

Complex Formation in the Molten Systems NaF–MgF₂ and Na₃AlF₆–MgF₂

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Three different structural models for the solution of magnesium fluoride in molten sodium fluoride and molten cryolite have been studied. Liquidus curves calculated for these systems are compared with solid-liquid phase diagrams in the literature. The results indicate that the presence of MgF₄²⁻ ions is more probable than MgF₃⁻ or Mg²⁺ ions in these melts.

Magnesium fluoride may be considered as a promising additive to the bath of the Hall-Héroult process.¹ Very little has been published in the open literature on cell operation experiences with baths containing magnesium fluoride, but a few papers are available.^{2–4} Soviet smelters are reported as continuing to use magnesium fluoride in the bath.⁵ For economic reasons magnesium oxide is actually added. It reacts with aluminium fluoride in the bath and forms magnesium fluoride and alumina.

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.⁶ The major disadvantage is a reduction of the electrical conductivity in the melt.⁷ Addition of magnesium fluoride has been reported to improve the current efficiency both in laboratory cells⁸ and industrial cells.²

In the present paper we will study the behaviour of magnesium fluoride in cryolite melts

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from a more fundamental point of view. Various structural models for the solution of magnesium fluoride in molten sodium fluoride and molten cryolite are examined. Liquidus curves calculated for these systems are compared with phase diagrams reported in the literature. This gives information about the most probable magnesium-containing species present in these melts.

THEORETICAL BASIS

We consider a binary mixture where A is the solvent and B is the solute. The melting point of pure A is T_m (K), and the standard molar enthalpy of melting is ΔH_m^0 . At any temperature T the activity $a_{A,l}$ of A in the melt in equilibrium with pure solid A is given by the equation

$$\ln a_{A,l} = -\frac{\Delta H_m^0}{R} \left(\frac{1}{T_m} - \frac{1}{T} \right) \quad (1)$$

where R is the gas constant. Pure molten A at the temperature T is selected as the standard state with unit activity. It is assumed that the difference in heat capacity between solid and liquid A is so small that it may be neglected. In cases where A forms a solid solution with B, the expression on the left-hand side of eqn. (1) is replaced by $\ln(a_{A,l}/a_{A,s})$.

If the solvent A dissociates on melting, this influences the activity of A in the melt. If we assume the mixture to be ideal, the mole fraction x_A of undissociated A is given by the equation

$$\ln x_A = -\frac{\Delta H_m^0}{R} \left(\frac{1}{T_{m,h}} - \frac{1}{T} \right) \quad (2)$$

where $T_{m,h}$ is the hypothetical melting point of pure, undissociated A. Assuming that the heat of dissociation is zero, the degree of dissociation has no influence on the heat of melting ΔH_m^0 . Eqn. (2) may be used to calculate the liquidus curve of A for various selected dissociation schemes for the solute B. This gives a method of testing these dissociation schemes and obtaining information about the ionic species formed in the melt.

SYSTEMS

NaF-MgF₂. In this system the formation of the congruently melting compound NaMgF₃ with a melting point of 1029 °C has been reported.⁹ No solid solution of MgF₂ in NaF has been found.

Three models for the solution of MgF₂ in molten NaF will be considered:

- i. MgF₂ dissociates into Mg²⁺ and 2F⁻ ions,
- ii. MgF₂ reacts with F⁻ and forms MgF₃⁻,
- iii. MgF₂ reacts with 2F⁻ and forms MgF₄²⁻.

Data for the melting point of NaF, $T_m=1269$ K, and the heat of melting, $\Delta H_m^0=33.4$ kJ.mol⁻¹, were used⁶ to calculate the liquidus curves shown in Fig. 1. It is seen that the formation of MgF₄²⁻ agrees better with the experimental data than any of the other model assumptions. The difference between the curves for MgF₄²⁻ and MgF₃⁻ is significant, and the assumption of Mg²⁺ ions formed gives the worst fit of the three models.

Na₃AlF₆-MgF₂. This system does not form a simple binary system. By cooling a molten mixture with a low content of magnesium fluoride, the solid compound NaMgF₃ will precipitate



At higher contents of MgF₂ the incongruently melting compound Na₂MgAlF₇ is formed, and presumably⁵ also Na₂Mg₂Al₃F₁₅. MgF₂ forms a solid solution with cryolite, the composition of which may be taken from the phase diagram.^{6,9}

It is generally accepted that the cryolite anion is partly dissociated according to the reaction



The equilibrium constant of this reaction⁶ is $K=0.06$ at 1008 °C. This gives a degree of dissociation $\alpha=0.30$ in pure molten cryolite.

