

# Algebraic analysis of the equations for calculation of the degree of dissociation of cryolite anions\*

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The equations for calculation of the degree of dissociation  $d$  of complex anion  $\text{AlF}_6^{3-}$  were analyzed using methods of advanced algebra. Binary mixtures containing lithium cryolite  $\text{Li}_3\text{AlF}_6$  as one component were chosen as the object of this study. It has been proved that in the case of the systems  $\text{Li}_3\text{AlF}_6-\text{LiF}$  and  $\text{Li}_3\text{AlF}_6-\text{BaF}_2$ , there is just one real solution in the interval  $(0;1)$  and therefore the degree of dissociation  $d$  can be determined unambiguously. However, in the case of the system  $\text{Li}_3\text{AlF}_6-\text{AlF}_3$  two solutions for the quantity  $d$  may exist in the mentioned interval. A method enabling to determine which of the solutions has physical meaning is reported.

One of the fundamental questions in the theory of aluminium production based on the electrolysis of molten mixtures containing cryolite and alumina is the question of the dissociation of anions  $\text{AlF}_6^{3-}$ . Grjotheim [1] used the classic thermodynamic approach for the study of this problem. He gave for the first time a reasonable, though not direct, evidence of a partial dissociation of complex cryolite anions. His method was based in principle on the comparison of the experimental and theoretically calculated shapes of liquidus curves of  $\text{Na}_3\text{AlF}_6$  in the system containing  $\text{NaF}$  and  $\text{AlF}_3$ . Grjotheim's approach, which started a new period in the development of the theory on aluminium electrolysis, found a wide-spread use in the study of dissociation in both sodium and lithium cryolites. The works by Brynestad [2, 3], Rolin [4, 5], Rolin and Bernard [6], Jenssen [7], and other authors [8, 9] should be mentioned.

The calculation of a liquidus curve is based on the generalized Le Chatelier—Schröder equation which gives the temperature dependence of liquidus  $T_i$  of a component  $i$  on its activity  $a_i$  in a solution. For obtaining the relation  $a_i = f(x_i)$  (where  $x_i$  is the mole fraction of the given substance in the solution) all the authors used the Temkin model of

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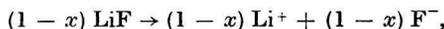
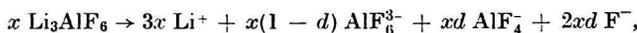
the ideal ionic solutions [10]. The method of calculation of the degree of dissociation  $d$  of anions  $\text{AlF}_6^{3-}$  based on this definition of activity leads to the equations of the third degree with respect to the quantity  $d$ . All the authors quoted above considered apparently as self-evident the fact that in solving these equations there was just one root in the interval (0;1) which had physical meaning.

However, *Vrbenská* [11] drew attention to the fact that when computing the degree of dissociation  $d$  in the system  $\text{Li}_3\text{AlF}_6 - \text{AlF}_3$  two results were obtained in the interval (0;1). This finding is important because it results in the statement that two different temperatures of primary crystallization might exist for one concentration as it follows from the character of the dependence  $T_i = f(d)$ . But the temperature of liquidus of a given component in a solution is in most cases and also in the case of the system  $\text{Li}_3\text{AlF}_6 - \text{AlF}_3$  an unambiguous function of the composition of the solution. Hence if the validity of Grjotheim's approach to the determination of the degree of dissociation is to be proved it is necessary to analyze the equations for the determination of the quantity  $d$  with respect to the number of roots in the interval (0;1) and if several values of  $d$  exist there to find out a method how to determine which of them is correct from the viewpoint of physical reality.

We are dealing with three important systems in this work, viz.: A.  $\text{Li}_3\text{AlF}_6 - \text{LiF}$ , B.  $\text{Li}_3\text{AlF}_6 - \text{BaF}_2$ , C.  $\text{Li}_3\text{AlF}_6 - \text{AlF}_3$ .

#### A. Discussion of the equation for calculation of $d$ in the system $\text{Li}_3\text{AlF}_6 - \text{LiF}$

Let  $x$  be the mole fraction of  $\text{Li}_3\text{AlF}_6$  in this system. We assume the following scheme of dissociation:



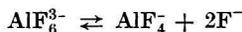
$$\sum \text{ cations} = 1 + 2x,$$

$$\sum \text{ anions} = 1 + 2xd.$$

The activities of different kinds of ions can be expressed as

$$a_{\text{Li}^+} = 1, \quad a_{\text{AlF}_6^{3-}} = \frac{x(1-d)}{1+2xd}, \quad a_{\text{AlF}_4^-} = \frac{xd}{1+2xd}, \quad a_{\text{F}^-} = \frac{1+2xd-x}{1+2xd}.$$

