

Calculation of isotherms in the phase diagram of the system $\text{Li}_3\text{AlF}_6\text{—LiF—CaF}_2$

*J. VRBENSKÁ and ^bI. KOŠTENSKÁ

^aDepartment of Electrotechnology, Slovak Technical University,
CS-812 19 Bratislava

^bDepartment of Chemical Technology of Inorganic Substances,
Slovak Technical University, CS-812 37 Bratislava

Received 3 September 1985

*Dedicated to the memory of Professor Ing. M. Malinovský, DrSc.,
April 2, 1926—December 15, 1984*

Isotherms in the phase diagram of the system $\text{Li}_3\text{AlF}_6\text{—LiF—CaF}_2$ were calculated using different models of the melt. It was found that the model respecting partial thermal dissociation of complex anion AlF_6^{3-} , temperature dependence of $\Delta H(\text{fus}, \text{CaF}_2)$ and assuming dissociation of CaF_2 into CaF^+ and F^- gives the best agreement with experimental data. Decrease of the degree of thermal dissociation of cryolite anion with increasing concentration of components LiF and CaF_2 proves the beneficial effect of these substances in aluminium electrolyte on the decrease of fluorine emissions.

Рассчитаны изотермы фазовой диаграммы системы $\text{Li}_3\text{AlF}_6\text{—LiF—CaF}_2$ с использованием различных моделей расплава. Обнаружено, что модель, учитывающая частичную термическую диссоциацию комплексного аниона AlF_6^{3-} , температурную зависимость $\Delta H(\text{fus}, \text{CaF}_2)$ и предполагающая диссоциирование CaF_2 на CaF и F^- , находится в наилучшем согласовании с экспериментальными данными. Понижение степени термической диссоциации аниона криолита при увеличении концентрации компонентов LiF и CaF_2 свидетельствует о благоприятном действии этих соединений в алюминиевом электролите на снижение эмиссий фтора.

Investigation and construction of phase diagrams of new systems is usually very laborious. Till now it is based almost exclusively on experimental work. From the theoretical and practical point of view remarkable contribution to solution of this problem can be done on the basis of calculation of liquidus curves (generally of liquidus surfaces or volumes) using tabulated thermodynamic data. In the field of physical chemistry of molten salts suitability of different models for this purpose is

tested. It requires comparison of the calculated and experimental data on the temperature of primary crystallization and the agreement between them is considered as a measure of reliability of the assumptions and of physical meaning of the chosen model.

Survey of literature data on the studied system

The system $\text{Li}_3\text{AlF}_6\text{—LiF—CaF}_2$ is a part of the system $\text{LiF—CaF}_2\text{—AlF}_3$ which has been experimentally investigated by several authors [1—9]. The data unambiguously confirm that in this system a congruently melting compound Li_3AlF_6 is formed. Thus there exists the stable diagonal $\text{Li}_3\text{AlF}_6\text{—CaF}_2$ which divides the original system into two independent subsystems: $\text{Li}_3\text{AlF}_6\text{—LiF—CaF}_2$ and $\text{Li}_3\text{AlF}_6\text{—CaF}_2\text{—AlF}_3$. The first of this subsystems is the object of investigation in this paper.

This system has been experimentally reinvestigated in 1966 [10]. It was found that the phase diagrams of the binary systems $\text{Li}_3\text{AlF}_6\text{—LiF}$, $\text{Li}_3\text{AlF}_6\text{—CaF}_2$, and LiF—CaF_2 have a simple eutectic character. X-Ray analysis proved that no solid solutions are formed. Also the ternary system is a simple eutectic system without solid solutions. Composition coordinates and temperatures of eutectic points are summarized in Table 1.

In the cited paper [10] the experimental results were compared with calculations of the liquidus curves. The Le Chatelier—Shreder equation was used

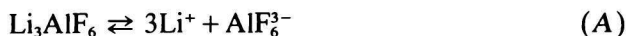
$$\ln a(i) = \frac{\Delta H(\text{fus}, i)}{R} \left(\frac{1}{T(\text{fus}, i)} - \frac{1}{T(i)} \right) \quad (1)$$

$a(i)$ is the activity of the i -th component, $\Delta H(\text{fus}, i)$ is the molar enthalpy of fusion of this component, $T(\text{fus}, i)$ is its temperature of fusion and $T(i)$ is the temperature of primary crystallization (liquidus temperature) of the i -th component.

