

MUTUAL RELATIONS BETWEEN EXCESS THERMODYNAMIC FUNCTIONS AND ACTIVITY COEFFICIENTS RELATED TO DIFFERENT STANDARD STATES IN SYSTEMS CONTAINING ELECTROLYTES AND NON-ELECTROLYTES

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General relations between excess thermodynamic functions and activity coefficients related to different standard states in systems of electrolytes and non-electrolytes are derived systematically and discussed from the point of view of their chemical-engineering applications.

The thermodynamic description of multicomponent system is usually based on the comparison of properties of its components in the solution with those in the defined standard state. Auxiliary thermodynamic functions, namely activity and activity coefficient, were introduced for this comparison^{1,2} and many different reference systems and standard states are used for this purpose (for detailed discussion see, *e.g.*, Hougén and Watson³, Van Ness and Abbott⁴).

If pure component at the temperature and pressure of the system is chosen as the standard state, the activity coefficient γ_i is normalized so that it holds

$$\gamma_i \rightarrow 1 \quad \text{as} \quad x_i \rightarrow 1 \quad \text{"type a"} . \quad (1)$$

Often, it is suitable to use the very diluted solution as a reference system and component in a hypothetical pure state (extrapolated from its behaviour in the infinitely diluted solution) as the standard state. The activity coefficient γ'_i is then normalized so that it holds

$$\gamma'_i \rightarrow 1 \quad \text{as} \quad x_i \rightarrow 0 \quad \text{"type b"} . \quad (2)$$

If molality is chosen as concentration variable, the component in hypothetical state extrapolated from its behaviour in infinite dilution to molality $m_i = 1$ is used as standard state; then

$$\gamma''_i \rightarrow 1 \quad \text{as} \quad m_i \rightarrow 0 \quad \text{"type c"} . \quad (3)$$

The important practical problem in the thermodynamics of solutions is a consistent expression of the dependence of activity coefficients in multicomponent systems (of all mentioned types) on temperature, pressure and especially on composition.

If the standard state and activity coefficients of "type a" are chosen for description of the system, the procedure based on the Gibbs function of balance the process during which a solution is formed from pure components is very suitable for this purpose (Scatchard⁵, Scatchard and Hamer⁶).

The difference between changes in Gibbs function associated with the real and ideal mixing process is called *Excess Gibbs Energy of Mixing*; the expression of its composition dependence is the further step of the procedure and the partial differentiation of excess Gibbs energy of mixing with respect to the moles of a component leads to the thermodynamically consistent equations expressing the concentration dependence of "type *a*" activity coefficients.

If the standard state and activity coefficients of "type *b*" are chosen for description of the system, it can be shown (Hála⁷) that it is convenient to start from the Gibbs function balance of a process in which an infinitely diluted solution is formed from a solution of given composition. The difference between changes of the Gibbs function associated with real and ideal dilution process is called *Excess Gibbs Energy of Dilution*; the expression of its composition dependence and following partial differentiation with respect to the moles of a component leads to the consistent equations expressing the concentration dependence of "type *b*" activity coefficients.

Both procedures just mentioned ("a" and "b") are elaborated in detail for systems of non-electrolytes.

The present paper is concerned with systems of electrolytes.

Excess Gibbs Energy of Mixing

Let us consider at first a process in which a solution is formed from pure components at constant temperature and pressure

$$\begin{aligned} n_B B + n_C C + \dots + n_R R + n_S S + \dots = \\ = [n_B B + n_C C + \dots + n_R R + n_S S = \dots]; [T, P], \end{aligned} \quad (4)$$

where n_i denotes moles of electrolytic component i ($i = B, C, \dots$), n_k moles of non-electrolytic component k ($k = R, S, \dots$), and the symbol $[T, P]$ emphasizes that the process proceeds at constant temperature and pressure.

Electrolytic components dissociate into cations and anions according to the reaction scheme



where ν_{i+} , ν_{i-} denote numbers of cations and anions formed by dissociation of a molecule i ($i = B, C, \dots$).

