

# Dissociation of the $\text{AlF}_6^{3-}$ anion in the systems $\text{Li}_3\text{AlF}_6\text{—CaF}_2$ , $\text{Li}_3\text{AlF}_6\text{—SrF}_2$ , and $\text{Li}_3\text{AlF}_6\text{—BaF}_2$

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Grjothheim's generalized method was applied to the systems  $\text{Li}_3\text{AlF}_6\text{—MF}_2$  ( $M = \text{Ca, Sr, Ba}$ ) for the calculation of the dissociation of the  $\text{AlF}_6^{3-}$  anion. The dissociation degree of  $\text{AlF}_6^{3-}$  in pure molten  $\text{Li}_3\text{AlF}_6$  was found to be equal to 0.30. Comparison of the theoretical and experimental data leads to the conclusion that  $\text{CaF}_2$  in this case mostly yields the  $\text{CaF}^+$  and  $\text{F}^-$  ions, whereas  $\text{SrF}_2$  and  $\text{BaF}_2$  dissociate into  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$ , respectively, and  $\text{F}^-$ . The described scheme of dissociation of the compounds of  $\text{MF}_2$  is in accordance with the cryoscopic measurements in the systems  $\text{NaCl—MF}_2$ .

Recently the phase diagrams of the systems  $\text{Li}_3\text{AlF}_6\text{—CaF}_2$ ,  $\text{Li}_3\text{AlF}_6\text{—SrF}_2$ , and  $\text{Li}_3\text{AlF}_6\text{—BaF}_2$  have been established [1]. A comparison of the experimental and calculated data is important to the understanding of the dissociation schemes of the complex anion  $\text{AlF}_6^{3-}$  in these systems. For calculation of the dissociation degree of the complex anion  $\text{AlF}_6^{3-}$  the same procedure was applied as used by Grjothheim [2] for the systems  $\text{Na}_3\text{AlF}_6\text{—NaF}$  and  $\text{Na}_3\text{AlF}_6\text{—AlF}_3$ . The applicability of this method was verified with the systems  $\text{Li}_3\text{AlF}_6\text{—LiF}$  and  $\text{Li}_3\text{AlF}_6\text{—AlF}_3$  [3]. In contrast to the cases studied in [2, 3], in the systems considered in this paper there are two kinds of cations:  $\text{Li}^+ + \text{M}^{2+}$ , or  $\text{Li}^+ + \text{MF}^+$ .

## Schemes of dissociation

The following assumptions have been employed in the calculation:

a) Molten  $\text{Li}_3\text{AlF}_6$  dissociates completely according to



and the  $\text{AlF}_6^{3-}$  anion partially continues dissociating according to the equilibrium scheme



The dissociation process of the type (B) is supposed not only by Grjothheim [2] but also by other authors [4–7]. For molten fluorides of the type  $\text{MF}_2$  the following schemes of dissociation are assumed



Then the equilibrium reaction partially takes place



b) The dissociation constant in equation (B) and the value of  $\Delta H_{\text{Li}_3\text{AlF}_6}^f$  are temperature independent.

c) The studied systems are in accordance with Temkin's model [8] of the activity of a component in an ideal ionic solution.

### *A survey of Grjotheim's method of calculation*

The degree of dissociation of the  $\text{AlF}_6^{3-}$  anion in pure  $\text{Li}_3\text{AlF}_6$  is denoted as  $b$ . The ions  $\text{Li}^+$ ,  $\text{AlF}_6^{3-}$ ,  $\text{AlF}_4^-$ , and  $\text{F}^-$  form an ideal ionic solution; then the procedure described in [3] leads to the expression of the activity of lithium cryolite:

$$a_{\text{Li}_3\text{AlF}_6} = \frac{1 - b}{1 + 2b}. \quad (1)$$

With respect to the scheme (B) the dissociation constant  $K_1$  of the  $\text{AlF}_6^{3-}$  anion in pure  $\text{Li}_3\text{AlF}_6$  is defined by equation

$$K_1 = \frac{a_{\text{AlF}_4^-} \cdot a_{\text{F}^-}^2}{a_{\text{AlF}_6^{3-}}} = \frac{4b^3}{(1 - b)(1 + 2b)^2} \quad (2)$$

