# Structural Species and Activities of Lithium Fluoride and Lithium Hexafluoroaluminate Dissolved in Molten Cryolite

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Liquidus curves have been calculated for the dissolution of LiF and $Li_3AlF_6$ in molten $Na_3AlF_6$, and the results are compared with published solid-liquid phase diagrams for these systems. It is assumed that both LiF and $Li_3AlF_6$ dissociate completely in molten cryolite to give $Li^+$ ions and $F^-$ or $AlF_6^{3-}$ ions, respectively. Mole fractions, activities and activity coefficients are then calculated for the species LiF, NaF, $Na_3AlF_6$, $Na_2AlF_5$ and $NaAlF_4$ in these systems. The addition of $Li_2CO_3$ to molten cryolite is also discussed, because of its industrial application as an additive to the bath in several aluminium smelters.

Addition of lithium carbonate to the bath in the Hall-Héroult process has been used quite extensively for many years now, and it is presently employed in several aluminium smelters worldwide. Pawlek[1] has made an extensive survey of the literature pertaining to the characteristics of lithium carbonate and its use in the aluminium industry.

When added to the cryolite bath, lithium carbonate dissociates, and when dissolved in the melt it behaves like lithium fluoride. Thus, we take a brief look here at the advantages and disadvantages of the presence of lithium fluoride in cryolite-alumina melts.

Lithium fluoride has several positive effects on the physicochemical properties of these melts. It lowers the liquidus temperature and the aluminium metal solubility in the bath, as well as the density and the viscosity, while it increases electrical conductivity and the interfacial tension between metal and bath. Its influence on the current and energy efficiencies of the Hall-Héroult process is therefore positive. Its main disadvantages concerning the physicochemical properties

of the bath are that it reduces the alumina solubility and the alumina dissolution rate. These effects, however, are typical of practically all additives, and can now be overcome satisfactorily, especially in the case of alumina reduction cells with centre-feeding, where the amount of alumina added may be controlled carefully. More serious objections are the relatively high price, about 3 US dollars per kg at the present time, of lithium carbonate and its adverse effect on the purity of the aluminium produced. This may necessitate a special cleaning process for the metal after tapping if a lithium content below a certain limit is required for the fabrication of the metal.

Lithium fluoride has been claimed to be the "best" possible additive for the Hall-Héroult bath. Although there is probably no single "optimum" bath composition for this process,[2] the addition of 2–4 mass % of lithium fluoride blended with other additives, for example magnesium fluoride, has obvious advantages with respect to the current and energy efficiencies.

The present work describes a study of lithium fluoride dissolved in cryolite melts. It is generally accepted that this compound forms one "foreign" species when added to molten cryolite, and it is therefore reasonable to assume that lithium fluoride dissociates according to eqn. (1):

$$LiF = Li^+ + F^- \tag{1}$$

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Thus, lithium fluoride is an $F^-$ donor and increases the basicity of the cryolite melt.

The method used in the work described here is to calculate the theoretical liquidus curves for cryolite in the systems $Na_3AlF_6$–LiF and $Na_3AlF_6$–$Li_3AlF_6$, and compare them with the best experimental data available in the literature. This method has previously been employed in similar model studies of the systems $Na_3AlF_6$–$MgF_2$,[3] and $Na_3AlF_6$–$CaF_2$,[4] giving information about the main structural species in those melts. In the present lithium-containing systems, the dissociation model apparently cannot be any other than that described by eqn. (1).

The purpose of the present work is also to test the reliability of the method of calculation,[3,4] and to see whether it gives reasonable results for lithium-containing cryolite melts. Mole fractions and activities are then calculated for the main species in the two systems $Na_3AlF_6$–LiF and $Na_3AlF_6$–$Li_3AlF_6$.

