Problems of the stability of the anion AlF_6^{3-} in the molten system $NaCl—Na_3AlF_6$*

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The course of the liquidus curve of NaCl in the system $NaCl—Na_3AlF_6$ was measured. The system exhibits a eutectic point with the coordinates of 89 mole % NaCl, 11 mole % Na_3AlF_6, $t_E = 737°C$. The solubility of Na_3AlF_6 in solid NaCl is negligible. Different dissociation schemes of Na_3AlF_6 in this system with an excess of NaCl were discussed and the effect of the nature of dissociation of Na_3AlF_6 on the liquidus of NaCl was determined. It has been proved that the assumption of the existence of the complex anions AlF_6^{3-} in melts of the system under consideration is consistent with the course of the liquidus curve of NaCl in the concentration range of $1.2—11.0$ mole % Na_3AlF_6.

The problems concerning the dissociation of Na_3AlF_6 and especially the question of the stability of the complex anion AlF_6^{3-} in the melting process are still topical, though many research workers have been occupied with them already.

It has been supposed for à long time that molten cryolite represents a mixture of the ions Na^+ and AlF_6^{3-}, the latter one partially dissociating into Al^{3+} and F^-. Another assumption told that melting led to partial thermal dissociation of cryolite into 3NaF and AlF_3 with a subsequent electrolytic dissociation of all constituents present in the melt [1—5].

Boner [6] published his essentially different opinions on the dissociation of cryolite according to which the melting process runs by the reaction

$$Na_3AlF_6(s) \rightarrow NaAlF_4(l) + 2NaF(l). \qquad (A)$$

NaF in the melt is dissociated into Na^+ and F^-, while $NaAlF_4$ forms an undissociated molecular solution.

Boner's suggestions were accepted with a certain mistrust until *Howard* [7] proved the existence of $NaAlF_4$ in quenched samples by means of X-ray techniques.

Grjotheim [8] suggested that in the melting of cryolite the complete dissociation into $3Na^+$ and AlF_6^{3-} as well as the partial dissociation takes place according to the reaction

$$AlF_6^{3-} \rightarrow AlF_4^- + 2F^-. \qquad (B)$$

The dissociation degree according to (B) was determined by means of thermodynamic analysis of the liquidus curves of Na_3AlF_6 in systems with NaF and AlF_3. The value

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of 30% established by Grjotheim was essentially proved also by other authors [9, 10].

The first attempt of direct quantitative measurements of the dissociation of molten cryolite was done by *Solomons et al.* [11]. Using Raman spectroscopy they found for the dissociation degree of AlF_6^{3-} according to (*B*) a surprisingly high value of 70—75%.

Petit and *Ngo Tuang* [12] applied cryometry to prove that a very small amount of Na_3AlF_6 yields 10 new particles in an excess of molten $BaCl_2$ demonstrating that a total dissociation of Na_3AlF_6 takes place to give $3Na^+$, Al^{3+} (or an Al-containing ion), and $6F^-$. This result indicates that the dissociation character of Na_3AlF_6 depends on its concentration in the mixture under consideration.

Recently *Dewing* [13, 14] published papers in which he considered the dissociation of AlF_6^{3-} according to (*B*) to be total or practically total. Dewing is convinced that Grjotheim's assumption [8] that the molten systems $Na_3AlF_6 + NaF$ and $Na_3AlF_6 + AlF_3$, respectively, may be considered as ideal ionic solutions is not satisfactorily fulfilled.

It should also be stated that the method used by Grjotheim requires precise measurements of the liquidus temperature of Na_3AlF_6. *Malinovský* [15] advised upon the necessity that, should the values of the dissociation degree of AlF_6^{3-} according to (*B*) be reliable, the accuracy of the measurements for high concentrations of Na_3AlF_6 must be better than 0.1°C.

