

Dissociation Equilibria in Molten Cryolite: The Presence of AlF_5^{2-} Ions

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Feng, N. X. and Kvanvde, H., 1986. Dissociation Equilibria in Molten Cryolite: The Presence of AlF_5^{2-} Ions. – Acta Chem. Scand. A 40: 622–630.

The ionic structure of cryolite melts is discussed. Contrary to previous opinions in the literature, it is assumed that molten cryolite is partly dissociated into more than one type of aluminium-containing ionic species. Model calculations, using liquidus temperatures and thermodynamic data from the literature, then show that the most probable dissociation reaction of molten cryolite may be written as: $\text{Na}_3\text{AlF}_6(\text{l}) = 1.8 \text{NaF}(\text{l}) + 0.8 \text{NaAlF}_4(\text{l}) + 0.2 \text{Na}_2\text{AlF}_5(\text{l})$. Thermodynamic data and activities for $\text{Na}_3\text{AlF}_6(\text{l})$ were calculated, giving the standard heat of formation of $\text{Na}_2\text{AlF}_5(\text{l})$ from the elements: $\Delta H_f^\circ(\text{Na}_2\text{AlF}_5(\text{l})) = -2791 \text{ kJ mol}^{-1}$ at 1285 K. By use of this dissociation model, the molar volumes of the species were calculated. Literature data for the degree of ionization to Na^+ and F^- in molten sodium fluoride were then used to calculate the equivalent conductances and the transference numbers of Na^+ and F^- in these melts. For the cryolite composition, $t_{\text{Na}^+} = 0.93$ was obtained, which confirms that almost all the current through the electrolyte used in the Hall-Héroult process is transported by Na^+ ions.

The ionic structure of molten cryolite has been discussed extensively for more than sixty years now.¹ Several dissociation species are possible in cryolite melts, at least in theory, and some of these are listed in Table 1. First, it should be noted that molten cryolite is completely dissociated into Na^+ and AlF_6^{3-} . The latter ions further dissociate partially, mainly into AlF_4^- and F^- [eqn. (1)]. The existence of AlF_4^- has been firmly established from cryoscopic measurements² and density data,³ and later confirmed by Raman spectroscopic measurements.⁴ The equilibrium constant and the degree of dissociation for the re-



action are reasonably well established, the latter being about 0.3 in pure molten cryolite at tem-

peratures around 1300 K. Thermodynamic data and activities are available in the literature for both $\text{Na}_3\text{AlF}_6(\text{l})$ and $\text{NaAlF}_4(\text{l})$, as well as for the pure constituents $\text{NaF}(\text{l})$ and $\text{AlF}_3(\text{s})$.¹ Among the ionic species in Table 1, only AlF_6^{3-} and AlF_4^- have been positively identified spectroscopically. However, there are strong indications that Al_2F_7^- ions exist in melts with very low cryolite ratios, close to the saturation limit of AlF_3 .⁵

Mass spectrometric and vapour pressure measurements have established the presence of $\text{Na}_2\text{AlF}_5(\text{g})$ in the vapour phase above solid and molten cryolite.^{5,6} Although the existence of a species in the vapour phase does not necessarily imply that the same species is present in the melt to any appreciable extent, it has to be present *in principle*. However, its partial pressure in the vapour does not give any direct information about its activity in the melt.

The basic idea in the present paper is that molten cryolite may dissociate to give more than one type of aluminium-containing dissociation species. Although there is no doubt that AlF_4^- is the dominant dissociation product, small amounts of AlF_5^{2-} may be present too. The purpose of the

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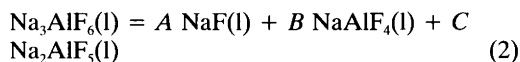
Table 1. Possible ionic species present in NaF/AlF₃ melts. Cryolite ratio is defined as the molar ratio of NaF to AlF₃ in the melt.

| Species | Corresponding cryolite ratio | Mol fraction of AlF ₃ |
|---|------------------------------|----------------------------------|
| AlF ₆ ³⁻ | 3/1 | 0.250 |
| Al ₂ F ₁₁ ⁵⁻ | 5/2 | 0.286 |
| AlF ₅ ²⁻ | 2/1 | 0.333 |
| Al ₃ F ₁₄ ⁵⁻ | 5/3 | 0.375 |
| Al ₂ F ₉ ³⁻ | 3/2 | 0.400 |
| AlF ₄ ⁻ | 1/1 | 0.500 |
| Al ₂ F ₇ ⁻ | 1/2 | 0.667 |

present work was, then, to determine activities and thermodynamic data for Na₂AlF₅(l) in cryolite melts, and thus furnish some evidence for the suggestion that the AlF₆³⁻ ion may dissociate to give both AlF₄⁻ and AlF₅²⁻. The results were then used to calculate molar volumes, electrical conductivities and transference numbers in NaF/AlF₃ melts.

