Dissociation of the anions AlF_6^{3-} in the system Na_3AlF_6—Na_2SO_4

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Dedicated to Professor Ing Dr Jaroslav Malkovský on his 75th birthday

The course of the liquidus of Na_2SO_4 in the system Na_3AlF_6—Na_2SO_4 was determined. The eutectic point was found to be at 9.0 mole % Na_3AlF_6 and 91.0 mole % Na_2SO_4, $t_E = 794.5°C$. The solubility of Na_3AlF_6 in solid Na_2SO_4 is negligible. The course of the liquidus curve of Na_2SO_4 in the composition interval of 91.0—96.0 mole % Na_2SO_4 is consistent with the assumption that the anions AlF_6^{3-} undergo thermal dissociation according to the scheme $AlF_6^{3-} \rightleftharpoons AlF_4^- + 2F^-$. At a very low content of Na_3AlF_6 in Na_2SO_4 a total destruction of the anions AlF_4^- takes place under the formation of 7 new elementary particles from each molecule of Na_3AlF_6 in molten Na_2SO_4. In the eutectic point of the system Na_3AlF_6—Na_2SO_4 the degree of thermal dissociation of AlF_6^{3-} anions according to the given scheme equals 0.67. The calculated dissociation degree of pure cryolite is 0.21. The conclusions of some other papers concerning the given problems are discussed.

Измерен ход ликвидуса Na_2SO_4 в системе Na_3AlF_6—Na_2SO_4. Обнаружена эвтектическая точка при 9,0 мол. % Na_3AlF_6 и 91,0 мол. % Na_2SO_4, $t_E = 794,5°C$. Растворимость Na_3AlF_6 в твердом Na_2SO_4 пренебрежимо мала. Ход кривых ликвидуса Na_2SO_4 в интервале состава 91,0—96,0 мол. % Na_2SO_4 консистентный в соответствии с предпосылкой того, что анионы AlF_6^{3-} диссоциируют термически по схеме $AlF_6^{3-} \rightleftharpoons AlF_4^- + 2F^-$. При очень низком содержании Na_3AlF_6 в Na_2SO_4 происходит также полное разложение анионов AlF_4^-, причем из одной молекулы Na_3AlF_6 образуется в расплаве Na_2SO_4 7 новых элементарных частиц. В эвтектической точке системы Na_3AlF_6—Na_2SO_4 степень термической диссоциации анионов AlF_6^{3-} по указанной схеме равна 0,67. Рассчитанная степень термической диссоциации чистого криолита равна 0,21. Обсуждаются заключения некоторых работ, посвященных этой тематике.

As indicated by numerous papers [1—11], the thermal dissociation of cryolite in the liquid state is a topical problem in the research of fused salts. Several authors applied to their study the classical thermodynamic approach, described *e.g.* by *Glasstone* [12]. Its principle lies in comparing the experimentally established course of the liquidus of Na_3AlF_6 in the system Na_3AlF_6—MA with the course calculated under certain simplifying assumptions. In this case, however, the system Na_3AlF_6—MA has to fulfil several conditions [1, 2, 4, 5]. In 1959 *Grjotheim et al.* [13] suggested for the determination of the character of thermal dissociation of Na_3AlF_6 not to analyze liquidus curve of Na_3AlF_6, but that of the component MA in the system Na_3AlF_6—MA (the method of "the second component"). As the component MA sodium sulfate was chosen. This forms with cryolite a system with a eutectic. In the composition interval with a high content of Na_3AlF_6 there is a wide region of solid solutions, while the Na_3AlF_6 is practically insoluble in solid Na_2SO_4 just as it is required if applying the method of "the second component". The data published by *Grjotheim et al.* [13] were confirmed in [14].

