Determination of the excess thermodynamic functions of components of binary salt melts in infinitely diluted solution on the basis of the ideal associated solution model

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*Dedicated to Associate Professor K. Matiašovský, DrSc.,
in honour of his 60th birthday*

The authors pointed out that beside the heteronuclear associates, type A_IB_J, the homonuclear associates, types A_i and B_j, are also necessary for the adequate thermodynamic description of the molten salt systems. With any number of associates, types A_i, B_j, and A_IB_J, being considered, the explicit formulas for calculation of the partial molar excess thermodynamic functions extrapolated to the infinitely diluted solution for components A and B were obtained in the system A—B.

The trial calculations have proved that it is necessary to consider the homonuclear associates, types A_i and B_j, not only from the theoretical point of view, but also that of the practice even if the stability of the heteronuclear associates, type A_IB_J, is much greater (with more orders of magnitude) than that of the homonuclear ones. The possible methods of determination of the model parameters have been also discussed.

In order to describe the thermodynamic functions of liquid mixtures *Dolezalek* [1] firstly assumed that the interactions between the constituting components result in associates. *Prigogine* and *Defay* [2] created the theory of associated solution models, which was used until the end of the sixties exclusively for the thermodynamic description of systems at low temperatures, mainly for solutions containing organic components.

The application of the associated mixture model to the molten salts started in the last 20 years [3—11]. In the early seventies the "ionic" form of the associated solution models was developed [3—5], in which the excess mixing functions were calculated related to the ideal ionic Temkin's model [12]. The common feature of these models in the $M'X—M''X_2$ systems (where M'' is a bivalent metal and X is a halogen element) was the assumption of the existence of $M''X_4^{2-}$ complex anions (associates), when the $M''X_2$ content was low. According to *Pelton* [3] this complex anion exists in the whole concentration range, moreover, the pure $M''X_2$ melt consists of 50 % $M''X_4^{2-}$ anions and 50 % M''^{2+} cations. The model of *Flengas* and *Kucharski* [4] differs from that describing the

pure $M''X_2$ melt in entirely dissociated form (M''^{2+}, X^-), while *Maroni* and his coworkers [5] supposed the existence of "polymers" $(M''X_2)_p$ in pure phase $M''X_2$.

The spectroscopic investigation of *Volkov* [13—15] and other researchers proved unambiguously that $M''X_4^{2-}$ complex anions are formed really in the mole fraction interval $0 < x(M''X_2) < 0.33$. At the same time it was also proved experimentally that in a given $M'X$—$M''X_2$ system the stability (and the thermodynamic and kinetic parameters) of the $M''X_4^{2-}$ complex anions is determined by the interactions arising between this complex anion and the M'^+ cations settled in the outer ionic sphere. It follows from this that the models may be and must be constructed on the basis of the $M_2'[M''X_4]$ heteronuclear complex instead of the $M''X_4^{2-}$ complex anion, and so, if $M'X$ is denoted as A and $M''X_2$ as B, the model applied to the classic, "molecular" form of the model A—A_2B—B. So, the associated solution model was applied to the molten salts in this form [6—11] from the middle of the seventies and, in this manner, the mathematical apparatus used for calculations became simpler, as well.

The researchers applied the ideal [6—8, 10], or in some cases the regular [9, 11] associated solution models to molten salt systems. The use of the latter one is advantageous especially in cases, when the mixing of the components is restricted in the melt phase, *i.e.* $\partial^2 G/\partial x^2 < 0$ (as *e.g.* in the LiCl—KCl—AlCl$_3$ system [9]); and $\partial^2 G_i^E/\partial x_i^2 < 0$ (as *e.g.* in the MCl—AlCl$_3$ system where i = AlCl$_3$ [11]), because from the ideal associated solution model the values of both $\partial^2 G/\partial x^2$ and $\partial^2 G_i^E/\partial x_i^2$ can be exclusively positive.