Calculation procedure

As in the majority of the studies reported on the dissociation of molten cryolite, the ideality assumption is also applied here. This means that the melt is treated as an ideal ionic mixture and the activity then set equal to the mol fraction of the ionic species under consideration. The dissociation reaction of molten cryolite may be written formally as shown in eqn. (2), where the stoichiometric



metric coefficients *A*, *B* and *C* are related through the mass balance eqns. (3), (4) and (5).

$$\text{Sodium: } A + B + 2C = 3 \quad (3)$$

$$\text{Aluminium: } B + C = 1 \quad (4)$$

$$\text{Fluorine: } A + 4B + 5C = 6 \quad (5)$$

However, even though we apparently have here three eqns. with three unknowns, the eqns. are not independent, and we end up with two eqns., (6) and (7).

$$A - B = 1 \quad (6)$$

$$B + C = 1 \quad (7)$$

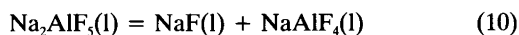
The equilibrium constant *K*₀ for the dissociation reaction (2) may be written as eqn. (8), where *a*

$$K_0 = \frac{a_{\text{NaF}}^A \cdot a_{\text{NaAlF}_4}^B \cdot a_{\text{Na}_2\text{AlF}_5}^C}{a_{\text{Na}_3\text{AlF}_6}} \quad (8)$$

denotes activity. From the ideality assumption, the activity may be set equal to the mol fraction *N* of the ions, as given in eqn. (9). We now intro-

$$K_0 = \frac{N_{\text{NaF}}^A \cdot N_{\text{NaAlF}_4}^B \cdot N_{\text{Na}_2\text{AlF}_5}^C}{N_{\text{Na}_3\text{AlF}_6}} \quad (9)$$

duce the weighed-in mol fraction *x* of aluminium fluoride in the system NaF/AlF₃, and *r*₀, the degree of dissociation of Na₃AlF₆(l). Furthermore, the species Na₂AlF₅(l) may dissociate according to eqn. (10) and the equilibrium constant *K*₁



for this reaction may be written as eqn. (11). The degree of dissociation of Na₂AlF₅(l) in the

$$K_1 = \frac{N_{\text{NaF}} \cdot N_{\text{NaAlF}_4}}{N_{\text{Na}_2\text{AlF}_5}} \quad (11)$$

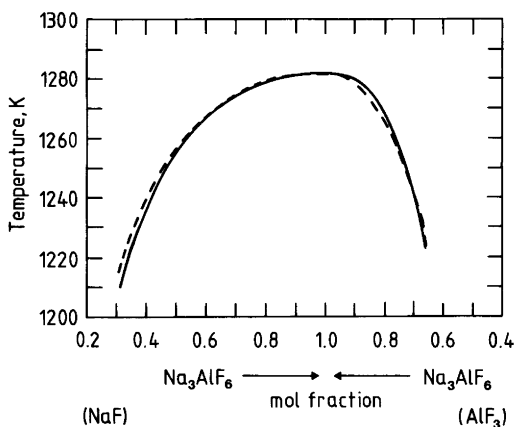


Fig. 1. Experimental and calculated temperatures of primary crystallization of the system NaF/AlF₃. Solid line: measured temperatures.¹ Dashed line: calculated values according to dissociation reaction (2), see text.

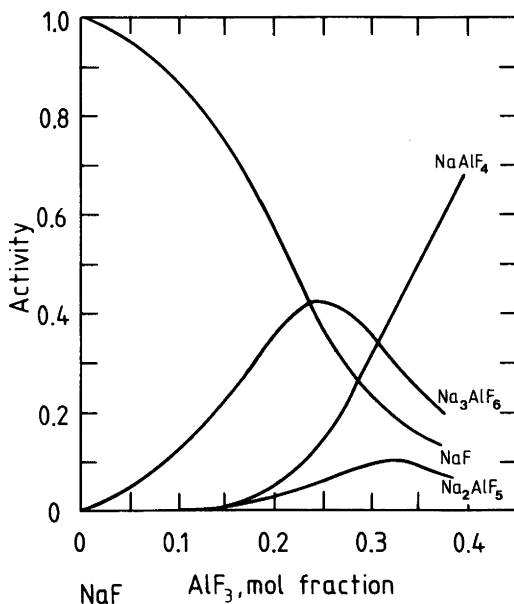


Fig. 2. Activities of NaF, Na_3AlF_6 , Na_2AlF_5 and NaAlF_4 in NaF/ AlF_3 melts at 1280 K.

melt at its stoichiometric composition is denoted by r_1 .

