Inconsistency of the Thermodynamic Model of Molten Salt Mixtures Based on the Ion Equivalent Fractions

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Thermodynamics of molten salt mixtures is discussed. It is shown that the model for entropy of mixing based on the equivalent fractions does not obey the Gibbs—Duhem equation.

Molten salt mixtures are the electrolytes consisting of positively and negatively charged atoms or groups of atoms. For some molten salt mixtures the same concept of ideal thermodynamic behaviour as for non-electrolyte solutions can be used. As an example, the mixtures of alkali metal halides with common cation or common anion can be mentioned. As it was firstly pointed out by *Hildebrand* [1] the entropy of mixing of the system AgBr in molten alkali metal bromides is in the first approximation ideal and the excess partial Gibbs energy (which equals the partial molar heat of solution) of either component is proportional to the square of the mole fraction of the other. This so-called regular thermodynamic model usually describes well thermodynamic behaviour of the mixtures of univalent salts with common cation or common anion.

Situation is more complex when the mixture consists of different cations and anions (reciprocal systems) or if the mixture contains ions of different charge. In the case of these mixtures it generally does not hold

$$\lim_{x_i \to 1} \frac{\mathrm{d}a_i}{\mathrm{d}x_i} = 1 \qquad (1)$$

where a_i and x_i are the activity and the mole fraction of the i-th component, respectively. This means that entropy of mixing of the molten salt systems might be different from entropy of mixing of the classical ideal solution, which is defined by the relationship

$$\Delta S_{\mathrm{mix,id}} = -R \sum_i n_i \ln x_i \qquad (2)$$

$\Delta S_{\mathrm{mix,id}}$ is the ideal entropy of mixing and n_i is the amount of substance of the i-th component. As mentioned above in molten salt mixtures the relationships (1) and (2) are not generally valid. This problem is solved in a number of models of molten salt mixtures [2—12].

Temkin [2] suggested that in salt mixture the entropy of mixing is determined by the number of permutations among different ions of the same sign and of the same charge. Thus in the ideal Temkin ionic model the cations mix randomly in the cation solution and the anions mix randomly in anion solution. Entropy of mixing in each of these solutions is given by the relationship (2). Enthalpies of mixing in each solution equal zero and the same holds for mixing of the cation and anion solutions.

Let us consider a solution which is formed by mixing of n_1 of salt $\mathrm{M}_p\mathrm{A}_q$ (1) and n_2 of salts $\mathrm{N}_r\mathrm{B}_s$ (2) (n_i denotes the amount of substance in moles). M and N denote cations and A, B are the anions. According to the Temkin model [2] the entropy of mixing of the system is as follows (T denotes quantities in the Temkin model)

$$\Delta S_{\mathrm{T,mix}} = -R(n_{\mathrm{M}} \ln x_{\mathrm{T,M}} + n_{\mathrm{N}} \ln x_{\mathrm{T,N}} + $$
$$+ n_{\mathrm{A}} \ln x_{\mathrm{T,A}} + n_{\mathrm{B}} \ln x_{\mathrm{T,B}}) \qquad (3)$$

$n_{\mathrm{M}}, n_{\mathrm{N}}, n_{\mathrm{A}}, n_{\mathrm{B}}$ are the amounts of substance of ions in the mixture. As mentioned above, the Temkin model considers separately the solution of cations of the same charge and anions of the same charge. Thus in the relationship (3) $x_{\mathrm{T,M}}, x_{\mathrm{T,N}}$ denote the ionic fractions of cations in the cation solution and $x_{\mathrm{T,A}}, x_{\mathrm{T,B}}$ denote the ionic fractions of anions in the anion solution. These ionic fractions are defined as follows

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

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

As $\Delta H_{\mathrm{mix}} = 0$, $\Delta G_{\mathrm{mix}} = -T\Delta S_{\mathrm{mix}}$, and

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

Thus for the activities of components in the Temkin ideal ionic solution we get the expressions

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

Flood and *Urnes* [3] used this model for the description of the thermodynamic behaviour of the salt mixtures $MgCl_2$—AlkCl (Alk = Na, K, Rb). They assumed that divalent Mg^{2+} cations mix randomly with monovalent alkali metal cations.

