

Liquidus Curve and Density of the Molten System Li_3AlF_6 — Na_3AlF_6

M. MALINOVSKÝ, M. PAUČÍROVÁ and K. MATIAŠOVSKÝ

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

Received July 19, 1968

It has been found by TA that there is a minimum on the liquidus curve of the system Li_3AlF_6 — Na_3AlF_6 , the coordinates of which are 62.5 mole % (56.25 weight %) Li_3AlF_6 , 719°C.

By hydrostatic measurement the densities of the molten components and their molten mixtures in the system Li_3AlF_6 — Na_3AlF_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, Li_3AlF_6 , possible. In this case alumina will be dissolved in molten Li_3AlF_6 — Na_3AlF_6 (with regard to C. R.* it will be a neutral electrolyte) or in Li_3AlF_6 — Na_3AlF_6 — AlF_3 (with regard to C. R. an acidic electrolyte).

b) An addition of LiF alone, without AlF_3 , is added so that there would be a certain lithium fluoride excess in the melt (*i.e.* not compensated by AlF_3). Alumina will be dissolved in the molten $\text{LiF} + \text{Na}_3\text{AlF}_6$ in which a small amount of Li_3AlF_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 Li_3AlF_6 — Na_3AlF_6 is justified.

Liquidus curve of the molten system Li_3AlF_6 — Na_3AlF_6

The system Li_3AlF_6 — Na_3AlF_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 Li_3AlF_6 , the natural mineral cryolite 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 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.

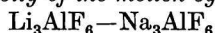
and *Saksonov* [3] identified by X-ray methods the compounds $\text{Li}_3\text{Na}_6\text{Al}_3\text{F}_{18}$, $\text{Li}_6\text{Na}_3\text{Al}_3\text{F}_{18}$ and $\text{Li}_{15}\text{Na}_3\text{Al}_6\text{F}_{36}$ which form, according to the experimental results of the latter authors, with the fundamental components Li_3AlF_6 and Na_3AlF_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 Li_3AlF_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

Literature data on the liquidus curve of the system Li_3AlF_6 — Na_3AlF_6

Melting point Li_3AlF_6 °C	Melting point Na_3AlF_6 °C	Composition at the temperature minimum point		Corresponding temperature °C	Characteristics of the system	References
		mole % Li_3AlF_6	weight % Li_3AlF_6			
785	1000	66.06	60.0	723	continuous solid solutions	[1]
782	1012	67.92	62.0	710	simple eutectic system	[2]
783	1009	62.29	56.0	713	two discrete solid solutions	[4]
783	1004	61.00	54.7	720	continuous solid solutions	[5]
782	1009	67.92	62.0	716	the system has an eutectic point	[6]
770	1000	67.80	61.87	680	a simple eutectic system	[7]
782	1007	62.50	56.22	719	—	this work

Density of the molten system

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 % Li_3AlF_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 LiF „for single crystals“, from 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).

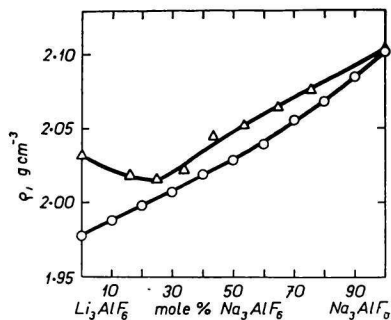


Fig. 1. Density of the system Li_3AlF_6 — Na_3AlF_6 at 1000°C .

△ *Mašovec* [9]
○ this work

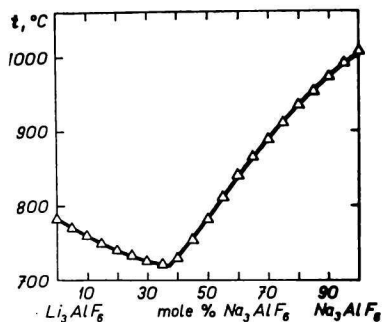


Fig. 2. Liquidus curve for Li_3AlF_6 — Na_3AlF_6 .

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_3AlF_6 and the mixtures with very high Li_3AlF_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_3AlF_6 in the papers [9, 14, 15] are graphically compared with those determined in the present work.

In Fig. 4, the data for Li_3AlF_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 $\text{Li}_3\text{AlF}_6 - \text{Na}_3\text{AlF}_6$ system, $t \in [950; 1050]^\circ\text{C}$

Composition		a	$-b \times 10^3$
mole % Li_3AlF_6	mole % Na_3AlF_6		
0	100	3.0220	0.92
10	90	2.9845	0.90
20	80	2.9880	0.92
30	70	2.9860	0.93
40	60	2.9400	0.90
50	50	2.9385	0.91
60	40	2.9290	0.91
70	30	2.9270	0.92
80	20	2.9080	0.91
90	10	2.8780	0.89
100	0	2.8180	0.84

The 1000°C isotherm of density for $\text{Li}_3\text{AlF}_6 - \text{Na}_3\text{AlF}_6$ is confronted with data cited by *Mašovec* and *Petrov* [9] (in Fig. 1).