## Theoretical basis

For a binary mixture in which **A** is the solvent, the activity $a_{A(l)}$ of **A** in the melt in equilibrium with pure solid **A** may be given by eqn. (2):

$$\ln a_{A(l)} = \frac{\Delta H_m^\circ}{R}\left(\frac{1}{T_m} - \frac{1}{T}\right) \tag{2}$$

Here, $\Delta H_m^\circ$ is the standard molar enthalpy of melting of **A**, $T_m$ is the absolute melting point of pure **A**, $T$ is an arbitrary absolute temperature and $R$ is the universal gas constant. Pure molten **A** at the temperature $T$ is then chosen as the standard state (Raoultian activity scale).

If **A** dissociates partly on melting, this influences the activity of **A** in the melt. The hypothetical melting point of pure, undissociated **A** must then be introduced instead of $T_m$ in eqn. (2). If we assume that the heat of dissociation is zero, the degree of dissociation of **A** in the melt does not have any influence on the enthalpy of melting, $\Delta H_m^\circ$.

In the case of a system with a solid solution, eqn. (2) may be written:

$$\ln \frac{a_{A(l)}}{x_A} = \frac{\Delta H_m^\circ}{R}\left(\frac{1}{T_m} - \frac{1}{T}\right) \tag{3}$$

where $x_A$ is the mole fraction of **A** in the solid solution. The term $x_A$ stems from the assumption of an ideal solid solution with $x_A = a_A$.

Eqn. (3) was used to calculate the liquidus curve for **A** for the actual dissolution model of the solute. The liquidus temperature $T$ was determined when the Temkin activity was available.[5]
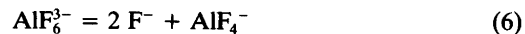
## Systems

$Na_3AlF_6$. In this system, complete dissociation of sodium hexafluoroaluminate is generally accepted.[6] Furthermore, it is assumed here that the hexafluoroaluminate ion is partly dissociated according to eqn. (4):[7]

$$AlF_6^{3-} = 1.8\ F^- + 0.8\ AlF_4^- + 0.2\ AlF_5^{2-} \tag{4}$$

The equilibrium constant for this reaction is $K_o = 0.47$ at 1284 K, and a value for the enthalpy of dissociation $\Delta H_{diss}^\circ = 64.0$ kJ mol$^{-1}$ was used.[7] The equilibrium constant $K$ at any other temperature $T$ may be calculated by eqn. (5):

$$\ln \frac{K}{K_o} = \frac{\Delta H_{diss}^\circ}{R}\left(\frac{1}{T_o} - \frac{1}{T}\right) \tag{5}$$

It should be noted here that eqn. (4) is slightly different from the conventional form of the dissociation reaction:[6]

$$AlF_6^{3-} = 2\ F^- + AlF_4^- \tag{6}$$

However, the results reported in the present work are not altered significantly if the reaction is assumed to follow eqn. (6) rather than eqn. (4) above.

$Na_3AlF_6$–$LiF$. For this system, the experimentally determined phase diagram of Holm and Holm[8] was used as a reference. Some solid solution is present on the cryolite side of this system, as seen from Fig. 1.