Considering the dissociation scheme



it holds for the equilibrium constant of dissociation of the complex anion  $\text{AlF}_6^{3-}$

$$K = \frac{a_{\text{AlF}_4^-} \cdot a_{\text{F}^-}^2}{a_{\text{AlF}_6^{3-}}} = \frac{(1+2xd-x)^2 d}{(1-d)(1+2xd)^2}. \quad (1)$$

Eqn (1) can be expanded according to the powers of  $d$ :

$$4x^2(K+1)d^3 + 4x(1-x+K-Kx)d^2 + [(x-1)^2 + K(1-4x)]d - K = 0. \quad (2)$$

The domain of definition of the equilibrium dissociation constant  $K$  is (0; $\infty$ ). (3)

The domain of definition of the degree of dissociation  $d$  of  $\text{AlF}_6^{3-}$  in the studied mixture is  $(0;1)$ . (4)

The mole fraction  $x$  is from the interval  $(0;1)$ . (5)

In order to find the number of positive roots of eqn (2) with respect to  $d$  we shall use Descartes' Rule of Signs: "The number of positive roots of an equation  $f(d) = 0$  equals maximally the number of changes in sign in the sequence of coefficients of the polynomial  $f(d)$ . If it is lower then it is lower by an even number." (6)

And further, Bolzano–Cauchy theorem will be used: "If at the terminal points of the interval  $\langle a;b \rangle$  holds that  $f(a) \cdot f(b) < 0$  then the equation  $f(d) = 0$  has an odd number of roots in this interval. If  $f(a) \cdot f(b) > 0$  then the equation  $f(d) = 0$  has an even number of roots." (7)

Let us consider  $0 < x < 1$  and  $0 < K$ , then it holds for each coefficient of eqn (2)  $4x^2(K+1) > 0$ ,  $4x(K+1)(1-x) > 0$ ,  $(x-1)^2 + K(1-4x) \geq 0$  (the sign may be arbitrary), and the last coefficient  $-K < 0$ .

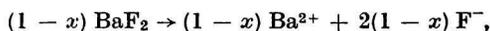
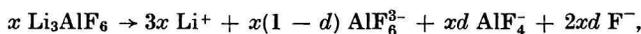
There is always only one change in sign and hence according to eqn (6) there is one positive root. According to (7) and (4) it holds that  $f(0) \cdot f(1) < 0$  or  $f(0) = -K < 0$ ,  $f(1) = (x+1)^2 > 0$ .

*Summary:* Eqn (2) has always only one positive root in the interval  $(0;1)$ .

The same result can be achieved if we consider the system  $\text{Li}_3\text{AlF}_6\text{--CaF}_2$  with  $\text{CaF}_2$  dissociating according to the scheme  $\text{CaF}_2 \rightarrow \text{CaF}^+ + \text{F}^-$ . Correctness of this assumption has been shown in [12].

### B. Discussion of the equation for calculation of $d$ in the system $\text{Li}_3\text{AlF}_6\text{--BaF}_2$

Let  $x$  (defined in agreement with (5)) be the mole fraction of  $\text{Li}_3\text{AlF}_6$ . We assume the following scheme of dissociation:



$$\sum \text{cations} = 1 + 2x,$$

$$\sum \text{anions} = 2 + 2xd - x;$$

$$a_{\text{Li}^+} = \frac{3x}{1+2x}, \quad a_{\text{Ba}^{2+}} = \frac{1-x}{1+2x}, \quad a_{\text{AlF}_6^{3-}} = \frac{(1-d)x}{2+2xd-x},$$

$$a_{\text{AlF}_4^-} = \frac{xd}{2+2xd-x}, \quad a_{\text{F}^-} = \frac{2(1+xd-x)}{2+2xd-x}.$$

For the equilibrium constant of dissociation it may be set

$$K = \frac{4(1+xd-x)^2 d}{(1-d)(2+2xd-x)^2} \quad (8)$$

or after rearrangement with respect to  $d$

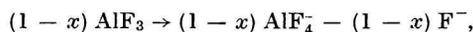
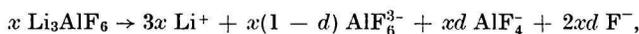
$$4x^2(K+1)d^3 + 8x(1-x)(1+K)d^2 + [4(x-1)^2 + K(5x^2 - 12x + 4)]d - K(x-2)^2 = 0. \quad (9)$$

We shall use the theorems (6) and (7) and take into account (3) and (4). Then it holds for each coefficient:  $4x^2(K+1) > 0$ ,  $8x(K+1)(1-x) > 0$ ; the expression  $4(x-1)^2 + K(5x^2 - 12x + 4)$  can be positive or negative, and the last term  $-K(x-2)^2 < 0$ . There is always only one change in sign and therefore there is only one positive root. It holds that  $f(0) \cdot f(1) < 0$  or  $-K(x-2)^2 < 0$  and  $4 > 0$ .