Combining equations (4) and (5), we can write

$$\begin{aligned} n_B(\nu_{B+} B_+ + \nu_{B-} B_-) + n_C(\nu_{C+} C_+ + \nu_{C-} C_-) + \dots + n_R R + n_S S + \dots = \\ = [n_B(\nu_{B+} B_+ + \nu_{B-} B_-) + n_C(\nu_{C+} C_+ + \nu_{C-} C_-) + \dots + \\ + n_R R + n_S S + \dots]; [T, P]. \end{aligned} \quad (6)$$

The change of Gibbs function associated with the mixing process is then given as

follows

$$\begin{aligned} \Delta G_{\text{mix}} = & n_B [(v_{B+}\mu_{B+} + v_{B-}\mu_{B-}) - (v_{B+}\mu_{B+}^0 + v_{B-}\mu_{B-}^0)] + \\ & + n_C [(v_{C+}\mu_{C+} + v_{C-}\mu_{C-}) - (v_{C+}\mu_{C+}^0 + v_{C-}\mu_{C-}^0)] + \dots \\ & + n_R(\mu_R - \mu_R^0) + n_S(\mu_S - \mu_S^0) + \dots, \end{aligned} \quad (7)$$

where μ_{i+} , μ_{i-} denote the chemical potentials of cations and anions of the electrolyte i ($i = B, C, \dots$), μ_k denotes the chemical potential of the non-electrolyte k ($k = R, S, \dots$), and the superscript 0 denotes the state of pure component.

In solutions, cations and anions are present in such a ratio, for the solution to be externally electroneutral; therefore the effects of both ion kinds are investigated simultaneously during all experiments. This fact is the reason for introducing so-called mean thermodynamic functions, *e.g.*, the mean chemical potential of ions defined by the equation

$$v_i \mu_{i\pm} = v_{i+} \mu_{i+} + v_{i-} \mu_{i-}, \quad (8)$$

where $\mu_{i\pm}$ denotes the mean chemical potential of ions of the electrolyte i and v_i ($v_i = v_{i+} + v_{i-}$) the total number of ions produced by dissociating one molecule of the electrolyte i .

With respect to relation (8), equation (7) takes the form

$$\begin{aligned} \Delta G_{\text{mix}} = & n_B v_B (\mu_{B\pm} - \mu_{B\pm}^0) + n_C v_C (\mu_{C\pm} - \mu_{C\pm}^0) + \dots \\ & + n_R (\mu_R - \mu_R^0) + n_S (\mu_S - \mu_S^0) + \dots. \end{aligned} \quad (9)$$

On introducing the mean activity, mean mole fraction, mean activity coefficient of ions of the electrolyte i ($i = B, C, \dots$) and the activity, mole fraction, and activity coefficient of the non-electrolyte k ($k = R, S, \dots$),

$$v_i (\mu_{i\pm} - \mu_{i\pm}^0) = RT v_i \ln a_{i\pm} = RT v_i \ln x_{i\pm} + RT v_i \ln \gamma_{i\pm} \quad (10)$$

$$\mu_k - \mu_k^0 = RT \ln a_k = RT \ln x_k + RT \ln \gamma_k, \quad (11)$$

where

$$v_i \ln x_{i\pm} = v_{i+} \ln x_{i+} + v_{i-} \ln x_{i-} \quad (12)$$

$$v_i \ln \gamma_{i\pm} = v_{i+} \ln \gamma_{i+} + v_{i-} \ln \gamma_{i-}, \quad (13)$$

we obtain, on combining relations (9)–(13), the equation

$$\begin{aligned} \Delta G_{\text{mix}} = & \sum_i n_i RT v_i \ln x_{i\pm} + \sum_k n_k RT \ln x_k + \\ & + \sum_i n_i RT v_i \ln \gamma_{i\pm} + \sum_k n_k RT \ln \gamma_k. \end{aligned} \quad (14)$$

For an ideal solution (*), the activity coefficients of all constituents are equal to unity and the second term on the right-hand side of (14) vanishes

$$\Delta G_{\text{mix}}^* = \sum_i n_i v_i RT \ln x_{i\pm} + \sum_k n_k RT \ln x_k. \quad (15)$$

