Structural Species of Calcium Fluoride Dissolved in Cryolite Melts

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Various structural models for the dissolution of calcium fluoride in molten sodium fluoride and molten cryolite have been studied. Liquidus curves calculated for these systems were compared with published solid-liquid phase diagrams. Contrary to previous opinion in the literature, Ca^{2+} ions were *not* found to be the dominant calcium-containing species in these melts. The results indicated that CaF_3^- ions are formed when calcium fluoride is added to molten sodium fluoride, while both CaF_3^- and CaF^+ ions may be present in cryolite-calcium fluoride melts. Increasing acidity in cryolite melts will favour the formation of CaF^+ ions. Activity values in these systems were calculated. The addition of calcium oxide to molten cryolite is also discussed.

In spite of the large amount of research work published in recent years, as reviewed by Grjotheim et al.,[1] there still remain unsolved problems concerning the bath chemistry of the Hall-Héroult process for the production of aluminium. One such problem concerns the structure of the main additives dissolved in cryolite-alumina melts. The most common of these additives is calcium fluoride, which is always present in the bath of industrial alumina reduction cells owing to the presence of small amounts of calcium oxide in the alumina ore.

Typical calcium fluoride contents in the bath are in the range from 3 to 7 mass % CaF_2. Although there seems to be no "optimum" content, some aluminium producers add calcium fluoride deliberately. The main advantages of this addition are lower crystallization temperature, lower solubility of aluminium in the bath, higher interfacial tension between metal and bath, and lower vapour pressure. Calcium fluoride has been calculated to improve the current efficiency of the electrolysis process by 1 % for each mass per cent of CaF_2 added, and to reduce the energy consumption by 1 relative per cent for each per cent of CaF_2 in the bath.[2] However, calcium fluoride

also has some disadvantages, since it reduces the electrical conductivity and the alumina solubility in the bath, and increases the bath density. Nevertheless, it may be concluded that the addition of calcium fluoride, within limits, is usually beneficial to the operation of Hall-Héroult cells.

In the present work we discuss the structural behaviour of calcium fluoride and calcium oxide dissolved in cryolite-alumina melts. It is generally accepted that addition of calcium fluoride leads to formation of one "foreign" species in cryolite melts. It is further believed that Ca^{2+} ions may exist as such in these melts, and that they probably do not form any complexes with fluoride ions.[1] With this rather limited information available, we examined various structural models for the dissolution of calcium fluoride. We started with the simple binary system $NaF-CaF_2$, after which the systems $Na_3AlF_6-CaF_2$ and Na_3AlF_6-CaO were studied. On the basis of the selected structural models we calculated liquidus curves for these systems and compared them with phase diagrams reported in the literature.[3] The model giving the best agreement with the experimental data was then used to obtain information about the most probable calcium-containing species present in the melts.

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Theoretical basis

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

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

Here, ΔH_m° is the standard molar enthalpy of melting of A, T_m is the melting point of pure A in Kelvin, T is an arbitrary absolute temperature and R is the universal gas constant. Pure molten A at temperature T is chosen as the standard state.
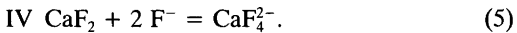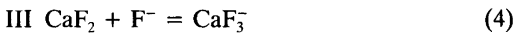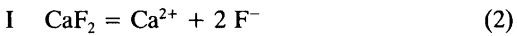
If A dissociates partly on melting, this influences the activity of A in the melt. The hypothetical melting point of pure, undissociated A must then be introduced instead of T_m in eqn. (1). If we assume that the heat of dissociation is zero, the degree of dissociation of A in the melt does not have any influence on the enthalpy of melting, ΔH_m°.

Eqn. (1) was used to calculate the liquidus curve for A for the various dissolution models. The liquidus temperature T was determined when the Temkin activity was given.[4]

Systems

NaF–CaF₂. For this system the phase diagram of Holm[3] was used. No solid solution of calcium fluoride in sodium fluoride has been found experimentally.