The degree of thermal dissociation of cryolite in equilibrium

$$Na_3AlF_6 \rightleftharpoons NaAlF_4 + 2NaF \qquad (A)$$

should be designated as d; apparently it holds that $d = f_1(x_1) = f_2(x_2)$; x_1 and x_2 are mole fractions of Na_3AlF_6 and Na_2SO_4, respectively; $(x_1 + x_2 = 1)$. If the temperature interval is not too wide $(T_2^f - T_2 \leqslant 100°C)$, for the equilibrium activity of the component MA in its saturated solution, $a_{2,eq}^l$, the known relation is valid

$$\ln a_{2,eq}^l = (\Delta H_2^f/R)(1/T_2^f - 1/T_2) \qquad (1)$$

where ΔH_2^f is the molar melting enthalpy of the pure component MA, T_2^f is the melting temperature [K] of the pure component MA, and T_2 is the temperature [K] of the liquidus of component MA in the liquid phase, when its equilibrium activity is equal to $a_{2,eq}^l$.

The activity $a_{2,eq}^l$ is a function of the parameter d. We choose different schemes of thermal dissociation and under the assumption of an ideal behaviour of the mixture Na_3AlF_6 + MA, we may express the quantity $a_{2,eq}^l$. If a proper scheme was chosen, then the slope of the linear dependence $\log a_{2,eq}^l = f(1/T_2^f - 1/T_2)$ is equal $\Delta H_2^f/R$. Since the systems $NaCl$—Na_2SO_4, $NaBr$—Na_2SO_4, and Na_2CO_3—Na_2SO_4 are nearly ideal, *Grjotheim et al.* [13] suggest that also the mixture of the ions Na^+, F^-, AlF_4^-, AlF_6^{3-}, and SO_4^{2-} (*i.e.* the molten binary system Na_3AlF_6—Na_2SO_4) will exhibit an ideal behaviour, thus justifying the application of Temkin's model of ideal ionic solutions [15].

In [13] it was stated, however, that for all the three chosen schemes

$$Na_3AlF_6 \rightleftharpoons 2NaF + NaAlF_4 \rightarrow 3Na^+ + 2F^- + AlF_4^- \qquad (B)$$

$$Na_3AlF_6 \rightleftharpoons 3NaF + AlF_3 \rightarrow 3Na^+ + Al^{3+} + 6F^- \qquad (C)$$

$$Na_3AlF_6 \rightleftharpoons 3Na^+ + AlF_6^{3-} \qquad (D)$$

the dependence $a^{\mathrm{l}}_{2,\mathrm{eq}}=\mathrm{f}(1/T)$ had the form of a curve, convex with respect to the axis of reciprocal temperature coordinates. According to *Grjotheim et al.* [13] this fact was due to a nonideal behaviour of the given system and they therefore suggested that $\Delta\bar{H}^{\mathrm{l}}_{\mathrm{Na_2SO_4,mix}}\neq 0$. In order to eliminate the effect of this quantity they drew tangents to the curves $a^{\mathrm{l}}_{2,\mathrm{eq}}=\mathrm{f}(1/T)$ for $x_2\rightarrow 1$ and from the slopes of these tangents they calculated the value of the parameter ΔH^{f}_2.

For the first of the above schemes, *i.e.* (*B*), the obtained value conforms very good with the calorimetric data. Thus it may be expected that at a low content of cryolite in the given system the anions $\mathrm{F^-}$, $\mathrm{AlF_4^-}$, and $\mathrm{SO_4^{2-}}$ are present in the melt.

The method used in [13] may be exactly justified. For a not too wide temperature interval $(T^{\mathrm{f}}_2-T_2)$ the simplified form of the general Le Chatelier—Shreder equation is valid [1]. If we consider the formation of a liquid solution from pure liquid substances "1" and "2", it holds

$$\Delta\bar{G}^{\mathrm{l}}_{2,\mathrm{mix}}=\Delta\bar{H}^{\mathrm{l}}_{2,\mathrm{mix}}-T\,\Delta\bar{S}^{\mathrm{l}}_{2,\mathrm{mix}} \tag{2}$$