The difference ($\Delta G_{\text{mix}} - \Delta G_{\text{mix}}^*$) for real systems is called excess Gibbs energy of mixing

$$\Delta G_{\text{mix}}^E = \Delta G_{\text{mix}} - \Delta G_{\text{mix}}^* = \sum_i n_i v_i RT \ln \gamma_{i\pm} + \sum_k n_k RT \ln \gamma_k. \quad (16)$$

On differentiating ΔG^E partially with respect to the moles of any component i , we obtain

$$\begin{aligned} \left(\frac{\partial \Delta G_{\text{mix}}^E}{\partial n_i} \right)_{T, P, n_i \neq j} &= v_i RT \ln \gamma_{i\pm} + \sum_j n_j v_j RT \frac{\partial \ln \gamma_{j\pm}}{\partial n_i} + \\ &+ \sum_k n_k RT \frac{\partial \ln \gamma_k}{\partial n_i} = v_i RT \ln \gamma_{i\pm} \end{aligned} \quad (17)$$

since according to Gibbs–Duhem equation

$$\sum_i n_i RT_i \left(\frac{\partial \ln \gamma_{i\pm}}{\partial n_i} \right)_{T, P, n_i \neq j} + \sum_k n_k RT \left(\frac{\partial \ln \gamma_k}{\partial n_i} \right)_{T, P, n_i \neq j} = 0. \quad (18)$$

Similarly for non-electrolytes it can be written

$$\left(\frac{\partial \Delta G^E}{\partial n_k} \right)_{T, P, n_i \neq j} = RT \ln \gamma_k. \quad (19)$$

As we can see from equations (17) and (18), if excess Gibbs energy of mixing is known as a function of composition, by relatively simple operation of partial differentiation with respect to n_i , or n_k , it is possible to obtain relations giving the dependence of activity coefficient of the constituent i or k on the composition of solution. Relations derived by this procedure, automatically satisfy the Gibbs–Duhem equation.

Excess Gibbs Energy of Dilution

If activity coefficients are normalized according to equation (2), it is suitable to start from the balance of a dilution process.

Let us consider a process during which a multicomponent mixture of electrolytic components B, C, \dots and non-electrolytes R, S, \dots is diluted with a large excess

of a mixed solvent

$$\begin{aligned} & [n_B B + n_C C + \dots + n_R R + n_S S + \dots] + [(\bar{n}_R - n_R) R + (\bar{n}_S - n_S) S + \dots] \\ & = [n_B B + n_C C + \dots + \bar{n}_R R + \bar{n}_S S + \dots]; [T, P]. \end{aligned} \quad (20)$$

In equation (4), n_B, n_C, \dots denote amounts of electrolytic components (in moles), n_R, n_S, \dots amounts of non-electrolytic components (in moles), the symbols in bracket the 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

$$\bar{n}_R \gg n_R, \bar{n}_S \gg n_S, \dots \quad (21)$$

$$\bar{n}_R / \bar{n}_S = n_R / n_S. \quad (22)$$

Taking into account the dissociation (5), the dilution process (20) can be written as follows

$$\begin{aligned} & [v_B(v_{B+} B_+ + v_{B-} B_-) + n_C(v_{C+} C_+ + v_{C-} C_-) + \dots + n_R R + n_S S + \dots] + \\ & + [(\bar{n}_R - n_R) R + (\bar{n}_S - n_S) S + \dots] = \\ & = [n_B(v_{B+} B_+ + v_{B-} B_-) + n_C(v_{C+} C_+ + v_{C-} C_-) + \dots + \\ & + \bar{n}_R R + \bar{n}_S S + \dots]; [T, P]. \end{aligned} \quad (23)$$

