MUTUAL RELATIONS BETWEEN EXCESS THERMODYNAMIC FUNCTIONS RELATED TO DIFFERENT REFERENCE STATES*

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General relations between excess thermodynamic functions and activity coefficients related to different standard states are derived in a thermodynamically exact way and discussed from the point of view of their chemical-engineering applications.

In a thermodynamic quantitative description of a multicomponent liquid system one usually proceeds by comparing properties of components in the solution with those in selected standard state. To facilitate this comparison, auxiliary thermodynamic functions were introduced, namely the activity and activity coefficient[1].

If the critical temperature of a component is higher than the temperature of the system, it is usual to choose the standard state as (for the details see, *e.g.*[2,3]): pure component at the temperature and pressure of the system. The activity coefficient γ_i is then normalized so that it holds:

a) $$\gamma_i \to 1 \quad \text{as} \quad x_i \to 1 \,. \tag{1}$$

If the critical temperature of a component is lower than the temperature of the system, it is suitable to choose the standard state as: component in a hypothetical pure state extrapolated from its behaviour in an infinitely diluted solution. The activity coefficient γ_i' is then normalized so that it holds

b) $$\gamma_i' \to 1 \quad \text{as} \quad x_i \to 0 \,. \tag{2}$$

The main practical task in the thermodynamics of mixed phases dwells in searching for a thermodynamically consistent description of the dependence of activity coefficients of both types on state variables, especially on composition.

In the case of type (*a*) activity coefficients, the method employed first by Scatchard[4] has proved satisfactory. His concept is based on the balance of a process during

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which a solution is formed from its pure components at the temperature and pressure of the system. The difference between changes in the Gibbs function associated with the real and ideal mixing process is equal to the so called excess Gibbs function of mixing. The expression of its composition dependence is a further step in the process and partial derivatives of this excess function with respect to the number of moles of a component lead to a thermodynamically consistent description of the concentration dependence of type (*a*) activity coefficients.

In this communication we will show that in the case of activity coefficients normalized according to Eq. (*2*) it is suitable to start from the balance of a process during which an infinitely diluted solution is formed from a solution of a given composition.

Let us consider a process during which a multicomponent mixture is diluted with a large excess of a mixed solvent

$$\begin{aligned}[][n_B\mathrm{B} + n_C\mathrm{C} + \ldots + n_R\mathrm{R} + n_S\mathrm{S} + \ldots] + [(\bar{n}_R - n_R)\mathrm{R} + (\bar{n}_S - n_S)\,\mathrm{S} + \ldots] &= \\ = [n_B\mathrm{B} + n_C\mathrm{C} + \ldots + \bar{n}_R\mathrm{R} + \bar{n}_S\mathrm{S} + \ldots]\,; &\qquad (3) \\ [T, P] &\end{aligned}$$

In this equation, B, C, ... R, S, denote components in the system, $n_B, n_C, \ldots, n_R, n_S$, their amounts in mol, the symbols in bracket denote solutions of a given composition and $[T, P]$ emphasizes that the process proceeds at constant temperature and pressure. The following relations hold between the amounts of components of the mixed solvent

$$\bar{n}_R \gg n_R\,, \quad \bar{n}_S \gg n_S\,, \ldots \qquad (4)$$

$$\bar{n}_R/\bar{n}_S = n_R/n_S\,. \qquad (5)$$

The change in the excess Gibbs function associated with the process described by Eq. (*3*) is given by the difference between values corresponding to the final and initial states of the system, namely

$$\begin{aligned}\Delta G^E_{\mathrm{dil}} = {} & n_B\bar{\mu}^E_B + n_C\bar{\mu}^E_C + \ldots + \bar{n}_R\bar{\mu}^E_R + \bar{n}_S\bar{\mu}^E_S + \ldots \\ & - n_B\mu^E_B - n_C\mu^E_C - \ldots - n_R\mu^E_R - n_S\mu^E_S - \ldots \\ & - \bar{n}_R\bar{\mu}^E_R - \bar{n}_S\bar{\mu}^E_S - \ldots + n_R\bar{\mu}^E_R + n_S\bar{\mu}^E_S + \ldots = \\ = {} & n_B(\bar{\mu}^E_B - \mu^E_B) + n_C(\bar{\mu}^E_C - \mu^E_C) + \ldots + \\ & + n_R(\bar{\mu}^E_R - \mu^E_R) + n_S(\bar{\mu}^E_S - \mu^E_S) + \ldots\,, \qquad (6)\end{aligned}$$

where μ^E_i ($= RT\ln\gamma_i$) is the excess chemical potential of component i (i = B, C, ...

