Comments on some models of molten salt mixtures

P. FELLNER

Institute of Inorganic Chemistry, Centre of Chemical Research,
Slovak Academy of Sciences, CS-842 36 Bratislava

The Temkin and Haase models of ideal ionic mixtures are compared. Assumptions on which the models are based are discussed. Examples are given that in many cases the classical thermodynamic relations, which do not take into account ionic structure of the systems, are correct and reliable for the description of thermodynamic or transport properties of the molten salt mixtures.

Сравниваются модели идеальных ионных смесей Темкина и Хаасе. Обсуждены предположения, на которых основываются обе модели. Приводятся примеры того, что во многих случаях классические термодинамические соотношения, не учитывающие ионной структуры систем, оказываются точными и справедливыми для описания термодинамических или транспортных свойств смесей расплавленных солей.

It is well-known that if we add a substance B to the melt of substance A, then it generally does not hold for the relationship between activity and mole fraction of the melt A [1] (the pure molten substance A is chosen as standard state)

$$\lim_{x_A \to 1} da_A/dx_A = 1 \qquad (1)$$

This deviation of molten salt mixtures from classical thermodynamic ideality results from that for mixing entropy of ideal ionic mixture it does not hold that

$$\Delta S_{mix} = -R(n_A \ln x_A + n_B \ln x_B) \qquad (2)$$

n_A, n_B are the amounts of substance A and B, respectively, from which the molten mixture is composed and x_A, x_B are corresponding mole fractions of these components in solution.

General discussion of the structure and thermodynamic properties of molten salts and their mixtures can be found in monographs [1, 2]. This paper deals with critical comparison of some models of ionic melts. Special attention is paid to the Temkin and Haase models. We shall discuss also the interpretation of equilibrium and/or kinetic phenomena in molten systems without considering their ionic character.

The Temkin model

The Temkin model of an ideal ionic mixture [3] belongs in the thermodynamics of molten salts among the most popular [1, 2]. We shall briefly outline the physical background of this model.

According to Temkin a fused salt may be described as two interlocking solutions: solution of cations and solution of anions. Cations mix randomly only in the cationic solution and anions in the anionic solution. In the case of ideal ionic mixture enthalpies of mixing accompanying these processes equal zero and similarly also enthalpy of mixing of the cationic and anionic solutions is equal to zero.

Let us consider a solution which is prepared by mixing n_1 moles of substance M_pA_q and n_2 moles of substance N_rB_s (M, N denote the cations and A, B the anions). According to Temkin we may consider separately solutions of cations and anions and the mixing entropy of final solution is obtained as a sum of the entropies of mixing of both ionic solutions. Applying the relationship (2) to both solutions (cationic and anionic) we obtain for an ideal ionic mixture the following relationship

$$\Delta S_{T, mix} = - R \left(n_M \ln x_{T,M} + n_N \ln x_{T,N} + n_A \ln x_{T,A} + n_B \ln x_{T,B} \right) \qquad (3)$$

where n_M, n_N, n_A, and n_B are the amounts of substance of ions in the mixture.

As we consider each of the ionic solutions separately we use in the relation (3) the so-called ionic fractions (denoted with symbol T) which are defined as follows

$$x_{T,M} = \frac{n_1 p}{n_1 p + n_2 r}; \qquad x_{T,N} = \frac{n_2 r}{n_1 p + n_2 r}$$

$$x_{T,A} = \frac{n_1 q}{n_1 q + n_2 s}; \qquad x_{T,B} = \frac{n_2 s}{n_1 q + n_2 s} \qquad (4)$$

Because we assume that $\Delta H_{mix} = 0$ it holds

$$\frac{\partial \Delta S_{mix}}{\partial n_1} = - R \ln a_1; \qquad \frac{\partial \Delta S_{mix}}{\partial n_2} = - R \ln a_2 \qquad (5)$$

Applying the relationship (5) to eqn (3) we finally obtain

$$a_{T,1} = x_{T,M}^p \cdot x_{T,A}^q; \qquad a_{T,2} = x_{T,N}^r \cdot x_{T,B}^s \qquad (6)$$

The symbol T at the activity denotes that we deal with activities in the ideal ionic solution which behaves according to the Temkin model.