But, in general, the use of the ideal associated solution model is more advantageous, because its mathematical apparatus is more easy to survey and the equilibrium constants connected with the formation of complex compounds can be determined independently of the model. The experimental data can be described by both these methods using the same number of parameters nearly with the same accuracy (see *e.g.* the ideal associated mixture model of *Wasai* and *Mukai* [16], as well as the regular associated one of *Sommer* [17] for molten metallic systems). In the ideal models the secondary effects are approached by means of a less stable complex instead of the "interaction parameters" used in the regular models. In the systems investigated by the authors this less stable complex is the AB in general, and the more stable one is A_2B [6—8]. We can say formally that AB is the product of the particular dissociation of the A_2B complex.

Let us now proceed to discussing the concentration range being rich in $M''X_2$. According to [13—15] the heteronuclear complexes are turning more and more into multi-homonuclear ones in the mole fraction interval $0.33 < x(M''X_2) < 1$, *i.e.* the following complexes appear: $M_2'[M_2''X_6]$, $M_{n<2}'[M_p''X_{2p+n}]$. At the same time, $(M''X_2)_p$ polymeric system can be found in the pure melt phase, in which the two neighbouring M''^{2+} ions are connected by X^- bridges.

According to *Volkov* [13, 15], the notion of thermodynamic and kinetic constants becomes meaningless for these multi-homonuclear complexes. His opinion was supported by experimental results, that the values of various structure-sensitive parameters (activity coefficient γ_i, magnetic susceptibility χ_m, molar absorption coefficient ε and the half width of band of electronic absorption spectra $\delta_{1/2}$) are not constant in the given concentration range in contrast to the diluted $M''X_2$ solutions.

According to our opinion the conclusion obtained from these experimental data is not acceptable. Namely, the γ_i, χ_m, ε, and $\delta_{1/2}$ values are constant in the diluted $M''X_2$ solutions only because more than 90 % of the $M''X_2$ component is only found in one type of complexes: $M_2'[M''X_4]$. On the other hand, in the concentrated solution of $M''X_2$ one can find various $M'_{n<2}[M''_pX_{2p+n}]$ and $(M''X_2)_p$ complexes the stabilities of which differ from each other, but not very much. So, the values of such macroscopic parameters as γ_i, χ_m, ε, and $\delta_{1/2}$ will be changed in the case of the changing of the $M''X_2$ concentration even, if we suppose that all the complexes denoted by concrete parameters p are imagined as individual ones with their own thermodynamic and kinetic constants, and, consequently, they are in equilibrium with each other and with the monomers $M''X_2$. So, according to our opinion, there is a reason for speaking about the equilibrium concentration of the monomers and of various B_p polymers in the pure $M''X_2$ phase at given temperature. The proportion of the monomers will increase and the average length of the "polymers" (parameter p) will decrease elevating the temperature.

The same conception is related to both pure melt phases $M''X_2$ and $M'X$. The formation of homonuclear complexes in alkali-halide melts has been supposed by *Smirnov* and coworkers [18] in their "autocomplex" model. Since then in the last 20 years the existence of the $M_n'[M'X_{n+1}]$ "autocomplexes" has been proved as a result of a lot of experiments, and their supposition has also been proved that energetically the formation of the $n + 1 = 4$ complexes, *i.e.* the tetrahedral configuration, is the most probable one [19].

Consequently, on the basis of experimental results in the $M'X—M''X_2$, *i.e.* A—B systems, it seems to be reasonable to take into consideration the homonuclear complexes (A_n and B_m) in addition to the heteronuclear A_nB_m ones, as well. At the same time in the publications using the molecular form of the associated mixture models [6—11] the homonuclear complexes have not been considered yet. Moreover, the authors started from the values of partial thermodynamic functions extrapolated to the infinitely diluted solutions of the A or B (eventually both) components for the empirical determination of the equilibrium values of heteronuclear complexes notwithstanding the fact that, as we can see later, these values are depending on the equilibrium constants not only of the complexes A_nB_m but also of the A_n and B_m type. If we do not take into consideration the effect of the A_n and B_m complexes the calculated by this manner equilibrium

constants referring to the A_nB_m complexes will differ from that measured or calculated independently of the thermodynamic mixing data. It means that the data used in the model and the real ones will always be inconsistent.