Assuming the partial dissociation of  $\text{AlF}_6^{3-}$  the experimentally determined melting point of pure  $\text{Li}_3\text{AlF}_6$  represents the temperature at which an invariant equilibrium exists between the solid compound  $\text{Li}_3\text{AlF}_6$  and the melt formed of a mixture of the ions  $\text{Li}^+$ ,  $\text{AlF}_6^{3-}$ ,  $\text{AlF}_4^-$ , and  $\text{F}^-$ . Then the hypothetical melting point of absolutely undissociated cryolite is expressed by the relation

$$\frac{1}{T_{\text{id}}^f} = \frac{1}{T_{\text{exp}}^f} + \frac{R}{\Delta H_{\text{Li}_3\text{AlF}_6}^f} \ln \frac{1 - b}{1 + 2b}. \quad (3)$$

The degree of dissociation of  $\text{AlF}_6^{3-}$  in the systems  $\text{Li}_3\text{AlF}_6 - \text{MF}_2$  in general differs from that in pure  $\text{Li}_3\text{AlF}_6$ . If  $d$  is this degree of dissociation and the dissociation of  $\text{MF}_2$  is considered to occur according to the scheme (C), then one mole of the melt with the mole fraction of  $\text{Li}_3\text{AlF}_6$  being  $X$ , yields  $3X$  moles  $\text{Li}^+$ ,  $(1 - X)$  moles  $\text{M}^{2+}$ ,  $(1 - d)X$  moles  $\text{AlF}_6^{3-}$ ,  $Xd$  moles  $\text{AlF}_4^-$  and  $[2Xd + 2(1 - X)]$  moles  $\text{F}^-$ .

The dissociation constant  $K_2$  of  $\text{AlF}_6^{3-}$  in the melt  $\text{Li}_3\text{AlF}_6 + \text{MF}_2$  equals

$$K_2 = \frac{4(1 +Xd - X)^2 d}{(1 - d)(2 + 2Xd - X)^2} \quad (4)$$

and the activity of  $\text{Li}_3\text{AlF}_6$  is

$$a_{\text{Li}_3\text{AlF}_6/\text{MF}_2} = a_{\text{Li}^+}^3 \cdot a_{\text{AlF}_6^{3-}} = \frac{27X^4(1 - d)}{(1 + 2X)^3(2 + 2Xd - X)}. \quad (5)$$

The temperature of the primary crystallization  $T$  of lithium cryolite under the discussed conditions is given by equation

$$\frac{1}{T} = \frac{1}{T_{\text{id}}^f} - \frac{R}{\Delta H_{\text{Li}_3\text{AlF}_6}^f} \ln a_{\text{Li}_3\text{AlF}_6/\text{MF}_2} \quad (6)$$

The expressions for the activities of the dissociation schemes (D) and (E) of  $\text{MF}_2$  should be arranged according to the chosen dissociation model. The dissociation degree of  $\text{MF}^+ \rightleftharpoons \text{M}^{2+} + \text{F}^-$  is denoted as  $e$ .

### Calculation

a) The values of  $K_1$  and  $T_{\text{id}}^f$  of  $\text{Li}_3\text{AlF}_6$  are calculated from equations (2) and (3). The interval of the dissociation degrees was chosen from 0.05 to 0.95.

b) Since for ideal ionic solutions the equality

$$K_1 = K_2$$

is valid, we can set equal equations (2) and (4). In this way we can calculate  $d$  for the chosen values of  $X$  and  $b$  (eventually for  $e$ ).

c) The theoretical value of the temperature of primary crystallization of  $\text{Li}_3\text{AlF}_6$  in the systems with  $\text{MF}_2$  can be determined from equation (6) by substituting the chosen values for  $X$  and the corresponding values of  $d$  or  $e$ .

