ON THE ACTIVITY COEFFICIENTS OF COMPONENTS IN MOLTEN SALTS

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The classical activity coefficient is shown to be unsuitable for a characterization of the interaction of components in molten salts. A better approach consists in the use of the "global" activity coefficient by which the model activity must be multiplied to give the thermodynamic activity, or of the suggested "internal" activity coefficient by which the concentration variable is multiplied in the expression for the model activity to become identical with the thermodynamic activity. The conclusions are illustrated on a LiF–NaCl melt. The interrelation between the global and the internal activity coefficients is analyzed. It is suggested that the internal activity coefficient may find application is statistical modelling of melt systems.

Consider a binary liquid-phase system. The partial molar Gibbs energy of the *i*-th component obeys the well-known relationship

$$\bar{G}_i^l = G_i^{0,l} + RT \ln a_i = G_i^{0,l} + RT \ln \gamma_i x_i\,, \qquad (1)$$

where a_i is the thermodynamic activity of the *i*-th component in the solution, x_i is its mole fraction, and γ_i is its „classical" activity coefficient. The state of the pure liquid *i*-th substance at the temperature and pressure of the system is chosen as the standard state.

With respect to the nature of the interaction between the components in solution, the deviation is either positive, $\gamma_i > 1$, or negative, $\gamma_i < 1$. In the former case the interaction is weaker than as corresponds to the ideal solution and the partial molar enthalpy of mixing $\Delta\bar{H}_{i,\mathrm{mix}}^{l/0,l}$ is usually positive; in the latter case the reverse is true.

For a melt system in which the two components exist in the ionic state, the classical activity coefficient fails to serve as a quantity characterizing properly the interaction of the components.

Consider a melt system MA-NB$_2$ in which the components are completely dissociated to $M^+ + A^-$ and $N^{2+} + 2\,B^-$ ions. We shall express the component activities in terms of the models of Temkin[1] (Tem) and of Haase[2] (Ha), and of a universal model[3] (un). For the three models we have

$$a_{\mathrm{MA,Tem}} = x_{\mathrm{MA}}^2/(2 - x_{\mathrm{MA}}) \tag{2}$$

$$a_{\mathrm{MA,Ha}} = 4x_{\mathrm{MA}}^2/(3 - x_{\mathrm{MA}})^2 \tag{3}$$

$$a_{\mathrm{MA,un}} = x_{\mathrm{MA}}^3 . \tag{4}$$

The activity coefficients $\gamma_{\mathrm{MA}} = a_{\mathrm{MA}}/x_{\mathrm{MA}}$ then are

$$\gamma_{\mathrm{MA,Tem}} = x_{\mathrm{MA}}/(2 - x_{\mathrm{MA}}) \tag{5}$$

$$\gamma_{\mathrm{MA,Ha}} = 4x_{\mathrm{MA}}/(2 - x_{\mathrm{MA}})^2 \tag{6}$$

$$\gamma_{\mathrm{MA,un}} = x_{\mathrm{MA}}^2 . \tag{7}$$

These values differ from unity and depend on the mole fraction of the component. This is a consequence of the fact that in general the melt system does not obey, in the classical conception, Raoult's law or Henry's law, hence, the relations

$$\lim \mathrm{d}a_{\mathrm{MA}}/\mathrm{d}x_{\mathrm{MA}} = 1 (x_{\mathrm{MA}} \rightarrow 1) \tag{8}$$

$$\lim \mathrm{d}a_{\mathrm{MA}}/\mathrm{d}x_{\mathrm{MA}} = k_{\mathrm{H}} (x_{\mathrm{MA}} \rightarrow 0) \tag{9}$$

are not satisfied (k_{H} is Henry's constant). From this point of view, ionic systems are usually divided into two classes, *viz.* 1st kind systems or solutions for which relations (*8*) and (*9*) are valid, and 2nd kind systems or solutions for which one or both of Eqs (*8*) and (*9*) do not hold true[4,5].