The mol fractions of the species NaF(l), NaAlF_4 (l), Na_2AlF_5 (l) and Na_3AlF_6 (l), and the equilibrium constants K_0 and K_1 may then be expressed by the stoichiometric coefficients A , B and C , the dissociation degrees r_0 and r_1 , and the weighed-in mol fraction x of AlF_3 in the melt. The eqns. for the mol fractions of the above-mentioned four species become somewhat different in the two concentration ranges where $0 \leq x < 0.25$ and $0.25 \leq x \leq 0.50$. These eqns. are straightforward, but rather complex and need not be written here.

From phase diagram theory, the activity of cryolite may be expressed by eqn. (12), where

$$\ln a_{\text{Na}_3\text{AlF}_6} = \frac{\Delta H_{m,\text{hypo}}^\circ}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \quad (12)$$

$\Delta H_{m,\text{hypo}}^\circ$ is the heat of melting of pure Na_3AlF_6 (l) at the melting point T_0 of hypothetical, undissociated cryolite, T is the absolute temperature of melting (the liquidus temperature) and R is the universal gas constant. By introduction of the ideality assumption, eqn. (12) may be rewritten as eqn. (13).

$$\frac{1}{T_0} = \frac{1}{T_c} + \frac{R}{\Delta H_f^\circ} \cdot \ln N_{\text{Na}_3\text{AlF}_6} \quad (13)$$

If $N_{\text{Na}_3\text{AlF}_6}$ is known at its real melting point T_c ($= 1284 \text{ K}$), eqn. (13) may be used to calculate T_0 , the melting point of hypothetical, undissociated cryolite. When the equilibrium constant K_1 at temperature T_1 is known or can be estimated, the equilibrium constant K_2 at a different temperature, T_2 , may be calculated by eqn. (14),

$$\ln \frac{K_2}{K_1} = \frac{\Delta H_d^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (14)$$

where ΔH_d° is the heat of dissociation of pure molten cryolite.

The calculation procedure was as follows: A pair of values for the equilibrium constants K_0 and K_1 was chosen, and values for the degrees of dissociation r_0 and r_1 were then calculated from the mol fractions and the expressions for the equilibrium constants, eqns. (9) and (11). The mol fraction of Na_3AlF_6 in pure cryolite was calculated, and the temperature T_c was then calculated from eqn. (13). Values for the heats of dissociation of pure Na_3AlF_6 and Na_2AlF_5 were then chosen, and for each set of values eqn. (14) was used to calculate equilibrium constants at temperatures T , equal to the measured liquidus temperatures from the literature. The degrees of dissociation and the mol fractions were calculated, and finally the liquidus temperatures were calculated from eqn. (12). The best fit between experimental and calculated temperatures was then determined in order to obtain the most probable dissociation scheme for molten cryolite.

The following experimental data were used in

Table 2. Activity values for the main ionic species present in molten cryolite at 1280 K.

| Species | Present data | Kvande ⁵ | Sterten and Mæland ⁷ |
|---------------------------|--------------|---------------------|---------------------------------|
| Na_3AlF_6 | 0.42 | 1 ^a | 1 ^a |
| NaF | 0.36 | 0.38 | 0.35 |
| NaAlF_4 | 0.14 | 0.15 | 0.12 |
| Na_2AlF_5 | 0.06 | — | — |

^a Defined as equal to unity because of a different choice of standard state for Na_3AlF_6 in these studies.

the present calculations: The liquidus temperatures in the system NaF/AlF₃, taken from the literature,¹ and the heat of melting of pure cryolite, $\Delta H_m^\circ = 107 \text{ kJ mol}^{-1}$, taken from the measurements of Sterten and Mæland.⁷ The latter value may be expressed by the eqn.:

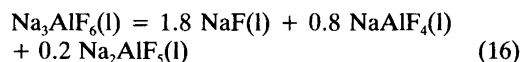
$$\Delta H_m^\circ = \Delta H_{m,\text{hypo}}^\circ + r_0 \cdot \Delta H_d^\circ (\text{Na}_3\text{AlF}_6) + r_0 \cdot r_1 \cdot \Delta H_d^\circ (\text{Na}_2\text{AlF}_5) \quad (15)$$

Dewing¹⁷ has reported the existence of small amounts of solid solutions of AlF₃ in cryolite, but this has been neglected in the present calculations.

Results and discussion

The best fit between measured and calculated temperatures is shown in Fig. 1. It is seen that the agreement is quite satisfactory. The "best" values for the degrees of dissociation are $r_0 = 0.33$ at the Na₃AlF₆ composition and $r_1 = 0.1$ at the Na₂AlF₅ composition.