Fig. 2 shows the results obtained in the present work. The agreement between the theoretical and the experimental data is quite satisfactory for mole fractions of LiF up to about 0.25. The calculated liquidus temperatures are seen to be lower than those measured, the difference reaching about 10 °C for a mole fraction of LiF of 0.5.
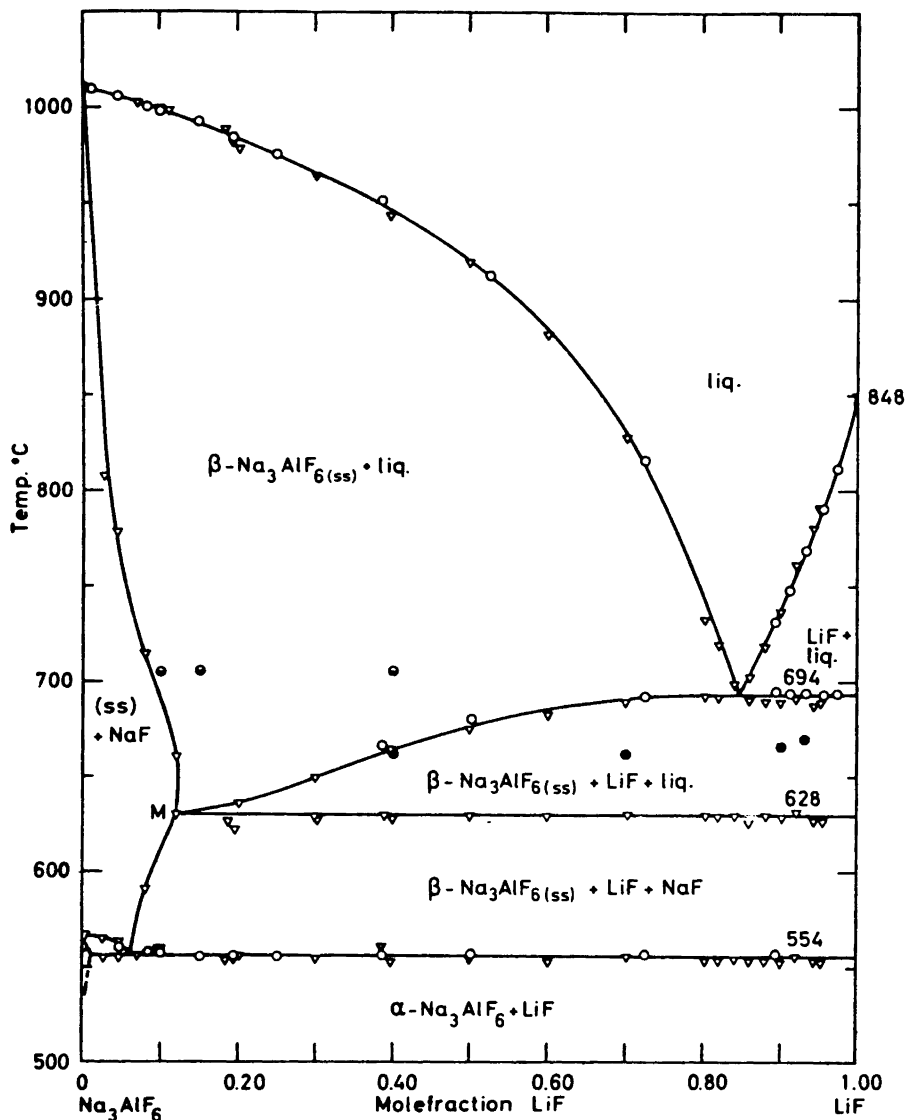
Fig. 1. The phase diagram of the system Na₃AlF₆−LiF according to Holm and Holm.[8]

Fig. 3 shows the calculated mole fractions and the activities of the species LiF, NaF, NaAlF₄, Na₂AlF₅ and Na₃AlF₆. The calculation procedure has been described previously.[4] The activities of the latter three aluminium-containing species decrease with increasing mole fraction of LiF, while LiF clearly shows the opposite behaviour. Sodium fluoride shows slightly increasing activity with increasing LiF content, which implies a relatively strong positive deviation from ideality for NaF in these melts.

The calculated activity coefficients are given in Table 1. The activity coefficient for NaAlF₄ decreases slightly, while those for Na₃AlF₆ and Na₂AlF₅ show a more significant decrease. The activity coefficient for NaF increases drastically with increasing mole fraction of LiF in the melt, which is somewhat surprising. On the other hand,
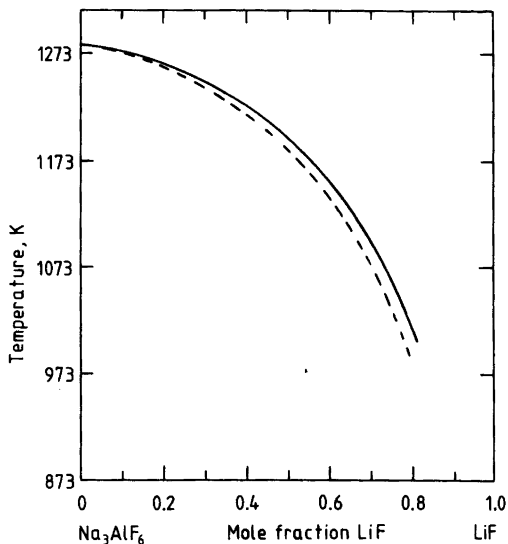
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Fig. 2. Comparison of calculated and experimental[8] liquidus curves for cryolite in the system $Na_3AlF_6$–LiF. The dashed line is calculated.