... R, S, ...) in the original solution and $\bar{\mu}_i^E$ ($= RT \ln \bar{\gamma}_i$) is the excess chemical potential of component i in the infinitely dilute solution.

After introducing excess chemical potentials $\mu_i^{E'}$ and activity coefficients γ_i' defined through the relations

$$\mu_i^{E'} = \mu_i^E - \bar{\mu}_i^E = RT \ln \gamma_i' = RT \ln \gamma_i/\bar{\gamma}_i \,, \tag{7}$$

where the dashed superscript emphasizes the choice of an infinitely diluted solution as the reference system, and after introducing a new excess function $\Delta G^{E'}$, through

$$\Delta G^{E'} = (-\Delta G^E_{\text{dil}}) \,, \tag{8}$$

relation (*6*) can be written in a formally simple form

$$\Delta G^{E'} = n_B \mu_B^{E'} + n_C \mu_C^{E'} + \ldots + n_R \mu_R^{E'} + n_S \mu_S^{E'} + \ldots \tag{9}$$

Partial differentiation with respect to the number of moles of component *i* leads further to

$$\left(\frac{\partial \Delta G^{E'}}{\partial n_i}\right)_{T,P,n_{j \neq i}} = \mu_i^{E'} + \sum_k n_k \left(\frac{\partial \mu_k^{E'}}{\partial n_i}\right)_{T,P,n_{k \neq i}} \tag{10}$$

According to the Gibbs–Duhem relation, the second term on the right-hand side of Eq. (*10*) is equal to zero

$$\sum_k n_k \left(\frac{\partial \mu_k^{E'}}{\partial n_i}\right)_{T,P,n_{k \neq i}} = 0 \,, \tag{11}$$

so that, by connecting Eqs (*10*), (*11*) and (*7*), we obtain the final form

$$\left(\frac{\partial \Delta G^{E'}}{\partial n_i}\right)_{T,P,n_{j \neq i}} = \mu_i^{E'} = RT \ln \gamma_i' = RT \ln \gamma_i/\bar{\gamma}_i \,. \tag{12}$$

It is obvious from the resulting equation (*12*) that if we know the concentration dependence of the excess function $\Delta G^{E'}$, it is possible to express consistently the concentration dependence of type (*b*) activity coefficients by a simple mathematical operation, *i.e.*, by partial differentiation with respect to the number of moles of a component.

Eq. (*6*) was derived by a general method for a mixed solvent. If the solvent is the pure component R, its chemical potential is equal to that of the pure component R;

since it holds

$$\bar{\mu}_{\mathrm{R}}^{\mathrm{E}} = RT \ln \bar{\gamma}_{\mathrm{R}} = 0 \, ; \quad [x_{\mathrm{R}} \rightarrow 1] \tag{13}$$

and, by connecting Eqs (*13*) and (*12*), we obtain

$$\mu_{\mathrm{R}}^{\mathrm{E}'} = \mu_{\mathrm{R}}^{\mathrm{E}} = RT \ln \gamma'_{\mathrm{R}} = RT \ln \gamma_{\mathrm{R}} \, ; \quad [x_{\mathrm{S}} \rightarrow 0 \, , \ldots] \, . \tag{14}$$

Further it will be shown how the process described by Eq. (*3*) can be replaced by the following steps:

$$n_{\mathrm{B}}\mathrm{B} + n_{\mathrm{C}}\mathrm{C} + \ldots + n_{\mathrm{R}}\mathrm{R} + n_{\mathrm{S}}\mathrm{S} + \ldots = [n_{\mathrm{B}}\mathrm{B} + n_{\mathrm{C}}\mathrm{C} + \ldots + n_{\mathrm{R}}\mathrm{R} + n_{\mathrm{S}}\mathrm{S} + \ldots] \quad [T, P] \tag{15}$$

$$\Delta G_{\mathrm{a}}^{\mathrm{E}} = n_{\mathrm{B}}\mu_{\mathrm{B}}^{\mathrm{E}} + n_{\mathrm{C}}\mu_{\mathrm{C}}^{\mathrm{E}} + \ldots + n_{\mathrm{R}}\mu_{\mathrm{R}}^{\mathrm{E}} + n_{\mathrm{S}}\mu_{\mathrm{S}}^{\mathrm{E}} + \ldots \tag{16}$$

