKUĆINA**

Gibbsova energija miješanja



Razdvojeni plinovi



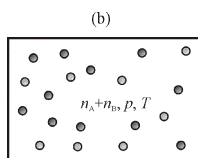
$$G_1 = n_A \mu_A^* + n_B \mu_B^*$$

$$\mu_B^* = \left(\mu_B^\circ + RT \ln \frac{p}{p^\circ} \right) \quad \mu_A^* = \left(\mu_A^\circ + RT \ln \frac{p}{p^\circ} \right)$$

$$G_1 = n_A \left(\mu_A^\circ + RT \ln \frac{p}{p^\circ} \right) + n_B \left(\mu_B^\circ + RT \ln \frac{p}{p^\circ} \right)$$

Pomiješani plinovi

$$G_2 = n_A \mu_A + n_B \mu_B$$



$$\mu_A = \left(\mu_A^\circ + RT \ln \frac{p_A}{p^\circ} \right) \quad \mu_B = \left(\mu_B^\circ + RT \ln \frac{p_B}{p^\circ} \right)$$

$$G_2 = n_A \left(\mu_A^\circ + RT \ln \frac{p_A}{p^\circ} \right) + n_B \left(\mu_B^\circ + RT \ln \frac{p_B}{p^\circ} \right)$$

$$G_2 = n_A \left(\mu_A^\circ + RT \ln \frac{p_A}{p^\circ} \right) + n_B \left(\mu_B^\circ + RT \ln \frac{p_B}{p^\circ} \right)$$

$$p_A = x_A p \quad p_B = x_B p$$

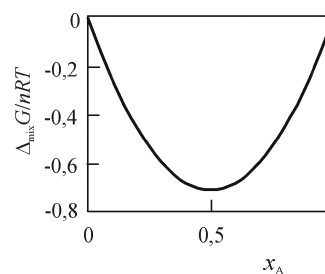
$$G_2 = n_A \left(\mu_A^\circ + RT \ln x_A + RT \ln \frac{p}{p^\circ} \right) + n_B \left(\mu_B^\circ + RT \ln x_B + RT \ln \frac{p}{p^\circ} \right)$$

Gibbsova energija miješanja
idealnih plinova:

$$\Delta G_{\text{mix}} = G_2 - G_1$$

$$\Delta G_{\text{mix}} = n_A RT \ln x_A + n_B RT \ln x_B$$

$$\Delta G_{\text{mix}} = nRT (x_A \ln x_A + x_B \ln x_B)$$

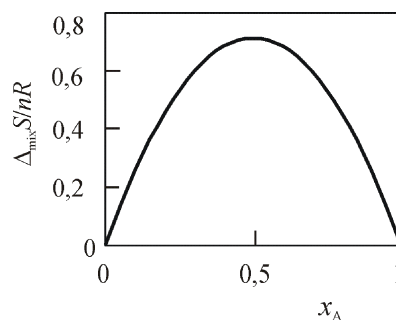


$$dG = Vdp - SdT$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \quad \Delta S_{\text{mix}} = -\left(\frac{\partial \Delta G_{\text{mix}}}{\partial T}\right)_p$$

$$\Delta S_{\text{mix}} = -n_A R \ln x_A - n_B R \ln x_B$$

$$\Delta S_{\text{mix}} = -nR(x_A \ln x_A + x_B \ln x_B)$$



$$\Delta H_{\text{mix}} = \Delta G_{\text{mix}} + T\Delta S_{\text{mix}} = 0$$

Miješanje tekućina koje tvore idealnu smjesu

$$\Delta G_{\text{mix}} = nRT(x_A \ln x_A + x_B \ln x_B)$$

$$\Delta S_{\text{mix}} = -nR(x_A \ln x_A + x_B \ln x_B)$$

$$\Delta H_{\text{mix}} = 0$$

Promjena Gibbsove energije s napredovanjem kemijske reakcije

$$\left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_{j \neq i}} = \tilde{G}_i = \mu_i$$

$$dG_i = \mu_i dn_i$$

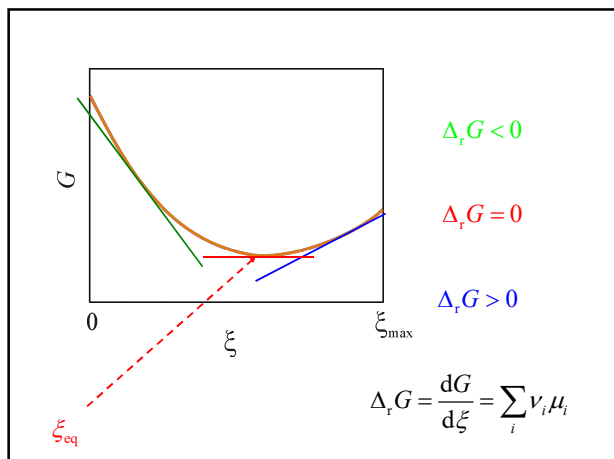
$$dn_i = v_i d\xi_i$$

$$dG_i = \sum_i v_i \mu_i d\xi_i \quad p, T = \text{konst.}$$

Gibbsova energija u reakcijskom sustavu

$$\Delta_r G = \frac{dG}{d\xi} = \sum_i v_i \mu_i$$

$$\Delta_r G^\circ = \frac{dG^\circ}{d\xi} = \sum_i v_i \mu_i^\circ$$



Gibbsova energija u reakcijskom sustavu

$$\Delta_r G = \frac{dG}{d\xi} = \sum_i \nu_i \mu_i \quad \Delta_r G^\circ = \frac{dG^\circ}{d\xi} = \sum_i \nu_i \mu_i^\circ$$