Förland [4, 5] proposed to solve the deficiency of the model based on random mixing of ions with different charges [3] by the assumption that the ions can bring to the solution also vacancies. He showed [4, 5] that the heat of mixing in the systems Na_2CO_3—$CaCO_3$ and K_2CO_3—$CaCO_3$ can be described by a simple regular solution model if the composition of the system is expressed by the so-called equivalent fractions. According to *Förland* [4, 5] one can assume that a quasi-lattice exists with the anions occupying the anion region of the lattice while the cations mix on the cation portion of the lattice. For every Ca^{2+} cation added from $CaCO_3$ to the solvent Na_2CO_3, a "vacancy" is also added.

According to [5], for the case in which M^{q+}, N^{s+} and the cation vacancies are randomly distributed over the cation sites, the entropy of mixing due to this disorder of the three species M^{q+}, N^{s+} and CV^- (cation vacancy) over all cation sites is

$$\Delta S_{mix} = -R \left(n_{M^{q+}} + n_{N^{s+}} + n_{CV^-} \right) \cdot$$
$$\cdot \left(\frac{n_{M^{q+}}}{n} \ln \frac{n_{M^{q+}}}{n} + \frac{n_{N^{s+}}}{n} \ln \frac{n_{N^{s+}}}{n} + \frac{n_{CV^-}}{n} \ln \frac{n_{CV^-}}{n} \right) -$$
$$- S_{M_pA_q} - S_{N_rB_s} \qquad (7)$$

where n_i denotes the number of moles of each species and n is the number of moles of cation sites. The last two terms is the entropy due to the disorder in the distribution of M^{q+} and CV^- in pure M_pA_q and the entropy due to disorder in N_rB_s, respectively. If this distribution is assumed to be random, then

$$S_{M_pA_q} = -Rpqn_1 \left(\frac{1}{q} \ln \frac{1}{q} + \frac{q-1}{q} \ln \frac{q-1}{q} \right)$$

$$S_{N_rB_s} = -Rrsn_2 \left(\frac{1}{s} \ln \frac{1}{s} + \frac{s-1}{s} \ln \frac{s-1}{s} \right) \quad (8)$$

This gives

$$\Delta S_{mix} = -R \left(n_1pq + n_2rs \right) \cdot$$
$$\cdot \left(x_{F,M} \ln x_{F,M} + x_{F,N} \ln x_{F,N} \right) \qquad (9)$$

where $x_{F,i}$ denotes equivalent fractions of i

$$x_{F,M} = \frac{n_1pq}{n_1pq + n_2rs} \quad x_{F,N} = \frac{n_2rs}{n_1pq + n_2rs} \qquad (10)$$

In a similar way one can obtain relationships for anions

$$x_{F,A} = \frac{n_1pq}{n_1pq + n_2rs} \quad x_{F,B} = \frac{n_2rs}{n_1pq + n_2rs} \qquad (11)$$

Detailed discussion of this model can be found in monographs [5, 6]. Another model of molten salt mixtures was proposed by *Herasimenko* [7]. It became more popular in the version published by *Haase* [8, 9].

In this paper we will show that the Förland's model does not obey the Gibbs—Duhem equation in all cases and thus it is not consistent from the thermodynamic point of view.