By use of the values $K_0 = 0.045$ and $K_1 = 0.81$ at 1280 K, the mol fractions (or activities) of NaF, NaAlF₄, Na₂AlF₅ and Na₃AlF₆ in the melt were calculated. The results are presented in Fig. 2. The values of the stoichiometric coefficients in eqn. (2) are: $A = 1.8$, $B = 0.8$ and $C = 0.2$. This gives the eqn. (16). The activity data for the



cryolite composition may be read from Fig. 2; they are compared with literature data in Table 2.

Table 2 shows that there is very good agreement between the activity values for NaF and

Table 3. Heats of reaction for different dissociation reactions in cryolite melts at 1285 K.

| Reaction | $\Delta H^\circ_{\text{reaction}}/\text{kJ mol}^{-1}$ |
|--|---|
| $\text{Na}_3\text{AlF}_6 = 1.8 \text{ NaF} + 0.8 \text{ NaAlF}_4 + 0.2 \text{ Na}_2\text{AlF}_5$ | 64.0 |
| $\text{Na}_2\text{AlF}_5 = 2 \text{ NaF} + \text{NaAlF}_4$ | 70.4 |
| $\text{Na}_3\text{AlF}_6 = \text{NaF} + \text{Na}_2\text{AlF}_5$ | 38.2 |
| $\text{Na}_2\text{AlF}_5 = \text{NaF} + \text{NaAlF}_4$ | 32.2 |
| $\text{Na}_2\text{AlF}_5 = 2 \text{ NaF} + \text{AlF}_3(\text{s})$ | 26.0 ^a |

^aUsing auxiliary data from Sterten and Mæland.⁷

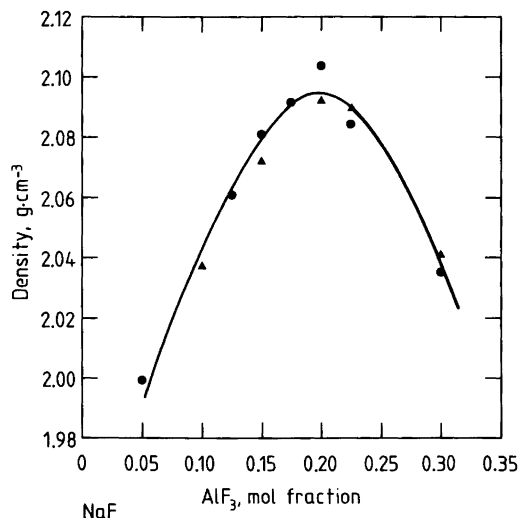


Fig. 3. Densities of NaF/AlF₃ melts at 1284 K. Filled triangles: experimental data.¹¹ Filled circles: experimental data.¹² Solid line: calculated values.

NaAlF₄ in the three studies compared. No data for the activity of Na₂AlF₅ are available in the literature, but the present value of 0.06 appears reasonable. This activity value increases with increasing mol fraction of AlF₃ in the melt up to the stoichiometric composition of Na₂AlF₅ (mol fraction of AlF₃ = 0.333), where the maximum activity value for this species is reached. Fig. 2 shows that the activity of Na₂AlF₅ then decreases again for higher mol fractions of AlF₃ in the melt.

The hypothetical melting point of pure, undissociated Na₃AlF₆ was found to be 1424 K, which is in excellent agreement with the results of Grjotheim² and Paučirová *et al.*⁸ The corresponding heat of melting was found to be 92 kJ mol⁻¹. Table 3 gives the heats of reaction that were calculated from the present work. No data concerning Na₂AlF₅(l) have been found in the literature.

Data in the literature (in kJ mol⁻¹) for the reaction given by eqn. (17) are as follows: 48.5,



Kvande;⁵ 71.1, Sterten and Mæland;⁷ 64.0, Rolin;⁹ 75.3, Holm.¹⁰ These data give an average ΔH° value of 64.7 kJ mol⁻¹, as compared to the present value of 70.4 kJ mol⁻¹. Thus, the agree-

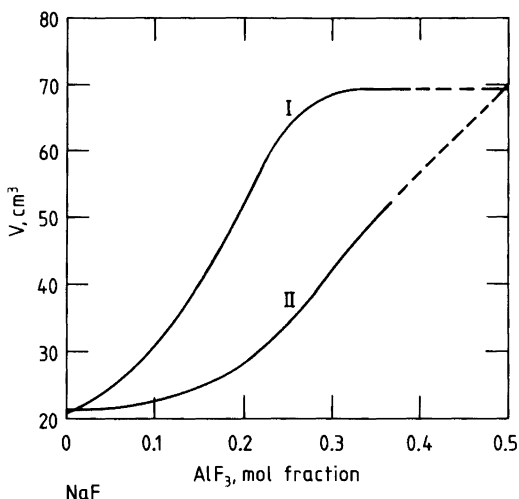


Fig. 4. Molar and equivalent molar volumes of NaF/AlF₃ melts at 1284 K. Curve I: molar volume. Curve II: equivalent molar volume.

ment is satisfactory when the assumptions made are taken into account.