$$\bar{n}_{\mathrm{R}}\mathrm{R} + \bar{n}_{\mathrm{S}}\mathrm{S} + \ldots = [\bar{n}_{\mathrm{R}}\mathrm{R} + \bar{n}_{\mathrm{S}}\mathrm{S} + \ldots] \, , \quad [T, P] \tag{17}$$

$$\Delta G_{\mathrm{b}}^{\mathrm{E}} = \bar{n}_{\mathrm{R}}\bar{\mu}_{\mathrm{R}}^{\mathrm{E}} + \bar{n}_{\mathrm{S}}\bar{\mu}_{\mathrm{S}}^{\mathrm{E}} + \ldots \tag{18}$$

$$[n_{\mathrm{B}}\mathrm{B} + n_{\mathrm{C}}\mathrm{C} + \ldots + \bar{n}_{\mathrm{R}}\mathrm{R} + \bar{n}_{\mathrm{S}}\mathrm{S}] = n_{\mathrm{B}}\mathrm{B} + n_{\mathrm{C}}\mathrm{C} + \ldots + \bar{n}_{\mathrm{R}}\mathrm{R} + \bar{n}_{\mathrm{S}}\mathrm{S} + \ldots \, , \quad [T, P] \tag{19}$$

$$-\Delta G_{\mathrm{c}}^{\mathrm{E}} = -n_{\mathrm{B}}\bar{\mu}_{\mathrm{B}}^{\mathrm{E}} - n_{\mathrm{C}}\bar{\mu}_{\mathrm{C}}^{\mathrm{E}} - \ldots - \bar{n}_{\mathrm{R}}\bar{\mu}_{\mathrm{R}}^{\mathrm{E}} - \bar{n}_{\mathrm{S}}\bar{\mu}_{\mathrm{S}}^{\mathrm{E}} - \ldots \tag{20}$$

$$[n_{\mathrm{R}}\mathrm{R} + n_{\mathrm{S}}\mathrm{S} + \ldots] = n_{\mathrm{R}}\mathrm{R} + n_{\mathrm{S}}\mathrm{S} + \ldots \, , \quad [T, P] \tag{21}$$

$$-\Delta G_{\mathrm{d}}^{\mathrm{E}} = -n_{\mathrm{R}}\bar{\mu}_{\mathrm{R}}^{\mathrm{E}} - n_{\mathrm{S}}\bar{\mu}_{\mathrm{S}}^{\mathrm{E}} - \ldots \tag{22}$$

By algebraic addition of contributions (*16*), (*18*), (*20*) and (*22*) we obtain the relation which is identical with the equation (*6*)

$$\Delta G^{\mathrm{E}'} = \Delta G_{\mathrm{a}}^{\mathrm{E}} + \Delta G_{\mathrm{b}}^{\mathrm{E}} - \Delta G_{\mathrm{c}}^{\mathrm{E}} - \Delta G_{\mathrm{d}}^{\mathrm{E}} = $$
$$= n_{\mathrm{B}}(\mu_{\mathrm{B}}^{\mathrm{E}} - \bar{\mu}_{\mathrm{B}}^{\mathrm{E}}) + n_{\mathrm{C}}(\mu_{\mathrm{C}}^{\mathrm{E}} - \bar{\mu}_{\mathrm{C}}^{\mathrm{E}}) + \ldots + n_{\mathrm{R}}(\mu_{\mathrm{R}}^{\mathrm{E}} - \bar{\mu}_{\mathrm{R}}^{\mathrm{E}}) + n_{\mathrm{S}}(\mu_{\mathrm{S}}^{\mathrm{E}} + \bar{\mu}_{\mathrm{S}}^{\mathrm{E}}) + \ldots \tag{23}$$

Eqs (*12*) and (*23*) are directions for mutual recalculations of activity coefficients and excess thermodynamic functions related to different reference systems and facilitate the use of practically verified assumptions of the concentration dependence of the excess thermodynamic function of mixing.

REFERENCES

1. Lewis G. N.: Proc. Amer. Acad. Arts Sci. *43*, 259 (1907); Z. Phys. Chem. (Leipzig) *61*, 129 (1907).
2. Hála E., Pick J., Fried V., Vilím O.: *Vapour–Liquid Equilibrium.* Pergamon Press, Oxford 1967.
3. Prausnitz J. M.: *Molecular Thermodynamics of Fluid-Phase Equilibria.* Prentice-Hall, Englewood Cliffs 1969.
4. Scatchard G.: Chem. Rev. *8*, 321 (1931).

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