О вычислении $\mu(x)$ в многокомпонентных системах

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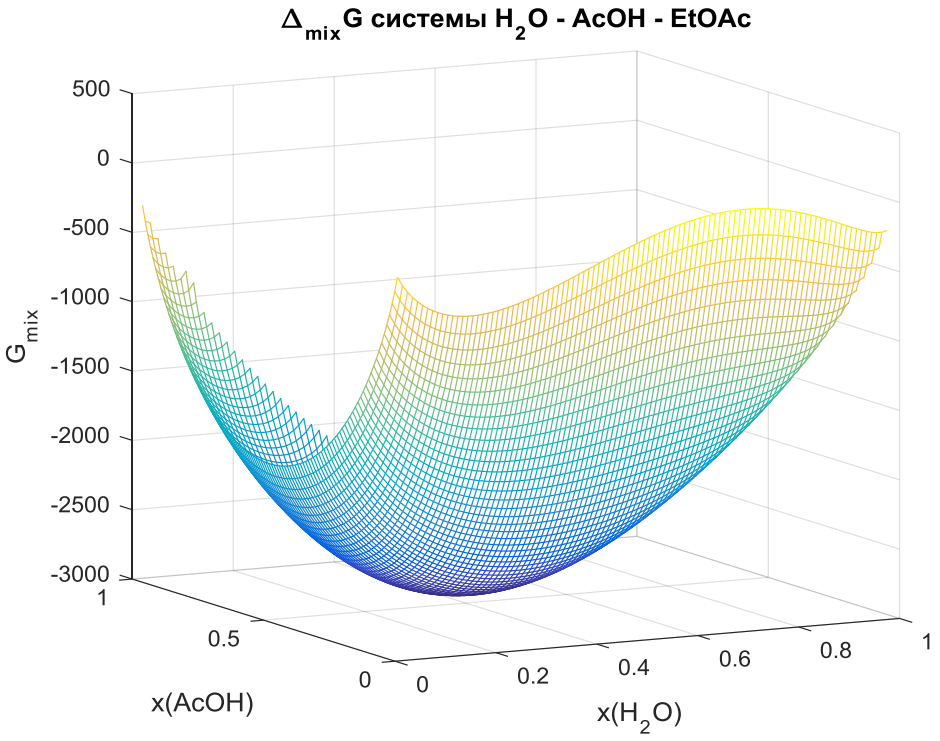
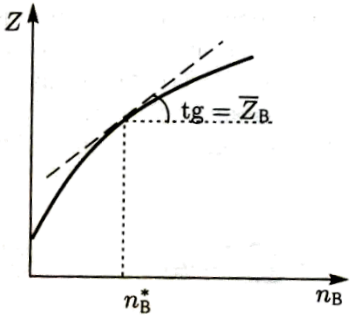
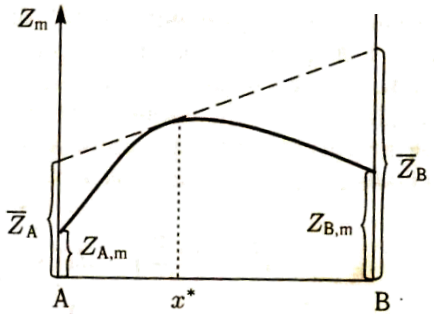
История







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

$$\overline{Z}_B = \left(\frac{\partial Z}{\partial n_B}\right)_{p,T,n_A}$$

$$\overline{Z}_A = \frac{Z - n_B\overline{Z}_B}{n_A}$$

$$\overline{Z}_i = Z_m - \sum_{i=1}^{K-1} x_i \left(\frac{\partial Z_m}{\partial x_i}\right)_{p,T}$$

$$\overline{Z}_B = Z_m + (1-x)\left(\frac{\partial Z_m}{\partial x}\right)_{p,T}$$

$$\overline{Z}_A = Z_m - x\left(\frac{\partial Z_m}{\partial x}\right)_{p,T}$$

$$\bar{Z}_i = Z_m - \sum_{i=1}^{K-1} x_i \left(\frac{\partial Z_m}{\partial x_i}\right)_{p,T}$$