The heat of reaction for eqn. (18) may be used to calculate the standard heat of formation of Na₂AlF₅(l) from the elements by combining the literature data with the present data. This gives the value in eqn. (19).

$$\Delta H_f^\circ(\text{Na}_2\text{AlF}_5(\text{l})) = -2791 \text{ kJ mol}^{-1} \quad (19)$$

Heats of vaporization are available from the mass spectrometric measurements of Kolosov *et al.*,⁶ giving the corresponding value for the gaseous species Na₂AlF₅(g) shown in eqn. (20). The va-

$$\Delta H_f^\circ(\text{Na}_2\text{AlF}_5(\text{g})) = -2582 \pm 21 \text{ kJ mol}^{-1} \quad (20)$$

pour pressure measurements made by Kvande⁵ showed that the heat of vaporization of Na₂AlF₅(g) at its stoichiometric melt composition is probably a little less than 204 ± 15 kJ mol⁻¹. If this value (which is valid for the cryolite composition) is used, the vaporization data^{5,6} give the value

$$\Delta H_f^\circ(\text{Na}_2\text{AlF}_5(\text{l})) = -2786 \pm 26 \text{ kJ mol}^{-1} \quad (21)$$

which agrees very well with the value in eqn. (19).

Calculation of molar volumes, equivalent conductances and transference numbers in NaF/AlF₃ melts

In this part of the work, we have used the dissociation reaction described by eqn. (16) to calculate molar volumes, electrical conductivities and transference numbers in NaF/AlF₃ melts containing up to 35 mol % AlF₃, corresponding to a cryolite ratio of 1.86 (on a molar basis). For this purpose, we combine the calculated mol fractions of the main species NaF, Na₃AlF₆, Na₂AlF₅ and NaAlF₄ (see Fig. 2) with experimental data from the literature for the density and the electrical conductivity.¹

Molar volumes. The molar volumes of the species were assumed to be additive and independent of the total composition of the melt. For pure molten sodium fluoride, the molar volume, V_{NaF} , may be calculated from the simple eqn. (22), where

$$V_{\text{NaF}} = \frac{M_{\text{NaF}}}{d_{\text{NaF}}} \quad (22)$$

M_{NaF} is the molar mass of NaF (42 g mol⁻¹), and d_{NaF} is the experimentally measured density (1.95 g cm⁻³).³ From eqn. (22), $V_{\text{NaF}} = 21.5 \text{ cm}^3 \text{ mol}^{-1}$ may be calculated. On the basis of the assumptions above, the density of NaF/AlF₃ melts may be expressed by eqn. (23). Here, N is the mol

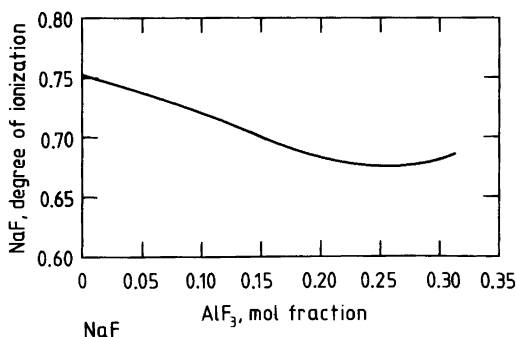


Fig. 5. Degree of ionization of NaF into Na⁺ and F⁻ in NaF/AlF₃ melts at 1273 K.¹²

$$d = \frac{N_{\text{NaF}} \cdot M_{\text{NaF}} + N_{\text{Na}_3\text{AlF}_6} \cdot M_{\text{Na}_3\text{AlF}_6} + N_{\text{Na}_2\text{AlF}_5} \cdot M_{\text{Na}_2\text{AlF}_5} + N_{\text{NaAlF}_4} \cdot M_{\text{NaAlF}_4}}{N_{\text{NaF}} \cdot V_{\text{NaF}} + N_{\text{Na}_3\text{AlF}_6} \cdot V_{\text{Na}_3\text{AlF}_6} + N_{\text{Na}_2\text{AlF}_5} \cdot V_{\text{Na}_2\text{AlF}_5} + N_{\text{NaAlF}_4} \cdot V_{\text{NaAlF}_4}} \quad (23)$$