The following two models for relationship between activity and mole fraction of components were used:

a) The system was assumed to be ideal; $a(i) = x(i)$.

b) The Temkin model of ideal ionic mixtures was used [11]; in this case the activity equals the product of cationic and anionic fractions. The following dissociation schemes were assumed



The enthalpies of fusion of pure components were taken from literature [12—14]. Their temperature dependence was neglected.

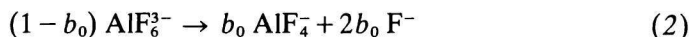
Table 1

Composition coordinates and temperature of eutectic points in the studied systems [10]

System	$\frac{x(\text{Li}_3\text{AlF}_6)}{\text{mole \%}}$	$\frac{x(\text{LiF})}{\text{mole \%}}$	$\frac{x(\text{CaF}_2)}{\text{mole \%}}$	T/K	Calculated according to the Temkin model			
					$\frac{x(\text{Li}_3\text{AlF}_6)}{\text{mole \%}}$	$\frac{x(\text{LiF})}{\text{mole \%}}$	$\frac{x(\text{CaF}_2)}{\text{mole \%}}$	T/K
$\text{Li}_3\text{AlF}_6\text{—LiF}$	29.5	70.5	—	988	38	62	—	953
$\text{Li}_3\text{AlF}_6\text{—CaF}_2$	56.5	—	43.5	976	55	—	45	908
LiF—CaF_2	—	79.0	21.0	1038	—	83	17	1053
$\text{Li}_3\text{AlF}_6\text{—LiF—CaF}_2$	25	23	52	938	31	44	25	873

The variant *b*) gave better agreement between experimental and calculated data. It was concluded that the behaviour of the system approaches the Temkin model of perfect ionic solutions. As seen from Table 1 the difference in composition does not exceed 10 %. However, the difference in the eutectic temperatures is rather high. It follows that the model does not describe behaviour of the studied system with sufficient precision and one should seek a possibility for improving the agreement with experiment.

It is known that cryolite anion thermally dissociates. *Grjothheim* [15] used for solution of this problem the *Glasstone's* idea [16]. He assumed that cryolite completely electrolytically dissociates into sodium cations and anions AlF_6^{3-} which further partly thermally dissociate according to the scheme



b_0 is the degree of thermal dissociation of AlF_6^{3-} in the melt of pure cryolite. In the mixture this parameter is denoted as b . It is generally different from b_0 .

It is obvious that the thermal dissociation will influence the activities of components and consequently the calculated liquidus curves. Application of this procedure to the calculation of liquidus curves of Li_3AlF_6 in its mixtures with CaF_2 , SrF_2 , BaF_2 , and LiF , respectively, gave better agreement with experimental liquidus curves of Li_3AlF_6 [17] in relevant binary systems. The best fit was obtained for $b_0 = 0.25$ [12]. Simultaneously it has been shown [17] that in the system Li_3AlF_6 — CaF_2 calcium fluoride does not dissociate according to the scheme (C) but rather according to the scheme



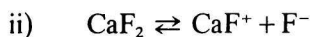
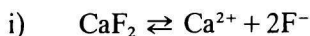
Refined calculation of isotherms

Calculation of isotherms of the phase diagram of the system Li_3AlF_6 — LiF — CaF_2 presented here differs from that used in paper [10] in the following details:

- partial thermal dissociation of anion AlF_6^{3-} is taken into account;
- two possibilities of dissociation of CaF_2 according to the scheme (C) or (D) are considered;

- at the calculation of liquidus curve of CaF_2 the temperature dependence of the enthalpy of fusion $\Delta H(\text{fus}, \text{CaF}_2)$ is taken into account. This includes also the polymorphic transition of $\text{CaF}_2(\alpha)$ into $\text{CaF}_2(\beta)$ at 1424 K. (In the case of liquidus curves of Li_3AlF_6 or LiF the temperature dependence of the enthalpy of fusion can be neglected because the temperature ranges in remarkably smaller interval than in the case of liquidus of CaF_2 (ca. 550 K).)