Four models for the dissolution of calcium fluoride were considered:

I $CaF_2 = Ca^{2+} + 2\,F^-$　　　　　　(2)

II $CaF_2 = CaF^+ + F^-$　　　　　　(3)

III $CaF_2 + F^- = CaF_3^-$　　　　　　(4)

IV $CaF_2 + 2\,F^- = CaF_4^{2-}.$　　　　　(5)

Data for the melting point of sodium fluoride (T_m = 1269 K) and the enthalpy of melting (ΔH_m° = 33.4 kJ mol⁻¹) were then used to calculate the liquidus curves shown in Fig. 1. It is seen that model III, involving the formation of CaF_3^- ions, agrees much better with the experimental data than any of the other models considered.
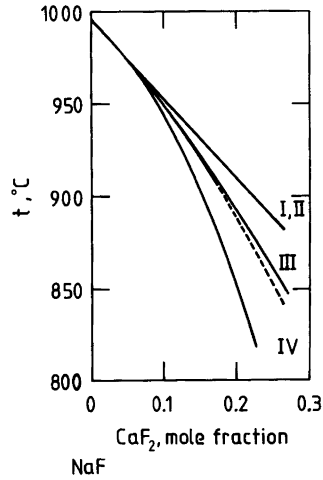

Fig. 1. Comparison of experimental and calculated liquidus curves in the system NaF–CaF₂. Models I to IV are described in the text and the experimental data (dashed line) are from Holm.[3]

In the calculation of the activities of NaF and CaF₂ it was assumed that NaF is completely dissociated into Na⁺ and F⁻ ions. N_0 mol of NaF then give N_0 mol of Na⁺ ions and N_0 mol of F⁻ ions. Addition of N_1 mol of CaF₂ gives N_1 mol of CaF_3^- ions but also consumes N_1 mol of F⁻ ions, so that the remaining total amount of F⁻ ions in the melt becomes N_0-N_1. This leads to the following expressions for the activities:

$$a_{NaF} = \frac{N_0-N_1}{N_0}\qquad(6)$$

$$a_{CaF_2} = \frac{N_1}{N_0}.\qquad(7)$$

These activities are plotted in Fig. 2, together with the corresponding mole fractions, as a function of the mole fraction of calcium fluoride added. It is seen that the activity of NaF shows a small negative deviation from ideality, whereas that of CaF₂ shows the opposite trend. The activity coefficients are given in Table 1.

Na₃AlF₆–CaF₂. The phase diagram of Holm[3,6] was used in the present calculations. He found no sign of any solid solution of calcium fluoride in cryolite. It may be noted that Dewing[20] reported
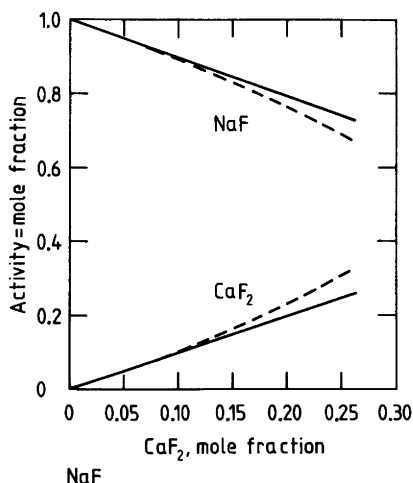
147

Fig. 2. Activities and mole fractions in the system NaF–CaF$_2$ at 1268 K. —— activities; — — — mole fractions.

Table 1. Activity coefficients in the system NaF–CaF$_2$ at 1268 K.

Mole fraction of CaF$_2$	γ_{NaF}	γ_{CaF_2}
0	1	–
0.05	0.997	1.06
0.10	0.989	1.10
0.15	0.965	1.17
0.20	0.940	1.25

NaF–CaF$_2$. In the cryolite system, the activity and concentration of sodium fluoride are lower than in the latter system, and the availability of F$^-$ ions for the reaction involved in model III is restricted. Thus, model II is equally probable in molten Na$_3$AlF$_6$–CaF$_2$.