Развитие событий

Лысенко В.А. Журнал физической химии, 2002, том 76, №12, с. 2199-2203

Это объясняется тем, что данные функции являются составной частью аналитического описания энергии Гиббса раствора, для которого уравнение Гиббса–Дюгема выполняется автоматически. Для доказательства последнего утверждения используем выражение для химического потенциала компонента в многокомпонентной системе [10]

$$\mu_i = G_m + \left(\frac{\partial G_m}{\partial x_i}\right) - \sum_{k=1}^{n} x_k \left(\frac{\partial G_m}{\partial x_k}\right),$$

Hillert M. // Physica B. 1981. V. 103. №1. P.31

One can easily show that the partial Gibbs energy can be calculated from the molar quantity

$$G_i^r = G_m^r + \partial G_m^r / \partial x_i^r - \sum_j x_j^r \, \partial G_m^r / \partial x_j^r. \qquad (12)$$

$$\mu_i = G_m + \left(\frac{\partial G_m}{\partial x_i}\right) - \sum_{k=1}^{n} x_k \left(\frac{\partial G_m}{\partial x_k}\right)$$

Предпосылки к решению

Для двойных систем

$$\begin{cases} \mu_A = G_m - x \cdot \left(\dfrac{\partial G_m}{\partial x}\right)_{p,T} \\ \mu_B = G_m + (1-x) \cdot \left(\dfrac{\partial G_m}{\partial x}\right)_{p,T} \end{cases}$$

$$\begin{cases} \mu_1 = G_m - x_2 \cdot \left(\dfrac{\partial G_m}{\partial x_2}\right) \\ \mu_2 = G_m - x_1 \cdot \left(\dfrac{\partial G_m}{\partial x_1}\right) \end{cases}$$

Для тройных систем

$$\begin{cases} \mu_1 = G_m - x_2 \cdot \left(\dfrac{\partial G_m}{\partial x_2}\right)_{x_3} - x_3 \cdot \left(\dfrac{\partial G_m}{\partial x_3}\right)_{x_2} \\ \mu_2 = G_m - x_1 \cdot \left(\dfrac{\partial G_m}{\partial x_1}\right)_{x_3} - x_3 \cdot \left(\dfrac{\partial G_m}{\partial x_3}\right)_{x_1} \\ \mu_3 = G_m - x_1 \cdot \left(\dfrac{\partial G_m}{\partial x_1}\right)_{x_2} - x_2 \cdot \left(\dfrac{\partial G_m}{\partial x_2}\right)_{x_1} \end{cases}$$

Попытка разобраться

$$\mu_i = G_m + \left(\frac{\partial G_m}{\partial x_i}\right) - \sum_{k=1}^{n} x_k \left(\frac{\partial G_m}{\partial x_k}\right)$$

$$\mu_A = G_m + \frac{\partial G_m}{\partial x_A} - x_A \frac{\partial G_m}{\partial x_A} - x_B \frac{\partial G_m}{\partial x_B} - x_C \frac{\partial G_m}{\partial x_C}$$

$$= G_m + (x_B + x_C) \frac{\partial G_m}{\partial x_A} - x_B \frac{\partial G_m}{\partial x_B} - x_C \frac{\partial G_m}{\partial x_C}$$

$$= G_m - x_B \left(\frac{\partial G_m}{\partial x_B} - \frac{\partial G_m}{\partial x_A}\right) - x_C \left(\frac{\partial G_m}{\partial x_C} - \frac{\partial G_m}{\partial x_A}\right)$$

$$\bar{Z}_i = Z_m - \sum_{i=1}^{K-1} x_i \left(\frac{\partial Z_m}{\partial x_i}\right)_{p,T}$$