The change in the excess Gibbs function associated with the process described by equation (23) is given by the difference between the values corresponding to the final and initial states of the system, *viz.*

$$\begin{aligned} \Delta G_{dil}^E & = n_B RT(v_{B+} \ln \bar{\gamma}_{B+} + v_{B-} \ln \bar{\gamma}_{B-}) + n_C RT(v_{C+} \ln \bar{\gamma}_{C+} + v_{C-} \ln \bar{\gamma}_{C-}) + \dots \\ & + n_R RT \ln \bar{\gamma}_R + n_S RT \ln \bar{\gamma}_S + \dots \\ & - n_B RT(v_{B+} \ln \gamma_{B+} + v_{B-} \ln \gamma_{B-}) - n_C RT(v_{C+} \ln \gamma_{C+} + v_{C-} \ln \gamma_{C-}) + \dots \\ & - n_R RT \ln \gamma_R - n_S RT \ln \gamma_S - \dots \end{aligned} \quad (24)$$

After introducing the mean activity coefficients defined by equation (13) we can write

$$-\Delta G_{dil}^E = \sum_i n_i RT v_i \ln \frac{\bar{\gamma}_{i\pm}}{\gamma_{i\pm}} + \sum_k n_k RT \ln \frac{\bar{\gamma}_k}{\gamma_k}. \quad (25)$$

The next step is the definition of activity coefficients normalized to the standard

state *b*

$$\gamma'_{i\pm} = \frac{\gamma_{i\pm}}{\bar{\gamma}_{i\pm}}; \quad [i = B, C, \dots] \quad (26)$$

$$\gamma'_k = \frac{\gamma_k}{\bar{\gamma}_k}; \quad [k = R, S, \dots]. \quad (27)$$

On combining equation (25)–(27) we arrive at the final, formally simple form

$$-\Delta G_{dil}^E = \sum_i n_i RT v_i \ln \gamma'_{i\pm} + \sum_k n_k RT \ln \gamma'_k. \quad (28)$$

Partial differentiation with respect to moles of component *i* and *k* (taking into account corresponding Gibbs–Duhem relations) leads further to

$$\left[\frac{\partial(-\Delta G_{dil}^E)}{\partial n_i} \right]_{T,P,n_j \neq i} = RT v_i \ln \gamma'_{i\pm} = RT v_i \ln \frac{\gamma_{i\pm}}{\bar{\gamma}_{i\pm}} \quad (29)$$

$$\left[\frac{\partial(-\Delta G_{dil}^E)}{\partial n_k} \right]_{T,P,n_j \neq k} = RT \ln \gamma'_k = RT \ln \frac{\gamma_k}{\bar{\gamma}_k}. \quad (30)$$

It is obvious that, if we know the concentration dependence of excess Gibbs energy of dilution ($-\Delta G_{dil}^E$), it is possible to express consistently the concentration dependence of activity coefficients normalized to the standard state “*b*” by a simple mathematical operation, *i.e.*, by partial differentiation with respect to moles of a component.

DISCUSSION

Equation (28) was derived by a general method for mixed solvent. If the solvent is the pure component *R*, its chemical potential in a very diluted solution is equal to that of the pure component *R*; since it holds

$$RT \ln \bar{\gamma}_R = 0; \quad [x_R \rightarrow 1] \quad (31)$$

we obtain by combining equations (27) and (31),

$$RT \ln \gamma'_R = RT \ln \gamma_R; \quad [x_k \neq R \rightarrow 0]. \quad (32)$$

Further, it can be shown that the process described by equation (23) can be replaced by four mixing steps:

a)

$$\begin{aligned} n_{\text{B}}(v_{\text{B}+}B_{+} + v_{\text{B}-}B_{-}) + n_{\text{C}}(v_{\text{C}+}C_{+} + v_{\text{C}-}C_{-}) + \dots + n_{\text{R}}R + n_{\text{S}}S + \dots = \\ = [n_{\text{B}}(v_{\text{B}+}B_{+} + v_{\text{B}-}B_{-}) + n_{\text{C}}(v_{\text{C}+}C_{+} + v_{\text{C}-}C_{-}) + \dots + \\ + n_{\text{R}}R + n_{\text{S}}S + \dots]; [T, P] \end{aligned} \quad (33)$$