Using procedure described in [15—17] the relationships for activity and dissociation constant $K^0(\text{dis})$ of pure molten Li_3AlF_6 were derived for two alternatives based on two possible schemes of dissociation of CaF_2



For thermal dissociation of Li_3AlF_6 it follows

$$K^0(\text{dis}) = \frac{4b_0^3}{(1-b_0)(1+2b_0)^2} \quad (3)$$

b_0 was adopted to be 0.25 for both models. Then $K^0(\text{dis}) = 0.03704$ and for activities of components it follows

$$a(\text{Li}_3\text{AlF}_6) = \left(\frac{3x+y}{1+2x}\right)^3 \cdot \frac{x(1-b)}{1+2xb+z} \quad (4\text{i})$$

$$a(\text{Li}_3\text{AlF}_6) = \left(\frac{3x+y}{1+2x}\right)^3 \cdot \frac{x(1-b)}{1+2xb} \quad (4\text{ii})$$

$$a(\text{LiF}) = \frac{3x+y}{1+2x} \cdot \frac{2xb+y+z}{1+2xb+z} \quad (5\text{i})$$

$$a(\text{LiF}) = \frac{3x+y}{1+2x} \cdot \frac{2xb+y+z}{1+2xb} \quad (5\text{ii})$$

$$a(\text{CaF}_2) = \frac{z}{1+2x} \cdot \left(\frac{2xb+y+z}{1+2xb+z}\right)^2 \quad (6\text{i})$$

$$a(\text{CaF}_2) = \frac{z}{1+2x} \cdot \frac{2xb+y+z}{1+2xb} \quad (6\text{ii})$$

$$a(\text{LiAlF}_4) = \frac{3x+y}{1+2x} \cdot \frac{xb}{1+2xb+z} \quad (7\text{i})$$

$$a(\text{LiAlF}_4) = \frac{3x+y}{1+2x} \cdot \frac{xb}{1+2xb} \quad (7\text{ii})$$

$$K(\text{dis}) = \frac{(2xb+y+z)^2 b}{(1-b)(1+2xb+z)^2} \quad (8\text{i})$$

$$K(\text{dis}) = \frac{(2xb+y+z)^2 b}{(1-b)(1+2xb)^2} \quad (8\text{ii})$$

In the relations (4—8) x , y , z denote the mole fractions of Li_3AlF_6 , LiF , and CaF_2 , respectively. The degree of dissociation of AlF_6^{3-} in the mixture (it is denoted as b) was calculated under the assumption

$$K^0(\text{dis}) = K(\text{dis}) \quad (9)$$

After introducing the activities into eqn (1) the corresponding temperatures of primary crystallization of components were calculated. In the case of CaF_2 the temperature dependence of the enthalpy of fusion was taken into account

$$\ln a(\text{CaF}_2) = \frac{\Delta H(\text{fus}, \text{CaF}_2)}{R} \left(\frac{1}{T(\text{fus}, \text{CaF}_2)} - \frac{1}{T(\text{CaF}_2)} \right) + f(\Delta C_p(l/s)) \quad (10)$$

In this way three temperatures of primary crystallization were obtained for each composition point in the ternary system. The highest value of the temperature was considered as that corresponding to the solidus—liquidus equilibrium and it was used for construction of surfaces of monovariant equilibrium. The used thermodynamic data are presented in Table 2. The results are plotted in Figs. 1 and 2. With respect to extended numerical results only the calculated data for composition

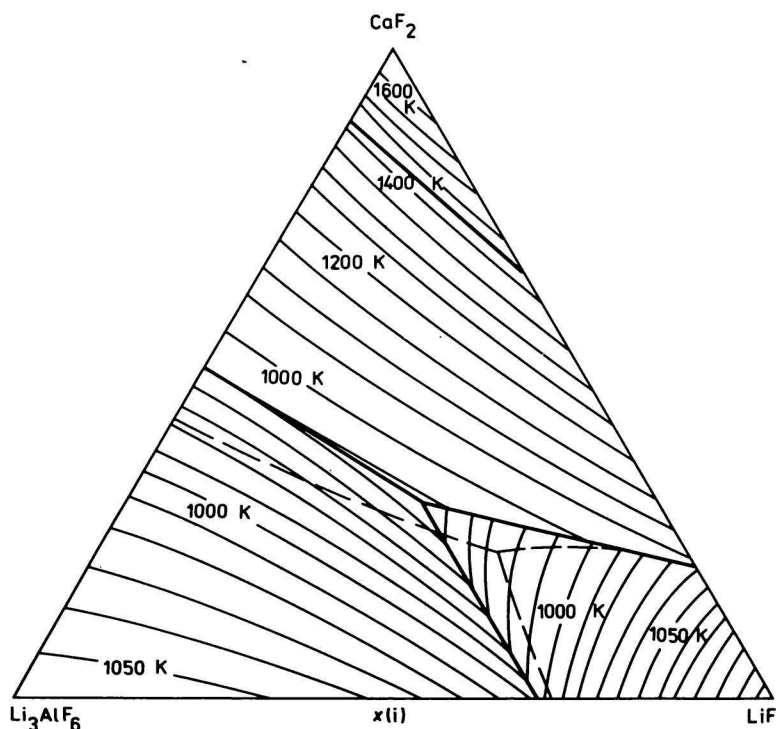


Fig. 1. Isotherms in the system Li_3AlF_6 — LiF — CaF_2 calculated according to the variant ii).
 ————— Calculated; - - - - - experimental.

