Phase diagram of the system LiF—NaF—Na$_2$SO$_4$ and its thermodynamic analysis

II. Calculation of the phase diagram according to the molecular model

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Phase diagram of the ternary reciprocal system LiF—NaF—Na$_2$SO$_4$ was calculated according to the molecular model of molten salts. This model assumes that in an ideal molten mixture electrically neutral ionic pairs "molecules" (in this case Li$^+$·F$^-$, Na$^+$·F$^-$, 2Li$^+$·SO$_4^{2-}$, 2Na$^+$·SO$_4^{2-}$, and 3Na$^+$·FSO$_4^{3-}$) mix randomly. Model composition of the system, i.e. mole fractions of ionic pairs, can be calculated taking into account simultaneous chemical equilibria among components of the molten mixture.

Using the calculated model mole fractions of components, liquidus curves of pseudobinary systems LiF—Na$_2$SO$_4$ and LiF—Na$_3$FSO$_4$ and liquidus surfaces in the reciprocal ternary system LiF—NaF—Na$_2$SO$_4$ were calculated. Agreement between calculated and experimental data is good.

In the first paper [1] the results of experimental investigation of the ternary system LiF—NaF—Na$_2$SO$_4$ were presented. In this work the thermodynamic analysis of this reciprocal system containing incongruently melting compound will be discussed. This system is interesting from two aspects:

1. It allows to characterize quantitatively the interaction of fluoride and sulfate ions in the melts;
2. It is suitable for verification of thermodynamic models of molten mixtures.
and systems containing the compound which partly thermally dissociates under melting.

In the present work the thermodynamic analysis of the system LiF—NaF—Na$_2$SO$_4$ is based on the molecular model of molten salt mixtures [2, 3]. This model assumes that in an ideal molten mixture molecules (ionic pairs) and not the ions mix randomly as it is assumed in ionic concepts of molten mixtures [4, 5]. Model composition of the melt, i.e. the mole fractions of ionic pairs in the molten mixture, is calculated on the basis of simultaneous chemical equilibria among components of the mixture. For example, in the melt of the system LiF—NaF—Na$_2$SO$_4$ one can assume random mixing of molecules Li$^+ \cdot F^-$, Na$^+ \cdot F^-$, $2Na^+ \cdot SO_4^{2-}$, $2Li^+ \cdot SO_4^{2-}$, $3Na^+ \cdot FSO_4^{3-}$.

Suitability of the model for description of the behaviour of thermodynamic properties of molten mixtures is tested by comparing the experimental and calculated solid—liquid phase equilibria in the studied system.

Congruently melting compound Na$_3$FSO$_4$ formed in the system NaF—Na$_2$SO$_4$ allows to divide the ternary system LiF—NaF—Na$_2$SO$_4$ into two subsystems, viz. LiF—NaF—Na$_3$FSO$_4$ and LiF—Na$_2$SO$_4$—Na$_3$FSO$_4$. Thus special attention was paid to the boundary systems LiF—Na$_2$SO$_4$ and LiF—Na$_3$FSO$_4$. The boundary systems NaF—Na$_3$FSO$_4$ and Na$_2$SO$_4$—Na$_3$FSO$_4$ have been discussed in detail in paper [6]. Thermodynamic behaviour of the system LiF—NaF is not very far from ideality [7].

**Theoretical**

*Calculation of model composition of the molten mixture LiF—NaF—Na$_2$SO$_4***

Calculation of model composition in the whole range of the system LiF—NaF—Na$_2$SO$_4$ is based on the assumption that the molten mixture consists of the following molecules (ionic pairs): Li$^+ \cdot F^-$, Na$^+ \cdot F^-$, $2Li^+ \cdot SO_4^{2-}$, $2Na^+ \cdot SO_4^{2-}$, $3Na^+ \cdot FSO_4^{3-}$. Their content in the melt (i.e. the model composition of the melt) is given by the following chemical reactions

$$Na^+ \cdot F^- (l) + 2Na^+ \cdot SO_4^{2-} (l) = 3Na^+ \cdot FSO_4^{3-} (l) \quad K_1 = 0.89 \quad (A)$$

$$2(Li^+ \cdot F^- (l)) + 2Na^+ \cdot SO_4^{2-} (l) = 2(Na^+ \cdot F^- (l)) + 2Li^+ \cdot SO_4^{2-} (l) \quad K_2 = 0.01 \quad (B)$$