$$\begin{aligned} (\Delta G_{\text{mix}}^{\text{E}})_{\text{a}} = RT(n_{\text{B}}v_{\text{B}} \ln \gamma_{\text{B}\pm} + n_{\text{C}}v_{\text{C}} \ln \gamma_{\text{C}\pm} + \dots + \\ + n_{\text{R}} \ln \gamma_{\text{R}} + n_{\text{S}} \ln \gamma_{\text{S}} + \dots) \end{aligned} \quad (34)$$

b)

$$\bar{n}_{\text{R}}R + \bar{n}_{\text{S}}S + \dots = [\bar{n}_{\text{R}}R + \bar{n}_{\text{S}}S + \dots]; [T, P] \quad (35)$$

$$(\Delta G_{\text{mix}}^{\text{E}})_{\text{b}} = RT(\bar{n}_{\text{R}} \ln \bar{\gamma}_{\text{R}} + \bar{n}_{\text{S}} \ln \bar{\gamma}_{\text{S}} + \dots) \quad (36)$$

c)

$$\begin{aligned} [n_{\text{B}}(v_{\text{B}+}B_{+} + v_{\text{B}-}B_{-}) + n_{\text{C}}(v_{\text{C}+}C_{+} + v_{\text{C}-}C_{-}) + \dots + \bar{n}_{\text{R}}R + \bar{n}_{\text{S}}S + \dots] = \\ = n_{\text{B}}(v_{\text{B}+}B_{+} + v_{\text{B}-}B_{-}) + n_{\text{C}}(v_{\text{C}+}C_{+} + v_{\text{C}-}C_{-}) + \dots + \\ + \bar{n}_{\text{R}}R + \bar{n}_{\text{S}}S + \dots; [T, P] \end{aligned} \quad (37)$$

$$\begin{aligned} -(\Delta G_{\text{mix}}^{\text{E}})_{\text{c}} = -RT(n_{\text{B}}v_{\text{B}} \ln \bar{\gamma}_{\text{B}\pm} + n_{\text{C}}v_{\text{C}} \ln \bar{\gamma}_{\text{C}\pm} + \dots + \\ + n_{\text{R}} \ln \bar{\gamma}_{\text{R}} + n_{\text{S}} \ln \bar{\gamma}_{\text{S}} + \dots) \end{aligned} \quad (38)$$

d)

$$[n_{\text{R}}R + n_{\text{S}}S + \dots] = n_{\text{R}}R + n_{\text{S}}S + \dots; [T, P] \quad (39)$$

$$(-\Delta G_{\text{mix}}^{\text{E}})_{\text{d}} = -RT(n_{\text{R}} \ln \gamma_{\text{R}} + n_{\text{S}} \ln \gamma_{\text{S}} + \dots). \quad (40)$$

By (algebraic) addition of contributions (34), (36), (38), and (40), we obtain the relation which is identical with equation (25)

$$\begin{aligned} (-\Delta G_{\text{dil}}^{\text{E}}) = (\Delta G_{\text{mix}}^{\text{E}})_{\text{a}} + (\Delta G_{\text{mix}}^{\text{E}})_{\text{b}} + (-\Delta G_{\text{mix}}^{\text{E}})_{\text{c}} + (-\Delta G_{\text{mix}}^{\text{E}})_{\text{d}} = \\ = \sum_{\text{i}} n_{\text{i}} RT v_{\text{i}} \ln \frac{\gamma_{\text{i}\pm}}{\bar{\gamma}_{\text{i}\pm}} + \sum_{\text{k}} n_{\text{k}} RT \ln \frac{\gamma_{\text{k}}}{\bar{\gamma}_{\text{k}}}. \end{aligned} \quad (41)$$

Equations (26), (27), and (41) are directions for mutual conversion of excess functions and activity coefficients related to different standard states. They facilitate the use of theoretical models and of different empirical procedures (*e.g.*, series expansions which take into account boundary conditions) in chemical-engineering practice.