fraction, M is the molar mass and V is the molar volume of the species indicated by the subscript. The values of the mol fractions N were taken from the data shown in Fig. 2, the molar masses are known, and V_{NaF} was found from eqn. (22) above. This still leaves three unknowns in eqn. (23), viz. $V_{\text{Na}_3\text{AlF}_6}$, $V_{\text{Na}_2\text{AlF}_5}$ and V_{NaAlF_4} . We therefore fitted eqn. (23) to some selected experimental literature data.^{11,12} The resulting curve for the density of NaF/AlF₃ melts at 1284 K is shown in Fig. 3. The calculated densities show good agreement with the experimental data, and the best fit was obtained with the following values (in cm³ mol⁻¹) of the molar volumes in eqn. (23): $V_{\text{Na}_3\text{AlF}_6} = 95.7$;

$$V = N_{\text{NaF}} \cdot V_{\text{NaF}} + N_{\text{Na}_3\text{AlF}_6} \cdot V_{\text{Na}_3\text{AlF}_6} + N_{\text{Na}_2\text{AlF}_5} \cdot V_{\text{Na}_2\text{AlF}_5} + N_{\text{NaAlF}_4} \cdot V_{\text{NaAlF}_4} \quad (24)$$

$V_{\text{Na}_2\text{AlF}_5} = 81.2$; $V_{\text{NaAlF}_4} = 69.6$. The data for Na₃AlF₆ and NaAlF₄ are in excellent agreement with the values of $V_{\text{Na}_3\text{AlF}_6} = 95.0$ cm³ mol⁻¹ and $V_{\text{NaAlF}_4} = 67.3$ cm³ mol⁻¹ at 1273 K, reported by Frank and Foster.³ No previous data for $V_{\text{Na}_2\text{AlF}_5}$ are available, but the above value fits in reasonably well with the two other data. The molar vol-

ume V of the NaF/AlF₃ melt may be calculated from eqn. (24), which is identical to the denominator in eqn. (23). The *equivalent* molar volume V_{equiv} of the melt may be defined by eqn. (25).

$$V_{\text{equiv}} = N_{\text{NaF}} \cdot V_{\text{NaF}} + \frac{1}{3} N_{\text{Na}_3\text{AlF}_6} \cdot V_{\text{Na}_3\text{AlF}_6} + \frac{1}{2} N_{\text{Na}_2\text{AlF}_5} \cdot V_{\text{Na}_2\text{AlF}_5} + N_{\text{NaAlF}_4} \cdot V_{\text{NaAlF}_4} \quad (25)$$

The calculated values for the molar and the *equivalent* molar volumes of the mixture are shown in Fig. 4. It is seen that both these volumes increase with increasing mol fraction of AlF₃ in the melt. For pure molten sodium fluoride the volumes are equal, but when AlF₃ is added the molar volume becomes higher than the *equivalent* molar volume. Fig. 4 shows that the curves approach each other again for compositions with mol fractions of AlF₃ above 0.35. They will probably be almost identical at the NaAlF₄ composition, due to the definitions given by eqns. (24) and (25).

Degree of ionization of sodium fluoride. Frank and Foster¹³ have studied the degree of ionization to Na⁺ and F⁻ ions in molten sodium fluoride. They found that the assumption of complete ionization of NaF to Na⁺ and F⁻ did not give results that were in agreement with the experimental measurements of the electrical conductivity. However, when incomplete ionization was assumed, good agreement was found. This result

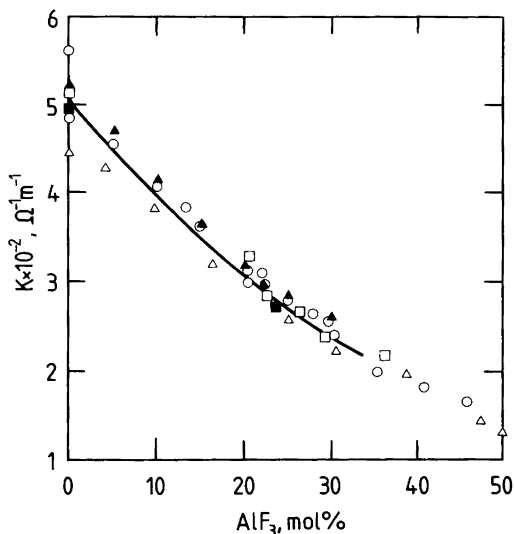


Fig. 6. Electrical conductivity of NaF/AlF₃ melts at 1273 K. Points: experimental data from the literature.² Solid line: calculated values.