Table 2

Thermodynamic data of pure components [18]

Component	$\frac{\Delta H(\text{fus})}{\text{kJ mol}^{-1}}$	$\frac{\Delta H(\alpha \rightleftharpoons \beta)}{\text{kJ mol}^{-1}}$	$\frac{T(\text{fus})}{\text{K}}$	$\frac{T(\alpha \rightleftharpoons \beta)}{\text{K}}$	$\frac{C_p(l^0)}{\text{J K}^{-1} \text{mol}^{-1}}$	$\frac{C_p(s^0)}{\text{J K}^{-1} \text{mol}^{-1}}$	b_0
Li_3AlF_6	86.29	—	1058	—	—	—	0.25
LiF	27.09	—	1121	—	—	—	1.0
$\text{CaF}_2(\alpha)$	29.71	4.77	1691	1424	100	$108 + 10.5 \times 10^{-3} T$	1.0
$\text{CaF}_2(\beta)$	34.48	—	1679.5	—	—	$60 + 30.5 \times 10^3 T + 1.97 \times 10^5 T^{-2}$	1.0

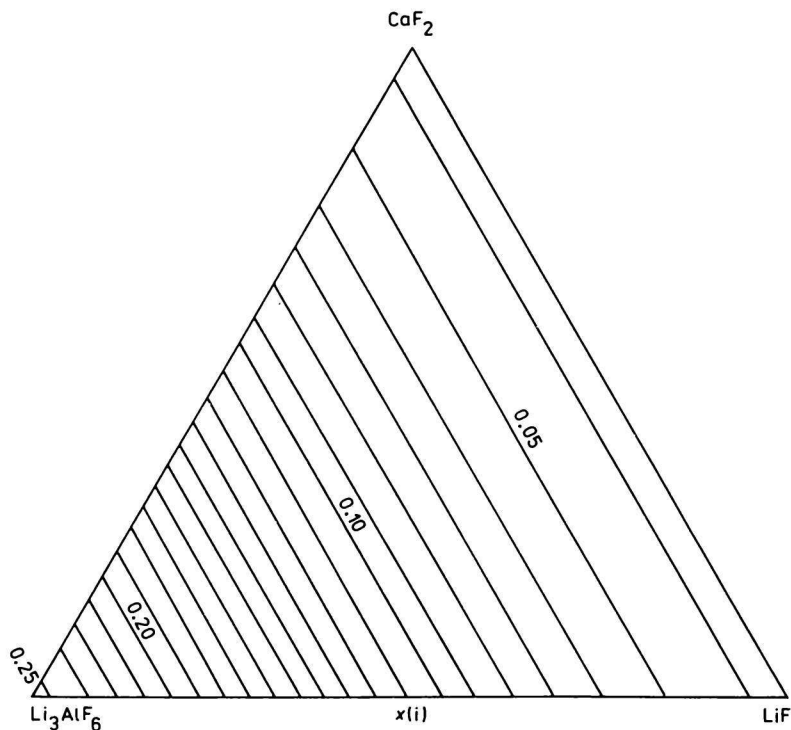


Fig. 2. Isopleths of the coefficient of dissociation of AlF_6^{3-} in the system Li_3AlF_6 — LiF — CaF_2 calculated according to the variant ii).

and temperature of binary and ternary eutectic points are given in Table 3. The agreement is evaluated in percents of the difference between the calculated and experimental value.

Results and discussion

The system Li_3AlF_6 — LiF — CaF_2 contains a complex compound which partly thermally dissociates under melting. One of the products of the dissociation are the ions F^- which are present also in the other two components. Thus the system can be considered as a system with common anion. It follows that the decrease of concentration of Li_3AlF_6 must cause also a decrease in the degree of thermal dissociation of the anion AlF_6^{3-} . This was confirmed by calculations.