These results led us to combine the models II and III to give another model:

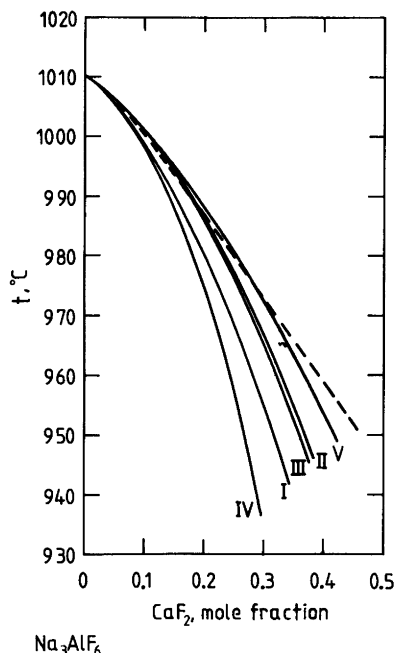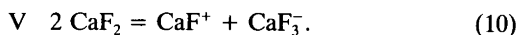$$\text{V} \quad 2\,CaF_2 = CaF^+ + CaF_3^-. \qquad (10)$$

Fig. 3. Comparison of experimental and calculated liquidus curves in the system Na$_3$AlF$_6$–CaF$_2$. Models I to V are described in the text and the experimental data (dashed line) are from Holm.[3,6]

that some solid solution was formed, but this has been neglected here. It is generally accepted that dissociation of sodium hexafluoroaluminate is complete in cryolite melts.[1] Furthermore, it is assumed that the hexafluoroaluminate ion is partly dissociated according to eqn. (8):[5]

$$AlF_6^{3-} = 1.8\,F^- + 0.8\,AlF_4^- + 0.2\,AlF_5^{2-}. \qquad (8)$$

The equilibrium constant for this reaction has the value $K_0 = 0.047$ at 1284 K, and a value for the enthalpy of dissociation $\Delta H^\circ_{diss} = 64.0$ kJ mol^{-1} was used.[5] The equilibrium constant K at any other temperature T may be calculated from eqn. (9):

$$\ln \frac{K}{K_0} = \frac{\Delta H^\circ_{diss}}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right). \qquad (9)$$

Models I–IV [eqns. (2–5)] were also used for the system Na$_3$AlF$_6$–CaF$_2$, and the calculated liquidus curves are shown in Fig. 3. It is seen that models II and III give better agreement than models I and IV, but in no case can the agreement be considered as satisfactory. On the basis of the available data we cannot distinguish between the results of models II and III.

It is interesting to note the difference between these results and those obtained for the system

This model was used to calculate a new liquidus curve, also shown in Fig. 3. It is seen that the agreement of this model with the experimental data is satisfactory. Thus, it may be concluded that the present calculations indicate model V to be the most probable dissociation reaction for calcium fluoride in molten cryolite.

In the calculation of the activities of the species

$$a_{\text{NaF}} = \frac{3N_0}{3N_0 + \frac{1}{2}N_1} \cdot \frac{1.8\,r\,N_0}{\frac{1}{2}N_1 + N_0 + 1.8\,r\,N_0} \tag{11}$$

$$a_{\text{NaAlF}_4} = \frac{3N_0}{3N_0 + \frac{1}{2}N_1} \cdot \frac{0.8\,N_0}{\frac{1}{2}N_1 + N_0 + 1.8\,r\,N_0} \tag{12}$$

$$a_{\text{Na}_2\text{AlF}_5} = \left(\frac{3N_0}{3N_0 + \frac{1}{2}N_1}\right)^2 \cdot \frac{0.2\,N_0}{\frac{1}{2}N_1 + N_0 + 1.8\,r\,N_0} \tag{13}$$

$$a_{\text{Na}_3\text{AlF}_6} = \left(\frac{3N_0}{3N_0 + \frac{1}{2}N_1}\right)^3 \cdot \frac{(1-r)N_0}{\frac{1}{2}N_1 + N_0 + 1.8\,r\,N_0} \tag{14}$$

$$a_{\text{CaF}_2} = \left(\frac{N_1}{3N_0 + \frac{1}{2}N_1}\right)^{\frac{1}{2}} \cdot \left(\frac{\frac{1}{2}N_1}{\frac{1}{2}N_1 + N_0 + 1.8\,r\,N_0}\right)^{\frac{1}{2}} \cdot \tag{15}$$

in the system Na$_3$AlF$_6$–CaF$_2$, it was assumed that the degree of dissociation of cryolite is r. Thus, the number of mol of Na$_3$AlF$_6$ is $1-r$, for NaF it is $1.8\,r$, for NaAlF$_4$ it is $0.8\,r$ and for Na$_2$AlF$_5$ it is $0.2\,r$ [eqn. (8)]. The total number of mol of the four species is then $1 + 1.8\,r$.