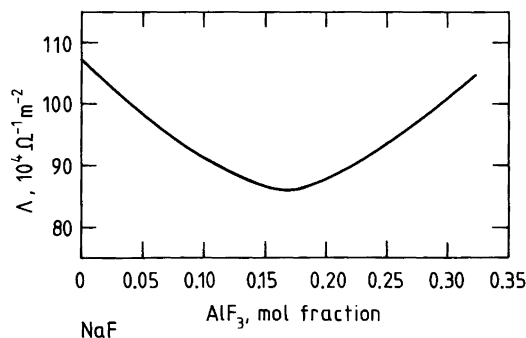


Fig. 7. Equivalent molar conductance in NaF/AlF₃ melts at 1284 K.

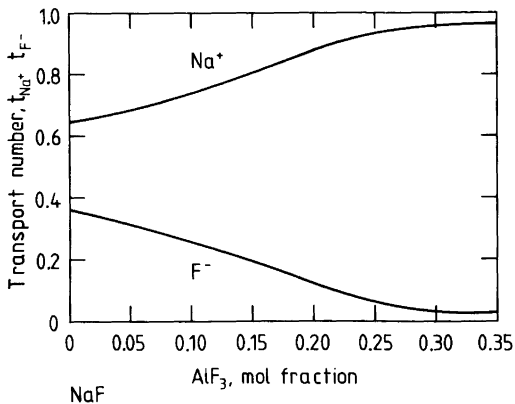


Fig. 8. Transference numbers of Na^+ and F^- in NaF/AlF_3 melts at 1284 K.

was interpreted from the viewpoint of a "defect" molten salt structure. Sodium fluoride was found to be 68% "ionized" at 1273 K. The "non-ionized" sodium fluoride was considered to be Na^+F^- ion-pairs that diffuse via paired cation-anion vacancies, and thus do not contribute to the electrical conductivity. More recently, Ran *et al.*¹² reported data for the degree of ionization of sodium fluoride in NaF/AlF_3 melts. Their results are shown in Fig. 5. The degree of ionization in pure sodium fluoride was found to be 0.75, which is a little higher than the value of 0.68 reported by Frank and Foster.¹³ Increasing content of AlF_3 in the melt caused the degree of ionization to decrease down to a minimum value of 0.675 in molten cryolite. Further addition of aluminium fluoride then gave an increasing degree of ionization again.

Electrical conductivity. In general, the experimental data available from the literature for the electrical conductivity of NaF/AlF_3 melts are in good agreement.¹ Most of the electric current is carried by the Na^+ ions, while the rest is carried by F^- ions. Large anions like AlF_6^{3-} , AlF_5^{2-} and AlF_4^- are not considered very likely to take part in the process. The electrical conductivity, K , of NaF/AlF_3 melts may be calculated by the eqn.

$$K = \frac{1}{V} [(\beta \cdot N_{\text{NaF}} + 3N_{\text{Na}_3\text{AlF}_6} + 2N_{\text{Na}_2\text{AlF}_5} + N_{\text{NaAlF}_4}) \cdot \lambda_{\text{Na}^+} + \beta \cdot N_{\text{NaF}} \cdot \lambda_{\text{F}^-}] \quad (26)$$

(26), where β is the degree of ionization of NaF , λ_{Na^+} and λ_{F^-} are the equivalent ionic conductances of Na^+ and F^- , V is the real molar volume of the melt as given by eqn. (24), and N is the mol fraction, as before.

In pure molten sodium fluoride the ratio of the equivalent ionic conductances may be written as

$$\frac{\lambda_{\text{Na}^+}}{\lambda_{\text{F}^-}} = \frac{t_{\text{Na}^+}}{t_{\text{F}^-}} \quad (27)$$

eqn. (27), where t_{Na^+} and t_{F^-} are the transference- or transport numbers of Na^+ and F^- in the melt. Grjotheim *et al.*¹⁴ measured the transference number of Na^+ to be $t_{\text{Na}^+} = 0.64 \pm 0.05$ in pure molten sodium fluoride. Thus, $t_{\text{F}^-} = 0.36 \pm$ and the ratio $t_{\text{Na}^+}/t_{\text{F}^-}$ in eqn. (27) becomes 1.78. We have used the value of $\beta = 0.75$ from Fig. 5, the electrical conductivity, $K = 5.0 \text{ ohm}^{-1}\text{cm}^{-1}$, from the literature,¹⁵ and the molar volume, $V_{\text{NaF}} = 21.5 \text{ cm}^3\text{mol}^{-1}$, to calculate the values of the equivalent conductances of the two ions in molten sodium fluoride. Combination of eqns. (26) and (27) thus gave $\lambda_{\text{Na}^+} = 91.5 \text{ ohm}^{-1}\text{cm}$ and $\lambda_{\text{F}^-} = 51.3 \text{ ohm}^{-1}\text{cm}$. Eqn. (26) was then used to calculate the electrical conductivity of various NaF/AlF_3 melts. The results are shown as a solid line in Fig. 6; the agreement with the literature data is satisfactory.