Fig. 3. Activities and mole fractions in the system $Na_3AlF_6$–LiF at 1284 K. Dashed lines: activities. Solid lines: mole fractions. I: $Na_2AlF_5$, II: $NaAlF_4$, III: $Na_3AlF_6$, IV: NaF, V: LiF.

the increase in the activity coefficient for LiF is about as one would expect.

*Na₃AlF₆–Li₃AlF₆.* This system is very complex, as shown by the phase diagram published by Holm and Holm.[8] A wide domain of solid solution exists in this system, as seen from Fig. 4.

In the calculation it was assumed that $Li_3AlF_6$ was completely dissociated according to eqn. (7):
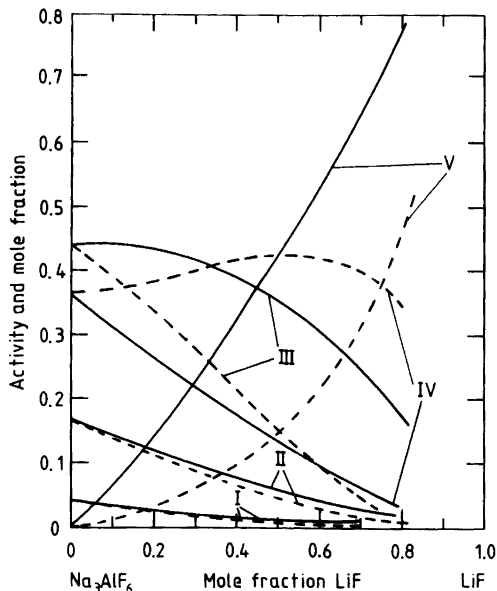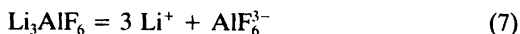
$$Li_3AlF_6 = 3\ Li^+ + AlF_6^{3-} \tag{7}$$

Furthermore, the hexafluoroaluminate ions dissociate further according to eqn. (4) above.

The results are shown in Fig. 5. In this case the calculated liquidus temperatures are higher than those found experimentally. Good agreement with the data of Holm and Holm[8] is obtained only for low mole fractions of LiF (values less than about 0.1), while the deviation becomes quite substantial at higher mole fractions (it is more

Table 1. Activity coefficients for the main species in the system $Na_3AlF_6$–LiF at 1284 K.