The relations (6) for Temkin's activity can be obtained also in a simpler way using formalism of thermodynamics. Chemical potential of substance in solution can be expressed as a sum of chemical potentials of the ions from which the substance is composed. We may write for chemical potential of each ion

$$\mu_{T,i} = \mu_{T,i}^0 + RT \ln x_{T,i} \qquad (i = M, N, A, B) \tag{7}$$

Then for the first component (and similarly for the second component) it follows

$$\mu_{T,1} = p\, \mu_{T,M} + q\, \mu_{T,A}$$
$$\mu_{T,1}^0 + RT \ln a_{T,1} = p\, [\mu_{T,M}^0 + RT \ln x_{T,M}] + q\, [\mu_{T,A}^0 + RT \ln x_{T,A}] \tag{8}$$

From this equation we readily obtain the resulting expression (6) for Temkin's activities.

The Haase model

The *Haase* model [4, 5] appeared later than the Temkin model. At the derivation of his model, Haase used the approach of thermodynamic formalism similar to that discussed here in connection with the Temkin model. In contradistinction to Temkin, Haase assumes that all ions in ideal ionic mixture can mix randomly. In accordance with this assumption he defines mole fractions of ions in molten mixture. We shall denote these mole fractions of ions in mixture by the symbol H after *Herasimenko* who used them in one of the first models of melts [6].

$$x_{H,M} = \frac{n_1 p}{n_1(p+q) + n_2(r+s)}; \qquad x_{H,N} = \frac{n_2 r}{n_1(p+q) + n_2(r+s)}$$
$$x_{H,A} = \frac{n_1 q}{n_1(p+q) + n_2(r+s)}; \qquad x_{H,B} = \frac{n_2 s}{n_1(p+q) + n_2(r+s)} \tag{9}$$

According to this model, also the melt of pure component M_pA_q is regarded as solution obtained by mixing the solutions of cations M^{q+} and anions A^{p-}. Therefore, the entropy of mixing of n_1 moles of substance M_pA_q with n_2 moles of substance N_rB_s is calculated so that we subtract from entropy of formation of given mixture of ions the contributions of pure components.

$$\Delta S_{H,mix} = -R\,[(n_M \ln x_{H,M} + n_A \ln x_{H,A} + n_N \ln x_{H,N} + n_B \ln x_{H,B}) - $$
$$ - (n_M \ln x_{H,M}^0 + n_A \ln x_{H,A}^0 + n_N \ln x_{H,N}^0 + n_B \ln x_{H,B}^0)] \tag{10}$$

The upper index 0 denotes the mole fraction of cations or anions in pure substance.

By application of the relation (5) to eqn (10) we obtain the expressions for activities of components in Haase's ideal ionic mixture

$$a_{H,1} = (x_{H,M}/x_{H,M}^0)^p \cdot (x_{H,A}/x_{H,A}^0)^q$$
$$a_{H,2} = (x_{H,N}/x_{H,N}^0)^r \cdot (x_{H,B}/x_{H,B}^0)^s \tag{11}$$

Comparison of the Temkin and Haase models

Both models of ideal ionic mixtures are compared by *Markov* in his monograph on thermodynamics of molten salts [7]. Also *Haase* [5] outlined comparison of his approach with the Temkin model. However, in neither case is the discussion exact. Markov supposes that both models are actually identical. Haase, on the other hand, points out as an interesting feature, that the Temkin model coincides with his model in the case of ionic melts of the type NaCl—KCl or NaCl—NaBr. However,

Table 1

Activity of the first component in ideal ionic mixture of the systems MA—NA$_2$, MA—NΛ$_3$, and MA—NB$_2$, respectively.
The activities are calculated as function of mole fraction x of this component according to the Temkin or Haase models

MA—NA$_2$: $a_{T,1} = x$; $a_{H,1} = 4x(2-x)/(3-x)^2$
MA—NA$_3$: $a_{T,1} = x$; $a_{H,1} = x(3-2x)/(x-2)^2$
MA—NB$_2$: $a_{T,1} = x^2/(2-x)$; $a_{H,1} = [2x/(3-x)]^2$