The main advantage of procedures based on excess Gibbs energy of mixing or dilution is the possibility to deduce by a simple mathematical procedure – partial differentiation with respect to moles of a component – thermodynamically consistent equations expressing the dependence of activity coefficients of different types of all components on the composition of a multicomponent system.

APPENDIX

The composition of an electrolyte solution is frequently indicated by means of the molality, *i.e.*, as the number of moles of solute *per* one kg solvent. The molality tends to infinity as $x_i \rightarrow 1$ and is therefore unsuitable for high concentration region. (Typical examples are systems with strong mineral acids where a continuous set of liquid solutions from high dilution to the pure solute is accessible.)

In that case the mole fraction is used as concentration variable and activity *a* or *b* characterize the thermodynamic state of the system.

For this reason the mutual conversion of activity coefficients of different types is desirable. The particular conversion formulas are summarized in the following tables:

Variables Expressing the Composition of Electrolyte Solution

$$x_j = \frac{v_j n_j}{\sum_i v_i n_i + \sum_k n_k} \quad [i, j \dots \text{electrolytes}] \quad (A-1)$$

$$x_s = \frac{n_s}{\sum_i v_i n_i + \sum_k n_k} \quad [k, s \dots \text{non-electrolytes}] \quad (A-2)$$

$$x'_s = \frac{n_s}{\sum_k n_k} \quad (A-3)$$

$$m_j = \frac{v_j n_j}{(\sum_k n_k) \bar{M}} \quad \bar{M} = \sum_k x'_k M_k \quad (A-4)$$

M_k ... molecular mass of non-electrolyte *k* (in kg kmol⁻¹)

$$x_{j\pm}^{v_j} = \frac{(v_{j+} n_j)^{v_{j+}} (v_{j-} n_j)^{v_{j-}}}{(\sum_i v_i n_i + \sum_k n_k)^{v_j}} = v_{j+}^{v_{j+}} v_{j-}^{v_{j-}} \left(\frac{n_j}{\sum_i v_i n_i + \sum_k n_k} \right)^{v_j} \quad (A-5)$$

$$m_{j\pm}^{v_j} = \frac{(v_{j+} n_j)^{v_{j+}} (v_{j-} n_j)^{v_{j-}}}{[(\sum_k n_k) \bar{M}]^{v_j}} = v_{j+}^{v_{j+}} v_{j-}^{v_{j-}} \left[\frac{n_j}{(\sum_k n_k) \bar{M}} \right]^{v_j} \quad (A-6)$$

Mean Activity Coefficients of Ions of Electrolyte Related to Different Standard States

Definition

$$\begin{aligned}
 v_i \mu_{i\pm} &= v_i \mu_{i\pm}^0 + RT v_i \ln x_{i\pm} + RT v_i \ln \gamma_{i\pm} = \\
 &= v_i \mu_{i\pm}^{0'} + RT v_i \ln x_{i\pm} + RT v_i \ln \gamma'_{i\pm} = \\
 &= v_i \mu_{i\pm}^{0''} + RT v_i \ln m_{i\pm} + RT v_i \ln \gamma''_{i\pm}.
 \end{aligned}
 \tag{A-7}$$

Normalization

$$\begin{aligned}
 \gamma_{i\pm} &\rightarrow 1 \quad \text{as} \quad x_i \rightarrow 1 \\
 \gamma'_{i\pm} &\rightarrow 1 \quad \text{as} \quad \sum_i x_i \rightarrow 0 \\
 \gamma''_{i\pm} &\rightarrow 1 \quad \text{as} \quad \sum_i m_i \rightarrow 0.
 \end{aligned}
 \tag{A-8}$$

Mutual conversion

$$\gamma'_{i\pm} = \frac{\gamma_{i\pm}}{\lim_{\sum_i x_i \rightarrow 0} \gamma_{i\pm}} = \gamma''_{i\pm} (1 + \bar{M} \sum_i m_i)
 \tag{A-9}$$

$$\gamma_{i\pm} = \frac{\gamma'_{i\pm}}{\lim_{x_i \rightarrow 1} \gamma'_{i\pm}}.
 \tag{A-10}$$

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