According to the definition, it holds

$$\Delta\bar{G}^{\mathrm{l}}_{2,\mathrm{mix}}=\bar{G}^{\mathrm{l}}_2-G^{0,\mathrm{l}}_2=RT\ln a^{\mathrm{l}}_2 \tag{3}$$

For the case of formation of a liquid solution which is in equilibrium with solid substance "2", the activities in eqns (*1*) and (*3*) are equal and it holds

$$\ln a^{\mathrm{l}}_{2,\mathrm{eq}}=(\Delta\bar{H}^{\mathrm{l}}_{2,\mathrm{mix}}/RT_2)_{\mathrm{eq}}-(\Delta\bar{S}^{\mathrm{l}}_{2,\mathrm{mix}}/R)_{\mathrm{eq}}=(\Delta H^{\mathrm{f}}_2/R)(1/T^{\mathrm{f}}_2-1/T_2) \tag{4}$$

For a system with the behaviour of Temkin's ideal solution $\Delta\bar{H}^{\mathrm{l}}_{2,\mathrm{mix}}=0$ and therefore

$$\ln a^{\mathrm{l}}_{2,\mathrm{eq,Tem}}=-(\Delta\bar{S}^{\mathrm{l}}_{2,\mathrm{mix}}/R)_{\mathrm{eq}}=(\Delta H^{\mathrm{f}}_2/R)(1/T^{\mathrm{f}}_2-1/T_2) \tag{5}$$

The term $a^{\mathrm{l}}_{2,\mathrm{eq,Tem}}$ stands for the equilibrium activity of substance "2" in the liquid solution expressed according to Temkin. In a number of cases the behaviour of real solutions differs from the one postulated by Temkin's model. Then it holds

$$\ln a^{\mathrm{l}}_{2,\mathrm{eq}}\neq\ln a^{\mathrm{l}}_{2,\mathrm{eq,Tem}}$$

This deviation from an ideal behaviour according to Temkin's model can be expressed quantitatively as the partial molar enthalpy of mixing of $\mathrm{Na_2SO_4}$, $\Delta\bar{H}^{\mathrm{l}}_{2,\mathrm{mix}}$, however, it must be assumed that the value of the partial molar excess entropy of mixing of $\mathrm{Na_2SO_4}$, $\Delta\bar{S}^{\mathrm{ex,l}}_{2,\mathrm{mix}}$, is negligible. Then it holds

$$\ln a^{\mathrm{l}}_{2,\mathrm{eq}}=\ln a^{\mathrm{l}}_{2,\mathrm{eq,Tem}}+(\Delta\bar{H}^{\mathrm{l}}_{2,\mathrm{mix}}/RT_2)_{\mathrm{eq}} \tag{6}$$

and with respect to eqn (*4*)

$$\ln a^{\mathrm{l}}_{2,\mathrm{eq,Tem}}=(\Delta H^{\mathrm{f}}_2/R)(1/T^{\mathrm{f}}_2-1/T_2)-(\Delta\bar{H}^{\mathrm{l}}_{2,\mathrm{mix}}/RT_2)_{\mathrm{eq}} \tag{7}$$

For $x_2 \rightarrow 1$, $\Delta \bar{H}^{l}_{2,\mathrm{mix}} \rightarrow 0$ and consequently $a^{l}_{2,\mathrm{eq,Tem}} \rightarrow a^{l}_{2,\mathrm{eq}}$.

In order to approximate the experimental values to the straight line with the slope $\Delta H^{f}_{2}/R$, *Grjotheim et al.* [13] suggested that in the molten mixture Na_3AlF_6—Na_2SO_4 the thermal dissociation of the AlF_6^{3-} anions according to the scheme $AlF_6^{3-} \rightleftharpoons AlF_4^{-} + 2F^{-}$ took place. The degree of this dissociation is assumed to be dependent on cryolite content in the melt.

