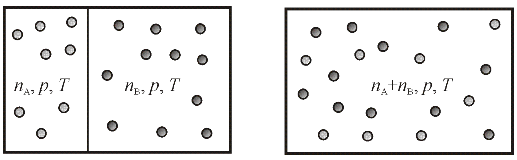
PROMJENE TERMODINAMIČKIH VELIČINA PRILIKOM MIJEŠANJA PLINOVA I TEKUĆINA

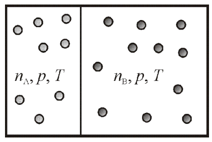
Gibbsova energija miješanja

(a) (b)



Razdvojeni plinovi

(a)



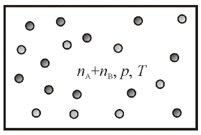
$$G_1 = n_A \mu_A{}^* + n_B \mu_B{}^*$$

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

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

Pomiješani plinovi

(b)



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

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

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

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

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

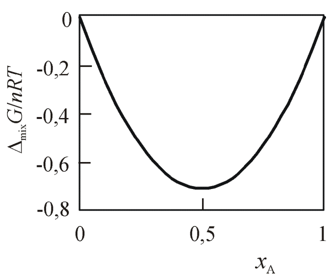
$$G_2 = n_A \left(\mu_A{}^\circ + RT \ln x_A + RT \ln \frac{p}{p^\circ} \right) + n_B \left(\mu_B{}^\circ + RT \ln x_B + RT \ln \frac{p}{p^\circ} \right)$$

Gibbsova energija miješanja idealnih plinova:

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

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

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

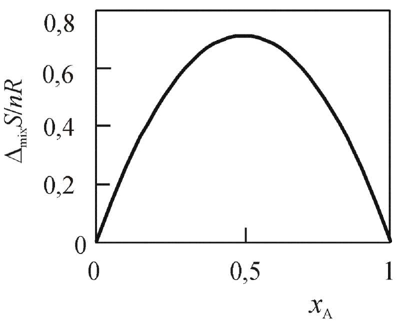


$$dG = V dp - S dT$$

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

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

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



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

Miješanje tekućina koje tvore idealnu smjesu

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

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

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

Promjena Gibbsove energije s napredovanjem kemijske reakcije

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

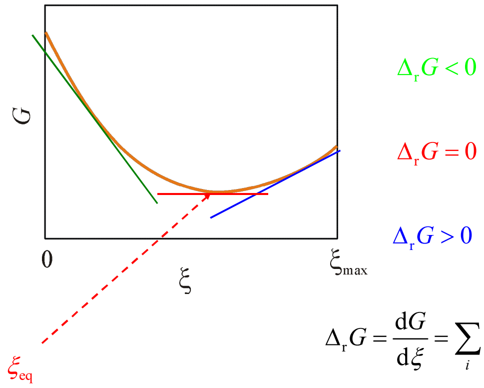
$$dG_i = \mu_i dn_i$$

$$dn_i = \nu_i d\xi_i$$

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

Gibbsova energija u reakcijskom sustavu

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



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

Gibbsova energija u reakcijskom sustavu

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

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

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

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

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

Standardna konstanta ravnoteže

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

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

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

Standardna konstanta ravnoteže

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

$$\prod_i \left(a_i^{\nu_i} \right)^{eq} = Q_e \qquad \prod_i \left(a_i^{\nu_i} \right)^{eq} = K^\circ$$

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

Disocijacija vode

$$H_2O(l) \rightleftarrows H^+(aq) + OH^-(aq)$$

$$K^\circ = \frac{a(H^+)a(OH^-)}{a(H_2O)}$$

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

EMPIRIJSKE KONSTANTE RAVNOTEŽA

Tlačna konstanta ravnoteže

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

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

Racionalna konstanta ravnoteže

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

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

Koncentracijska konstanta ravnoteže

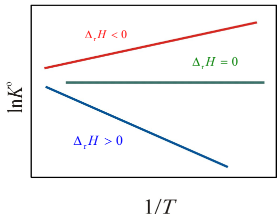
$$K_c = \prod_i \left(c_i^{\text{eq}}\right)^{\nu_i}$$

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

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

- A(l) ⇄ A(g)

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

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

Talište otopine

A(s) ⇄ A(l)

$-\mu(\text{s}) + \mu(\text{l}) = 0$

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

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

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

$$T_\mathrm{f} = \frac{\Delta_\mathrm{fus} H^\circ}{\Delta_\mathrm{fus} S^\circ - R \ln x_l}$$

$$T_\mathrm{f}^* = \frac{\Delta_\mathrm{fus} H^\circ}{\Delta_\mathrm{fus} S^\circ}$$

$$\Delta T_\mathrm{f} = T_\mathrm{f}^* - T_\mathrm{f} = K_\mathrm{f} \sum_i b_i$$

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

krioskopska konstanta

$$K_\mathrm{f} = \frac{M_\mathrm{A} R T_\mathrm{f}^{*2}}{\Delta_\mathrm{fus} H^\circ}$$

krioskopska konstanta

$$M_\mathrm{B} = \frac{K_\mathrm{f} m_\mathrm{B}}{\Delta T_\mathrm{f}\, m_\mathrm{A}}$$

određivanje molarne mase otopljene tvari krioskopijom

Vrelište otopine

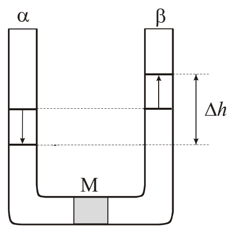
$$K_\mathrm{b} = \frac{M_\mathrm{A} R T_\mathrm{b}^{*2}}{\Delta_\mathrm{vap} H^\circ}$$

ebulioskopska konstanta

$$M_\mathrm{B} = \frac{K_\mathrm{b} m_\mathrm{B}}{\Delta T_\mathrm{b}\, m_\mathrm{A}}$$

određivanje molarne mase otopljene tvari ebulioskopijom

osmotski tlak



osmotski tlak

Osmotska ravnoteža: $\mu_\mathrm{A}^*(p^\alpha) = \mu_\mathrm{A}(p^\beta, c_\mathrm{B})$

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

$$x_\mathrm{B} = 1 - x_\mathrm{A} \qquad \ln(1-x) \approx -x$$

$$RT\, x_\mathrm{B} = \Pi\, V_\mathrm{m,A}$$

osmotski tlak

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

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

$\Pi = c_B RT$

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

osmometrijsko određivanje molarne mase tvari B