In order to solve this contradiction in this paper — as a first step — the authors make an attempt to determine the values of the various partial molar excess thermodynamic functions extrapolated to the infinitely diluted solution using the ideal associated solution model, taking into consideration both homonuclear (A_n, B_m) and heteronuclear (A_nB_m) complexes. Consequently we will consider the equilibrium system which contains complexes of optional quality and quantity, which are in equilibrium with each other and with the A_1 and B_1 monomers. The model of the system is

$$A_1; \quad \sum_{i=2}^{n} A_i; \quad \sum_{I=1}^{N} \sum_{J=1}^{M} A_I B_J; \quad \sum_{j=2}^{m} B_j; \quad B_1 \tag{1}$$
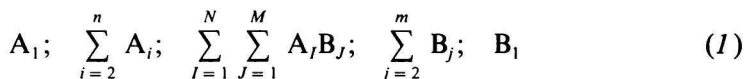
Determination of the equilibrium mole fractions in pure phases A and B

Let us consider a pure phase A of n_A quantity in which $(n-1)$ homonuclear A_i complexes are present beside the A_1 monomers. The equation

$$n_A = n_{A_1}^0 + \sum_{i=2}^{n} i n_{A_i}^0 \tag{2}$$

connects the equilibrium amounts of substances $n_{A_i}^0$ with n_A. All the complexes being in equilibrium with all the other $(n-2)$ complexes and with monomers A_1, the following, altogether $(n-1)$ independent chemical equilibriums can be written

$$i A_1 = A_i \tag{3}$$

in order to characterize the equilibrium of the system. As the condition of the $(n-1)$ equilibrium, $(n-1)$ independent mathematical equations must be written in the following way

$$K_{A_i} = x_{A_i}^0 / (x_{A_1}^0)^i \tag{4}$$

where K_{A_i} is the equilibrium constant of the A_i complex determined by equilibrium (3), and $x_{A_i}^0$ is the equilibrium mole fraction of the A_i complex in pure phase A.

So, n unknown quantities, which are the equilibrium mole fractions of the monomer and the complexes, can be found in the system of equations constructed from eqn (2) and from $(n-1)$ eqns of (4) type. If the values of equilibrium constants K_{A_i} as parameters are known, the equilibrium mole fractions in pure phase A can be determined.

Analogously, we need the values of equilibrium constants of $(m-1)$ B_j complexes for the calculation of the equilibrium mole fractions of the monomer B_1 and $(m-1)$ homonuclear complexes B_j in the pure phase B of n_B quantity. In this case eqns $(2-4)$ will be modified in the following way

$$n_B = n_{B_1}^0 + \sum_{j=2}^{m} j n_{B_j}^0 \qquad (2a)$$

$$j B_1 = B_j \qquad (3a)$$

$$K_{B_j} = x_{B_j}^0 / (x_{B_1}^0)^j \qquad (4a)$$

Determination of the equilibrium mole fractions in the A—B system

If we mix $\{n_A\}$ mol of pure phase A and $\{n_B\}$ mol of pure phase B we get a melt, the composition of which will be determined by eqn (1). Let us denote the equilibrium amounts of substances in such an equilibrium system with n_k, where the index k denotes any of the components, listed in eqn (1).

The following balance equations are valid between the initial and equilibrium amounts of substances

$$n_A = n_{A_1} + \sum_{i=2}^{n} i n_{A_i} + \sum_{I=1}^{N} \sum_{J=1}^{M} I n_{A_I B_J}$$
$$\qquad (5)$$
$$n_B = n_{B_1} + \sum_{j=2}^{m} j n_{B_j} + \sum_{I=1}^{N} \sum_{J=1}^{M} J n_{A_I B_J}$$

The total amount of substances of the equilibrium solution is

$$n_s = n_{A_1} + n_{B_1} + \sum_{i=2}^{n} n_{A_i} + \sum_{j=2}^{m} n_{B_j} + \sum_{I=1}^{N} \sum_{J=1}^{M} n_{A_I B_J} \qquad (6)$$