Mole fraction x	MA—NA$_2$		MA—NA$_3$		MA—NB$_2$	
	$a_{T,1}$	$a_{H,1}$	$a_{T,1}$	$a_{H,1}$	$a_{T,1}$	$a_{H,1}$
1.0	1.0	1.0000	1.0	1.0000	1.0000	1.0000
0.9	0.9	0.89796	0.9	0.89256	0.73636	0.73469
0.8	0.8	0.79339	0.8	0.77778	0.53333	0.52893
0.7	0.7	0.68809	0.7	0.66272	0.37692	0.37051
0.6	0.6	0.58333	0.6	0.55102	0.25714	0.25000
0.5	0.5	0.48000	0.5	0.4444	0.16667	0.16000
0.4	0.4	0.37870	0.4	0.34375	0.10000	0.09467
0.3	0.3	0.27984	0.3	0.24913	0.05294	0.04938
0.2	0.2	0.18367	0.2	0.16049	0.02222	0.02041
0.1	0.1	0.09037	0.1	0.07756	0.00526	0.00476

it is easy to prove that both models give identical expressions for activity in ideal ionic mixture if the following conditions are fulfilled

$$p/r = q/s \quad \text{or} \quad p/r = (p+q)/(r+s) \qquad (12)$$

For example, in the systems of the type MA_q—NB_q it holds for both models that $a_1 = a(MA_q) = x^{q+1}$ (x being the mole fraction of component MA_q in mixture). In the case of the system with common ion (e.g. the system of the type MA_q—NA_q) it holds $a(MA_q) = x$.

When the conditions (12) are not fulfilled the models yield different expressions for the activity of components in ideal ionic mixture. It is interesting that even when the expressions for activities obtained according to the Temkin or Haase models are different the numerical values of activities which follow from the models are often very close.

This feature of both models is demonstrated in Table 1 where numerical values of activity in ideal ionic mixture calculated according to the Temkin and Haase models are compared.

Discussion

From the derivation of both models of ionic mixtures it is apparent that the assumptions on which the models are based need not be fulfilled in systems of real ionic melts. For example, according to the Temkin model we assume that the ions carrying different charge (but of the same sign) can mutually replace regardless of this charge. It is also hardly acceptable that ions of remarkably different size can randomly mix without any other effect. An attempt to overcome these difficulties has been done by Norwegian researchers [2]. Many questions, however, remain unsolved.

As far as the Haase model is concerned, it follows from its derivation that the model is only formal. From the point of view of statistical thermodynamics the model can hardly be approved.

The key problem, however, seems to be the inability of both models to describe the behaviour of real reciprocal systems, i.e. of the systems having different cations and different anions. Even in the simplest case, e.g. the mixture $MA + NB$, these models fail. It can be objected that it is a result of remarkable deviation from ideality of these systems. In this case namely, it is necessary to take into account also the reaction [8]

$$MA + NB = MB + NA \qquad \Delta G \neq 0 \qquad (13)$$

Therefore it follows that the discussed models are suitable only for description of the systems with common ion. This special case, however, can be treated successfully also from the point of view of classical thermodynamics which does not take into account structure of the system. We assume that this classical approach to the thermodynamics of molten systems should be preferred to the concepts based on models that use the quantities which are not attainable to physical measurement (*e.g.* chemical potentials of ions, entropy of mixing of cationic and anionic solutions, *etc.*). When we use the classical approach we need not make corrections for charge of ions because we consider only neutral groups of particles (molecules). For example, in the system $KCl—SnCl_2$ we consider the groups KCl, $SnCl_2$, $KSnCl_3$, and $KSnCl_7$. We tested that this approach is suitable for the calculation of phase diagrams of the systems in which compounds are formed. When we use the Temkin or Haase models we get unrealistic picture of these systems [9].

Another example of a successful application of the formal classical approach to molten salt problems is the study of cathodic reaction in the molten mixture $NaCl—KCl—AlCl_3$. At low concentrations of $AlCl_3$ this substance is almost completely bound to the complex anion $AlCl_4^-$ [10]. In the interpretation of measurements of vapour pressure over this melt [10] as well as at the study cathodic process in this system [11] it is necessary to take into account the thermal dissociation

$$MAlCl_4 = MCl + AlCl_3 \qquad (14)$$

Even if the equilibrium of this reaction is shifted to the left side of eqn (*14*) the existence of a neutral species $AlCl_3$ is useful for explanation of mechanism of the cathodic process. It is apparent that the equilibrium constant of the reaction depends on the nature of cation M. This is not quite obvious when we use the ionic models. Furthermore, the Temkin or Haase models are unable to treat the system containing neutral species. This confirms again usefulness of the classical approach.

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