From the measured density values ρ of mixtures in the system $\text{Li}_3\text{AlF}_6 - \text{Na}_3\text{AlF}_6$ 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

$$V = a + bx_1 + cx_1^2 + dx_1^3 = V_2^0 + bx_1 + cx_1^2 + dx_1^3 \quad (1)$$

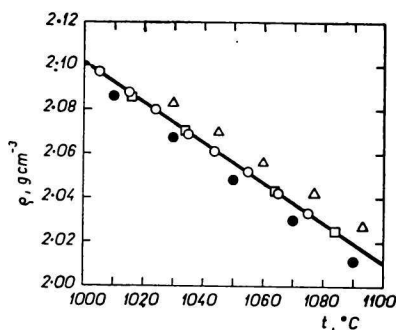


Fig. 3. Density of Na_3AlF_6 as a function of temperature.

- \triangle Abramov [14]
- \square Mašovec [9]
- \bullet Edwards [15]
- \circ this work

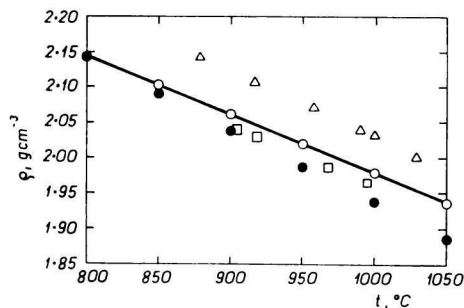


Fig. 4. Density of Li_3AlF_6 as a function of temperature.

- \triangle Mašovec [9]
- \square Kostukov [17]
- \bullet Maicev [16]
- \circ this work

x_i is mole fraction

V_i^0 is molar volume

the indexes 1 and 2 indicate Li_3AlF_6 and Na_3AlF_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

t , °C	V_2^0	b	c	d	Mean error
950	97.796	-14.203	-5.479	1.961	±0.067
1000	99.874	-14.165	-5.620	1.698	±0.044
1050	102.109	-14.606	-4.910	1.042	±0.075

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 ΔV^E :

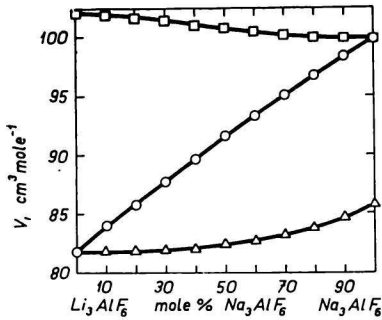


Fig. 5. Dependence of the molar volume and of partial molar volumes of the components of the system $\text{Li}_3\text{AlF}_6 - \text{Na}_3\text{AlF}_6$ on concentration at 1000°C .

- molar volume
 △ $\bar{V}_{\text{Li}_3\text{AlF}_6}$
 □ $\bar{V}_{\text{Na}_3\text{AlF}_6}$

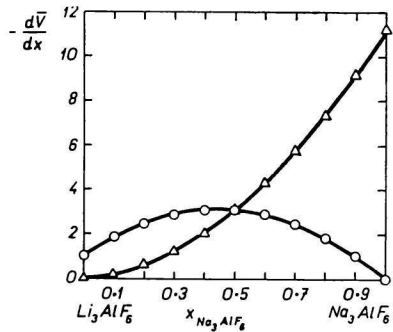


Fig. 6. Dependence $-\text{d}\bar{V}_i/\text{d}x_i$ as a function of composition at 1000°C for the system $\text{Li}_3\text{AlF}_6 - \text{Na}_3\text{AlF}_6$.

- $-\frac{\text{d}\bar{V}_{\text{Na}_3\text{AlF}_6}}{\text{d}x_{\text{Na}_3\text{AlF}_6}}$ △ $-\frac{\text{d}\bar{V}_{\text{Li}_3\text{AlF}_6}}{\text{d}x_{\text{Li}_3\text{AlF}_6}}$

$$\Delta V^E = V - V_{id} = x_1 \bar{V}_1 + x_2 \bar{V}_2 - (x_1 V_1^0 + x_2 V_2^0). \quad (9)$$

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

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

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

Hence we may write

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

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

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

$$\frac{\text{d}\Delta V^E}{\text{d}x_1} = -(c + d) + 2cx_1 + 3dx_1^2 = 0. \quad (12)$$

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

$$\left(\frac{d^2 \Delta V^E}{dx_1^2}\right)_{x_1=0.435} = 2c + 6dx_1 = -11.24 + 4.32 < 0$$

it is a maximum the coordinates of which are $(x_1)_{\max} = 0.435$; $\Delta V^E_{\max} = 0.782 \text{ cm}^3 \text{ mol}^{-1}$. In Fig. 7 the functions ΔV^E and $\Delta V^E/x_1(1-x)$ at 1000°C are shown.