Попытка разобраться

$$dG_m = \frac{\partial G_m}{\partial x_A} dx_A + \frac{\partial G_m}{\partial x_B} dx_B + \frac{\partial G_m}{\partial x_C} dx_C$$

$$= \frac{\partial G_m}{\partial x_A} d(1 - x_B - x_C) + \frac{\partial G_m}{\partial x_B} dx_B + \frac{\partial G_m}{\partial x_C} dx_C$$

$$= \underbrace{\left(\frac{\partial G_m}{\partial x_B} - \frac{\partial G_m}{\partial x_A}\right)}_{\left(\frac{\partial G_m}{\partial x_B}\right)_{x_C}} dx_B + \underbrace{\left(\frac{\partial G_m}{\partial x_C} - \frac{\partial G_m}{\partial x_A}\right)}_{\left(\frac{\partial G_m}{\partial x_C}\right)_{x_B}} dx_C$$

В точности формула со слайда №4

$$\mu_A = G_m - x_B \left(\frac{\partial G_m}{\partial x_B} - \frac{\partial G_m}{\partial x_A}\right) - x_C \left(\frac{\partial G_m}{\partial x_C} - \frac{\partial G_m}{\partial x_A}\right) = G_m - x_B \cdot \left(\frac{\partial G_m}{\partial x_B}\right)_{x_C} - x_C \cdot \left(\frac{\partial G_m}{\partial x_C}\right)_{x_B}$$

Проверка формулы

4.1.3.3. *Quaternary Systems*

The fourth-order equation of the general Wohl expansion (I–159) for a quaternary system has the form

$$\frac{\Delta G^E}{2.303RT}\frac{1}{q_1x_1+q_2x_2+q_3x_3+q_4x_4} = 2z_1z_2a_{12} + 2z_1z_3a_{13}$$
$$+ 2z_1z_4a_{14} + 2z_2z_3a_{23} + 2z_2z_4a_{24} + 2z_3z_4a_{34} + 3z_1^2z_2a_{112}$$
$$+ 3z_1z_2^2a_{122} + 3z_1^2z_3a_{113} + 3z_1z_3^2a_{133} + 3z_1z_4^2a_{144} + 3z_1^2z_4a_{114}$$
$$+ 3z_2^2z_3a_{223} + 3z_2z_3^2a_{233} + 3z_2^2z_4a_{224} + 3z_2z_4^2a_{244} + 3z_3^2z_4a_{334}$$
$$+ 3z_3z_4^2a_{344} + 6z_1z_2z_3a_{123} + 6z_1z_2z_4a_{124} + 6z_1z_3z_4a_{134}$$
$$+ 6z_2z_3z_4a_{234} + 4z_1^3z_2a_{1112} + 6z_1^2z_2^2a_{1122} + 4z_1z_2^3a_{1222}$$
$$+ 4z_1^3z_3a_{1113} + 6z_1^2z_3^2a_{1133} + 4z_1z_3^3a_{1333} + 4z_1^3z_4a_{1114}$$
$$+ 6z_1^2z_4^2a_{1144} + 4z_1z_4^3a_{1444} + 4z_2^3z_3a_{2223} + 6z_2^2z_3^2a_{2233}$$
$$+ 4z_2z_3^3a_{2333} + 4z_2^3z_4a_{2224} + 6z_2^2z_4^2a_{2244} + 4z_2z_4^3a_{2444}$$
$$+ 4z_3^3z_4a_{3334} + 6z_3^2z_4^2a_{3344} + 4z_3z_4^3a_{3444} + 12z_1^2z_2z_3a_{1123}$$
$$+ 12z_1^2z_3z_4a_{1134} + 12z_1z_2^2z_3a_{1223} + 12z_1z_2^2z_4a_{1224} + 12z_1z_2z_3^2a_{1233}$$
$$+ 12z_1z_2z_4^2a_{1244} + 12z_1z_3^2z_4a_{1334} + 12z_1z_3z_4^2a_{1344} + 12z_1^2z_2z_4a_{1124}$$
$$+ 12z_2^2z_4a_{2234} + 12z_2z_3^2z_4a_{2334} + 12z_2z_3z_4^2a_{1244} + 24z_1z_2z_3z_4a_{1234}.$$