As to the character of the dissociation of Na_3AlF_6 conclusions may be drawn, however, not only from the course of its liquidus curve in the systems $Na_3AlF_6 — NaF$ and $Na_3AlF_6 — AlF_3$, but also from that of a substance, let us denote it MA, in systems with Na_3AlF_6. The substance MA has to fulfil certain conditions:

1. It must form with cryolite a system with eutecticum and the solubility of Na_3AlF_6 in the solid substance MA must be zero.

2. The melting enthalpy of MA must be reliably known.

3. The eutectic point in the system $MA — Na_3AlF_6$ should contain about 90 mole % MA, in order that along the liquidus curve of MA, the solution of $MA — Na_3AlF_6$ might be considered to be practically an ideal one.

4. The liquidus of MA must be reliably measurable. These properties are to be found *e.g.* in chlorides and sulfates of alkali metals.

In the present study NaCl was taken for the substance MA. The fact that it has a common cation with Na_3AlF_6 lets expect the concentration interval of ideal behaviour of the melt $NaCl — Na_3AlF_6$ to be sufficiently wide. It is known that the system, *e.g.* $NaF — NaCl$ with a common cation is considerably nearer to the ideal behaviour than *e.g.* $NaF — KCl$.

Though the equilibrium "solidus—liquidus" in the system $NaCl — Na_3AlF_6$ has been measured several times, the published data are practically inapplicable to our purposes, except the important fact, to which all the authors agree, that the given system is a simple eutectic one. *Phillips et al.* [16], *Kuvakin* and *Kusakin* [17], *Rolin* and *Bernard* [18], *Yaguchi et al.* [19] published diagrams of the liquidus of the given system in weight %, *Bukhalova et al.* [20] in equivalent %, but none of these works presented any numerical values concerning the liquidus of NaCl, and the published graphical data could not be reliably converted into mole %. Besides, it must be stated that the results by *Kuvakin* and *Kusakin* [17] are apparently erroneous.

Matiašovský and *Malinovský* [21] published the phase diagram of the discussed system in mole %, but the number of the measurements done by them in the region of primary crystallization of NaCl is not sufficient. *Madhavan et al.* [22] presented the liquidus diagram of $NaCl — Na_3AlF_6$ also in mole %, the scheme dimensions being however too small for practical use. In addition, the liquidus curve of NaCl appears to be concave

with respect to the concentration axis, a scarcely probable circumstance considering the condition of the existence of an inflection point on the liquidus curves [23].

The above said made it necessary carefully to remeasure the liquidus of NaCl in the system under consideration.

Experimental

The region of primary crystallization of NaCl in the phase diagram of $NaCl-Na_3AlF_6$ was studied by the TA method. The chemicals used were of "single crystal" purity. The melting points were: NaCl 800.8°C; NaF 995°C; Na_2SO_4 884.8°C (for calibration purposes). Na_3AlF_6 was synthesized with NaF and AlF_3, prepared by sublimation of the pure product in a platinum apparatus at 1260—1320°C. The salts were melted in covered Pt-crucibles, the sample weight being 20 g, cooling rate 1—2°/min. The cooling curves were recorded with an automatic compensating line recorder EZ 11; the zero stability was tested with a special reference power supply of low voltage. The reproducibility of the measurements was ±1°C. The experimental results are listed in Table 1.

Table 1

Experimental data of the system $NaCl-Na_3AlF_6$

NaCl [mole %]	Na_3AlF_6 [mole %]	TPC [°C]	TPC [K]	T_E [°C]	T_E [K]
99.75	0.25	796.0	1069.0	—	—
99.50	0.50	794.0	1067.0	—	—
99.25	0.75	791.5	1064.5	—	—
99.0	1.0	789.5	1062.5	729	1002
98.5	1.5	786.5	1059.5	735	1008
98.0	2.0	784.0	1057.0	735	1008
97.0	3.0	778.5	1051.5	737	1010
96.0	4.0	772.0	1045.0	738	1011
95.0	5.0	766.5	1039.5	737	1010
94.0	6.0	761.0	1034	736	1009
93.0	7.0	755.0	1028	736	1009
92.0	8.0	750.0	1023	736	1009
91.0	9.0	746.0	1019	737	1010
90.0	10.0	741.5	1014.5	737.5	1010.5
89.0	11.0	—	—	737	1010

TPC = temperature of primary crystallization.