Let x_1 and x_2 be the mole fractions of Na_3AlF_6 and Na_2SO_4, respectively. If the degree of thermal dissociation of Na_3AlF_6 into $NaAlF_4$ and $2NaF$ is designated as d, then in the equilibrium mixture there exist

$x_1(1-d)$ moles of AlF_6^{3-}
$x_1 d$ moles of AlF_4^{-}
$2x_1 d$ moles of F^{-}
$3x_1 + 2x_2$ moles of Na^{+}

The equilibrium constant of thermal dissociation according to the scheme $AlF_6^{3-} \rightleftharpoons AlF_4^{-} + 2F^{-}$ in the given mixture can be expressed as follows

$$K_{\mathrm{dis}} = \frac{4x_1^2 d^3}{(1-d)(1+2x_1 d)^2} \tag{8}$$

When deriving the relation (*8*) it was assumed that the considered molten mixture behaved like Temkin's ideal solution. Further it has been assumed that the constant of the thermal dissociation K_{dis} is temperature independent. This assumption can be satisfactorily fulfilled when the analyzed liquidus curve does not cover a too wide temperature interval. In the given case this interval corresponds to the difference $(T^{f}_{Na_2SO_4} - T_E) < 100$°C and therefore it can be expected that the postulate $K_{\mathrm{dis}} \neq f(T)$ does not introduce any greater inaccuracy into the results. The degree of thermal dissociation, d, is supposed to be unambiguously defined by eqn (*8*).

According to Temkin, for the activity of Na_2SO_4 the equation holds

$$a^{l}_{2,\mathrm{eq,Tem}} = x^{2}_{Na^+}\, x_{SO_4^{2-}} = \frac{x_2}{1+2(1-x_2)\,d} \tag{9}$$

The value of K_{dis} determined by *Grjotheim* [1] equals 0.06 (at the melting temperature of cryolite 1010°C). Then for a given x_1 we can determine the value of d from eqn (*8*), that of $a^{l}_{2,\mathrm{eq,Tem}}$ from eqn (*9*) and we can draw the dependence $\ln a^{l}_{2,\mathrm{eq,Tem}} = f(1/T)$. Though the points obtained in this way are situated nearer to the straight line with the "correct" slope, the deviation, *e.g.* for the eutectic point is still considerable. Therefore in [13] also the value $K_{\mathrm{dis}} = 0.02$ has been used in order to approximate the points still more to the straight line. Nevertheless, the points fit to the straight line with the slope $\Delta H^{f}_{2}/R$ only then, if $K_{\mathrm{dis}} = 0.013$, this value being clearly different from $K_{\mathrm{dis}} = 0.06$ [1], or $K_{\mathrm{dis}} = 0.037$ [2].

The results presented in [13] support the dissociation scheme $AlF_6^{3-} \rightarrow AlF_4^{-} + 2F^{-}$, with $d = 50$—70%. The values obtained yield, however, a lower equilibrium dissociation constant than those found by other methods. The considered system does not behave apparently like Temkin's ideal solution at a higher content of cryolite in Na_2SO_4 and therefore the efforts to "approximate" the experimental points to the theoretical curve by choosing a low value of the dissociation constant is questionable.

Further, in [13] the authors did not consider the possibility of a total destruction of the anions AlF_6^{3-} at a low content of cryolite in the melt; such destruction has been found for $x_{Na_3AlF_6} \rightarrow 0$ in the system Na_3AlF_6—$BaCl_2$ [16] and also in the system Na_3AlF_6—NaCl [17] by means of the cryometric method.

