31. ZADATAK

Koeficijent aktiviteta komponente (1) u dvokomponentnoj otopini ovisi, pri stalnom tlaku i temperaturi, o sastavu prema sljedećem empirijskom izrazu:

$$\ln \gamma_1 = a x_2^2 + b x_2^3 + c x_2^4 .$$

Parametri *a*, *b* i *c* pritom ne ovise o sastavu.

Treba prirediti izraze koji opisuju ovisnost koeficijenta aktiviteta komponente(2), odnosno ekscesne Gibbsove energije o sastavu u istoj dvokomponentnoj otopini.

GIBBS-DUHEMOVA JEDNADŽBA

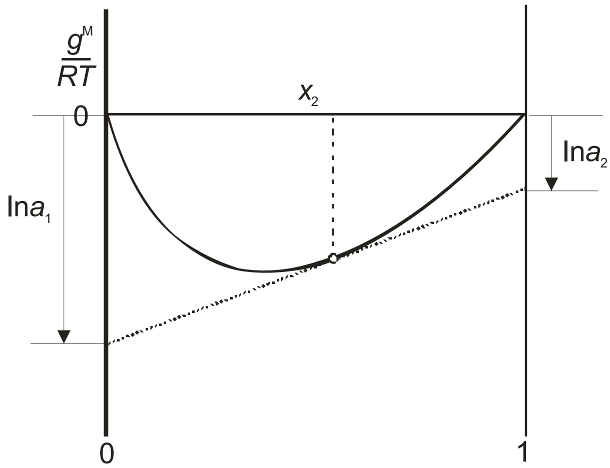
Daje međuovisnost parcijalnih molarnih veličina u višekomponentnim sustavima:

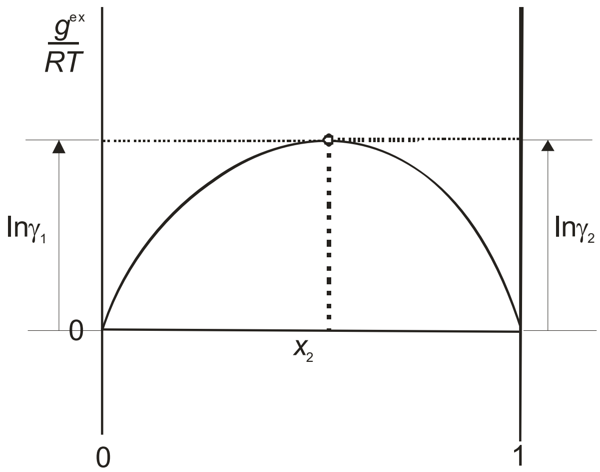
$$\sum n_{\mathrm{i}} d\bar{y}_{\mathrm{i}} = 0$$

$$\sum x_{\mathrm{i}} d\bar{y}_{\mathrm{i}} = 0$$

Veza ekscesne Gibbsove energije i koeficijenta aktiviteta:

$$\frac{g^{\mathrm{ex}}}{RT} = \sum x_{\mathrm{i}} \ln \gamma_{\mathrm{i}}$$





Logaritam koeficijenta aktiviteta jest parcijalna molarna veličina:

$$\sum x_{\mathrm{i}} d \ln \gamma_{\mathrm{i}} = 0$$

$$x_1 d \ln \gamma_1 + x_2 d \ln \gamma_2 = 0$$

$$x_2 d \ln \gamma_2 = -x_1 d \ln \gamma_1$$

$$d\ln\gamma_2 = -\frac{x_1}{x_2} d\ln\gamma_1$$

$$\int_{\ln\gamma_2(x_2=1)}^{\ln\gamma_2(x_2)} d\ln\gamma_2 = -\int_{x_2=1}^{x_2} \frac{x_1}{x_2} d\ln\gamma_1$$

$$x_1 = 1 - x_2$$

$$\frac{\partial \ln\gamma_1}{\partial x_2} = \frac{1}{\partial x_2}\partial\left(ax_2^2 + bx_2^3 + cx_2^4\right)$$

$$\frac{\partial \ln\gamma_1}{\partial x_2} = 2ax_2 + 3bx_2^2 + 4cx_2^3$$

$$d\ln\gamma_1 = \left(2ax_2 + 3bx_2^2 + 4cx_2^3\right)dx_2$$

Uvrštavanje:

$$\int_{\ln\gamma_2(x_2=1)}^{\ln\gamma_2(x_2)} d\ln\gamma_2 = -\int_{x_2=1}^{x_2} \frac{1-x_2}{x_2}\left(2ax_2 + 3bx_2^2 + 4cx_2^3\right)dx_2$$

Integriranje:

$$\ln\gamma_2 - 0 = -\int_{x_2=1}^{x_2} (1-x_2)\left(2a + 3bx_2 + 4cx_2^2\right)dx_2$$

$$\ln\gamma_2 - 0 = -\int_{x_2=1}^{x_2} \left[2a + (3b-2a)x_2 + (4c-3b)x_2^2 - 4cx_2^3\right]dx_2$$

$$\ln\gamma_2 = -\left.\left(2ax_2 + \frac{3b-2a}{2}x_2^2 + \frac{4c-3b}{3}x_2^3 - \frac{4c}{4}x_2^4\right)\right|_1^{x_2}$$

$$\ln\gamma_2 = -\left(2a\left(x_2-1\right)+\frac{3b-2a}{2}\left(x_2^2-1\right)+\frac{4c-3b}{3}\left(x_2^3-1\right)-\frac{4c}{4}\left(x_2^4-1\right)\right)$$

$$x_2 = 1 - x_1$$

$$\ln\gamma_2 = \left(a+\frac{3b}{2}+2c\right)x_1^2 - \left(b+\frac{8c}{3}\right)x_1^3 + cx_1^4$$

Ekscesna Gibbsova energija:

$$\frac{g^{\mathrm{ex}}}{RT} = x_1\ln\gamma_1 + x_2\ln\gamma_2$$

$$\frac{g^{\mathrm{ex}}}{RT} = x_1\left(ax_2^2+bx_2^3+cx_2^4\right)+x_2\left[\left(a+\frac{3b}{2}+2c\right)x_1^2-\left(b+\frac{8c}{3}\right)x_1^3+cx_1^4\right]$$

$$\frac{g^{\mathrm{ex}}}{RT} = x_1x_2\left[ax_2+bx_2^2+cx_2^3+\left(a+\frac{3b}{2}+2c\right)x_1-\left(b+\frac{8c}{3}\right)x_1^2+cx_1^3\right]$$

$$\frac{g^{\mathrm{ex}}}{RT} = x_1x_2\left[a+b+c-\left(\frac{b}{2}+c\right)x_1+\frac{c}{3}x_1^2\right]$$

Korektan izraz za ekscesnu Gibbsovu energiju!