Theoretical

The measurement results should yield information how the dissociation character of cryolite changes along the liquidus curve of NaCl from the eutectic point E to the figurative point of pure NaCl. In addition, it was desirable to verify the absence of solid solutions of Na_3AlF_6 in NaCl.

To obtain the necessary information, the experimentally found liquidus of NaCl should be compared with the calculated course; then the general form of the Le Chatelier—Schröder equation may be applied
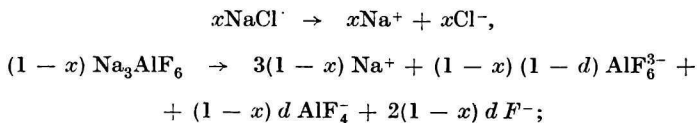
$$RT \ln a_i = -\Delta H_i^f(1 - T/T_i^f) + \int_T^{T_i^f} \Delta C_P^{l/s} \, dT - T \int_T^{T_i^f} \Delta C_P^{l/s} \, d \ln T. \qquad (1)$$

If the studied temperature interval (T_i^f, T) is sufficiently narrow, then all terms containing $\Delta C_P^{l/s}$ may be neglected. For the given case, if $i = \mathrm{NaCl}$, $T_i^f = 800.8°\mathrm{C}$, $T = 737°\mathrm{C}$, the temperature interval is $63.8°\mathrm{C}$. Then eqn (1) may be written in the following way

$$T = \frac{\Delta H_i^f}{\Delta S_i^f - R \ln a_i}. \tag{2}$$

Further the form of the relation $a_i = \mathrm{f}(x_i)$ should be known. For this purpose the Temkin model of ideal ionic solutions [24] was used in the case of cryolite several times already. It was assumed that NaCl dissociated into $\mathrm{Na^+} + \mathrm{Cl^-}$ and $\mathrm{Na_3AlF_6}$ into $3\mathrm{Na^+}$ and $\mathrm{AlF_6^{3-}}$ and that the anion $\mathrm{AlF_6^{3-}}$ further dissociated according to (B). To the existence of the anions $\mathrm{AlF_4^-}$ most of the scientists agree. The question at issue is, to what degree the anion $\mathrm{AlF_6^{3-}}$ dissociates.

Let the mole fraction of NaCl be equal to x, then it holds

$$x\mathrm{NaCl} \rightarrow x\mathrm{Na^+} + x\mathrm{Cl^-},$$

$$(1 - x)\,\mathrm{Na_3AlF_6} \rightarrow 3(1 - x)\,\mathrm{Na^+} + (1 - x)(1 - d)\,\mathrm{AlF_6^{3-}} +$$
$$+ (1 - x)\,d\,\mathrm{AlF_4^-} + 2(1 - x)\,d\,F^-;$$

d being the dissociation degree.

$$a_{\mathrm{NaCl}} = x_{\mathrm{Na^+}} \cdot x_{\mathrm{Cl^-}}; \quad x_{\mathrm{Na^+}} = 1,$$

$$a_{\mathrm{NaCl}} = \frac{x}{1 + 2d(1 - x)}; \quad \lim_{x \to 1} \frac{\mathrm{d}a}{\mathrm{d}x} = 1 + 2d.$$