In this case the equilibrium mole fraction of component k can be expressed as

$$x_k = \frac{n_k}{n_s} \qquad (7)$$

The complexes are in equilibrium both with each other and the monomers in the system, therefore $N M$ independent chemical equilibriums of

$$I A_1 + J B_1 = A_I B_J \qquad (8)$$

type can be written beside $(n-1)$ eqns of type (3) and $(m-1)$ eqns of type $(3a)$. The conditions of equilibriums of types (3), $(3a)$, and (8) are as follows

$$K_{A_i} = x_{A_i} / (x_{A_1})^i \qquad (9)$$

$$K_{B_j} = x_{B_j}/(x_{B_1})^j \tag{10}$$

$$K_{A_I B_J} = x_{A_I B_J}/(x_{A_1})^I (x_{B_1})^J \tag{11}$$

The integral molar excess mixing functions

When the mixing process of components A and B is accompanied by formation of heteronuclear and by dissociation of homonuclear complexes the integral molar excess mixing functions ΔY^E contain two terms

$$\Delta Y^E = \Delta Y_{ass} + \Delta Y^E_{conf} \tag{12}$$

where ΔY_{ass} is connected with the formation and dissociation of the associates, and ΔY^E_{conf} is connected with the configuration entropy.

The ΔY^E functions, the values of which are equal to zero for the ideal solutions (e.g. if $Y = H$, or V, or $(\partial H/\partial T)_p = C_p$, or $(\partial V/\partial T)_p = \beta$, etc.), do not contain a configuration term and in this case $\Delta Y^E = \Delta Y_{ass}$.

Firstly, let us examine the ΔY_{ass} term of eqn (12). A two-phase system is given. One of the phases contains $\{n_A\}$ mol of pure component A, the other one contains $\{n_B\}$ mol of pure component B. The integral function, which characterizes the initial state of mixing process, related to one mole of the system can be written as follows

$$\Delta Y_{ass,init} = \frac{1}{n_A + n_B} \left[\sum_{i=2}^{n} n^0_{A_i} \Delta Y^0_{A_i} + \sum_{j=2}^{m} n^0_{B_j} \Delta Y^0_{B_j} \right] \tag{13}$$

The final state of mixing process can be characterized by the following integral function

$$\Delta Y_{ass,fin} = \frac{1}{n_A + n_B} \left[\sum_{i=2}^{n} n_{A_i} \Delta Y^0_{A_i} + \sum_{I=1}^{N} \sum_{J=1}^{M} n_{A_I B_J} \Delta Y^0_{A_I B_J} + \sum_{j=2}^{m} n_{B_j} \Delta Y^0_{B_j} \right] \tag{14}$$

where

$$\Delta Y^0_{A_i} = Y^0_{A_i} - i\,Y^0_A$$

$$\Delta Y^0_{B_j} = Y^0_{B_j} - j\,Y^0_B \tag{15}$$

$$\Delta Y^0_{A_I B_J} = Y^0_{A_I B_J} - (I\,Y^0_A + J\,Y^0_B)$$

It follows from eqn (15) that $\Delta Y^0_{A_1} = \Delta Y^0_{B_1} = 0$, even if A or B are not elements but compounds. That is why we have to speak about the "associate quantities of formation" which are not equal to the common thermodynamic functions of formation from elements.

The change of the integral quantity ΔY_{ass}, accompanied by the mixing process, can be calculated as the difference between eqns (14) and (13).

Let us now examine the second term of eqn (12), the configuration entropy. The integral configuration entropy terms, which characterize the initial and final states of mixing process, can be written as follows

$$\Delta S^{\text{E}}_{\text{conf, init}} = \frac{-R}{n_{\text{A}} + n_{\text{B}}} \left[\sum_{i=1}^{n} n^0_{\text{A}_i} \ln x^0_{\text{A}_i} + \sum_{j=1}^{m} n^0_{\text{B}_j} \ln x^0_{\text{B}_j} \right] \tag{16}$$

$$\Delta S^{\text{E}}_{\text{conf, fin}} = \frac{-R}{n_{\text{A}} + n_{\text{B}}} \left[\sum_{i=1}^{n} n_{\text{A}_i} \ln x_{\text{A}_i} + \sum_{I=1}^{N} \sum_{J=1}^{M} n_{\text{A}_I\text{B}_J} \ln x_{\text{A}_I\text{B}_J} + \sum_{j=1}^{m} n_{\text{B}_j} \ln x_{\text{B}_j} \right] +$$
$$+ R(x_{\text{A}} \ln x_{\text{A}} + x_{\text{B}} \ln x_{\text{B}}) \tag{17}$$