Experimental

The system Na_3AlF_6—Na_2SO_4 was investigated using TA method in the composition range 0—12 mole % Na_3AlF_6. Fifteen mixtures from the region of the primary crystallization of Na_2SO_4 and three from that of Na_3AlF_6 were measured. Some of the experimental data are listed in Table 1. The parameters of the eutectic point are 9 mole % Na_3AlF_6 and 91 mole % Na_2SO_4, the temperature of the eutectic crystallization being 794.5 ± 0.5°C. The fact that the temperature of eutectic crystallization has been recorded on the cooling curves also at low contents of Na_3AlF_6 (Table 1) indicates that cryolite is practically insoluble in solid Na_2SO_4. It is well known that the classical thermodynamic approach can be applied to the

Table 1

System Na_3AlF_6—Na_2SO_4
Experimental data on TPC and T_E

Na_3AlF_6 mole %	Na_2SO_4 mole %	TPC °C	T_E °C
0.00	100.00	884.8	—
0.10	99.90	881.5	796.0
0.25	99.75	877.0	—
0.50	99.50	872.0	—
0.75	99.25	869.0	789.0
1.00	99.00	866.0	795.0
2.00	98.00	852.0	794.0
3.00	97.00	842.0	796.0
4.00	96.00	832.5	795.0
5.00	95.00	823.0	794.0
6.00	94.00	815.0	794.5
7.00	93.00	808.0	795.0
8.00	92.00	800.0	794.5
9.00	91.00	—	794.0

TPC — temperature of primary crystallization.

determination of the character of thermal dissociation of the substance MB on the basis of the course of the liquidus curve of the substance MA only when the substance MB is insoluble in the solid MA. This condition is apparently fulfilled in the given case.

Results and discussion

Because the difference $T_2^{\mathrm{f}} - T_{\mathrm{E}} = 884.8\,°\mathrm{C} - 794.5\,°\mathrm{C} = 90.3\,°\mathrm{C}$ is less than 100°C, it is possible to neglect the dependence of the enthalpy of melting of Na_2SO_4 on temperature. For calculation of $a^{\mathrm{l}}_{2,\mathrm{eq}}$ eqn (*1*) can be used; it holds

$$\Delta H_2^{\mathrm{f}} = 23.72\ \mathrm{kJ\ mol^{-1}} = 5.67\ \mathrm{kcal\ mol^{-1}} \quad [18]$$

The cryometric treatment of experimental results shows that for $x_2 \rightarrow 1$ it holds that $k_{1/2} \rightarrow 7$. The correction factor decreases rapidly with increasing content of cryolite in Na_2SO_4 and it reaches the value of 2.2 at the eutectic composition. In the case of a total decomposition according to the scheme $AlF_6^{3-} \rightarrow Al^{3+} + 6F^-$, $k_{1/2} = 7$. If the complete decomposition $AlF_6^{3-} \rightarrow AlF_4^- + 2F^-$ takes place, then $k_{1/2} = 3$. Consequently, the existence of the equilibrium

$$AlF_6^{3-} \rightleftharpoons AlF_4^- + 2F^-$$

requires that $k_{1/2} < 3$. Therefore it was necessary to calculate the values of the correction factors in dependence on composition. To this purpose the "universal" relationship

Table 2

Numerical values of the activity of Na_2SO_4 in the molten Na_3AlF_6—Na_2SO_4 mixtures calculated on the basis of eqn (*1*) and the values of the correction factor $k_{1/2}$ computed using eqn (*10*)

Mole fraction of Na_2SO_4 x_2	$-(1/T_2^{\mathrm{f}} - 1/T_2)\cdot 10^5$	Activity of Na_2SO_4 $a^{\mathrm{l}}_{2,\mathrm{eq}}$	Correction factor $k_{1/2}$
1.0000	0.0000	1.0000	7.0
0.9990	0.2468	0.9930	6.9
0.9975	0.5856	0.9832	6.6
0.9950	0.9653	0.9728	5.5
0.9925	1.1946	0.9665	4.4
0.9900	1.4252	0.9600	4.0
0.9800	2.5175	0.9308	3.5
0.9700	3.3145	0.9098	3.1
0.9600	4.0850	0.8900	2.9
0.9500	4.8688	0.8704	2.7
0.9400	5.5395	0.8539	2.6
0.9300	6.1346	0.8394	2.4
0.9200	6.8241	0.8230	2.3
0.9100	7.3035	0.8119	2.2