The activity coefficient of a component in solution of a given composition depends appreciably on the model applied. Let us treat, for instance, a LiF + NaCl melt saturated with LiF at 1 043 K. For the activity of LiF we have

$$\ln a_{\mathrm{LiF}} = (\Delta H_{\mathrm{LiF}}^{\mathrm{f}}/R)\,(1/T_{\mathrm{LiF}}^{\mathrm{f}} - 1/T)\,, \tag{10}$$

where $\Delta H_{\mathrm{LiF}}^{\mathrm{f}}$ is the fusion enthalpy of LiF, 27·105 kJ mol^{-1}, and T^{f} is its fusion temperature, which according to JANAF (ref.[6]) is 1 121·3 K.

Since $T_{\mathrm{LiF}}^{\mathrm{f}} - T = 78{\cdot}3\ \mathrm{K} < 100\ \mathrm{K}$, the temperature dependence of $\Delta H_{\mathrm{LiF}}^{\mathrm{f}}$ can be neglected. At 1 043 K, Eq. (*10*) affords the value of $a_{\mathrm{LiF}} = 0{\cdot}800$. As is found in the phase diagram[7], x_{LiF} then is 0·850. Thus the classical activity coefficient is $\gamma_{\mathrm{LiF}} = a_{\mathrm{LiF}}/x_{\mathrm{LiF}} = 0{\cdot}9458$, indicating a negative departure from ideality ($\gamma < 1$).

Now, let us determine the activity of LiF based on some models. A condition imposed on a model expressing the activity of component *i* along the liquidus in a simple eutectic system $i - j$ is that it must satisfy the limiting criterion, *viz.*

$$\lim \mathrm{d}a_i/\mathrm{d}x_i = k^{\mathrm{St}}_{j,i}\,, \quad (x_i \to 1)\,, \tag{11}$$

where $k^{\mathrm{St}}_{j,i}$ is Stortenbeker's correction factor, numerically equal to the number of new particles that appear in the system of pure component *i* if one molecule of component *j* is introduced. In the LiF–NaCl system (LiF = *i*, NaCl = *j*), NaCl is supposed to be completely dissociated into Na^+ and Cl^- ions, hence $k^{\mathrm{St}}_{\mathrm{NaCl,LiF}} = 2$. This assumption can be verified by using experimental data. For $x_{\mathrm{LiF}} \to 1$, Eq. (*10*) gives

$$\lim \mathrm{d}T/\mathrm{d}x_{\mathrm{LiF}} = k^0_{\mathrm{LiF}} = \left[R(T^f_{\mathrm{LiF}})^2/\Delta H^f_{\mathrm{LiF}}\right] \lim \mathrm{d}a_{\mathrm{LiF}}/\mathrm{d}x_{\mathrm{LiF}} \tag{12}$$

or

$$k^0_{\mathrm{LiF}} = \left[R(T^f_{\mathrm{LiF}})^2/\Delta H^f_{\mathrm{LiF}}\right] k^{\mathrm{St}}_{\mathrm{NaCl,LiF}}\,. \tag{13}$$

Substituting for the slope k^0_{LiF} the experimentally found value[7] of approximately 800 K, we obtain $k^{\mathrm{St}}_{\mathrm{NaCl,LiF}} = 2{\cdot}07 \approx 2{\cdot}0$.

It can be demonstrated that the limiting criterion (*11*) is met by the models of Temkin and Haase as well as by the universal model, but not by the model of strictly regular solutions, in which

$$RT \ln \gamma_i = w(1 - x_i)^2\,, \tag{14}$$

and thus

$$a_{\mathrm{LiF}} = \gamma_{\mathrm{LiF}} x_{\mathrm{LiF}} = x_{\mathrm{LiF}} \exp\left[w(1 - x_{\mathrm{LiF}})^2/RT\right] \tag{15}$$

and for $x_{\mathrm{LiF}} \to 1$,

$$\lim \mathrm{d}a_{\mathrm{LiF}}/\mathrm{d}x_{\mathrm{LiF}} = 1\,, \tag{16}$$

hence a value different from $k^{\mathrm{St}}_{\mathrm{NaCl,LiF}}$. The model of strictly regular solutions is obviously unsuitable for the calculation of the activity of LiF along its liquidus in the system with NaCl, and will therefore be abandoned.