Verifying of the Thermodynamic Consistency of the Förland's Model

Let us consider a solution, which is formed by mixing of n_1 moles of salt M_pA_q (1) and n_2 moles of salts N_rB_s (2). M and N denote cations and A, B are the anions. The equivalent fractions of both cations and anions are defined by eqn (7). Activities of components M_pA_q and N_rB_s in ideal solution are defined in a similar way as in the Temkin model (see eqn (6)). In this case, however, the equivalent fractions instead of ion fractions are used. It follows

$$a_{F,1} = \left(\frac{n_1pq}{n_1pq + n_2rs} \right)^{p+q}$$
$$a_{F,2} = \left(\frac{n_2rs}{n_1pq + n_2rs} \right)^{r+s} \qquad (12)$$

Symbol F in the index denotes the Förland's model. According to the Gibbs—Duhem equation it holds

$$n_1 d \ln a_{F,1} + n_2 d \ln a_{F,2} = 0 \qquad (13)$$

or

$$n_1 \left(\frac{\partial \ln a_{F,1}}{\partial n_1} \right)_{n_2} + n_2 \left(\frac{\partial \ln a_{F,2}}{\partial n_1} \right)_{n_2} = 0 \qquad (14)$$

We apply now eqn (14) to the relationships (12)

$$\frac{\partial \ln a_{F,1}}{\partial n_1} = \frac{1}{a_{F,1}} \cdot \frac{\partial a_{F,1}}{\partial n_1} \qquad (15)$$

$$\frac{\partial a_{F,1}}{\partial n_1} = (p+q) \cdot \left(\frac{n_1pq}{n_1pq + n_2rs} \right)^{p+q-1} \cdot$$
$$\cdot \frac{n_2rspq}{(n_1pq + n_2rs)^2} \qquad (16)$$

and thus

$$\frac{\partial \ln a_{F,1}}{\partial n_1} = \frac{(p+q) n_2rs}{n_1 (n_1pq + n_2rs)} \qquad (17)$$

Table 1. Sum of Eqn (19) as a Function of Stoichiometric Coefficients of Compounds M_pA_q and N_rB_s for p, q, r, $s \in \langle 0, 4 \rangle$

p	q	r	s	$(p+q)\,rs - (r+s)\,pq$	p	q	r	s	$(p+q)\,rs - (r+s)\,pq$
1	1	1	1	0	1	4	1	4	0
1	1	1	2	1	1	4	2	2	4
1	1	1	3	2	1	4	2	3	10
1	1	1	4	3	1	4	2	4	16
1	1	2	2	4	1	4	3	3	21
1	1	2	3	7	1	4	3	4	32
1	1	2	4	10	1	4	4	4	48
1	1	3	3	12	2	2	2	2	0
1	1	3	4	17	2	2	2	3	4
1	1	4	4	24	2	2	2	4	8
1	2	1	2	0	2	2	3	3	12
1	2	1	3	1	2	2	3	4	20
1	2	1	4	2	2	2	4	4	32
1	2	2	2	4	2	3	2	3	0
1	2	2	3	8	2	3	2	4	4
1	2	2	4	12	2	3	3	3	9
1	2	3	3	15	2	3	3	4	18
1	2	3	4	22	2	3	4	4	32
1	2	4	4	32	2	4	2	4	0
1	3	1	3	0	2	4	3	3	6
1	3	1	4	1	2	4	3	4	16
1	3	2	2	4	2	4	4	4	32
1	3	2	3	9	3	3	3	3	0
1	3	2	4	14	3	3	3	4	9
1	3	3	3	18	3	3	4	4	24
1	3	3	4	27	3	4	3	4	0
1	3	4	4	40	3	4	4	4	16

The expression for $\partial \ln a_{F,2}/\partial n_1$ can be derived in a similar way.

$$\frac{\partial \ln a_{F,2}}{\partial n_1} = -\frac{(r+s)\,pq}{n_1 pq + n_2 rs} \qquad (18)$$

The Gibbs—Duhem equation is fulfilled when the sum of the partial derivatives (17) and (18) multiplied by the amount of substance n_i (see eqn (14)) equals zero.

$$\text{Sum} = (p+q)rs - (r+s)pq = 0 \qquad (19)$$

For some combinations of p, q, r, s eqn (19) is evaluated in Table 1. It follows that, in general, the Förland's model does not fulfil the Gibbs—Duhem equation.

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