$$\ln a^{1}_{2,\mathrm{eq}} = k_{1/2} \ln x_2 \tag{10}$$

has been used. Here $k_{1/2}$ denotes a parameter numerically equal to the number of elementary particles (entities), which arise in the system formed by pure substance "2" (*i.e.* by pure Na_2SO_4) when introducing 1 molecule of substance "1" (*i.e.* Na_3AlF_6) [19]. The results of calculations according to eqns (*1*) and (*10*) are presented in Table 2. With respect to the value of $k_{1/2}$ there exist two regions in the composition interval 0—9 mole % Na_3AlF_6:

a) 0—3.5 mole % Na_3AlF_6, where it holds $k_{1/2} \geqslant 3$; in this region a total decomposition of AlF_6^{3-} anions and a partial decomposition of AlF_4^- anions evidently takes place. For $x_1 \rightarrow 0$ also the latter decomposition is complete and thus $k_{1/2} = k^{\mathrm{St}}_{1/2} = 7$. It is clear that as far as $k_{1/2} \geqslant 3$, eqns (*8*) and (*9*) cannot be applied to this case.

b) 3.5—9 mole % Na_3AlF_6, where it holds $k_{1/2} < 3$; in this composition region the equilibrium $AlF_6^{3-} \rightleftharpoons AlF_4^- + 2F^-$ can be suggested. In Fig. 1 the measured values of the liquidus temperature of Na_2SO_4 in coordinates $\log x_2 = \mathrm{f}(1/T_2^{\mathrm{f}} - 1/T_2)$ are presented as well as the tangents to the liquidus curve of Na_2SO_4 for $x_2 \rightarrow 1$, for alternatively 1 to 7 new (foreign) particles arising from 1 molecule of Na_3AlF_6.

It is evident that the conclusions which follow from the data presented in Fig. 1 hold the better the lower is the content of cryolite in the melt.

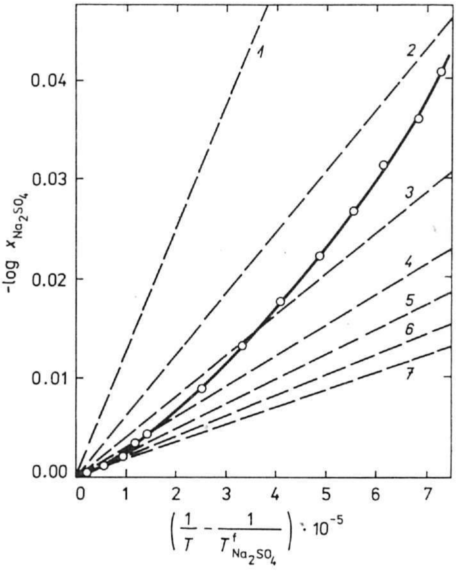

Fig. 1. System Na_3AlF_6—Na_2SO_4.
Experimental values of liquidus temperature of Na_2SO_4 in the coordinates $(1/T - 1/T^{\mathrm{f}}_{Na_2SO_4})$ *vs.* $\log x_{Na_2SO_4}$.
1. $k = 1$; *2.* $k = 2$; *3.* $k = 3$; *4.* $k = 4$; *5.* $k = 5$; *6.* $k = 6$; *7.* $k = 7$.

The above-mentioned relations enable to determine the degree d of thermal dissociation of AlF_6^{3-} anions. From eqn (*9*) it follows

$$d = \frac{x_2 - a^{1}_{2,\mathrm{eq,Tem}}}{2(1 - x_2)\, a^{1}_{2,\mathrm{eq,Tem}}} \tag{11}$$