### Results of calculation and their comparison with experimental data

Calculations of the liquidus curves of  $\text{Li}_3\text{AlF}_6$  were performed with a digital computer MINSK 22. In accordance with the published results [9, 10] the values  $\Delta H_{\text{Li}_3\text{AlF}_6}^f = 20.5 \text{ kcal mol}^{-1}$  and  $T_{\text{Li}_3\text{AlF}_6}^f = 1055 \text{ K}$  were used. With respect to the extent of results we list in Table 1 only those results, which enable us to make conclusions on the dissociation degree of the  $\text{AlF}_6^{3-}$  anion.

Table 1

Comparison of experimentally found and calculated values of liquidus curves

Mole fraction of $\text{Li}_3\text{AlF}_6$	Liquidus of $\text{Li}_3\text{AlF}_6$ in systems with $\text{MF}_2$ , [°C]					
	$\text{CaF}_2$		$\text{SrF}_2$		$\text{BaF}_2$	
	Experimentally found	Calculated $b = 0.30$ $e = 0.10$	Experimentally found	Calculated $b = 0.30$ $e = 0.80$	Experimentally found	Calculated $b = 0.30$ $e = 0.95$
1.0	782	782	782	782	782	782
0.95	777	776.11	777	775.96	775	775.91
0.90	769	769.75	768.5	769.08	766	768.88
0.85	763	762.60	760	761.02	757	760.60
0.80	755	754.56	750.5	751.62	745	750.70
0.70	738	735.13	725.5	728.29	717	726.63
0.60	714	709.96	691	698.11	686	695.49

### Discussion

In discussing the plausibility of the obtained results it should be kept in mind what simplifications have been made in calculations.

First, the validity of Temkin's model of an ideal ionic solution is supposed. The dissociation model of lithium cryolite may be considered, according to equations (A) and (B), as reliably verified.

Concerning the dissociation schemes of other components of the  $\text{MF}_2$  type, the possibilities expressed by equations (C), (D), and (E) were considered. Comparison of the measured and calculated results excluded the applicability of the dissociation scheme (C) for the system  $\text{Li}_3\text{AlF}_6\text{--CaF}_2$  and the scheme (D) for the systems  $\text{Li}_3\text{AlF}_6\text{--SrF}_2$  and  $\text{Li}_3\text{AlF}_6\text{--BaF}_2$ . But the used method of calculation did not yield unambiguous information whether for the dissociation of  $\text{CaF}_2$  in systems with  $\text{Li}_3\text{AlF}_6$  the dissociation model (D) or (E) and similarly for  $\text{SrF}_2$  and  $\text{BaF}_2$  the model (C) or (E) is valid.

In order to verify the most probable dissociation scheme of  $\text{MF}_2$  the cryoscopic method was used. The systems studied were  $\text{NaCl--CaF}_2$ ,  $\text{NaCl--SrF}_2$ , and  $\text{NaCl--BaF}_2$  [11] because the liquidus curve of  $\text{NaCl}$  in these systems is approximately in the same temperature range as that of  $\text{Li}_3\text{AlF}_6$  in systems with the same components. Cryoscopic measurements showed that in the concentration range of 0.5–2 mole %,  $\text{MF}_2$  in the system  $\text{NaCl--MF}_2$  each molecule of  $\text{CaF}_2$ ,  $\text{SrF}_2$ , and  $\text{BaF}_2$  brought into the molten  $\text{NaCl}$  2.15, 2.80, and 2.95 new particles, respectively. The best applicable explanation for these results lies in the idea of the coexistence of the ions  $\text{MF}^+$ ,  $\text{M}^{2+}$ , and  $\text{F}^-$ , according to equation (E). Table 1 shows that the experimental data are in good agreement with those obtained by calculations, when considering the dissociation degree of  $\text{AlF}_6^{3-}$  in pure  $\text{Li}_3\text{AlF}_6$  to be  $b = 0.30$ . Thus  $\text{CaF}_2$  dissociates completely into the  $\text{CaF}^+$  and  $\text{F}^-$  ions; the former partially continues to dissociate (up to 10%) into  $\text{Ca}^{2+}$  and  $\text{F}^-$ ; this dissociation makes for  $\text{SrF}_2$  approx. 80% and for  $\text{BaF}_2$  95%.