In the three models (mod) regarded, *i.e.*, Temkin's, Haasé's, and the universal model, the activity of LiF for $x_{\mathrm{LiF}} = 0{\cdot}850$ is $a_{\mathrm{LiF,mod}} = x^2_{\mathrm{LiF}} = 0{\cdot}7225$, and the activity coefficient,

$$\gamma_{\mathrm{LiF,mod}} = a_{\mathrm{LiF}}/a_{\mathrm{LiF,mod}} \tag{17}$$

is 1·1127 for all of the three models. An appreciable positive departure from ideality is apparent. Thus, for one and the same system we obtain a negative departure from ideality in the classical thermodynamic approach and a positive departure for the above three models. From the physical point of view, the latter models are preferred to the former model with regard to the fact that these satisfy the limiting criterion (*11*).

Numerically the activity and the activity coefficient of LiF in the system can be assessed also in a different manner. The composition of the liquid system is $x_{\mathrm{LiF}} = 0{\cdot}85$, $x_{\mathrm{NaCl}} = 0{\cdot}15$, $x_{\mathrm{LiF}} + x_{\mathrm{NaCl}} = 1$. Since, however, NaCl is present in the form of Na^+ and Cl^- ions, the formal composition of the solution should be regarded as 0·85 mol LiF, 0·15 mol Na^+, and 0·15 mol Cl^{-1} rather than 0·85 mol LiF + + 0·15 mol NaCl. The sum of moles then is 1·15 and the „true" mole fraction of LiF is $x^{\mathrm{tr}}_{\mathrm{LiF}} = 0{\cdot}85/1{\cdot}15 = 0{\cdot}7391$. This is a value approaching that of the model activity $a_{\mathrm{LiF,mod}} = 0{\cdot}7225$. The "true" activity coefficient then is $\gamma^{\mathrm{tr}}_{\mathrm{LiF}} = a_{\mathrm{LiF}}/x^{\mathrm{tr}}_{\mathrm{LiF}} = 0{\cdot}8039/0{\cdot}7391 = 1{\cdot}0877$, a value close to the above model value of 1·1127. The diluting effect of Na^+ and Cl^- ions on lithium fluoride results in a weakening of the interaction in the Li^+–F^- complexes playing the role of LiF molecules. This weakening of interaction (with respect to the pure LiF melt) is manifested by a positive departure from ideality (the activity coefficient of LiF is greater than unity).

The activity coefficient defined by Eq. (*17*) will be referred to as the "global" activity coefficient; it is frequently used in papers of Grjotheim and his research group[8] when treating Temkin's model.

We have

$$a_i = \gamma_{i,\mathrm{mod}} a_{i,\mathrm{mod}} ; \tag{18}$$

the global activity coefficient thus relates, in the role of a coefficient, the "model" activity $a_{i,\mathrm{mod}}$ with the thermodynamic activity.

In all of the three models under cnsideration the activity of the component is a function of its mole fraction solely, so it can be written as[9]

$$a_{i,\mathrm{mod}} = f(x_{i,\mathrm{mod}}) \tag{19}$$

and

$$a_i = \gamma_{i,\mathrm{mod}} \cdot f(x_{i,\mathrm{mod}}) . \tag{20}$$

Here $f(x_{i,\mathrm{mod}})$ denotes the mathematical operation that must be performed on x_i to convert it into the activity of component i in the model in question.