Using eqn (*1*) we find $a^{1}_{2,\mathrm{eq,E}} = 0.8119$. For Temkin's ideal solution $a^{1}_{2,\mathrm{eq,E}} = a^{1}_{2,\mathrm{eq,E,Tem}}$; from eqn (*11*) it follows that $d = 0.67$. The parameters $x_2 = 0.91$ and $d = 0.67$ inserted into eqn (*8*) yield the value $K_{\mathrm{dis}} = 0.024$, which corresponds to the value of the thermal dissociation of pure cryolite, $b = 0.21$. Even though these data do not differ appreciably from the values of $K_{\mathrm{dis}} = 0.037$ and $b = 0.25$ reported in [2], it is evident that the melts of the system Na_3AlF_6—Na_2SO_4 do not behave quite ideally, as postulated by Temkin's model. Their deviation from the Temkin ideal ionic solution can be expressed quantitatively as the magnitude of the partial molar enthalpy of mixing of Na_2SO_4 in the given solution. For the sake of simplicity we shall suggest (as it has been done above) that the value of the excess partial entropy of mixing of Na_2SO_4 is negligible.

We have mentioned already that $a^{1}_{2,\mathrm{eq,E}} = 0.8119$. The most probable value of the degree of the thermal dissociation of pure cryolite is 0.25 [2, 10], which corresponds to the dissociation constant $K_{\mathrm{dis}} = 0.037$. This value together with the value of $x_{1,\mathrm{E}} = 0.09$ inserted into eqn (*8*) yields $d_{\mathrm{E}} = 0.73$. Then from eqn (*9*) we can calculate that $a^{1}_{2,\mathrm{eq,E,Tem}} = 0.8043$.

From eqn (*6*) it follows

$$\Delta \bar{H}^{1}_{2,\mathrm{mix,E}} = RT \ln \left(a^{1}_{2,\mathrm{eq,E}}/a^{1}_{2,\mathrm{eq,E,Tem}}\right) = 81.76\ \mathrm{J\ mol^{-1}} \tag{12}$$

Suggesting that the system behaves like a strictly regular solution it holds

$$\Delta \bar{H}^{1}_{2,\mathrm{mix,E}} = \omega(1 - x_{2,\mathrm{E}})^2$$

from which $\omega = 10\,094\ \mathrm{J\ mol^{-1}}$ can be determined. For the solution with the composition $x_2 = 0.5$ the partial molar enthalpy of mixing of Na_2SO_4 would reach

Table 3

Comparison of the main parameters of thermal dissociation of cryolite in the system Na_3AlF_6—Na_2SO_4

Ref.	$a^{1}_{2,\mathrm{eq,E}}$	d_{E}		According to Temkin	
		According to Temkin	According to the universal relationship	K_{dis}	b
[13]	0.8215	0.58	0.53	0.013	0.17
This paper	0.8119	0.67	0.60	0.024	0.21

the value of 2523.5 J mol^{-1}. Consequently, Na_2SO_4 exhibits a weak positive deviation from an ideal ionic behaviour in this solution.

For the processing of the experimental results also the universal relationship [19] has been used. For the eutectic point E in the system Na_3AlF_6—Na_2SO_4 it holds

$$\ln a^{1}_{2,\mathrm{eq},\mathrm{E}} = k_{1/2} \ln x_{2,\mathrm{E}} \tag{13}$$

As $a^{1}_{2,\mathrm{eq},\mathrm{E}} = 0.8119$ and $x_{2,\mathrm{E}} = 0.91$, $k_{1/2} = 2.2$. From the equation of the thermal dissociation of cryolite

$$x_1(1-d)\ \mathrm{Na_3AlF_6} \rightleftarrows x_1 d\ \mathrm{NaAlF_4} + 2x_1 d\ \mathrm{NaF} \tag{E}$$

it follows that the sum of the ions equals $1 + 2d = k_{1/2}$. Consequently $d = 0.60$.

Analogical calculations have been made also using the data presented by *Grjotheim et al.* [13]. The results are confronted in Table 3.

Drawing conclusions we may state that the application of the method of "the second component" to the study of the thermal dissociation of cryolite confirms the data obtained by other methods [2, 10], according to which it holds for cryolite that $b \doteq 0.25$.

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