Other simplifying assumptions are those of the temperature independence of the dissociation constant and of the enthalpy of fusion for pure  $\text{Li}_3\text{AlF}_6$ . Since the liquidus curve of lithium cryolite runs in a relatively narrow temperature range (782–680°C) those assumptions should not cause any significant error.

In equation (3) the experimentally established value of  $\Delta H_{\text{Li}_3\text{AlF}_6}^f$  was taken into calculation, *i.e.* the enthalpy of dissociation of  $\text{Li}_3\text{AlF}_6$  was not considered; (the same was done by Rolin [5]). According to the published results [12], the value of  $\Delta H_{\text{Li}_3\text{AlF}_6}^{\text{dis}}$  is 11.2 kcal mol<sup>-1</sup>. In his studies of the dissociation of  $\text{AlF}_6^{3-}$  in molten  $\text{Na}_3\text{AlF}_6$ , Grjotheim took into account the respective quantity for sodium cryolite which led to the decrease in the originally calculated degree of dissociation  $b$  by approx. 0.02. With respect to the thermodynamic analogy of lithium and sodium cryolites [9] the same correction can also be assumed for the results presented in this paper.

In accordance with Temkin's model of ideal ionic solutions the type of cations in the compound  $\text{MF}_2$  has not been taken account of in the calculations. This simplification is valid with a sufficient accuracy only for lower concentrations of  $\text{MF}_2$  in  $\text{Li}_3\text{AlF}_6$ . For comparison of the calculated and experimental data for these systems, only the narrow concentration range of 0–15 mole %  $\text{MF}_2$  was considered because the experimental liquidus curves of  $\text{Li}_3\text{AlF}_6$  in systems with  $\text{SrF}_2$  and  $\text{BaF}_2$  are nearly identical. Therefore the effect of the different character of the  $\text{M}^{2+}$  cations on the dissociation of  $\text{AlF}_6^{3-}$  may be neglected in this concentration range.

In our calculations we considered the degree of dissociation  $e$  at the equilibrium  $\text{CaF}^+ \rightleftharpoons \text{Ca}^{2+} + \text{F}^-$  as concentration and temperature independent. It should be discussed to what extent this assumption is justified.

Along the liquidus curve of  $\text{Li}_3\text{AlF}_6$  the following equations apply:

$$a_{\text{CaF}^+} = \frac{(1 - X)(1 - e)}{1 + 2X},$$

$$a_{\text{F}^-} = \frac{2dX + (1 - X)(1 + e)}{1 + X(2d - e) + e},$$

$$a_{\text{Ca}^{2+}} = \frac{(1 - X)e}{1 + 2X},$$

$$K_{\text{CaF}^+/\text{Li}_3\text{AlF}_6}^{\text{dis}} = \frac{[2dX + (1 - X)(1 + e)]e}{(1 - e)[1 + X(2d - e) + e]}. \quad (7)$$

The calculation of  $K_{\text{CaF}^+/\text{Li}_3\text{AlF}_6}^{\text{dis}}$  for  $X_{\text{Li}_3\text{AlF}_6} = 0.9$  yielded the value of 0.0458; for  $X_{\text{Li}_3\text{AlF}_6} = 0.6$  it was 0.0586. This difference between the values of  $K_{\text{CaF}^+/\text{Li}_3\text{AlF}_6}^{\text{dis}}$  is relatively small. Taking  $e = 0.08$  instead of 0.10 for  $X_{\text{Li}_3\text{AlF}_6} = 0.6$  the value of  $K_{\text{CaF}^+/\text{Li}_3\text{AlF}_6}^{\text{dis}} = 0.0455$ . Thus we conclude that in the concentration range of  $X_{\text{Li}_3\text{AlF}_6} = 0.9 - 0.6$  the value of the dissociation degree  $e$  has changed by less than 0.02 and therefore the assumption of the dissociation of  $\text{CaF}^+$  into  $\text{Ca}^{2+}$  and  $\text{F}^-$  by about 10% is satisfactorily proved.

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