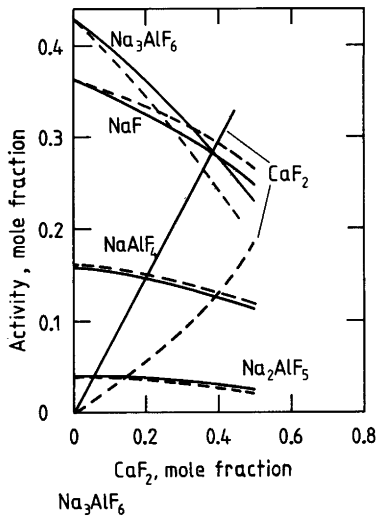As an illustration, the following eqns. for the activities are found when model V is used:

Here, N_0 is the weighed-in mole fraction of cryolite and N_1 is the corresponding mole fraction of calcium fluoride, while r is the degree of dissociation of cryolite according to eqn. (8).

The activities calculated according to model V are shown in Fig. 4. As expected, the activities of NaF and Na$_3$AlF$_6$ decrease and the activity of CaF$_2$ increases with increasing mole fraction of CaF$_2$ in the melt. It is seen that the activities of Na$_2$AlF$_5$ and NaAlF$_4$ also decrease, but considerably less than for NaF and Na$_3$AlF$_6$.

The mole fractions of these species are also shown in Fig. 4, and the corresponding calculated activity coefficients are given in Table 2. The activity coefficients of CaF$_2$, Na$_3$AlF$_6$ and Na$_2$AlF$_5$ decrease, while those of NaF and NaAlF$_4$ increase slightly with increasing mole fraction of CaF$_2$. However, for the aluminium-containing species, all the activity coefficients are close to unity, and the cryolite melt may therefore be regarded as an ideal ionic mixture.

Finally, it is noted here that the use of reaction (8), as suggested by the present authors,[5] rather than the previously accepted dissociation reaction for cryolite:[1]

Fig. 4. Activities and mole fractions in the system Na$_3$AlF$_6$–CaF$_2$ at 1284 K. —— activities; – – – mole fractions.

$$AlF_6^{3-} = 2F^- + AlF_4^- \qquad (16)$$

has no significant influence on the calculated values of the mole fractions and activities. Model V is the most probable also in this case.

Increasing bath acidity. The present results have shown that increasing bath acidity will favour the formation of CaF^+ ions rather than CaF_3^- ions. For the typical bath compositions used industrially, with cryolite ratios of about 2.2, model V will be the most probable. However, in extremely acidic baths it is quite possible that the major calcium-containing species will be CaF^+. In the molten AlF_3–CaF_2 system, for example, the major species are then probably CaF^+ and AlF_4^- ions.

Physicochemical properties. The effects of addition of calcium fluoride on the physicochemical properties of cryolite melts are well known from the literature.[1] Here, only two such properties will be mentioned. Calcium fluoride increases the viscosity of molten cryolite,[8] implying the formation of complex ions such as CaF^+ and CaF_3^- [eqn. (10)]. With regard to the vapour pressure, older literature data indicate a decrease with increasing calcium fluoride addition,[9-11] whereas more recent data seem to indicate that the vapour pressure of molten cryolite is unchanged, even by additions as large as 50 mol % CaF_2.[12] The present work shows that the activity of $NaAlF_4$, which is the major vapour species in this system, decreases slowly with increase in the mole fraction of added calcium fluoride, as may be seen from Fig. 4. This is in agreement with recent calculations by Ødegård.[13]
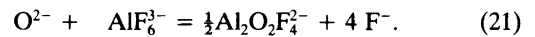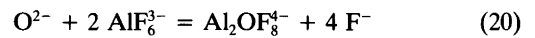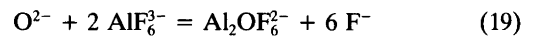
Na_3AlF_6–CaO. The phase diagram for the system Na_3AlF_6–CaO published by Abramov *et al.*[14] shows a eutectic point at about 33 mol % CaO, or

about 15 mass % CaO. However, the system is not quasi-binary, but is rather a complex section of the quaternary reciprocal system Na^+, Ca^{2+}, F^-, O^{2-}.