The last two terms of eqn (17) are equal to the configuration entropy of the ideal A—B solution. The requested quantity $\Delta S^{\text{E}}_{\text{conf}}$ can be obtained as the difference between eqns (17) and (16). The configuration term of the integral molar excess Gibbs function can be calculated by the well-known equation

$$\Delta G^{\text{E}}_{\text{conf}} = -T \, \Delta S^{\text{E}}_{\text{conf}} \tag{18}$$

Partial molar excess functions of the component A *concerning the infinitely diluted solution*

Later on we are going to deal with the requested equations only for the component A. The functions for the component B can be obtained analogously (see below eqns $(30, 31)$).

If the integral molar excess mixing function ΔY^{E} is known, the partial molar excess function for component A can be obtained by the following well-known equation

$$\Delta Y^{\text{E}}_{\text{A}} = \Delta Y^{\text{E}} + (1 - x_{\text{A}}) \frac{\partial \Delta Y^{\text{E}}}{\partial x_{\text{A}}} \tag{19}$$

If $x_{\text{A}} \to 0$ then $\Delta Y^{\text{E}} \to 0$ as well, and the requested quantity can be defined as follows

$$\Delta Y^{\text{E}\infty}_{\text{A}} = \lim_{x_{\text{A}} \to 0} \frac{\partial \Delta Y^{\text{E}}}{\partial x_{\text{A}}} \tag{20}$$

Let us introduce the following quantities

$$\nu_k = \lim_{x_{\text{A}} \to 0} \frac{\partial \left(\dfrac{n_k}{n_{\text{A}} + n_{\text{B}}} \right)}{\partial x_{\text{A}}} \qquad \zeta_k = \lim_{x_{\text{A}} \to 0} \frac{\partial \left(\dfrac{n_k \ln x_k}{n_{\text{A}} + n_{\text{B}}} \right)}{\partial x_{\text{A}}} \tag{21}$$

On the basis of comparison of eqns (12, 13, 14, 16, 17, and 20) it follows that in order to determine the requested quantities $\Delta Y_A^{E\infty}$ in explicit form the quantities v_k and ζ_k must be determined first.

Determination of $\Delta Y_{A,\text{ass}}^{E\infty}$

Using eqns (2—11) and definition (21) the following expressions for v_k were obtained after circuitous calculations

$$v_{A_i} = 0$$

$$v_{A_i}^0 = n_{A_i}^{01}$$

$$v_{A_I B_J} = \begin{cases} 0 & \text{if } I > 0 \\ CC_J & \text{if } I = 0 \end{cases} \tag{22}$$

$$v_{B_j} = -EE_j - x_{B_j}^0 \frac{F}{D}$$

$$v_{B_j}^0 = -n_{B_j}^{01}$$

where $v_{A_i}^0$ and $v_{B_j}^0$ are the quantities according to $n_{A_i}^0$ and $n_{B_j}^0$ occurring in eqn (13) and connected with the pure phases; $n_{A_i}^{01}$ and $n_{B_j}^{01}$ are the equilibrium amounts of substances of complexes A_i and B_j in 1 mol of pure phases A and B, respectively.

$$C_J = K_{AB_J}(x_{B_1}^0)^J \qquad CC_J = C_J / \left(1 + \sum_{J=1}^{M} C_J\right)$$

$$D = 1 + \sum_{j=2}^{m} (j-1) x_{B_j}^0$$

$$E_j = K_{B_j} j (x_{B_1}^0)^{j-1} \qquad EE_j = E_j / \left(1 + \sum_{j=2}^{m} E_j\right) \tag{23}$$

$$F = \sum_{J=1}^{M} J CC_J - \sum_{j=2}^{m} (j-1) EE_j$$

Using eqns (13, 14, 20—23) one can obtain for the requested quantity the following expression

$$\Delta Y_{A,\text{ass}}^{E\infty} = -\sum_{i=2}^{n} n_{A_i}^{01} \Delta Y_{A_i}^0 + \sum_{J=1}^{M} CC_J \Delta Y_{AB_J}^0 + \sum_{j=2}^{m} \left(n_{B_j}^{01} - EE_j - x_{B_j}^0 \frac{F}{D}\right) \Delta Y_{B_j}^0 \tag{24}$$

