On the calculation of phase diagrams of molten reciprocal systems

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It is proved that classical thermodynamic treatment of molten reciprocal mixtures satisfies criteria of thermodynamic consistency. On examples of the systems LiF—NaCl and LiF—KCl it is shown that the classical representation of the behaviour of molten reciprocal systems is suitable for calculation of the phase diagrams of these systems.

Показано, что классическое термодинамическое рассмотрение обратных расплавленных смесей отвечает критериям термодинамической согласуемости. На примерах систем LiF—NaCl и LiF—KCl показано, что классическое представление поведения обратных расплавленных систем удовлетворительно для расчета фазовых диаграмм этих систем.

Mixtures of molten salts which contain different cations and different anions are often called reciprocal systems. In the simplest case such reciprocal mixture contains two types of univalent cations M^+, N^+ and two types of univalent anions A^-, B^-.

Interpretation of thermodynamic properties of this class of liquid mixtures is usually based on the assumption of random distribution of cations in cationic and anions in anionic solutions [1—3], as it has been suggested by *Temkin* [1].

In this paper we shall demonstrate that thermodynamic behaviour of these systems can be represented by a simple classical thermodynamic model which does not require assumptions about structure of the melt or arrangement of the ions.

Let us assume a quasi-binary system which consists of substances $MA + NB$. This pair of substances is a stable diagonal of the reciprocal system M^+, N^+ // A^-, B^-. Reaction of both components in liquid phase is represented by the following reaction scheme

$$MA + NB = NA + MB \qquad \Delta G^0 > 0 \qquad (1)$$

For the equilibrium constant of this reaction it holds

$$K = \frac{a_{NA} \cdot a_{MB}}{a_{MA} \cdot a_{NB}} \qquad (2)$$

According to the classical thermodynamic approach we need not consider the existence of ions in the system but only the entities $N^+ \cdot A^-$, $M^+ \cdot A^-$, $M^+ \cdot B^-$, $N^+ \cdot B^-$. For easy survey we shall denote these entities as NA, MA, MB, and NB. The principles of thermodynamic consistency [4] require that for the reciprocal system M^+, N^+ // A^-, B^- it must hold

$$\lim_{x_{MA} \to 1} da_{MA}/dx_{MA} = 2 \tag{3}$$

The condition (3) follows from the fact that the substance NB introduces in the melt of pure substance MA two new species. According to our suggestion, these new species are not the ions N^+ and B^- but rather the ionic pairs $N^+ \cdot A^-$ and $M^+ \cdot B^-$.

Since the relationship (3) holds exactly only for infinite dilution of one component, we can use for its proof approximation of the Raoult and Henry laws. For $x \to 1$ the activity of the first component approaches its mole fraction (Raoult law) while the activity of the second component is proportional to its mole fraction (Henry law). Let us denote the first component MA and its mole fraction in the mixture x, the second component as NB and its mole fraction $(1 - x)$. The Henry constant is denoted as k. Then eqn (2) can be written in this approximation $(x \to 1)$ as

$$K = \frac{y^2 k_{NA} k_{MB}}{(x - y)(1 - x - y) k_{NB}} \tag{4}$$

where y is the mole fraction of the substances NA or MB which are formed due to the reaction (1). Thus it is assumed that the Raoult law holds for the activity of substance MA while for the activity of the components NB, NA, and MB the Henry approximation is correct. The true mole fraction of the component MA in the molten mixture is $(x - y)$. According to the relationship (3) it must hold

$$\lim_{x \to 1} d(x - y)/dx = 1 - dy/dx = 2 \tag{5}$$

By differentiation of the relationship (4) we obtain

$$\left(K' = K \frac{k_{NB}}{k_{NA} \cdot k_{MB}} \right)$$

$$dy/dx = -\frac{K' - 2K'x}{-K' + 2K'y - 2y} \tag{6}$$

$$\lim_{\substack{x \to 1 \\ y \to 0}} dy/dx = -1 \tag{7}$$
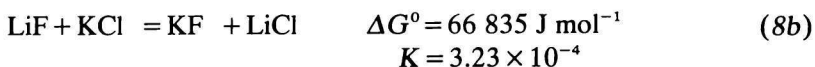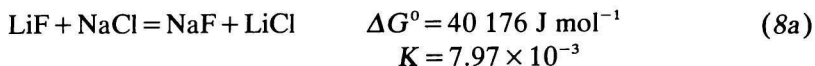
After introducing the result (7) into eqn (5) we readily find that the condition (5) is for $x \to 1$ fulfilled. It means that the approach used here for representation of the thermodynamic behaviour of the reciprocal systems is in agreement with the 1st criterion of thermodynamic consistency [4].

On examples of the systems LiF—NaCl and LiF—KCl we shall show how the proposed classical approach to the thermodynamic behaviour of reciprocal systems can be used for description of the phase diagrams of these systems. The systems LiF—NaCl and LiF—KCl are claimed to be of simple eutectic type [5], which means that no solid solutions are formed.

Thermodynamic data for pure components were taken from the JANAF tables [6]

$$
\begin{aligned}
T_f(\text{LiF}) &= 1121 \ \text{K} & \Delta H_f(\text{LiF}) &= 27 \ 087 \ \text{J mol}^{-1} \\
T_f(\text{NaCl}) &= 1073.8 \ \text{K} & \Delta H_f(\text{NaCl}) &= 28 \ 138 \ \text{J mol}^{-1} \\
T_f(\text{KCl}) &= 1044 \ \text{K} & \Delta H_f(\text{KCl}) &= 26 \ 284 \ \text{J mol}^{-1}
\end{aligned}
$$

Equilibrium constants of the corresponding chemical reactions are following ($T = 1000$ K)

$$
\text{LiF} + \text{NaCl} = \text{NaF} + \text{LiCl} \qquad
\begin{aligned}
\Delta G^\circ &= 40 \ 176 \ \text{J mol}^{-1} \\
K &= 7.97 \times 10^{-3}
\end{aligned}
\qquad (8a)
$$

$$
\text{LiF} + \text{KCl} = \text{KF} + \text{LiCl} \qquad
\begin{aligned}
\Delta G^\circ &= 66 \ 835 \ \text{J mol}^{-1} \\
K &= 3.23 \times 10^{-4}
\end{aligned}
\qquad (8b)
$$

Neglection of temperature dependence of the equilibrium constant had only little influence on the final result.