The departures from ideality can be corrected for also in another way. It is possible to determine the ideal mole fraction $x^{\mathrm{id}}_{i,\mathrm{mod}}$ having the property that the expression $f(x^{\mathrm{id}}_{i,\mathrm{mod}})$, which will be denoted $a^*_{i,\mathrm{mod}}$, will be identical with a_i. Generally, $x^{\mathrm{id}}_{i,\mathrm{mod}}$ is not identical with x_i; therefore it is convenient to introduce a new activity coefficient defined as

$$\Gamma_{i,\mathrm{mod}} = x^{\mathrm{id}}_{i,\mathrm{mod}}/x_i . \tag{21}$$

In order to distinguish this quantity from the global activity coefficient $\gamma_{i,\mathrm{mod}}$, it will be referred to as the „internal" activity coefficient.

We have then

$$a_i = a^*_{i,\mathrm{mod}} = f(x^{\mathrm{id}}_{i,\mathrm{mod}}) = f(\Gamma_{i,\mathrm{mod}} x_i)\,, \tag{22}$$

It will be clear that while by the global activity coefficient the entire function $a_{i,\mathrm{mod}}$ is multiplied, the quantity multiplied by the internal activity coefficient is the argument of the function $f(x_i)$. As follows from the definitions of the two types of activity coefficient (Eqs (*18*) and (*21*)), the internal activity coefficient is more closely related to the classical thermodynamic activity coefficient, $\gamma_i = a_i/x_i = x^{\mathrm{id}}_i/x_i$, than the global activity coefficient.

From the physical point of view, the global activity coefficient $\gamma_{i,\mathrm{mod}}$ characterizes the departure of the actual behaviour of component *i*, as a whole in the system under study, from the „ideal" behaviour within the scope of the model applied. The internal activity coefficient, on the other hand, characterizes the departure of the actual interaction from the „ideal" interaction as postulated by the model. The species of component *i* are usually ions, simple or complex, „produced" by electrochemical or thermal dissociation, or also molecules emerging from the partial thermal equilibrium dissociation of substance *i* in the solution. From this viewpoint, the internal activity coefficient can be expected to find application in the statistical treatment of melt system models.

There is a functional interdependence between the activity coefficients γ and Γ, as will be demonstrated on the system MA-NB$_2$. The above three models – Temkin's, Haase's, and the universal model – will be treated, and only component MA will be considered.

For Temkin's model we have

$$a_{\mathrm{MA}} = \gamma_{\mathrm{MA,Tem}} a_{\mathrm{MA,Tem}} = \gamma_{\mathrm{MA,Tem}} x^2_{\mathrm{MA}}/(2 - x_{\mathrm{MA}}) \tag{23}$$

and at the same time,

$$a_{\mathrm{MA}} = a^*_{\mathrm{MA,Tem}} = (\Gamma_{\mathrm{MA,Tem}} x_{\mathrm{MA}})^2/(2 - \Gamma_{\mathrm{MA,Tem}} x_{\mathrm{MA}})\,. \tag{24}$$

By eliminating a_{MA} from this system of equations we obtain a quadratic equation with respect to $\Gamma_{\mathrm{MA,Tem}}$, the solution of which is

$$\Gamma_{\mathrm{MA,Tem}} = -Z_{\mathrm{Tem}} + (Z^2_{\mathrm{Tem}} + 4Z_{\mathrm{Tem}}/x_{\mathrm{MA}})^{1/2}\,, \tag{25}$$

where

$$Z_{\mathrm{Tem}} = -\gamma_{\mathrm{MA,Tem}} x_{\mathrm{MA}}/2(2 - x_{\mathrm{MA}}) \tag{26}$$

(the other root lacks physical meaning).