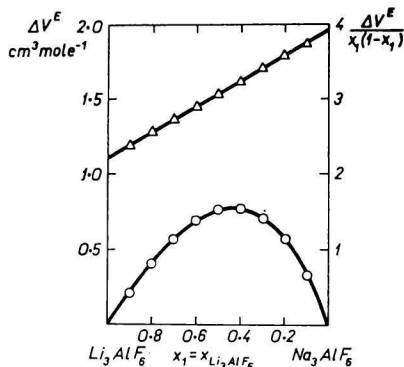


Fig. 7. Dependence of ΔV^E and $\Delta V^E/x_1(1-x_1)$ on concentration for the system Li_3AlF_6 - Na_3AlF_6 at 1000°C .
 $\circ \Delta V^E = f(x_1)$
 $\triangle \Delta V^E/x_1(1-x_1) = \psi(x_1)$

Discussion

As we see from Fig. 3, there is very good agreement between our density data for Na_3AlF_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_3AlF_6 , our data agree within 0.9% with values reported by *Kostukov et al.* [17] and they differ from *Malcev'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_3AlF_6 - Na_3AlF_6 at 1000°C increases monotonously from the density of Li_3AlF_6 towards the density of Na_3AlF_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_3AlF_6 in the paper [9].

The results of the density measurements show that the system Li_3AlF_6 - Na_3AlF_6 is very close to the ideal system. The maximal deviation ΔV^E is $0.782 \text{ cm}^3/\text{mole}$ and the ratio $100(\Delta V^E_{\max}/V_{id})$ (for identical concentration coordinate) = 0.85%. The composition of mixtures for which ΔV^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 $\Delta V^E/x_1(1-x) = \psi(x)$ 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.

* 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 $x_i \rightarrow 0$.

In praxis, the measurements of liquidus curve and densities for the system Li_3AlF_6 — Na_3AlF_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 Al_2O_3 , as well as their density are somewhat lower than the values of these parameters in the binary system Li_3AlF_6 — Na_3AlF_6 .

References

1. Drossbach P., *Z. Elektrochem. Angew. Phys. Chem.* **42**, 65 (1936).
2. Mašovec V. P., Petrov V. I., *Ž. Prikl. Chim.* **30**, 1695 (1957).
3. Beleckij M. S., Saksonov J. G., *Ž. Neorg. Chim.* **2**, 415 (1957).
4. Rolin M., Muhlethaler R., *Bull. Soc. Chim. France* **1964**, 2593.
5. Sílešová J., Matiašovský K., unpublished results.
6. Chin D. A., Hollingshead E. A., *J. Electrochem. Soc.* **113**, 736 (1966).
7. Babajan G. G., Edojan R. S., Manveljan M. G., *Arm. Chim. Ž.* **20**, 20 (1967).
8. Menzer G., *Z. Krist.* **66**, 457 (1927); **75**, 265 (1930).
9. Mašovec V. P., Petrov V. I., *Ž. Prikl. Chim.* **32**, 1526 (1959).
10. Matiašovský K., Malinovský M., Plško E., Kubík C., *Chem. Zvesti* **14**, 487 (1960).
11. Malinovský M., Čakajdová I., Matiašovský K., *Chem. Zvesti* **21**, 794 (1967).
12. Bruner E., *Z. Anorg. Chem.* **18**, 360 (1904).
13. Mellors G. V., Senderoff S., in the book *Proceedings of the First Australian Conference on Electrochemistry*, p. 578. Pergamon Press, Oxford, 1965.
14. Abramov G. A., Vetukov M. M., Gupalo I. P., Kostukov A. A., Ložkin L. N., *Teoretičeskije osnovy elektrometallurgii aluminija*, p. 88. Metallurgizdat, Moscow, 1953.
15. Edwards J. D., Taylor C. S., Russel A. S., *J. Electrochem. Soc.* **100**, 508 (1953).
16. Malcev V. T., Buchalova G. A., *Ž. Prikl. Chim.* **40**, 532 (1967).
17. Kostukov A. A., Pořakova G. V., according to [18].
18. Vetukov M. M., Siprija G. I., *Ž. Prikl. Chim.* **36**, 1905 (1963).
19. Hála E., Reiser A., *Fyzikální chemie*, Vol. I, p. 206. Publishing House of the Czechoslovak Academy of Sciences, Prague, 1960.
20. Kleppa O. J., Hersh L. S., *Discussions Faraday Soc.* **32**, 99 (1961).
21. Kleppa O. J., Toguri J. M., in the book *Selected Topics in High Temperature Chemistry*, p. 15. Edited by T. Førland, K. Grjotheim, K. Motzfeldt and S. Urnes. Universitets forlaget, Oslo, 1966.
22. Nooijer de B., *The Electrical Conductivity of Molten Nitrates and Binary Nitrates*. Rototype. University of Amsterdam, 1965.

Translated by V. Šašková