From eqn (24) one can conclude that the values of $\Delta Y_{A,\,ass}^{E\infty}$ can only be influenced by the heteronuclear associates 1 mol of which contains 1 mol of component A.

For $Y = H$ and S, respectively, the ΔY_k^0 values defined by eqn (15) will be negative for all thermodynamically stable associates, because their association heat of formation and association entropy change of formation are negative owing to their stability. Consequently it follows from eqns (23, 24) that the values of the functions ΔH_A^∞ and $\Delta S_{A,\,ass}^{E\infty}$ will be shifted to the positive direction by homonuclear associates, types A_i and B_j, and to the negative direction by heteronuclear associates, type AB_J.

<p align="center">Determination of $\Delta S_{A,\,conf}^{E\infty}$</p>

On the basis of eqns (2—11 and 21—23) the following expressions were obtained in a very circuitous way for the coefficient ζ_k

$$\zeta_A = 1 + \ln x_A$$

$$\zeta_B = -1$$

$$\zeta_{A_1} = (1 + \ln x_{A_1})/\left(1 + \sum_{J=1}^{M} C_J\right)$$

$$\zeta_{A_i} = 0 \qquad (\text{if } i > 1)$$

$$\zeta_{A_i}^0 = n_{A_i}^{01} \ln x_{A_i}^0 \qquad (\text{if } i \geq 1)$$

$$\zeta_{A_J B_J} = \begin{cases} 0 & (\text{if } I > 1) \\ C C_J (1 + \ln x_{AB_J}) & (\text{if } I = 1) \end{cases} \qquad (25)$$

$$\zeta_{B_1} = \left[\sum_{j=2}^{m} EE_j - 1 - x_{B_1}^0 \frac{F}{D}\right] \ln x_{B_1}^0 + \sum_{j=2}^{m} EE_j - 1$$

$$\zeta_{B_j} = -\left[EE_j + x_{B_j}^0 \frac{F}{D}\right] \ln x_{B_j}^0 - EE_j \qquad (\text{if } j > 1)$$

$$\zeta_{B_j}^0 = -n_{B_j}^{01} \ln x_{B_j}^0 \qquad (\text{if } j \geq 1)$$

Taking into consideration that

$$\lim_{x_A \to 0} (x_{A_1}/x_A) = D/\left(1 + \sum_{J=1}^{M} C_J\right)$$

$$\lim_{x_A \to 0} (x_{AB_J}/x_A) = D C C_J \qquad (26)$$

the following expression for partial excess configuration entropy was obtained

$$\Delta S_{A,\,conf}^{E\infty} = -R\left\{\ln D - \ln\left(1 + \sum_{J=1}^{M} C_J\right) + \sum_{J=1}^{M} CC_J \ln C_J - \sum_{i=1}^{n} n_{A_i}^{01} \ln x_{A_i}^{0} + \right.$$

$$\left. + \left[\sum_{j=2}^{m} EE_j + n_{B_1}^{01} - 1 - x_{B_1}^{0}\frac{F}{D}\right]\ln x_{B_1}^{0} - \sum_{j=2}^{m}\left[EE_j + x_{B_j}^{0}\frac{F}{D} - n_{B_j}^{01}\right]\ln x_{B_j}^{0}\right\} \quad (27)$$

where R is the universal gas constant.

It follows from eqn (27) that the value of $\Delta S_{A,\,conf}^{E\infty}$ will be shifted to the positive direction by the heteronuclear associates, type AB_J, and to the negative direction by the homonuclear associates, types A_i and B_j.