Data on excess Gibbs energy in the given systems are not available. Let us assume that in the first approximation the deviation of these systems from ideality can be represented by a regular model. Then we can write

$$
\begin{aligned}
G^E &= Ax(1-x) \\
RT \ln f_1 &= A(1-x)^2 \\
RT \ln f_2 &= Ax^2
\end{aligned}
\qquad (9)
$$

f_1, f_2 are the activity coefficients of LiF and NaCl or LiF and KCl. As we do not know the value of the parameter A, this is to be evaluated by comparing the experimental and calculated phase diagrams.

Because the mole fractions y of the substances resulting due to the reaction (1) are small we may consider their activity coefficients to be constant (Henry law). It follows that the constant K should be multiplied by the Henry constants and the resulting constant K is an adjustable parameter in this model. It was found, however, that it is not necessary and that good agreement between experimental and calculated data can be achieved without taking into account this deviation from

ideality. Then it holds for the equilibrium constant of the reaction (*8a*) or (*8b*)

$$K = \frac{y^2}{(x-y) \exp\left[-\dfrac{A}{RT}(1-x-y)^2\right] (1-x-y) \exp\left[-\dfrac{A}{RT}(x-y)^2\right]} \quad (10)$$

Numerical solution of eqn (*10*) yields for each value of the analytical mole fraction x corresponding value of the mole fraction y. These data are sufficient for calculation of the activity of components LiF and NaCl or LiF and KCl in corresponding systems.

Inserting these data into the LeChatelier—Shreder equation [7, 8]

$$\ln a_i = \frac{\Delta H_f}{R} (1/T_f - 1/T) \quad (11)$$

we can calculate the temperature of primary crystallization of the given component.

Comparison of the experimental and calculated data on the solid—liquid equilibria is presented in Figs. 1 and 2. The best agreement with experiment was achieved for the following values of the parameter A

LiF—NaCl: $A = -15\ 500$ J mol^{-1};
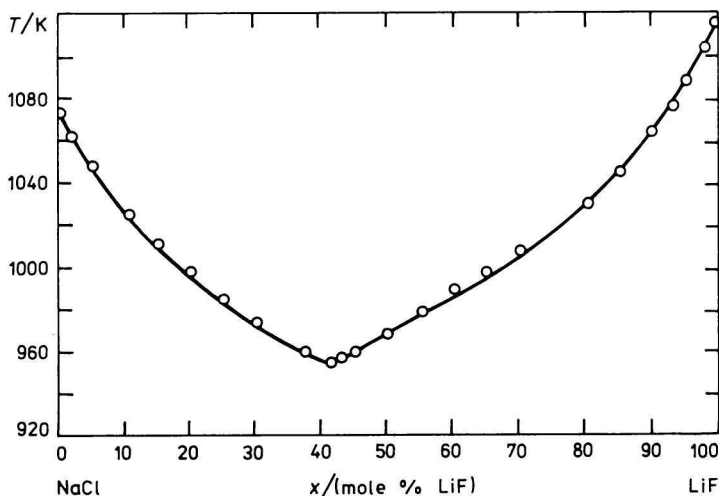LiF—KCl: $A = -17\ 000$ J mol^{-1}.

Fig. 1. Comparison of the experimental [5] and calculated phase diagram of the system NaCl—LiF.
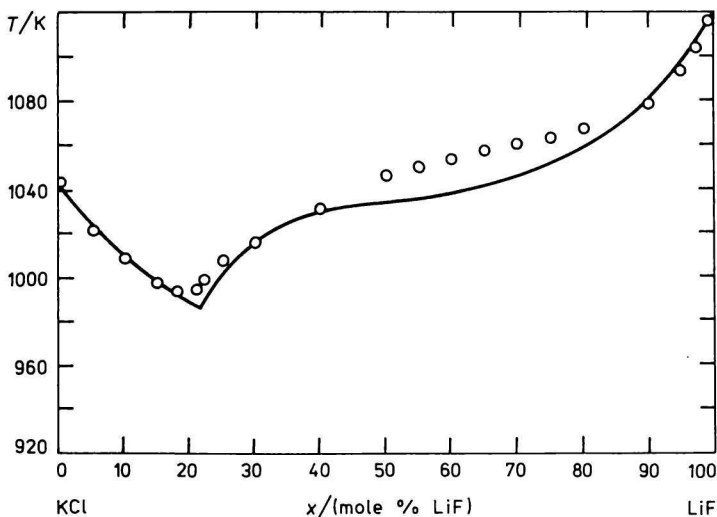O Experimental data; — calculation.

Fig. 2. Comparison of the experimental [5] and calculated phase diagram of the system KCl—LiF.
○ Experimental data; — calculation.

It can be seen from the figures that the calculated liquidus curves fit the experimental data quite well. The calculation showed that the amount of the components on the unstable diagonal of the reciprocal systems does not exceed 6 mole %.

Applicability of this approach to more complicated systems (the systems on cryolite basis with dissociating anions) is under study [9].

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