Limiting cases:

$$\text{For} \quad d = 0, \quad a = x; \quad \lim_{x \to 1} \frac{\mathrm{d}a}{\mathrm{d}x} = 1$$

and cryolite dissociates only according to the equation

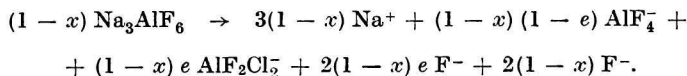$$\mathrm{Na_3AlF_6} \rightarrow 3\mathrm{Na^+} + \mathrm{AlF_6^{3-}}.$$
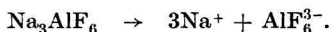
$$\text{For} \quad d = 1, \quad a = \frac{x}{3 - 2x}; \quad \lim_{x \to 1} \frac{\mathrm{d}a}{\mathrm{d}x} = 3$$

so that the dissociation runs according to the scheme

$$\mathrm{Na_3AlF_6} \rightarrow 3\mathrm{Na^+} + \mathrm{AlF_4^-} + 2F^-.$$
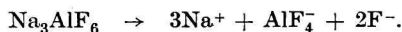
For sufficiently low concentrations of $\mathrm{Na_3AlF_6}$ in NaCl a change of the dissociation character of $\mathrm{AlF_6^{3-}}$ may be expected. Let us suggest in this connection a total dissociation of $\mathrm{AlF_6^{3-}}$ into $\mathrm{AlF_4^-}$ and $2F^-$ and a partial dissociation of $\mathrm{AlF_4^-} + 2\mathrm{Cl^-} \rightleftharpoons \mathrm{AlF_2Cl_2^-} + 2F^-$ characterized by the dissociation degree of e. For an exact calculation a consumption of $\mathrm{Cl^-}$ for the formation of the difluorodichloroaluminate anion is assumed.
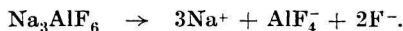
$$(1 - x)\,\mathrm{Na_3AlF_6} \rightarrow 3(1 - x)\,\mathrm{Na^+} + (1 - x)(1 - e)\,\mathrm{AlF_4^-} +$$
$$+ (1 - x)\,e\,\mathrm{AlF_2Cl_2^-} + 2(1 - x)\,e\,F^- + 2(1 - x)\,F^-.$$

$$a_{\mathrm{NaCl}} = \frac{x - 2e(1 - x)}{3 - 2x}; \quad \lim_{x \to 1} \frac{\mathrm{d}a}{\mathrm{d}x} = 3 + 2e.$$
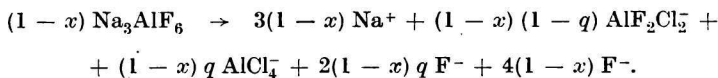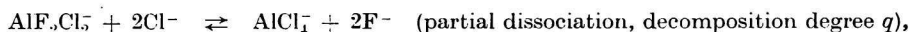
Limiting cases:
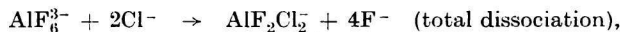
$$\text{For} \quad e = 0, \quad a = \frac{x}{3 - 2x}; \quad \lim_{x \to 1} \frac{da}{dx} = 3$$

cryolite dissociates according to the scheme

$$Na_3AlF_6 \quad \to \quad 3Na^+ + AlF_4^- + 2F^-.$$

$$\text{For} \quad e = 1, \quad a = \frac{3x - 2}{3 - 2x}; \quad \lim_{x \to 1} \frac{da}{dx} = 5.$$

For very low concentrations of Na_3AlF_6 in NaCl also the anions $AlF_2Cl_2^-$ may be expected to be unstable and gradually to begin further dissociation. Then for the dissociation of the cryolite anion the equations hold

$$AlF_6^{3-} + 2Cl^- \quad \to \quad AlF_2Cl_2^- + 4F^- \quad \text{(total dissociation)},$$

$$AlF_2Cl_2^- + 2Cl^- \quad \rightleftarrows \quad AlCl_4^- + 2F^- \quad \text{(partial dissociation, decomposition degree } q\text{)},$$

$$(1 - x)\, Na_3AlF_6 \quad \to \quad 3(1 - x)\, Na^+ + (1 - x)\,(1 - q)\, AlF_2Cl_2^- +$$

$$+ (1 - x)\, q\, AlCl_4^- + 2(1 - x)\, q\, F^- + 4(1 - x)\, F^-.$$

$$a_{NaCl} = \frac{x(3 + 2q) - 2(1 + q)}{3 - 2x}; \quad \lim_{x \to 1} \frac{da}{dx} = 5 + 2q.$$