Equilibrium constant $K_1$ was taken from literature [6]. Equilibrium constant $K_2$ was calculated from tabulated data on Gibbs energy of formation of pure molten components LiF, Li$_2$SO$_4$, NaF, and Na$_2$SO$_4$ at the temperature of 1000 K [8]. The temperature dependence of the equilibrium constants was
neglected at the calculation. It was also assumed that the melt behaves ideally from the thermodynamical point of view and thus the activities of components equal their mole fractions. We will briefly outline the procedure of these calculations.

Let us denote the weighed-in amounts of components of the ternary system as \(n^*(\text{LiF}), n^*(\text{NaF}),\) and \(n^*(\text{Na}_2\text{SO}_4).\) As a result of the chemical reactions \(A\) and \(B\) among components of the molten mixture it holds for real (model) amounts of substances of components

\[
\begin{align*}
n (\text{Li}^+ \cdot \text{F}^-) &= n^*(\text{LiF}) - 2n (2\text{Li}^+ \cdot \text{SO}_4^{2-}) \\
n (\text{Na}^+ \cdot \text{F}^-) &= n^*(\text{NaF}) - n (3\text{Na}^+ \cdot \text{FSO}_4^{3-}) + 2n (2\text{Li}^+ \cdot \text{SO}_4^{2-}) \\
n (2\text{Na}^+ \cdot \text{SO}_4^{2-}) &= n^*(\text{Na}_2\text{SO}_4) - n (3\text{Na}^+ \cdot \text{FSO}_4^{3-}) - n (2\text{Li}^+ \cdot \text{SO}_4^{2-})
\end{align*}
\]

Because the melt is thermodynamically ideal it follows from eqns \(A\) and \(B\)

\[
K_1 = \frac{y (3\text{Na}^+ \cdot \text{FSO}_4^{3-})}{y (\text{Na}^+ \cdot \text{F}^-) \cdot y (2\text{Na}^+ \cdot \text{SO}_4^{2-})}
\]

\[
K_2 = \frac{y^2 (\text{Na}^+ \cdot \text{F}^-) \cdot y (2\text{Li}^+ \cdot \text{SO}_4^{2-})}{y^2 (\text{Li}^+ \cdot \text{F}^-) \cdot y (2\text{Na}^+ \cdot \text{SO}_4^{2-})}
\]

For chosen weighed-in compositions of the ternary mixture, the system of nonlinear equations \((1-5)\) can be solved numerically and thus the model mole fractions \(y(i)\) can be calculated in the whole composition range of the system. For illustration model mole fractions in the pseudobinary system LiF—Na\(_2\)SO\(_4\) are plotted in Fig. 1 as function of weighed-in mole fractions of components.

**Calculation of equilibrium solidus—liquidus temperature**

Equilibrium solidus—liquidus temperature (the temperature of primary crystallization) of chosen sections of the ternary system LiF—NaF—Na\(_2\)SO\(_4\) was calculated according to the LeChatelier—Shreder equation

\[
\ln a(i) = \frac{\Delta H(fus,i)}{R} \frac{1}{[1/T(fus,i) - 1/T(i)]}
\]

\(a(i)\) is the activity of the \(i\)-th component in molten mixture, \(\Delta H(fus,i)\) and \(T(fus,i)\) are the enthalpy and temperature of fusion, respectively, \(T(i)\) is the temperature of solid—liquid equilibrium (temperature of primary crystallization) at given composition of the mixture. As we have said above it was assumed that activities of components equal their mole fractions. In the case of the
compound $3\text{Na}^+ \cdot \text{FSO}_4^{3-}$ which partly dissociates under melting its activity equals the ratio of mole fractions of this component in the melt of given composition and in the melt corresponding to stoichiometric composition of this component. It can be shown that this approach is identical with the procedure using hypothetical temperature of fusion of thermally undissociated component [7].

