Liquidus Curve and Density of the Molten System

$\text{Li}_3\text{AlF}_6—\text{Na}_3\text{AlF}_6$

M. MALINOVSKÝ, M. PAUČÍROVÁ and K. MATIAŠOVSKÝ

Institute of Inorganic Chemistry, Slovak Academy of Sciences,
Bratislava 9

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It has been found by TA that there is a minimum on the liquidus curve of the system $\text{Li}_3\text{AlF}_6—\text{Na}_3\text{AlF}_6$, the coordinates of which are 62.5 mole % (56.25 weight %) $\text{Li}_3\text{AlF}_6$, 719°C.

By hydrostatic measurement the densities of the molten components and their molten mixtures in the system $\text{Li}_3\text{AlF}_6—\text{Na}_3\text{AlF}_6$ as functions of temperature were determined. It was found that the molar volume of the mixture is, in this system, very close to the ideal volume. The excess molar volume was determined and the partial molar volumes of the components of the system were calculated.

Lithium fluoride is one of those additives which can favourably change the properties of the electrolyte for aluminium production. This substance may be added to the electrolyte in two ways:

a) As a mixture of LiF (instead of LiF the equivalent amount of $\text{Li}_2\text{CO}_3 + \text{AlF}_3$ may be added) in a ratio so as to make the formation of the lithium cryolite, $\text{Li}_3\text{AlF}_6$, possible. In this case alumina will be dissolved in molten $\text{Li}_3\text{AlF}_6—\text{Na}_3\text{AlF}_6$ (with regard to C. R.* it will be a neutral electrolyte) or in $\text{Li}_3\text{AlF}_6—\text{Na}_3\text{AlF}_6—\text{AlF}_3$ (with regard to C. R. an acidic electrolyte).

b) An addition of LiF alone, without $\text{AlF}_3$, is added so that there would be a certain lithium fluoride excess in the melt (i.e. not compensated by $\text{AlF}_3$). Alumina will be dissolved in the molten $\text{LiF} + \text{Na}_3\text{AlF}_6$ in which a small amount of $\text{Li}_3\text{AlF}_6$ is usually present, since as a rule, the original electrolyte has C. R. $< 3$. With regard to C. R., the molten $\text{LiF} + \text{Li}_3\text{AlF}_6 + \text{Na}_3\text{AlF}_6$ represent a basic electrolyte.

From this point of view, our interest in the investigation of the properties of the system $\text{Li}_3\text{AlF}_6—\text{Na}_3\text{AlF}_6$ is justified.

Liquidus curve of the molten system

$\text{Li}_3\text{AlF}_6—\text{Na}_3\text{AlF}_6$

The system $\text{Li}_3\text{AlF}_6—\text{Na}_3\text{AlF}_6$, especially its liquidus curve and the interaction of the components of the system, were studied by several authors [1—7]. The most important results of their investigations are listed in Table 1. [8] reports that, apart from $\text{Li}_3\text{AlF}_6$, the natural mineral cryolithionite occurs, the chemical composition of which may be expressed by the formula $\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}$. It is interesting that this compound was not reported by any of the above authors [1—7]. Beleckij

* C. R., i.e. the cryolite ratio, which is the ratio of the number of NaF (or NaF + LiF) moles to $\text{AlF}_3$ moles in the mixture. In the pure cryolite (i.e. a neutral electrolyte) the C. R. = 3; in acidic electrolytes it is $< 3$ and vice versa.
M. Malinovský, M. Pačírová, K. Matiašovský and Saksonov [3] identified by X-ray methods the compounds \( \text{Li}_3\text{Na}_e\text{Al}_3\text{F}_{18} \), \( \text{Li}_5\text{Na}_3\text{Al}_2\text{F}_{18} \) and \( \text{Li}_{15}\text{Na}_3\text{Al}_6\text{F}_{38} \) which form, according to the experimental results of the latter authors, with the fundamental components \( \text{Li}_5\text{AlF}_6 \) and \( \text{Na}_3\text{AlF}_6 \), as well as with each other, eutectic systems.