Another special feature of the studied system is the fact that the melting point of CaF_2 is about 500 K higher than melting points of the other components and

Table 3

Comparison of the experimental and calculated data on composition coordinates and temperature of eutectic points in the studied systems

System	$x(\text{Li}_3\text{AlF}_6)$ mole %	$x(\text{LiF})$ mole %	$x(\text{CaF}_2)$ mole %	$T(\text{E})$ K
Li₃AlF₆—LiF				
found	30.0	70.0	—	988
calc. (i)	31.4	68.6	—	999
Δ_r (i)/%	4.7	2.0	—	1.1
calc. (ii)	31.4	68.6	—	999
Δ_r (ii)/%	4.7	2.0	—	1.1
Li₃AlF₆—CaF₂				
found	56.5	—	43.5	976
calc. (i)	49.0	—	51.0	922
Δ_r (i)/%	13.3	—	17.2	5.5
calc. (ii)	49.5	—	50.5	951
Δ_r (ii)/%	12.4	—	16.1	2.6
LiF—CaF₂				
found	—	79.0	21.0	1038
calc. (i)	—	79.5	20.5	1039
Δ_r (i)/%	—	0.6	2.4	0.1
calc. (ii)	—	79.5	20.5	1039
Δ_r (ii)/%	—	0.6	2.4	0.1
Li₃AlF₆—LiF—CaF₂				
found	25.0	52.0	23.0	938
calc. (i)	44.8	8.6	46.6	921.5
Δ_r (i)/%	79.2	83.5	102.6	1.8
calc. (ii)	30.6	38.9	30.5	940.5
Δ_r (ii)/%	22.4	25.2	32.6	0.3

$$\Delta_r/\% = 100 \frac{|\text{found} - \text{calc.}|}{\text{found}}$$

moreover it has a polymorphic transition in solid phase. This makes the agreement between calculated and experimental data specially worth. The calculated and experimental eutectic temperatures differ less than by 6 %. The differences in composition coordinates are somewhat greater, especially in the system Li₃AlF₆—CaF₂ (ca. 13 %) and in the ternary system Li₃AlF₆—LiF—CaF₂ where the difference ranges from 8 to 103 %. As may be seen from Table 3

a better agreement with experiment for all investigated systems was achieved when the dissociation of CaF_2 into CaF^+ and F^- was assumed (the variant ii)). This result again confirms the justification of the second model of dissociation of CaF_2 . Calculation of the ternary eutectic point according to the variant i) gives unsatisfactory results.

References

1. Ruff, O. and Busch, W., *Z. Anorg. Allg. Chem.* 144, 87 (1925).
2. Bukhalova, G. A. and Bergman, A. G., *Dokl. Akad. Nauk SSSR* 66, 67 (1947).
3. Bukhalova, G. A. and Berezhnaya, V. T., *Zh. Neorg. Khim.* 2, 1049 (1957).
4. Roake, W., *J. Electrochem. Soc.* 104, 661 (1957).
5. Feodotieff, P. P. and Timofeeff, G. A., *Z. Anorg. Allg. Chem.* 206, 263 (1932).
6. Dergunov, E. P., *Dokl. Akad. Nauk SSSR* 60, 1185 (1948).
7. Malinovský, M., Čakajdová, I., and Matiašovský, K., *Chem. Zvesti* 21, 794 (1967).
8. Fedotjev, P. P. and Iljinskij, V. P., *Z. Anorg. Allg. Chem.* 129, 93 (1923).
9. Holm, J. L., *Acta Chem. Scand.* 19, 1512 (1965).
10. Vrbenská, J. and Malinovský, M., *Chem. Zvesti* 21, 818 (1967).
11. Temkin, M., *Acta Physicochem. URSS* 20, 411 (1945).
12. Ratkje, S. K. and Rytter, E., *J. Phys. Chem.* 78, 1499 (1974).
13. Douglas, T. and Dever, J. L., *J. Amer. Chem. Soc.* 76, 4826 (1954).
14. Abramov, G. A., Vetyukov, M. M., Gupalo, I. P., Kostyukov, A. A., and Lozhkin, L. N., *Teoreticheskie osnovy elektrometallurgii alyuminiya*. Metallurgizdat, Moscow, 1953.
15. Grjotheim, K., *Contribution to the Theory of the Aluminium Electrolysis*. Kgl. Norske Vidensk. Selsk. Skr., No. 5. F. Bruns, Trondheim, 1956.
16. Glasstone, S., *Textbook of Physical Chemistry*. 2nd Edition. Van Nostrand, New York, 1947.
17. Vrbenská, J., Koštenská, I., and Malinovský, M., *Chem. Zvesti* 27, 577 (1973).
18. Kelley, K. K., *Contribution to the Data on Theoretical Metallurgy*. Bull. 584. Bureau of Mines. U.S. Government Printing Office, Washington, 1960.

Translated by P. Fellner