Determination of the activity coefficient for component A *extrapolated to the infinitely diluted solution*

Using eqns (12) and (18) and the well-known relation for activity coefficients the following expression can be written

$$RT \ln \gamma_A^{\infty} = \Delta G_A^{E\infty} = \Delta G_{A,\,ass}^{\infty} - T\,\Delta S_{A,\,conf}^{E\infty} \quad (28)$$

Using eqns $(23, 24,$ and $27)$, after the reductions the following rather simple expression can be obtained for γ_A^{∞}

$$\gamma_A^{\infty} = \frac{D}{x_{A_1}^{0}\left(1 + \sum_{J=1}^{M} C_J\right)} \quad (29)$$

From eqn (29) it follows that heteronuclear associates, type AB_J, cause the negative, while homonuclear associates, types A_i and B_j, cause the positive deviation from the Raoult's law.

If the solution contains only homonuclear associates, types A_i and B_j, and their stabilities and stoichiometry are equal, the associates A_i increase the value γ_A^{∞} more than the associates B_j do, and the more they do so, the higher are their stabilities. If the system contains heteronuclear associates, type AB_J, as well, the influence of associates B_j becomes stronger and the higher are the values of K_{AB_J} and J.

The excess functions for the infinitely diluted solution of component B

Since the $\Delta Y_B^{E\infty}$ functions can be obtained analogously as the $\Delta Y_A^{E\infty}$ ones, we give here only the final equations for component B, which are necessary for the calculations

$$\Delta Y_{\mathrm{B, ass}}^{\mathrm{E}\infty} = -\sum_{j=2}^{m} n_{\mathrm{B}_j}^{01} \Delta Y_{\mathrm{B}_j}^0 + \sum_{I=1}^{N} CC_I \Delta Y_{\mathrm{A}_I\mathrm{B}}^0 + \sum_{i=2}^{n} \left[n_{\mathrm{A}_i}^{01} - EE_i - x_{\mathrm{A}_i}^0 \frac{F'}{D'} \right] \Delta Y_{\mathrm{A}_i}^0$$

$$\Delta S_{\mathrm{B, conf}}^{\mathrm{E}\infty} = -R \left\{ \ln D' - \ln\left(1 + \sum_{I=1}^{N} C_I\right) + \sum_{I=1}^{N} CC_I \ln C_I - \sum_{j=2}^{m} n_{\mathrm{B}_j}^{01} \ln x_{\mathrm{B}_j}^0 + \right.$$

$$\left. + \left[\sum_{i=2}^{n} EE_i + n_{\mathrm{A}_1}^{01} - 1 - x_{\mathrm{A}_1}^0 \frac{F'}{D'} \right] \ln x_{\mathrm{A}_1}^0 - \sum_{i=2}^{n} \left[EE_i + x_{\mathrm{A}_i}^0 \frac{F'}{D'} - n_{\mathrm{A}_i}^{01} \right] \ln x_{\mathrm{A}_i}^0 \right\} \quad (30)$$

$$\gamma_{\mathrm{B}}^{\infty} = \frac{D'}{x_{\mathrm{B}_1}^0 \left(1 + \sum_{I=1}^{N} C_I\right)}$$

where

$$C_I = K_{\mathrm{A}_I\mathrm{B}} (x_{\mathrm{A}_1}^0)^I \qquad CC_I = C_I \bigg/ \left(1 + \sum_{I=1}^{N} C_I\right)$$

$$D' = 1 + \sum_{i=2}^{n} (i-1) x_{\mathrm{A}_i}^0$$

$$E_i = K_{\mathrm{A}_i} i (x_{\mathrm{A}_1}^0)^{i-1} \qquad EE_i = E_i \bigg/ \left(1 + \sum_{i=2}^{n} E_i\right) \qquad (31)$$

$$F' = \sum_{I=1}^{N} I CC_I - \sum_{i=2}^{n} (i-1) EE_i$$

As it can be seen from eqns *(30, 31)* the partial molar values of component B extrapolated to the infinitely diluted solution are only influenced by the heteronuclear complexes 1 mol of which contains only 1 mol of component B (*i.e.* complexes $A_I B$). Similarly, as it could be seen for component A as well, the heteronuclear complexes cause a negative deviation while the homonuclear ones cause the positive deviation from the Raoult's law.