As we can see from Table 1, there is a fair agreement between the data for the temperature coordinate of the minimum on the liquidus curve of the system. The work [7] is an exception, since most probably, the reagents of lower purity grade were used, this assumption being corroborated by a lower value of the melting point of \( \text{Li}_3\text{AlF}_6 \). In contrast, the concentration coordinates differ a great deal. The opinions of different authors on the character of this system vary considerably.

### Table 1

<table>
<thead>
<tr>
<th>Melting point ( \text{Li}_3\text{AlF}_6 ) ( ^\circ\text{C} )</th>
<th>Melting point ( \text{Na}_3\text{AlF}_6 ) ( ^\circ\text{C} )</th>
<th>Composition at the temperature minimum point mole % weight %</th>
<th>Corresponding temperature ( ^\circ\text{C} )</th>
<th>Characteristics of the system</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>785</td>
<td>1000</td>
<td>66.06</td>
<td>60.0</td>
<td>723</td>
<td>continuous solid solutions [1]</td>
</tr>
<tr>
<td>782</td>
<td>1012</td>
<td>67.92</td>
<td>62.0</td>
<td>710</td>
<td>simple eutectic system [2]</td>
</tr>
<tr>
<td>783</td>
<td>1009</td>
<td>62.29</td>
<td>56.0</td>
<td>713</td>
<td>two discrete solid solutions [4]</td>
</tr>
<tr>
<td>783</td>
<td>1004</td>
<td>61.00</td>
<td>54.7</td>
<td>720</td>
<td>continuous solid solutions [5]</td>
</tr>
<tr>
<td>782</td>
<td>1009</td>
<td>67.92</td>
<td>62.0</td>
<td>716</td>
<td>the system has an eutectic point [6]</td>
</tr>
<tr>
<td>770</td>
<td>1000</td>
<td>67.80</td>
<td>61.87</td>
<td>680</td>
<td>a simple eutectic system [7]</td>
</tr>
<tr>
<td>782</td>
<td>1007</td>
<td>62.50</td>
<td>56.22</td>
<td>719</td>
<td>—</td>
</tr>
</tbody>
</table>

**Density of the molten system \( \text{Li}_3\text{AlF}_6 \) — \( \text{Na}_3\text{AlF}_6 \)**

In the literature we only find the data of Mašovec and Petrov [9], according to whom, on the density isotherm of the given system at 1000°C a distinct minimum may be observed, corresponding to the composition of about 70 weight % \( \text{Li}_3\text{AlF}_6 \) (Fig. 1). The authors do not explain the reason of the existence of this minimum.

**Experimental**

The mixtures of \( \text{Li}_3\text{AlF}_6 + \text{Na}_3\text{AlF}_6 \) were synthesized from \( \text{LiF} \) „for single crystals“, from \( \text{AlF}_3 \) prepared by sublimation in a platinum apparatus as described by Matiašovský et al. [10] and from the natural hand picked Greenland cryolite. The procedure as well as the recording of the cooling curves were the same as in the previous work [11]. Inaccuracies in recording the critical points on the cooling curves did not exceed \( \pm 2^\circ\text{C} \).

Even when TA, DTA and X-ray phase analysis were performed, no satisfactory answer could be given as to the character of this system which seems to be rather complicated. There is no doubt that it is not a system with a simple eutecticum. With regard to this we give only the experimentally determined liquidus curve of the system (Fig. 2).
Density was determined by the hydrostatic measurement method. A silit furnace of our own construction was used in which the vertical motion was achieved with the aid of an electromotor. A spherical platinum sinker, 25 mm in diameter, was suspended from an analytical balance pan by a platinum wire, 0.3 mm in diameter. With the aid of a special device it was possible to submerge the sinker in the melt to a constant depth. The volume of the sinker as a function of temperature was found by calibration in the melts NaCl and KCl over the temperature range 800—1050°C. The density values of NaCl and KCl reported by Bruner [12] were used for the calibration of the sinker. The volumes of the sinker determined from NaCl and KCl differed less than by 0.2%. The reproducibility of the measurement was better than 0.1%. The salts were weighed out in the amounts of 100 g to a platinum crucible. The device used allowed to record the temperature of the melt with a Pt—Pt10Rh thermocouple each time when the weight of the sinker changed by 10 mg. The molten pure Li$_3$AlF$_6$ and the mixtures with very high Li$_3$AlF$_6$ content tend to capillary elevation of the melt along the platinum wire. For this reason the sinker was submerged into the melt just closely prior to the beginning of the measurement. The density of the melt was calculated from the equation

$$\rho_t = \frac{G_1 - G_2}{V_t}$$

where $G_1$, $G_2$ is the weight of the sinker in the air and in the melt, respectively. $V_t$ is the volume of the sinker at temperature $t$.