Limiting cases:

$$\text{For} \quad q = 0, \quad a = \frac{3x - 2}{3 - 2x}; \quad \lim_{x \to 1} \frac{da}{dx} = 5.$$

$$\text{For} \quad q = 1, \quad a = \frac{5x - 4}{3 - 2x}; \quad \lim_{x \to 1} \frac{da}{dx} = 7.$$

The above schemes cover in principle all the possible dissociation processes of cryolite with respect to the number of new particles brought in molten NaCl by cryolite. The expressions deduced for the activity of NaCl were inserted into eqn (2). The temperature of primary crystallization was calculated in the concentration interval $x_{NaCl} = 1.00 - 0.85$ with a step of 0.01. The degrees of dissociation d, e, and q were in the interval of $(0;1)$ with a step of 0.1.

The computed values of the primary crystallization temperature of NaCl were graphically presented and compared with the experimental liquidus curve (Fig. 1). For the sake of simplicity only the following cases are given: $d = 0$, $d = 0.5$, $d = 1$, $e = 1$, and $q = 1$.

As the figure shows, the dissociation of complex hexafluoroaluminate anion varies with the concentration of Na_3AlF_6. An infinite dilution causes a total disintegration of the anion AlF_6^{3-} into seven new particles. At the concentration of 1.2 mole % Na_3AlF_6 the experimental liquidus curve intersects the theoretical, calculated for $d = 1$, thus indicating the total dissociation of AlF_6^{3-} into AlF_4^- and $2F^-$. With increasing cryolite concentration also the amount of AlF_6^{3-} increases; at the concentration of 6.5 mole % Na_3AlF_6 $d = 0.5$, *i.e.* half the decomposition of AlF_6^{3-} into AlF_4^-. At the eutectic composition and temperature (11 mole % Na_3AlF_6 and 737°C) $d = 0.4$.

Fig. 1. Part of the liquidus of NaCl in
the system NaCl—Na₃AlF₆.
—○—○— experimental liquidus curve.
1. theoretical liquidus curve for $d = 0$;
2. theoretical liquidus curve for $d = 0.5$;
3. theoretical liquidus curve for $d = 1$;
4. theoretical liquidus curve for $e = 1$;
5. theoretical liquidus curve for $q = 1$.
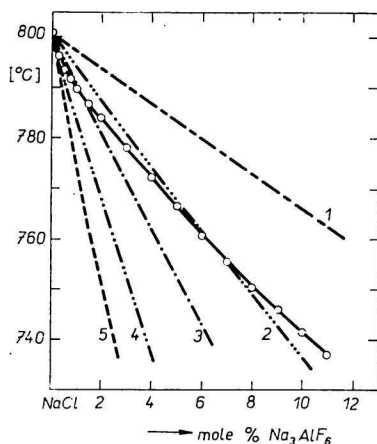
The experimental results concerning the liquidus curve of NaCl in a system with Na₃AlF₆ were then also used for the determination of the coefficient $k_{j/i}$, appearing in the "universal relationship" [25]. According to this, the activity of the i-th substance in a liquid binary system is given by

$$a_i = x_i^{k_{j/i}}. \tag{3}$$

The coefficient $k_{j/i}$ generally being a function of x_i, numerically equals the number of new (foreign) particles, arising in the system formed by the pure liquid substance "i", if 1 molecule of the substance "j" is introduced.