*Summary:* Eqn (9) has only one positive root in the interval (0;1). Correctness of the assumption about the dissociation of  $\text{BaF}_2$  according to the scheme  $\text{BaF}_2 \rightarrow \text{Ba}^{2+} + 2\text{F}^-$  has been verified experimentally [12].

### C. Discussion of the equation for calculation of $d$ in the system $\text{Li}_3\text{AlF}_6 - \text{AlF}_3$

Let  $x$  (which is defined in agreement with (5)) be the mole fraction of  $\text{Li}_3\text{AlF}_6$ . We assume the following dissociation:



$$\sum \text{cations} = 3x,$$

$$\sum \text{anions} = x(1+2d);$$

$$a_{\text{Li}^+} = 1, \quad a_{\text{AlF}_6^{3-}} = \frac{1-d}{1+2d}, \quad a_{\text{AlF}_4^-} = \frac{d}{1+2d}, \quad a_{\text{F}^-} = \frac{2xd - (1-x)}{1+2d}.$$

For the equilibrium constant of dissociation of  $\text{AlF}_6^{3-}$  it can be set

$$K = \frac{(1-x+xd)(2xd+x-1)^2}{x^3(1-d)(1+2d)^2} \quad (10)$$

or after rearrangement with respect to  $d$

$$4x^3(1+K)d^3 - 3[x(x-1)^2 + Kx^3]d - (x-1)^3 - Kx^3 = 0. \quad (11)$$

The less is  $x \in (0.95; 0.90, \dots, 0.05)$  the higher should be  $d$  in order to fulfil the inequality

$$d > \frac{1-x}{2x}.$$

(This inequality results from the requirement of positive value of  $a_{\text{F}^-}$ .)

With rising  $x$  the value of  $d$  decreases. It holds further  $0 < d < 1$ . With respect to these relations we obtain:

$$1 > d > \frac{1-x}{2x} > 0.$$

$$\text{a) } 1 > \frac{1-x}{2x}; \quad \text{b) } \frac{1-x}{2x} > 0.$$

$$x > \frac{1}{3}; \quad 1-x > 0.$$

$$x < 1$$

Thus the temperatures of liquidus found experimentally have to be related to the mixtures in which the mole fraction of lithium cryolite  $x$  is from the interval  $(1/3;1)$ .

If  $x > 1/3$  then  $d > 0$  and  $d < 1$ .

If  $x < 1/3$  then  $d > 1$  what cannot be accepted from the physical point of view.

For  $K$  and  $d$ , the relations (3) and (4) are valid. The number of positive roots of eqn (11) may be found by means of the theorem (6); see eqn (11).

We examine the sign of each coefficient:  $4x^3(1 + K) > 0$ ,  $-3[x(x - 1)^2 + Kx^3] < 0$ ; the third coefficient can be positive  $-[(x - 1)^3 + Kx^3] > 0$  if  $(x - 1)^3 + Kx^3 < 0$ ,

$$Kx^3 < (1 - x)^3$$

$$K < \frac{(1 - x)^3}{x^3}$$

There are two changes in sign here and therefore eqn (11) has two positive roots for

$$K < \frac{(1 - x)^3}{x^3}.$$

If the third coefficient is negative  $-[(x - 1)^3 + Kx^3] < 0$  then it must be  $(x - 1)^3 + Kx^3 > 0$ .

Consequently

$$K > \frac{(1 - x)^3}{x^3}.$$

In this case there is only one change in sign and therefore eqn (11) has only one positive root for

$$K > \frac{(1 - x)^3}{x^3}.$$

We have to make sure whether eqn (11) may have one or two positive roots in the interval  $(1/3;1)$ . For the existence of one positive root it holds

$$K > \frac{(1 - x)^3}{x^3} \Rightarrow x > \frac{1}{1 + \sqrt[3]{K}}. \quad (12)$$

We examine the possibility of the simultaneous validity of both relations:

$$\text{a) } x > 1/3 \quad \text{and} \quad x > \frac{1}{1 + \sqrt[3]{K}}.$$

It holds for  $K > 8$

$$\frac{1}{3} > \frac{1}{1 + \sqrt[3]{K}}.$$

For  $K < 8$

$$\frac{1}{3} < \frac{1}{1 + \sqrt[3]{K}}.$$

In both cases the mutual intersection of both intervals exists and therefore the obtained result satisfies also the condition  $x > 1/3$ .

$$\text{b) } x < 1 \quad \text{and} \quad x > \frac{1}{1 + \sqrt[3]{K}}$$

and hence

$$1 > \frac{1}{1 + \sqrt[3]{K}}.$$

The mutual intersection of both intervals exists and therefore the obtained result satisfies also the condition  $x < 1$ .