The correction to the surface tension was not made because, as it has been found [13], it lies within the limits of experimental error. Evaluating the measured data we found that in the interval 950—1050°C, the polytherms of densities for the individual mixtures are linear functions of temperature (Table 2).

In Fig. 3, the data reported on the dependence of density on the temperature for Na$_3$AlF$_6$ in the papers [9, 14, 15] are graphically compared with those determined in the present work.

In Fig. 4, the data for Li$_3$AlF$_6$ reported in the works [9, 16—18] are compared with our experimental results.
Table 2

Values of the constants in the relation \( \rho_t = a + bt \) for the molten Li₃AlF₆—Na₃AlF₆ system, \( t \in [950; 1050] ^\circ C \)

<table>
<thead>
<tr>
<th>Composition</th>
<th>mole % Li₃AlF₆</th>
<th>mole % Na₃AlF₆</th>
<th>( a )</th>
<th>(-b \times 10^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
<td>0</td>
<td>3.0220</td>
<td>0.92</td>
</tr>
<tr>
<td>10</td>
<td>90</td>
<td>10</td>
<td>2.9845</td>
<td>0.90</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>20</td>
<td>2.9880</td>
<td>0.92</td>
</tr>
<tr>
<td>30</td>
<td>70</td>
<td>30</td>
<td>2.9860</td>
<td>0.93</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>40</td>
<td>2.9400</td>
<td>0.90</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>50</td>
<td>2.9385</td>
<td>0.91</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>60</td>
<td>2.9290</td>
<td>0.91</td>
</tr>
<tr>
<td>70</td>
<td>30</td>
<td>70</td>
<td>2.9270</td>
<td>0.92</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
<td>80</td>
<td>2.9080</td>
<td>0.91</td>
</tr>
<tr>
<td>90</td>
<td>10</td>
<td>90</td>
<td>2.8780</td>
<td>0.89</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>100</td>
<td>2.8180</td>
<td>0.84</td>
</tr>
</tbody>
</table>

The 1000°C isotherm of density for Li₃AlF₆—Na₃AlF₆ is confronted with data cited by Mašovec and Petrov [9] (in Fig. 1).

From the measured density values \( \rho \) of mixtures in the system Li₃AlF₆—Na₃AlF₆ the molar volume \( V \) of the system was calculated. Using the least squares method for calculations of this kind (with the computer ZRA 1) we obtained the equation of the type \( V = f(x_1) \). Sufficient accuracy was attained when the function \( f(x_1) \) was expressed with the aid of a 3rd degree polynomial in \( x_1 \)

\[
V = a + bx_1 + cx_1^2 + dx_1^3 = V_0 + bx_1 + cx_1^2 + dx_1^3 \tag{I}
\]

![Fig. 3. Density of Na₃AlF₆ as a function of temperature.](image)

![Fig. 4. Density of Li₃AlF₆ as a function of temperature.](image)
$x_i$ is mole fraction

$V_i^0$ is molar volume

the indexes 1 and 2 indicate Li$_3$AlF$_6$ and Na$_3$AlF$_6$, respectively.

The values of the constants $V_2^0$, $b$, $c$, $d$ and their mean error for temperatures 950, 1000 and 1050°C are presented in Table 3. As we know, the following relation applies for the partial molar volume $\bar{V}_1$ of the first component of a binary system [19]:

$$\bar{V}_1 = V + x_2 \left( \frac{\partial V}{\partial x_1} \right)_{T, p} = V + (1 - x_1) \left( \frac{\partial V}{\partial x_1} \right)_{T, p}. \quad (2)$$

**Table 3**

Values of the constants in the polynomial $V = V_2^0 + bx_1 + cx_1^2 + dx_1^3$ as functions of temperature