As it has been found, the dependence $k_{j/i} = f(x)$ has a hyperbolic character and for the given case it may be expressed with sufficient accuracy by the relation

$$k_{j/i} = k_{j/i}^{\mathrm{St}} - \frac{(1 - x_i)}{a + b(1 - x_i)}, \tag{4}$$

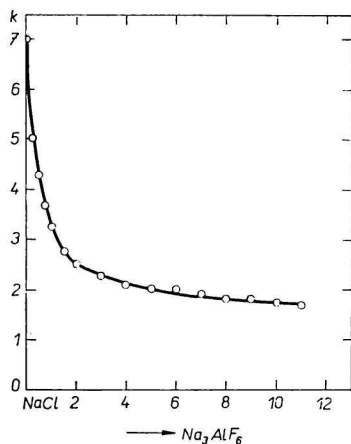where $k_{j/i}^{\mathrm{St}}$ is the Stortenbeker correction factor,

Fig. 2. Dependence of the coefficient $k_{j/i}$ from the universal melting relationship on the concentration of Na₃AlF₆ in the system NaCl—Na₃AlF₆.

a and b are constants ($a = 8.47 \times 10^{-4}$, $b = 1.82 \times 10^{-1}$).

The graphical representation of eqn (4) is in Fig. 2.

Introducing for $k_{j/i}$ from eqn (4) into eqn (3) and from there into eqn (2), we obtain a single relation for the calculation of the total liquidus curve of NaCl in the system with Na_3AlF_6.

Discussion

The results obtained assume that the melts of the system $NaCl - Na_3AlF_6$ obey either the Temkin model or that the activity of NaCl can be expressed using the universal relation. The exact fulfilment of the assumption is, however, by far not so essential as in the calculation method by *Grjotheim* [8]. While in Grjotheim's procedure a slight deviation of the liquidus temperature may considerably change the calculated dissociation degree of the anion AlF_6^{3-}, the method used in this study is free from this defect. This is clearly seen in Fig. 2. If the concentration of cryolite changes from $4-8$ mole $\%$ in the mixture, the coefficient $k_{j/i}$ varies from 2.15 down to 1.85 only. That means that a certain inaccuracy in the determination of the liquidus of NaCl would in principle not change the calculated result, showing that in a comparably wide concentration interval of Na_3AlF_6 in the mixture with NaCl is $1 < k_{j/i} < 3$. A relatively considerable "insensitiveness" of $k_{j/i}$ with respect to the concentration also means that even a certain deviation of the behaviour of melts saturated with NaCl from the ideal does not change in principle the results of calculation. If *e.g.* $k_{j/i} = 2$, then the most natural explanation is that from 1 molecule of Na_3AlF_6 the following particles non-common with NaCl are formed: 0.5 AlF_6^{3-}, 0.5 AlF_4^-, and F^-. Should the dissociation of AlF_6^{3-} into $AlF_4^- + 2F^-$ be total, then $k_{j/i}$ must equal 3.

Thus the results obtained unambiguously prove that the dissociation of AlF_6^{3-} is not total. The course of the dependence $k_{j/i} = f(x_{Na_3AlF_6})$ shows that with increasing cryolite concentration $k_{j/i}$ decreases. In the eutectic point E is $k_{j/i} = 1.75$ corresponding to the dissociation degree of anion AlF_6^{3-} of about 0.4. In melts with higher concentration of Na_3AlF_6 d may be expected therefore to be lower than this value; this finding is in complete agreement with the mentioned results by *Grjotheim* [8], *Frank* and *Foster* [9], and *Rolin* and *Bernard* [10]. The fact that for $x_{NaCl} \to 1$ $k_{j/i} = k_{j/i}^{St} = 7$ proves not only that for very low concentrations of cryolite a total decomposition of the ions AlF_6^{3-} takes place, but also that the solubility of Na_3AlF_6 in solid NaCl is practically negligible [26].

In conclusion it may be stated that the course of the liquidus curve of NaCl in the system $NaCl - Na_3AlF_6$ in the concentration range of $1.2-11.0$ mole $\%$ Na_3AlF_6 is consistent with the assumption according to which the melt consists of the ions Na^+, AlF_6^{3-}, AlF_4^-, and F^- and that Na_3AlF_6 does not form any solid solutions on the basis of NaCl.

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