Analogously in Haase's model,

$$\Gamma_{\mathrm{MA,Ha}} = -Z_{\mathrm{Ha}} + (Z_{\mathrm{Ha}}^2 + 3Z_{\mathrm{Ha}}/x_{\mathrm{MA}})^{1/2} \tag{27}$$

where

$$Z_{\mathrm{Ha}} = -3\gamma_{\mathrm{MA,Ha}}x_{\mathrm{MA}}/[(3 - x_{\mathrm{MA}})^2 - \gamma_{\mathrm{MA,Ha}}x_{\mathrm{MA}}^2]\,; \tag{28}$$

and in the universal model,

$$\Gamma_{\mathrm{MA,un}} = \gamma_{\mathrm{MA,un}}^{q}\,, \tag{29}$$

where

$$q = 1/k_{\mathrm{NB_2,MA}}^{\mathrm{St}}\,. \tag{30}$$

The activities and the activity coefficients $\gamma_{i,\mathrm{mod}}$ and $\Gamma_{i,\mathrm{mod}}$ for the three models and some system types are given in Table I.

The utility of the internal activity coefficient will be illustrated on the example of the systems MA–NB_2 and MA–NB_4 treated in terms of Haase's model. Let the global activity coefficients of component MA for a mole fraction if $x_{\mathrm{MA}} = 0{\cdot}9000$. be identical in the two systems, $\gamma_{\mathrm{MA,Ha}} = 1{\cdot}3878$ (see Table I, system MA–NB_4) This means that in the two systems the component MA departs from ideality in the same manner, as postulated by Haase's model. The internal activity coefficient for $x_{\mathrm{MA}} = 0{\cdot}9000$ is $\Gamma_{\mathrm{MA,Ha}} = 1{\cdot}1183$ for system MA–NB_2 and 1·0747 for system

TABLE I

Activities and activity coefficients of the component MA in the various models; $x_{\mathrm{MA}} = 0{\cdot}9000$, $a_{\mathrm{MA}} = 0{\cdot}8500$

System type	Activities and activity coefficients								
	Temkin's model			Haase's model			universal relation		
	a	γ	Γ	a	γ	Γ	a	γ	Γ
MA–MB	0·9000	0·9444	0·9444	0·9000	0·9444	0·9444	0·9000	0·9444	0·9444
MA–MB_2	0·8182	1·0389	1·0210	0·8163	1·0413	1·0218	0·8100	1·0494	1·0244
MA–MB_3	0·7500	1·1333	1·0494	0·7438	1·1428	1·0504	0·7290	1·1660	1·0525
MA–MB_4	0·6923	1·2278	1·0642	0·6805	1·2490	1·0652	0·6561	1·2955	1·0669
MA–NB	0·8100	1·0494	1·0244	0·8100	1·0494	1·0244	0·8100	1·0494	1·0244
MA–NB_2	0·7364	1·1543	1·0515	0·7347	1·1569	1·0518	0·7290	1·1660	1·0525
MA–NB_3	0·6750	1·2593	1·0656	0·6694	1·2698	1·0660	0·6561	1·2955	1·0669
MA–NB_4	0·6231	1·3642	1·0742	0·6125	1·3878	1·0747	0·5905	1·4394	1·0756

MA–NB_4. It can be thus inferred that in the former system the interaction of M^+ and A^- ions is appreciably lower, of that from the point of view of the interaction this system departs more from the ideal behaviour described by Haase's model, than the latter system. Such information, which is of importance in the structure elucidation of melt systems, cannot be derived from the global activity coefficient.

Two remarks in conclusion. First, the systems considered are ionic, but the conclusions arrived at hold also if the solution comprises neutral species only (*e.g.*, molecules) or both ions and neutral species; naturally, it is necessary to use a model in which allowance is made for this fact (Temkin's model, for instance, is here inapplicable). Second, while in the system considered the activity of a component depends on the mole fraction, it is independent of temperature. Should $a_{i,\mathrm{mod}}$ be a function of both, $a_{i,\mathrm{mod}} = f(x_{i,\mathrm{mod}}; T)$, the internal activity coefficient could only serve for a correction of the concentration coordinate, $a = f(\Gamma_{i,\mathrm{mod}} x_i; T)$.

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