<table>
<thead>
<tr>
<th>$t$, °C</th>
<th>$V_2^0$</th>
<th>$b$</th>
<th>$c$</th>
<th>$d$</th>
<th>Mean error</th>
</tr>
</thead>
<tbody>
<tr>
<td>950</td>
<td>97.796</td>
<td>-14.203</td>
<td>-5.479</td>
<td>1.961</td>
<td>±0.067</td>
</tr>
<tr>
<td>1000</td>
<td>99.874</td>
<td>-14.165</td>
<td>-5.620</td>
<td>1.698</td>
<td>±0.044</td>
</tr>
<tr>
<td>1050</td>
<td>102.109</td>
<td>-14.606</td>
<td>-4.910</td>
<td>1.042</td>
<td>±0.075</td>
</tr>
</tbody>
</table>

Substituting for $V$ from Eq. (1) in Eq. (2) and executing the mathematical operations as indicated above we get:

$$\bar{V}_1 = V_2^0 + b + 2cx_1 + (3d - c)x_1^2 - 2dx_1^3. \quad (3)$$

Inserting $x_1 = 1$ in equation (1) we can write:

$$(V)_{x_1=1} = V_1^0 = V_2^0 + b + c + d. \quad (4)$$

Substituting for $V_2^0$ from Eq. (4) in Eq. (3) we have

$$\bar{V}_1 = V_1^0 - (c + d) + 2cx_1 + (3d - c)x_1^2 - 2dx_1^3. \quad (5)$$

By analogy we get for $\bar{V}_2$ the following relation:

$$\bar{V}_2 = V - x_1 \left( \frac{\partial V}{\partial x_1} \right)_{T, p}. \quad (6)$$

Substituting for $V$ from Eq. (1) and executing the operations we get:

$$\bar{V}_2 = V_2^0 - cx_1^2 - 2dx_1^3. \quad (7)$$

Partial molar volumes $\bar{V}_1$, $\bar{V}_2$ and the volume $V$ at 1000°C are presented in Fig. 5. In Fig. 6, the dependences $-d\bar{V}_1/dx_1$ and $-d\bar{V}_2/dx_2$ as functions of composition at 1000°C are shown. The following relationship holds:

$$\left( \frac{d\bar{V}_1}{dx_1} \right)_{x_1=0.5} = \left( \frac{d\bar{V}_2}{dx_2} \right)_{x_2=0.5} = c + \frac{3}{2} d. \quad (8)$$

The deviation of the molar volume of the salt mixtures from the additive volume is an important constant. The following relation applies for this excess molar volume $\Delta V^e$: Chem. zvesti 23, 27—34 (1969)
Fig. 5. Dependence of the molar volume and of partial molar volumes of the components of the system Li₃AlF₆—Na₃AlF₆ on concentration at 1000°C.

- ○ molar volume
- △ \( \bar{V}_{\text{Li₃AlF₆}} \)
- □ \( \bar{V}_{\text{Na₃AlF₆}} \)

\[
\Delta V^E = V - V_{id} = x_1 \bar{V}_1 + x_2 \bar{V}_2 - (x_1 V^0_1 + x_2 V^0_2).
\] (9)

Inserting \( \bar{V}_1 \) and \( \bar{V}_2 \) from Eq. (5) and (7) in Eq. (9) and rearranging the equation we have for \( \Delta V^E \):

\[
\Delta V^E = -(c + d)x_1 + cx_1^2 + dx_1^3.
\] (10)

It follows from the physical character of the magnitude \( \Delta V^E \) that for \( x_1 = 0 \) and 1, \( \Delta V^E \) has zero value; at certain \( x_1 \in (0; 1) \) the function \( \Delta V^E \) reaches maximum. From this point of view there is just formal analogy between \( \Delta V^E \) and the additional enthalpy [20, 21], or with the "additional molar conductivity" \( \Delta \lambda^E \) [22].

Hence we may write

\[
\Delta V^E = x_1(1 - x_1)\psi(x_1) = -x_1(1 - x_1)[c + d(1 + x_1)].
\] (11)

The function \( \psi(x_1) \) is an integral rational function of the variable \( x_1 \). The function \( \psi(x_1) \) indicates the degree of deviation of the curve \( \Delta V^E = f(x_1) \) in the interval \( x_1 \in (0; 1) \) from the purely parabolic course.