$$\log\gamma_1 = \frac{\partial}{\partial n_1}\left(\frac{n\Delta G^E}{2.303RT}\right)_{P,T,n_2,n_3,n_4}$$
$$= x_2^2[A_{12} + 2x_1(A_{21} - A_{12} - D_{12}) + 3x_1^2D_{12}]$$
$$+ x_3^2[A_{13} + 2x_1(A_{31} - A_{13} - D_{13}) + 3x_1^2D_{13}]$$
$$+ x_4^2[A_{14} + 2x_1(A_{41} - A_{14} - D_{14}) + 3x_1^2D_{14}]$$
$$+ x_2x_3[A_{21} + A_{13} - A_{32} + 2x_1(A_{31} - A_{13}) + 2x_3(A_{32} - A_{23})$$
$$+ 3x_2x_3D_{23} - x_1(2 - 3x_1)\,C_{1123} - x_2(1 - 3x_1)\,C_{1223} - x_3(1 - 3x_1)\,C_{1233}]$$
$$+ x_2x_4[A_{21} + A_{14} - A_{42} + 2x_1(A_{41} - A_{14}) + 2x_4(A_{42} - A_{24})$$
$$+ 3x_2x_4D_{24} - x_1(2 - 3x_1)\,C_{1124} - x_2(1 - 3x_1)\,C_{1224} - x_4(1 - 3x_1)\,C_{1244}]$$
$$+ x_3x_4[A_{31} + A_{14} - A_{43} + 2x_1(A_{41} - A_{14}) + 2x_4(A_{43} - A_{34})$$
$$+ 3x_3x_4D_{34} - x_1(2 - 3x_1)\,C_{1134} - x_3(1 - 3x_1)\,C_{1334} - x_4(1 - 3x_1)\,C_{1344}]$$
$$+ x_2x_3x_4[2(A_{42} - A_{24}) + 3x_2C_{2234} + 3x_3C_{2334} + 3x_4C_{2344} + (1 - 3x_1)\,E_{1234}],$$

(I–236)

Hala E. Vapour-Liquid Equilibrium. Pergamon Press Ltd., Headington Hill Hall, Oxford, 1967

Проверка формулы

where n_i ($i = 1, 2, 3, 4$) are the moles of the ith constituent, n are the total moles, P is the total pressure, T is the absolute temperature and the various constants are given by the relations

$$A_{21} = 2a_{12} + 3a_{112} + 4a_{1112} \qquad A_{31} = 2a_{13} + 3a_{113} + 4a_{1113}$$
$$A_{12} = 2a_{12} + 3a_{122} + 4a_{1222} \qquad A_{13} = 2a_{13} + 3a_{133} + 4a_{1333}$$
$$D_{12} = 4a_{1112} + 4a_{1222} - 6a_{1122} \qquad D_{13} = 4a_{1113} + 4a_{1333} - 6a_{1133}$$
$$A_{41} = 2a_{14} + 3a_{114} + 4a_{1114} \qquad A_{32} = 2a_{23} + 3a_{223} + 4a_{2223}$$
$$A_{14} = 2a_{14} + 3a_{144} + 4a_{1444} \qquad A_{23} = 2a_{23} + 3a_{233} + 4a_{2333}$$
$$D_{14} = 4a_{1114} + 4a_{1444} - 6a_{1144} \qquad D_{23} = 4a_{2223} + 4a_{2333} - 6a_{2233}$$
$$A_{42} = 2a_{24} + 3a_{224} + 4a_{2224} \qquad A_{43} = 2a_{34} + 3a_{334} + 4a_{3334}$$
$$A_{24} = 2a_{24} + 3a_{244} + 4a_{2444} \qquad A_{34} = 2a_{34} + 3a_{344} + 4a_{3444}$$
$$D_{24} = 4a_{2224} + 4a_{2444} - 6a_{2244} \qquad D_{34} = 4a_{3334} + 4a_{3444} - 6a_{3344}$$