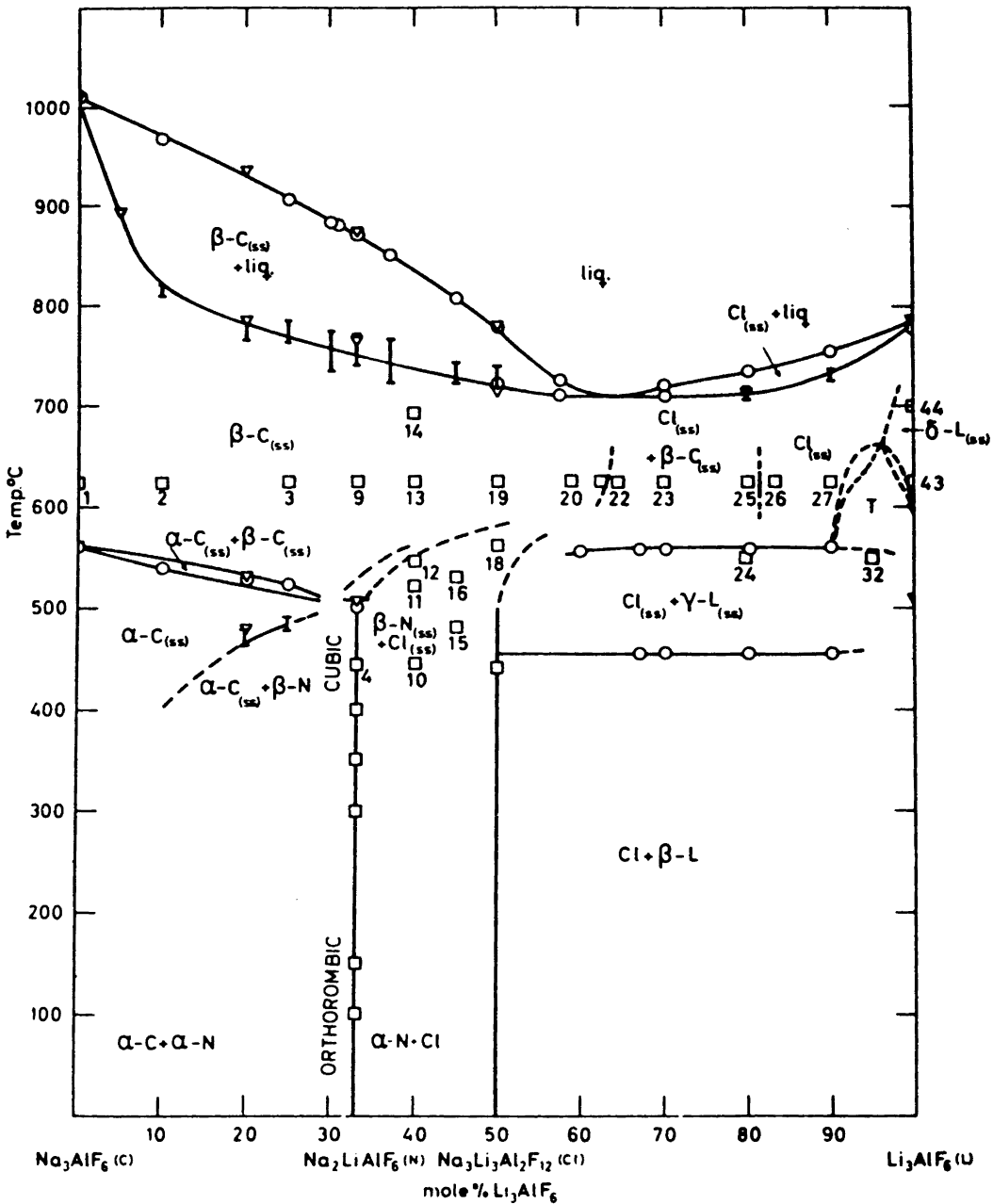| Mole fraction of LiF | $\gamma_{LiF}$ | $\gamma_{NaF}$ | $\gamma_{Na_3AlF_6}$ | $\gamma_{Na_2AlF_5}$ | $\gamma_{NaAlF_4}$ |
|---|---|---|---|---|---|
| 0 | – | 1 | 1 | 1 | 1 |
| 0.1 | 0.20 | 1.17 | 0.89 | 0.93 | 0.97 |
| 0.2 | 0.22 | 1.41 | 0.79 | 0.85 | 0.92 |
| 0.3 | 0.25 | 1.77 | 0.67 | 0.77 | 0.88 |
| 0.4 | 0.28 | 2.32 | 0.55 | 0.67 | 0.82 |
| 0.5 | 0.33 | 3.19 | 0.42 | 0.56 | 0.75 |
| 0.6 | 0.39 | 4.55 | 0.30 | 0.44 | 0.67 |
| 0.7 | 0.48 | 6.70 | 0.18 | 0.32 | 0.56 |
| 0.8 | 0.60 | 10.1 | 0.08 | 0.18 | 0.43 |