Values of enthalpies of fusion and temperatures of fusion used at the calculation are presented in Table 1.
Table 1

Data used in calculation of the phase diagram of the system LiF—NaF—Na$_2$SO$_4$ and its sections

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_{(\text{fus}, i)}/K$</th>
<th>$\Delta H_{(\text{fus}, i)}/(\text{J mol}^{-1})$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>1211.0</td>
<td>27074</td>
<td>[9]</td>
</tr>
<tr>
<td>NaF</td>
<td>1266.5</td>
<td>33302</td>
<td>[9]</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>1157.8</td>
<td>23012</td>
<td>[10]</td>
</tr>
<tr>
<td>Na$_3$FSO$_4$</td>
<td>1060.0</td>
<td>62280</td>
<td>[6, 11]</td>
</tr>
<tr>
<td>Li$_2$SO$_4$</td>
<td>1133.0</td>
<td>8319</td>
<td>[12]</td>
</tr>
</tbody>
</table>

Fig. 2. Phase diagram of the system LiF—Na$_2$SO$_4$. ——— Experimental; ——— calculated.
The system LiF—Na$_2$SO$_4$

From the point of view of thermodynamic analysis of the system LiF—NaF—Na$_2$SO$_4$ the system LiF—Na$_2$SO$_4$ is of primary importance. In this pseudobinary system there exists a region in which solid Na$_3$FSO$_4$ coexists in equilibrium with the melt. As it can be seen from Fig. 2, thermodynamic model proposed in this work predicts correctly such a behaviour of phase diagram of the system LiF—Na$_2$SO$_4$. The model predicts reasonably well the courses of liquidus curves of pure components. This seems to justify the approach used.

The system LiF—Na$_3$FSO$_4$

This system is interesting by that it contains a compound which partly dissociates under melting and besides it is a reciprocal system. In Fig. 3 the experimental and calculated phase diagrams of the system LiF—Na$_3$FSO$_4$ are compared. It can be seen that also in this case the agreement between experimental and calculated data is good.

![Graph of phase diagram of the system LiF—Na$_3$FSO$_4$.](image)

Fig. 3. Phase diagram of the system LiF—Na$_3$FSO$_4$. —— Experimental; —— calculated.
The system LiF—NaF—Na\textsubscript{2}SO\textsubscript{4}

This ternary reciprocal system is rather complicated. However, as we have seen above, the calculated and experimental data on the temperatures of primary crystallization for the boundary binary systems and for the section LiF—Na\textsubscript{3}FSO\textsubscript{4} of this ternary system are in good agreement. This makes it possible to predict that also experimental and calculated temperatures of solid—liquid equilibria in the ternary system will be in good agreement. In Fig. 4 the calculated and experimental curves of monovariant equilibria are plotted. The agreement between experiment and calculation is reasonably good.

![Phase diagram of the system LiF—NaF—Na\textsubscript{2}SO\textsubscript{4}.](image)

Fig. 4. Phase diagram of the system LiF—NaF—Na\textsubscript{2}SO\textsubscript{4}. —— Experimental; —— calculated.

No adjustable parameters except the value of equilibrium constant $K_1$ were used. (This constant was found by comparing experimental and calculated phase diagram of the system NaF—Na\textsubscript{2}SO\textsubscript{4} and thus it has to be considered as an...
adjustable parameter.) Thus it may be concluded that the molecular model describes well thermodynamic behaviour of the investigated system LiF—NaF—Na₂SO₄.

References


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