When calcium oxide is added to molten cryolite, it is most reasonable first to assume complete dissociation into Ca^{2+} and O^{2-} ions. However, these ions will react further with ions in the cryolite melt, for example as follows:

$$Ca^{2+} + \quad F^- = CaF^+ \qquad (17)$$

$$Ca^{2+} + 3\ F^- = CaF_3^- \qquad (18)$$

and

$$O^{2-} + 2\ AlF_6^{3-} = Al_2OF_6^{2-} + 6\ F^- \qquad (19)$$

$$O^{2-} + 2\ AlF_6^{3-} = Al_2OF_8^{4-} + 4\ F^- \qquad (20)$$

$$O^{2-} + \quad AlF_6^{3-} = \tfrac{1}{2}Al_2O_2F_4^{2-} + 4\ F^-. \qquad (21)$$

The three species $Al_2OF_6^{2-}$, $Al_2OF_8^{4-}$ and $Al_2O_2F_4^{2-}$ have been suggested to be the most important aluminium-oxygen-fluorine-containing ions in cryolite-alumina melts.[15] For small additions of alumina (or calcium oxide) the species $Al_2OF_8^{4-}$ was found to be the most important, whereas close to saturation $Al_2O_2F_4^{2-}$ was completely dominant.[15]

Thus, the dissolution of small amounts of calcium oxide in molten cryolite may tentatively be described by eqn. (22):

$$CaO + 2\ AlF_6^{3-} =$$

$$Al_2OF_8^{4-} + \tfrac{1}{2}\ CaF^+ + \tfrac{1}{2}\ CaF_3^- + 2\ F^-. \qquad (22)$$
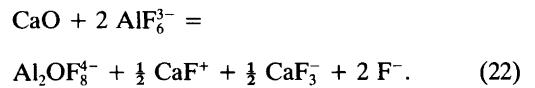
Dissolution then gives excess fluoride ions and thus decreases the acidity of the cryolite melt.

Table 2. Activity coefficients of the main species in the system Na_3AlF_6–CaF_2 at 1284 K.

Mole fraction of CaF_2	γ_{CaF_2}	γ_{NaF}	$\gamma_{Na_3AlF_6}$	$\gamma_{Na_2AlF_5}$	γ_{NaAlF_4}
0	–	1	1	1	1
0.1	0.38	1.02	0.98	0.99	1.01
0.2	0.40	1.03	0.95	0.98	1.03
0.3	0.42	1.04	0.91	0.97	1.04
0.4	0.45	1.05	0.86	0.96	1.05

This agrees with the results of Homsi et al.,[16] who reported that calcium oxide is an F$^-$ donor which increases the concentration of free fluoride ions in the melt. The main cause of the basic properties of calcium oxide in cryolite melts is therefore the mere presence of the oxide ions.

Concluding remarks

Addition of calcium fluoride has been reported to have little or no effect on the measured cryolite ratio, or on the ratio of sodium fluoride to aluminium fluoride.[17] Matiašovský et al.[18] found a very weak effect on the ratio, but practically within the range of experimental error. This lack of effect may be explained by the present model V:

$$2\ CaF_2 = CaF^+ + CaF_3^-. \tag{10}$$
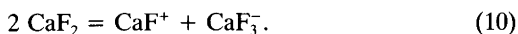
Thus, the main influence of calcium fluoride is on the degree of dissociation of the hexafluoroaluminate ion, owing to the effect of dilution. In that sense, calcium fluoride may have slight acidic (F$^-$ acceptor) properties in molten cryolite, as seen from the activities in Fig. 4.

It is interesting to note that calcium fluoride apparently behaves differently from magnesium fluoride in cryolite melts. The latter has definite acidic properties, and the formation of MgF$_4^{2-}$ ions has been found to be most probable in these melts.[19]

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