Equivalent conductances of NaF/AlF_3 melts. The equivalent conductance, Λ , of the melt was calculated from eqn. (28). As before, K is the elec-

$$\Lambda = K \cdot V_{\text{equiv.}} \quad (28)$$

trical conductivity and $V_{\text{equiv.}}$ the equivalent molar volume of the melt. The calculated results are shown in Fig. 7. The equivalent conductance decreases with increasing AlF_3 content in the melt, until it passes through a minimum value at a mol fraction of AlF_3 of 0.17, corresponding to a cryolite ratio of 4.9. It then increases again for higher AlF_3 content.

The results can be explained from the data in Fig. 6, which show that the electrical conductivity decreases steadily with increasing AlF_3 content, and from Fig. 4, which shows that the equivalent molar volume has the opposite variation. At low AlF_3 content (a mol fraction of $\text{AlF}_3 < 0.17$), the

$$t_{\text{Na}^+} = \frac{(\beta \cdot N_{\text{NaF}} + 3N_{\text{Na}_3\text{AlF}_6} + 2N_{\text{Na}_2\text{AlF}_5} + N_{\text{NaAlF}_4}) \cdot \lambda_{\text{Na}^+}}{(\beta \cdot N_{\text{NaF}} + 3N_{\text{Na}_3\text{AlF}_6} + 2N_{\text{Na}_2\text{AlF}_5} + N_{\text{NaAlF}_4}) \cdot \lambda_{\text{Na}^+} + \beta \cdot N_{\text{NaF}} \cdot \lambda_{\text{F}^-}} \quad (29)$$

$$t_{\text{F}^-} = \frac{\beta \cdot N_{\text{NaF}} \cdot \lambda_{\text{F}^-}}{(\beta \cdot N_{\text{NaF}} + 3N_{\text{Na}_3\text{AlF}_6} + 2N_{\text{Na}_2\text{AlF}_5} + N_{\text{NaAlF}_4}) \cdot \lambda_{\text{Na}^+} + \beta \cdot N_{\text{NaF}} \cdot \lambda_{\text{F}^-}} \quad (30)$$

increase is not very pronounced, and the product in eqn. (28) then decreases with increasing AlF_3 content, due to the dominant effect of the decreasing electrical conductivity. However, at AlF_3 contents higher than that corresponding to the cryolite composition, the *equivalent* molar volume increases much more rapidly, as seen from the slope of the curve given in Fig. 4, and the equivalent conductance then increases with further addition of AlF_3 , as shown in Fig. 7.

Transference numbers. The transference numbers of Na^+ and F^- in NaF/AlF_3 melts may be calculated from the eqns. (29) and (30). The calculated values for t_{Na^+} and t_{F^-} are shown in Fig. 8. It is seen that t_{Na^+} increases and t_{F^-} decreases with increasing AlF_3 content in the melt. For cryolite, values of $t_{\text{Na}^+} = 0.93$ and $t_{\text{F}^-} = 0.07$ are calculated. This means that almost all of the electric current in molten cryolite is transported by the Na^+ ions. In more acidic melts, which are now commonly used in the aluminium industry, even higher transference numbers for Na^+ are found (>0.95). This appears reasonable, since the concentration of F^- decreases with increasing content of AlF_3 in the melt.

Conclusion

The present work shows that the ionic structure of molten cryolite is more complex than has commonly been stated in the literature until now. The basic new idea presented here is that the AlF_6^{3-} ion dissociates partially to give another type of aluminium-containing species in addition to AlF_4^- , and that this species is AlF_5^{2-} . Model calculations of liquidus temperatures have yielded new thermodynamic data and activities for $\text{Na}_2\text{AlF}_5(\text{l})$. Further evidence for the existence of this species is found from the experimental data for the heat of vaporization of $\text{Na}_2\text{AlF}_5(\text{g})$.⁵ Craig and Brown¹⁶ have reported the existence of the corresponding compound CaAlF_5 in the molten system $\text{NaF}/\text{AlF}_3/\text{CaF}_2$.

Reasonable data for the molar volumes, equiv-

alent conductances and transference numbers in cryolite melts can be calculated on the basis of this new model for the dissociation of molten cryolite. This strengthens the argument for the existence of AlF_5^{2-} ions in these melts.

Note added in proof. Very recently, we have learned that Dewing¹⁸ has also postulated that Na_2AlF_5 must be an important species in cryolite melts.

Acknowledgement. The present work was supported financially by NORAD (Norwegian Agency for International Development), which granted a fellowship to Feng Nai Xiang. The work was done in Professor Kai Grjotheim's laboratory at the University of Oslo, and the authors hereby express their appreciation of his support and encouragement.

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Received July 18, 1986.