For the existence of two positive roots it must be valid:

$$K < \frac{(1-x)^3}{x^3} \quad \Rightarrow \quad x < \frac{1}{1 + \sqrt[3]{K}}. \quad (13)$$

We shall examine the possibility of this result with respect to the following condition for the mole fraction  $x: x \in (1/3; 1)$ .

$$\text{a) } x > \frac{1}{3} \quad \text{and} \quad x < \frac{1}{1 + \sqrt[3]{K}}.$$

For  $K > 8$  it holds

$$\frac{1}{3} > \frac{1}{1 + \sqrt[3]{K}}.$$

The mutual intersection of both intervals does not exist and therefore for  $K > 8$  the possibility of two positive roots does not exist either.

For  $K < 8$  it holds

$$\frac{1}{3} < \frac{1}{1 + \sqrt[3]{K}}.$$

The mutual intersection of both intervals exists and therefore the result (13) satisfies the condition  $x > 1/3$  for  $K < 8$ .

$$\text{b) } x < 1 \quad \text{and} \quad x < \frac{1}{1 + \sqrt[3]{K}}$$

and hence

$$1 > \frac{1}{1 + \sqrt[3]{K}}.$$

The mutual intersection exists and therefore the existence of two positive roots (13) satisfies also the condition  $x < 1$ .

*Summary:* Eqn (11) has one positive root for  $x \in (1/3; 1)$  and for  $d \in (0; 1)$  and  $K \in (0; \infty)$  if the relation

$$K > \frac{(1-x)^3}{x^3}$$

is valid.

Eqn (11) has two positive roots under the same conditions if  $K < 8$  and simultaneously

$$K < \frac{(1-x)^3}{x^3}.$$

Thus in the case of the system  $\text{Li}_3\text{AlF}_6 - \text{AlF}_3$  where the mole fraction of  $\text{Li}_3\text{AlF}_6$  has to be higher than 1/3 the equations for the determination of the degree of dissociation leads to two solutions in the interval (0;1) (assuming the value of the dissociation constant to be less than 8).

Because in the case of  $\text{Li}_3\text{AlF}_6$   $K \sim 0.06 \ll 8$  (see [8, 11]) this fact is practically and theoretically important. The existence of two values of  $d$  in the interval (0;1) has been confirmed by numerical calculations using a computer. From the physical point of view it is understandable (and the calculations confirmed it) that for the values of  $x$  which are near to one, the values of  $d$  are near to  $b$  ( $b$  is the degree of dissociation of complex anion  $\text{AlF}_6^{3-}$  in pure  $\text{Li}_3\text{AlF}_6$ ). For example, for  $x = 0.95$  we obtain the following pairs of the values  $b$  and  $d$ : (0.500, 0.501), (0.400, 0.402), (0.300, 0.302), (0.200, 0.204), (0.100, 0.106).

Because of physical reality (as it follows from the analysis of the relation  $K = f(x, d)$ ) if  $x$  decreases,  $d$  must increase and this increase is still steeper. The sequence of the real values of  $d$ , with the first term near to  $b$ , is the sequence raising with "acceleration" in the interval (0;1). When one expresses this condition in a mathematical way it follows that the sequence of values  $d$  and also the differences of all orders between them are always positive when the parameter  $x$  decreases uniformly. Therefore the following scheme may be written

$$x_1 > x_2 > x_3 > x_4 > x_5,$$

$$d_1 < d_2 < d_3 < d_4 < d_5.$$

$$\Delta_1^1 < \Delta_2^1 < \Delta_3^1 < \Delta_4^1,$$

$$\Delta_1^2 < \Delta_2^2 < \Delta_3^2,$$

$$\Delta_1^3 < \Delta_2^3,$$

where  $\Delta_i^j$  is the  $i$ -th difference of the  $j$ -th order with respect to the sequence of  $d_i$  values.

For  $x$  near to 1 the first term of the sequence (let us denote it as  $d_1$ ) is near to the value of the parameter  $b$ . The successive terms  $d_2, d_3, \dots, d_n$  have to fulfil the condition mentioned above. Practical verification proved that using this approach the sequence of real values of  $d$  is defined unambiguously.

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