*Fig. 4.* The phase diagram of the system Na$_3$AlF$_6$–Li$_3$AlF$_6$ according to Holm and Holm.[8]

than 40 °C at a mole fraction of 0.5). In this concentration range the calculated data in fact show better agreement with the measurements of Buk- halova and Maltsev,[9] but their data are probably less reliable than those of Holm and Holm.[6,8] The deviation is mainly caused by the present assump-
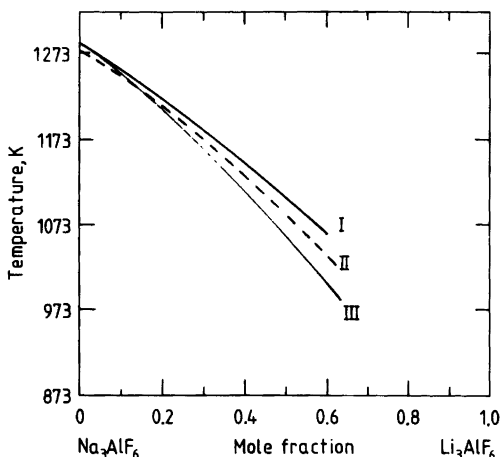
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Fig. 5. Comparison of calculated and experimental liquidus curves for cryolite in the system $Na_3AlF_6-Li_3AlF_6$. I: Calculated curve, II: experimental data from Bukhalova and Maltsev,[9] III: experimental data from Holm and Holm.[8]



Fig. 6. Activities and mole fractions in the system $Na_3AlF_6-Li_3AlF_6$ at 1284 K. Dashed lines: activities. Solid lines: mole fractions. I: NaF, II: $Na_3AlF_6$, III: LiF, IV: $NaAlF_4$, V: $Na_2AlF_5$.

tion of ideal behaviour of the solid solutions. Since we are interested here in the dissolution in *molten* cryolite, we have not attempted to account for the non-ideal behaviour of the solid solutions be changing our ionic models. Thus, some uncertainty in the results is unavoidable.

Fig. 6 shows the calculated mole fractions and the activities in the system $Na_3AlF_6-LiAlF_6$. The mole fractions show the expected behaviour. This is the case also for the activities of NaF, $Na_3AlF_6$, $Na_2AlF_5$ and $NaAlF_4$, since they decrease with increasing content of $Li_3AlF_6$. The activity coefficients are given in Table 2.
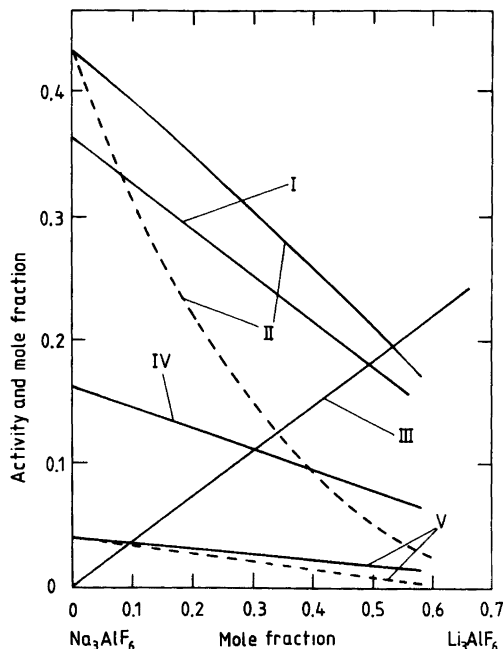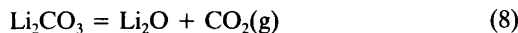
*Addition of $Li_2CO_3$.* The actual addition to the

bath of industrial alumina reduction cells is usually made in the form of $Li_2CO_3$ pellets. The dissolution of lithium carbonate may be described by the following reactions:
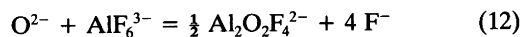
$$Li_2CO_3 = Li_2O + CO_2(g) \tag{8}$$

and

$$Li_2O = 2\,Li^+ + O^{2-} \tag{9}$$

Table 2. Activity coefficients for the main species in the system $Na_3AlF_6-Li_3AlF_6$ at 1284 K.

| Mole fraction of LiF | $\gamma_{LiF}$ | $\gamma_{NaF}$ | $\gamma_{Na_3AlF_6}$ | $\gamma_{Na_2AlF_5}$ | $\gamma_{NaAlF_4}$ |
|---|---|---|---|---|---|
| 0 | – | 1 | 1 | 1 | 1 |
| 0.1 | 1 | 1 | 0.81 | 0.90 | 1 |
| 0.2 | 1 | 1 | 0.64 | 0.80 | 1 |
| 0.3 | 1 | 1 | 0.49 | 0.70 | 1 |
| 0.4 | 1 | 1 | 0.36 | 0.60 | 1 |
| 0.5 | 1 | 1 | 0.25 | 0.50 | 1 |
| 0.6 | 1 | 1 | 0.16 | 0.40 | 1 |