Trial calculations

We shall try to find out, how the partial molar excess mixing functions depend on the number, stoichiometry and thermodynamic characteristics of the associates (Table 1).

We support the generalizations formulated in the preceding sections (Table 2). If we do not take the associates A_i and B_j into consideration it leads to great errors even if the stability of the associates, type $A_I B_J$, is much greater (with more orders of magnitude) than that of the associates A_i and B_j.

Table 1

The thermodynamic characteristics of associates used in the calculations at $T = 1000$ K

Associate	ΔH_k^0 kJ mol^{-1}	ΔS_k^0 J mol^{-1} K^{-1}	K_k
A_2	-35.0	-12.5	15.0
AB	-23.2	-7.0	7.0
AB_2	-100.0	-23.4	1.0×10^4
B_2	-18.0	-4.6	5.0

Conclusion

We have found out that the partial molar excess functions relating to the infinitely diluted solution can be influenced considerably by both the associates A_i and B_j. Consequently, it is necessary to take them into consideration if we want to get an adequate thermodynamic description of the molten salt systems $M'X$—$M''X_2$. At the same time, each new associate increases the number of model parameters by two new ones (ΔH_k^0, ΔS_k^0). Therefore, the introduction of the homonuclear associates can be performed in the following ways:

— taking into consideration only one associate (or some of them) with most favourable coordination, *e.g.* the associate type A_4 [18, 19] and/or A_6 [20] in pure alkali halide melts;

— taking into consideration such "polymer" associates of infinite quantity for which a connection can be created between their formation enthalpies and entropies by using only a few parameters, *e.g.* in pure $MnCl_2$, $CoCl_2$, $ZnCl_2$, *etc.* melts where tetrahedral cross-linked "structures" with undefined length will exist [15]. The obtained formulas can be used in both cases.

For using the associates A_i or B_j in the model as the first step it is necessary to determine their thermodynamic characteristics. These data can be calculated on the basis of the empirical mixing data of binary (or n-component) systems alone. But, the calculations should not be performed on the basis of empirical data measured in only one system A—B, because, in this case, a relatively small experimental error can cause great errors in the thermodynamic functions of A_i and B_j.

Practically, the task is related to that of construction of the table of ionic radii. It is necessary to assemble a thermodynamically closed system of quantities (nevertheless the task is much more complicated because of the much greater number of the possible phases and because beside the associates connected with the pure phases the heteronuclear associates must be also taken into

Table 2

The results of the trial calculations

Associate	ΔH_A^∞	$\Delta S_A^{E\infty}$	γ_A^∞	ΔH_B^∞	$\Delta S_B^{E\infty}$	γ_B^∞
	kJ mol^{-1}	J mol^{-1} K^{-1}		kJ mol^{-1}	J mol^{-1} K^{-1}	
A_2	15.3	2.9	4.4	2.0	−2.8	1.8
AB	−20.3	−3.0	0.13	−20.3	−3.0	0.13
AB_2	−100.0	−23.4	1.0×10^{-4}	0.0	0.0	1.0
B_2	1.5	−2.6	1.6	7.0	−1.5	2.8
A_2—B_2	16.8	0.35	7.2	9.0	−4.3	5.0
AB—A_2	−5.0	−0.05	0.55	−2.9	0.25	0.68
AB—B_2	−10.0	−3.7	0.47	−13.3	−4.5	0.35
AB—A_2—B_2	5.3	−0.81	2.1	4.1	−1.3	1.9
AB_2—AB	−99.9	−23.4	1.0×10^{-4}	−20.3	−3.0	0.13
AB_2—A_2	−84.8	−20.5	4.4×10^{-4}	2.0	−2.8	1.8
AB_2—B_2	−84.3	−29.0	1.3×10^{-3}	7.0	−1.5	2.8
AB_2—AB—A_2—B_2	−69.1	−26.1	5.6×10^{-3}	4.1	−1.3	1.9

consideration). But, for this purpose, more and more accurate experimental data are needed.

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