Now we again turn to the three models for the solution of MgF₂. Each of them will influence the concentration (and activity) of F⁻ ions in the melt. Thus, the concentrations of AlF₆³⁻ and AlF₄⁻ ions will change in order for the equilibrium of reaction (4) to be established. It is obvious that the mole fraction of the ions in the melt will depend on the model selected for the solution of MgF₂. If we insert the calculated mole fraction of AlF₆³⁻ in eqn. (2), we can calculate the liquidus curve of cryolite and compare it with the experimental curve. The necessary data were taken from Grjotheim *et al.*⁶

As an example, the real mole fraction N may be calculated from the following expressions, when the formation of MgF₄²⁻ ions is assumed:

$$N_{\text{AlF}_6^{3-}} = \frac{x(1-\alpha)}{2x+2x\alpha-1} \quad (5)$$

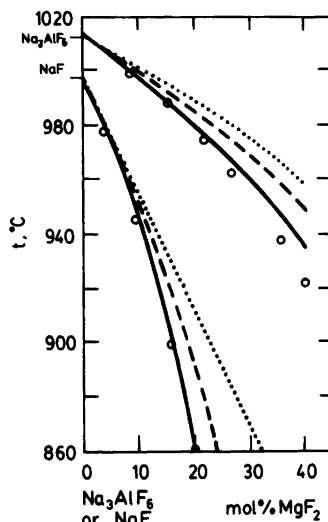


Fig. 1. Comparison of the experimental and calculated liquidus curves of NaF and Na₃AlF₆ in the systems NaF-MgF₂ (lower curves) and Na₃AlF₆-MgF₂ (upper curves). ○, experimental data;⁹ —, calculated assuming the formation of MgF₄²⁻ ions; ---, calculated assuming the formation of MgF₃⁻ ions; . . ., calculated assuming that MgF₂ dissociates into Mg²⁺ and 2F⁻.

$$N_{\text{F}^-} = \frac{2(xa+x-1)}{2x+2xa-1} \quad (6)$$

$$N_{\text{AlF}_4^-} = \frac{xa}{2x+2xa-1} \quad (7)$$

$$N_{\text{MgF}_4^{2-}} = \frac{1-x}{2x+2xa-1} \quad (8)$$

Here x denotes the weighed-in mole fraction of cryolite, and a is the degree of dissociation of cryolite ions.

Fig. 1 shows a comparison between the experimental and calculated liquidus curves for the system Na₃AlF₆–MgF₂. In this case also the best agreement is achieved for the model assuming the formation of MgF₄²⁻ ions, and the presence of these ions may be considered more likely than MgF₃ or Mg²⁺ ions.

Table 1 shows that the addition of MgF₂ has a considerable influence on the degree of dissociation of AlF₆³⁻ ions (when the formation of the MgF₄²⁻ ions is assumed). This explains why the addition of MgF₂ affects the physico-chemical properties of cryolite melts in qualitatively the same manner as the addition of AlF₃. This means that MgF₂ acts as an acid substance in molten cryolite.

DISCUSSION

In the literature very few papers have discussed the complex-forming ability of MgF₂ in cryolite

Table 1. The degree of dissociation a of the cryolite ion for various compositions in the system Na₃AlF₆–MgF₂.

Mole fraction of MgF ₂	Mass fraction of MgF ₂	Degree of dissociation a
0	0	0.30
0.05	0.02	0.33
0.10	0.03	0.37
0.15	0.05	0.42
0.20	0.07	0.47
0.25	0.09	0.53
0.30	0.11	0.61
0.35	0.14	0.69

melts. Dewing and van der Kouwe¹⁰ studied the reaction



The activity coefficient of MgF₂ was found to increase with both increasing AlF₃ and MgF₂ content. Numerical values of γ_{MgF_2} were reported to be 0.4 in molten cryolite and 1.1 in cryolite with 13 wt% AlF₃ in excess. These data show a negative deviation from ideality (Raoult's law), and should suggest that MgF₂ rather forms simple Mg²⁺ ions in melts more basic than corresponding to the cryolite composition. However, since the activity coefficient increases with increasing AlF₃ content, this should be taken as an indication of an increasing tendency to complex formation in more acidic melts.

Sokolov and Belyaev¹¹ and Kostyukov *et al.*⁵ reported that MgF₃⁻ ions are present in molten cryolite, and also in more basic melts. The latter authors used differential thermal analysis and X-ray methods to study sections in the phase diagrams of the system NaF–AlF₃–MgF₂. Thus, the formation of MgF₄²⁻ ions by the addition of MgF₂ to cryolite melts does not seem to have been suggested in the literature.

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