The $O^{2-}$ ions will react further with ions in the cryolite melt, for example with hexafluoroaluminate ions:

$$O^{2-} + 2\ AlF_6^{3-} = Al_2OF_6^{2-} + 6\ F^- \qquad (10)$$

$$O^{2-} + 2\ AlF_6^{3-} = Al_2OF_8^{4-} + 4\ F^- \qquad (11)$$

$$O^{2-} + AlF_6^{3-} = \tfrac{1}{2}\ Al_2O_2F_4^{2-} + 4\ F^- \qquad (12)$$

The three species $Al_2OF_6^{2-}$, $Al_2OF_8^{4-}$ and $Al_2O_2F_4^{2-}$ have been shown to be the most important aluminium-oxygen-fluorine-containing ions in cryolite-alumina melts.[10] For small contents of alumina, $Al_2OF_8^{4-}$ was found to be the most important species, while $Al_2O_2F_4^{2-}$ ions were completely dominant close to alumina saturation of the melt.[10]

Thus, the dissolution of small amounts of lithium carbonate in molten cryolite may tentatively be described by the following total reaction:

$$Li_2CO_3 + 2\ AlF_6^{3-} =$$
$$Al_2OF_8^{4-} + 2\ Li^+ + 4\ F^- + CO_2(g) \qquad (13)$$
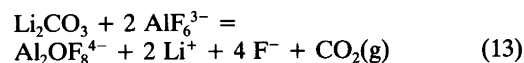
This reaction gives excess fluoride ions, and thus reduces the acidity of the cryolite melt. This will be the case irrespective of whether lithium fluoride or lithium carbonate is added.

## Concluding remarks

The present results agree quite well with those expected from the available data for the physico-chemical properties of lithium fluoride–containing cryolite melts. The increased electrical conductivity and the decreased viscosity do not indicate that the lithium ions react to form complex fluorine-containing species, but rather that they exist as discrete cations in these melts. The vapour pressure[11] increases with increasing addition of Li₃AlF₆ to Na₃AlF₆ up to a mole fraction of LiF of 0.5, but this has been shown to be due to the increased activity of AlF₃ in the melt, and not the appearance of LiAlF₄(g) in the vapour phase.[12]

No calculated activity data for the system Na₃AlF₆–LiF have been found in the literature, so the present data are new. For the corresponding system Na₃AlF₆–Li₃AlF₆, Dewing[12] derived activity data from measurements of the concentrations of Li and Na in aluminium in equilibrium with the melts at 1293 K. He concluded that Li₃AlF₆ is thermodynamically much less stable than Na₃AlF₆ and that LiF exists as such in a Na₃AlF₆ melt, the $F^-$ ions being more or less permanently attached to the $Li^+$ ions. The situation for NaF in dilute solution in Li₃AlF₆ is the converse, since it then is complexed strongly with AlF₃.

The present data for the activity coefficient for Na₃AlF₆ in the system Na₃AlF₆–Li₃AlF₆ given in Table 2 show fairly good agreement with those reported by Dewing.[12,13] However, he also calculated the activity of Li₃AlF₆ in these melts. This may be questionable, since the $Na^+$ and $Li^+$ ions and the cryolite ion $AlF_6^{3-}$ are completely dissociated in both Na₃AlF₆ and Li₃AlF₆. Thus, in the present work we have considered the ions $Na^+$, $Li^+$, $F^-$, $AlF_6^{3-}$, $AlF_5^{2-}$ and $AlF_4^-$ to be present in these melts. We have therefore calculated only the activities of NaF, LiF, Na₃AlF₆, Na₂AlF₅ and NaAlF₄, excluding the activity of the species Li₃AlF₆.

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