where

$$c_{123} = 3a_{112} + 3a_{133} + 3a_{223} - 6a_{123} + 4a_{1112} + 4a_{1333} + 4a_{2223}$$
$$c_{124} = 3a_{112} + 3a_{144} + 3a_{224} - 6a_{124} + 4a_{1112} + 4a_{1444} + 4a_{2224}$$
$$c_{134} = 3a_{113} + 3a_{144} + 3a_{334} - 6a_{134} + 4a_{1113} + 4a_{1444} + 4a_{3334}$$
$$c_{234} = 3a_{223} + 3a_{244} + 3a_{334} - 6a_{234} + 4a_{2223} + 4a_{2444} + 4a_{3334}.$$

$$C_{1123} = c_{123} + 4a_{1112} + 4a_{1113} - 12a_{1123} \qquad C_{1124} = c_{124} + 4a_{1112} + 4a_{1114} - 12a_{1124}$$
$$C_{1223} = c_{123} + 4a_{1222} + 4a_{2223} - 12a_{1223} \qquad C_{1224} = c_{124} + 4a_{1222} + 4a_{2224} - 12a_{1224}$$
$$C_{1233} = c_{123} + 4a_{1333} + 4a_{2333} - 12a_{1233} \qquad C_{1244} = c_{124} + 4a_{1444} + 4a_{2444} - 12a_{1244}$$
$$C_{1134} = c_{134} + 4a_{1113} + 4a_{1114} - 12a_{1134} \qquad C_{2234} = c_{234} + 4a_{2223} + 4a_{2224} - 12a_{2234}$$
$$C_{1334} = c_{134} + 4a_{1333} + 4a_{3334} - 12a_{1334} \qquad C_{2334} = c_{234} + 4a_{2333} + 4a_{3334} - 12a_{2334}$$
$$C_{1344} = c_{134} + 4a_{1444} + 4a_{3444} - 12a_{1344} \qquad C_{2344} = c_{234} + 4a_{2444} + 4a_{3444} - 12a_{2341}$$

$$E_{1234} = -(c_{123} + c_{124} + c_{134} + c_{234}) + 24a_{1234}, \qquad \text{(I-237)}$$

Проверка формулы

For a multicomponent solution, the excess Gibbs energy is

$$\frac{g^E}{RT} = -q \sum_{i=1}^{N} x_i \ln\left(\sum_{j=1}^{N} G_{ji} x_j \right) + p \sum_{i=1}^{N} x_i \frac{\sum_{j=1}^{N} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{N} G_{ki} x_k} \tag{35}$$

The activity coefficient is obtained by appropriate differentiation of Equation (35):

$$\ln \gamma_i = q \left(1 - \ln \sum_{j=1}^{N} x_j G_{ji} - \sum_{j=1}^{N} \frac{x_j G_{ij}}{\sum_{k=1}^{N} G_{kj} x_k} \right) + p \left[\frac{\sum_{j=1}^{N} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{N} G_{ki} x_k} + \sum_{j=1}^{N} \frac{x_j G_{ij}}{\sum_{k=1}^{N} G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_{l=1}^{N} x_l \tau_{lj} G_{lj}}{\sum_{k=1}^{N} G_{kj} x_k} \right) \right] \tag{38}$$

Renon, H. and Prausnitz, J. M. (1968), Local compositions in thermodynamic excess functions for liquid mixtures. AIChE J., 14: 135-144. doi:10.1002/aic.690140124