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

$$\Delta_r G = \sum_i \nu_i (\mu_i^\circ + RT \ln a_i)$$

$$\Delta_r G = \Delta_r G^\circ + RT \ln \prod_i a_i^{\nu_i}$$

$$\prod_i a_i^{\nu_i} = Q$$

Standardna konstanta ravnoteže

$$\Delta_r G^{\text{eq}} = 0$$

$$\Delta_r G^\circ + RT \ln \prod_i (a_i^{\nu_i})^{\text{eq}} = 0$$

$$\Delta_r G^\circ = -RT \ln \prod_i (a_i^{\nu_i})^{\text{eq}}$$

Standardna konstanta ravnoteže

$$\prod_i a_i^{\nu_i} = Q$$

$$\prod_i (a_i^{\nu_i})^{\text{eq}} = Q_e \quad \prod_i (a_i^{\nu_i})^{\text{eq}} = K^\circ$$

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

Disocijacija vode

$$\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$$

$$K^\circ = \frac{a(\text{H}^+)a(\text{OH}^-)}{a(\text{H}_2\text{O})}$$

$$K_w^\circ = a(\text{H}^+)a(\text{OH}^-) \quad K_w = c(\text{H}^+)c(\text{OH}^-)$$

EMPIRIJSKE KONSTANTE RAVNOTEŽA

Tlačna konstanta ravnoteže

$$K_p = \prod_i (p_i^{\text{eq}})^{\nu_i}$$

$$K^\circ = K_p (p^\circ)^{-\sum_i \nu_i} \prod_i (y_i^{\text{eq}})^{\nu_i}$$

Racionalna konstanta ravnoteže

$$K_x = \prod_i (x_i^{\text{eq}})^{\nu_i}$$

$$K^\circ = K_x \prod_i (y_i^{\text{eq}})^{\nu_i}$$

Koncentracijska konstanta ravnoteže

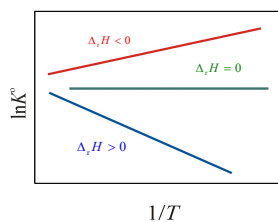
$$K_c = \prod_i (c_i^{\text{eq}})^{\nu_i}$$

$$K^\circ = K_c (c^\circ)^{-\sum_i \nu_i} \prod_i (y_i^{\text{eq}})^{\nu_i}$$

Ovisnost standardne konstante ravnoteže o temperaturi

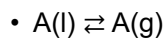
$$-RT \ln K^\circ = \Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ$$

$$\ln K^\circ = -\frac{\Delta_r H^\circ}{R} \cdot \frac{1}{T} + \frac{\Delta_r S^\circ}{R}$$



Koligativna svojstva

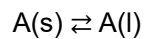
Tlak para otapala



$$p_A = p_A^* x_A \quad \Delta p_A = p_A^* - p_A = p_A^* x_B$$

$$p_A = p_A^* (1 - x_B)$$

Talište otopine



$$-\mu(s) + \mu(l) = 0$$

$$\mu^\circ(l) + RT_f \ln x_l = \mu^\circ(s) + RT_f \ln x_s$$

$$-RT_f \ln x_l = \mu^\circ(l) - \mu^\circ(s) =$$

$$= \Delta_{\text{fus}} G^\circ = \Delta_{\text{fus}} H^\circ - T_f \Delta_{\text{fus}} S^\circ$$

$$T_f = \frac{\Delta_{\text{fus}} H^\circ}{\Delta_{\text{fus}} S^\circ - R \ln x_i}$$

$$T_f^* = \frac{\Delta_{\text{fus}} H^\circ}{\Delta_{\text{fus}} S^\circ}$$

$$\Delta T_f = T_f^* - T_f = K_f \sum_i b_i$$

krioskopska konstanta

$$K_f = \frac{M_A R T_f^{*2}}{\Delta_{\text{fus}} H^\circ}$$

krioskopska konstanta

$$M_B = \frac{K_f m_B}{\Delta T_f m_A}$$

određivanje molarne
mase otopljene tvari
krioskopijom

Vrelište otopine

$$\Delta T_b = T_b - T_b^* = K_b \sum_i b_i$$

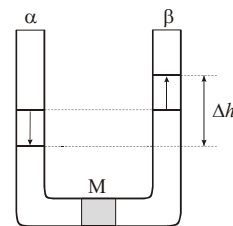
$$K_b = \frac{M_A R T_b^{*2}}{\Delta_{\text{vap}} H^\circ}$$

ebulioskopska konstanta

$$M_B = \frac{K_b m_B}{\Delta T_b m_A}$$

određivanje molarne
mase otopljene tvari
ebulioskopijom

osmotski tlak



osmotski tlak

Osmotska ravnoteža: $\mu_A^*(p^\alpha) = \mu_A(p^\beta, c_B)$

$$-RT \ln x_A^\beta = \Pi V_{m,A}$$

$$x_B = 1 - x_A \quad \ln(1 - x) \approx -x$$

$$RT x_B = \Pi V_{m,A}$$

osmotski tlak

$$x_B = \frac{n_B}{n_A + n_B} \approx \frac{n_B}{n_A} \quad (n_B \ll n_A)$$

$$V_{A,m} = V / n_A$$

$$\Pi = c_B RT$$

$$M_B = \frac{RT m_B}{\Pi V} = \frac{RT}{\Pi} \gamma_B$$

osmometrijsko određivanje molarne mase tvari B