The extreme on the curve \( \Delta V^E = f(x_1) \) occurs under condition that

\[
\frac{d \Delta V^E}{dx_1} = -(c + d) + 2cx_1 + 3dx_1^2 = 0.
\] (12)

By the solution of the equation (12) we have at 1000°C

\[
(x_1)_{1,2} = \frac{-c \pm \sqrt{c^2 + 3cd + 3d^2}}{3d}.
\]

In the given case \( (x_1)_1 = 1.772 \) (which has no physical meaning)
\( (x_1)_2 = 0.435 \)
since
\[
\left(\frac{\text{d}^2 \Delta V^E}{\text{d}x_1^2}\right)_{x_1=0.435} = 2c + 6dx_1 = -11.24 + 4.32 < 0
\]
it is a maximum the coordinates of which are \((x_1)_{\text{max}} = 0.435; \Delta V^E_{\text{max}} = 0.782 \text{ cm}^3 \text{ mol}^{-1}\). In Fig. 7 the functions \(\Delta V^E\) and \(\Delta V^E/x(1-x)\) at 1000°C are shown.

**Fig. 7.** Dependence of \(\Delta V^E\) and \(\Delta V^E/x_1(1-x_1)\) on concentration for the system Li\(_3\)AlF\(_6\) — Na\(_3\)AlF\(_6\) at 1000°C.

- \(\Delta V^E = f(x_1)\)
- \(\Delta V^E/x_1(1-x_1) = \psi(x_1)\)

**Discussion**

As we see from Fig. 3, there is very good agreement between our density data for Na\(_3\)AlF\(_6\) and those reported by Mašovec and Petrov [9]. The data of Abramov et al. [14] are about 0.45% higher and those of Edwards [15] about 0.40% lower than our results. As for the density of Li\(_3\)AlF\(_6\), our data agree within 0.9% with values reported by Kostukov et al. [17] and they differ from Mačcev’s data [16]. As we see from Fig. 4, the temperature coefficient of volume expansion reported in the work [16] largely differs from values found elsewhere.*

The density isotherm of the system Li\(_3\)AlF\(_6\) — Na\(_3\)AlF\(_6\) at 1000°C increases monotonously from the density of Li\(_3\)AlF\(_6\) towards the density of Na\(_3\)AlF\(_6\) (Fig. 1). We did not find the minimum on the isotherm reported by Mašovec et al. [9] which, most probably, is due to an incorrect density determination of pure Li\(_3\)AlF\(_6\) in the paper [9].

The results of the density measurements show that the system Li\(_3\)AlF\(_6\) — Na\(_3\)AlF\(_6\) is very close to the ideal system. The maximal deviation \(\Delta V^E\) is 0.782 cm\(^3\)/mole and the ratio 100(\(\Delta V^E_{\text{max}}/V_{\text{id}}\)) (for identical concentration coordinate) = 0.85%.

The composition of mixtures for which \(\Delta V^E\) is maximal \((x_1 = 0.435)\), differs basically from mixtures which have temperature minimum on the liquidus curve \((x_1 = 0.625)\).

It was found that the relationship \(\Delta V^E/x(1-x) = \psi(x)\) is very sensitive to small experimental inaccuracies. For this reason it is advisable to avoid constructing this dependence on the basis of experimental data and it is better to calculate it from the equation \(V = f(x)\) as we did in the present work.

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*The values of Mašovec and Petrov [9] are considerably higher (by 2.7%).*
As we see in Fig. 5, it holds that $\bar{V}_i$ ($i = 1, 2$) has maximal value for $x_i \to 0$. In praxis, the measurements of liquidus curve and densities for the system $\text{Li}_3\text{AlF}_6 - \text{Na}_3\text{AlF}_6$ may be used for a reasonably accurate determination of the dependence of these parameters for a neutral "lithium—sodium" electrolyte used in aluminium production on its composition in case that the alumina content in the melt drops to minimum (i.e. in the time of the anodic effect). The primary crystallization temperature of electrolytes containing several percents of $\text{Al}_2\text{O}_3$, as well as their density are somewhat lower than the values of these parameters in the binary system $\text{Li}_3\text{AlF}_6 - \text{Na}_3\text{AlF}_6$.

References

17. Kostukov A. A., Polakova G. V., according to [18].

Translated by V. Šašková