Строгий вывод

$$G = G_m \cdot \boldsymbol{n}$$

$$\boldsymbol{n} = \sum_{i=1}^{K} n_i$$

$$\mu_1 = \left(\frac{\partial G}{\partial n_1}\right)_{p,T,n_i \neq n_1} = \left(\frac{\partial G_m}{\partial n_1}\right)_{p,T,n_i \neq n_1} \cdot \boldsymbol{n} + G_m$$

$$\left(\frac{\partial G_m}{\partial n_1}\right)_{p,T,n_i \neq n_1} = \sum_{i \neq 1}^{K} \left(\frac{\partial G_m}{\partial x_i}\right)_{p,T,x_j \neq x_i} \cdot \left(\frac{\partial x_i}{\partial n_1}\right)_{p,T}$$

$$x_i = \frac{n_i}{\boldsymbol{n}} \quad \Rightarrow \quad \left(\frac{\partial x_i}{\partial n_1}\right)_{p,T,i \neq 1} = \frac{-n_i}{\boldsymbol{n}^2}$$

$$\mu_1 = \boldsymbol{n} \cdot \sum_{i \neq 1}^{K} \left(\frac{\partial G_m}{\partial x_i}\right)_{p,T,x_j \neq x_i} \cdot \frac{-n_i}{\boldsymbol{n}^2} + G_m = -\sum_{i \neq 1}^{K} x_i \cdot \left(\frac{\partial G_m}{\partial x_i}\right)_{p,T,x_j \neq x_i} + G_m$$

Соотнесение формул

$$\bar{Z}_i = Z_m - \sum_{i=1}^{K-1} x_i \left(\frac{\partial Z_m}{\partial x_i}\right)_{p,T} \quad \overset{?}{\Leftrightarrow} \quad \mu_i = G_m + \left(\frac{\partial G_m}{\partial x_i}\right) - \sum_{k=1}^{n} x_k \left(\frac{\partial G_m}{\partial x_k}\right)$$

$$\mu_1 = \left(\frac{\partial G}{\partial n_1}\right)_{p,T,n_i \neq n_1} = \left(\frac{\partial G_m}{\partial n_1}\right)_{p,T,n_i \neq n_1} \cdot \boldsymbol{n} + G_m$$

$$\left(\frac{\partial G_m}{\partial n_1}\right)_{p,T,n_i \neq n_l} = \sum_{i \neq l}^{K} \left(\frac{\partial G_m}{\partial x_i}\right)_{p,T,x_j \neq x_i} \cdot \left(\frac{\partial x_i}{\partial n_1}\right)_{p,T} \qquad \left(\frac{\partial x_1}{\partial n_1}\right)_{p,T} = \frac{\boldsymbol{n} - n_1}{\boldsymbol{n}^2}$$

$$\mu_1 = \left(\frac{\partial G_m}{\partial x_1}\right)_{\substack{p,T \\ x_j \neq x_1}} - \sum_{i \neq l}^{K} x_i \cdot \left(\frac{\partial G_m}{\partial x_i}\right)_{p,T,x_j \neq x_i} + G_m \qquad 1 < l \leq K$$

Заключение

Доказательство для двойной системы нестрогое!

$$Z = n_A \overline{Z}_A + n_B \overline{Z}_B,$$

$$Z_m = x_A \overline{Z}_A + x_B \overline{Z}_B = (1-x)\overline{Z}_A + x\overline{Z}_B = \overline{Z}_A + x\left(\overline{Z}_B - \overline{Z}_A\right),$$

$$\left(\frac{\partial Z_m}{\partial x}\right)_{p,T} = \overline{Z}_B - \overline{Z}_A, \qquad (6.14.а)$$

$$\overline{Z}_A = Z_m - x\left(\frac{\partial Z_m}{\partial x}\right)_{p,T}, \quad \overline{Z}_B = Z_m + (1-x)\left(\frac{\partial Z_m}{\partial x}\right)_{p,T}. \qquad (6.14.б)$$

Рекомендуемая формулировка

$$\mu_i = G_m - \sum_{j=1}^{K} x_j \cdot \left(\frac{\partial G_m}{\partial x_j}\right)_{p,T,x \neq x_j}$$

$$j \neq i$$

$$G_m = G_m(x_1, x_2, \dots, x_{i-1}, x_{i+1}, \dots, x_{K-1}, x_K)$$

Спасибо за внимание!