The data were fitted by a least squares treatment to equations of the type

$$H_T - H_{298.15} = a + b \times T$$

where b corresponds to the assumed constant heat capacity of the solid or the liquid over the limited temperature ranges in question; (*cf.* Table 1). The following equations were obtained:

solid $MgCl_2$: $H_T - H_{298.15} = 7407 + 20.92T$ $cal_{th}mol^{-1}$ ($\sigma = 96$)
liquid $MgCl_2$: $H_T - H_{298.15} = +837 + 22.18T$ $cal_{th}mol^{-1}$ ($\sigma = 58$) corresponding to

$$\Delta H_f(MgCl_2) = 8244 + 1.26T cal_{th}mol^{-1}$$

At the melting point 980 K this corresponds to an enthalpy of fusion

$$\Delta H_f(MgCl_2) = 9500 cal_{th}mol^{-1}$$

with an estimated uncertainty of 200 $cal_{th}mol^{-1}$. This value should be compared with the value given by Moore [3] and adopted by Kelley,[4] $\Delta H_f = 10\ 300$ $cal_{th}mol^{-1}$.

The agreement between the literature values and ours are excellent for solid $MgCl_2$,[3,4], while our data are about 4 % lower than those given for liquid $MgCl_2$.

Our heat capacity value for liquid $MgCl_2$, 22.17 $cal_{th}K^{-1}$ $mol^{-1}$ is, however, in good agreement with the value reported in literature,[4] 22.1 $cal_{th}K^{-1}$ $mol^{-1}$.

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# The Structure of Molten Sodium Tetrafluoro Aluminate, $NaAlF_4$

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The use of the term "complex" in ionic molten salt mixtures has been questioned on several occasions. Critic has been raised mainly because formation of complexes has been postulated in several molten salt solutions without reference to properties like the symmetry of the complex, its life time, *etc.* Despite these objections it has generally been accepted that complex ions may be formed in binary charge unsymmetrical mixtures like $AX\text{-}BX_2$, $AX\text{-}CX_3$ *etc.* The strong negative deviation from ideality which has often been found in certain concentration ranges in ionic mixtures of, for instance, $KF\text{-}BeF_2$, $RbF\text{-}BeF_2$,[1] and in certain $AlkCl\text{-}MgCl_2$ mixtures,[2] may very well justify the use of the term complex, despite the fact that important structural properties are not known. The term "complex" does not always mean the same thermodynamically as it does spectroscopically. This is because in spectroscopy one looks for interactions between the atoms in the complex, while the thermodynamical stability of the complex depends on the surroundings as well. This is particularly the case when dealing with ionic liquids or molten salts with a "lattice-like" structure.

In this paper the thermodynamic stability of the rather controversial $AlF_4^-$ion will be discussed. This ion has for some time been assumed to be a stable complex ion in mixtures of molten sodium fluoride and aluminium fluoride.[3] The present author has shown [4,5] how the degree of dissociation, or stability, of ionic complex ions can be calculated using enthalpy of mixing data. The equation.

$$\Delta H_C^M = \Delta H^{Diss} N_0(\alpha_1 - \alpha_0) \qquad (1)$$

where $\Delta H^{Diss}$ is the enthalpy of dissociation of the pure complex, $N_0$ is the weighed-in mol fraction of the complex, and $\alpha_0$ and $\alpha_1$ are the degrees of dissociations in the pure complex and in the mixture, respectively, was used to calculate the dissociation of cryolite, $Na_3AlF_6$, in molten $NaF\text{-}Na_3AlF_6$ mixtures.

*Table 1.* The degree of dissociation of $AlF_6^{3-}$ and the composition of different melts in the $Na_3AlF_6$-$AlF_3$ system.

| Composition mol fraction $AlF_3$ | $\Delta H^M$ cal $mol^{-1}$ | $\alpha$ | Mol fractions $AlF_6^{3-}$ | "$AlF_3$" | $F^-$ |
|---|---|---|---|---|---|
| 0 | 0 | 0.31 | 0.36 | 0.16 | 0.48 |
| 0.100 | −200 | 0.30 | 0.35 | 0.20 | 0.45 |
| 0.445 | +1000 | 0.39 | 0.21 | 0.40 | 0.39 |
| 0.575 | +2600 | 0.59 | 0.10 | 0.47 | 0.43 |
| 0.667 | +4100 | 0.87 | 0.02 | 0.51 | 0.47 |

The two most probable dissociation schemes for molten cryolite

(I) $Na_3AlF_{6(l)} = 3NaF_{(l)} + "AlF_{3(l)}"$

(II) $Na_3AlF_{6(l)} = 2NaF_{(l)} + NaAlF_{4(l)}$

were discussed. It was concluded that scheme II is of minor importance on the *NaF-side* of the system. The main species present in basic (NaF-rich) melts will be:

$Na^+$, $AlF_6^{3-}$, $F^-$, and "$AlF_3$"

In this dissociation scheme "$AlF_3$" is not supposed to be a separate species, but rather the inner and most stable part of the distorted $AlF_6^{3-}$-complex.

Here eqn. (1) will be used to calculate the dissociation of $Na_3AlF_6$ according to scheme I in molten mixtures of cryolite and aluminium fluoride.

*Calculations.* The weighed-in mol fractions are $N_0(Na_3AlF_6)$ and $N_1(AlF_3)$, and the degree of dissociation of $Na_3AlF_6$ in the mixture is $\alpha_1$. The mol fractions of the three main species assumed to be present are then given by

$$X_{AlF_6^{3-}} = \frac{N_0(1-\alpha_1)}{1+3N_0\alpha_1} \qquad (2a)$$

$$X_{AlF_3} = \frac{N_1+N_0\alpha_1}{1+3N_0\alpha_1} \qquad (2b)$$

$$X_{F^-} = \frac{3N_0\alpha_1}{1+3N_0\alpha_1} \qquad (2c)$$

These ionic fractions are given in Table 1 as a function of $N_1$, together with the enthalpies of mixing measured in the system $Na_3AlF_6$-$AlF_3$ by Holm.[6] On the NaF side of the system NaF-$AlF_3$ the best value for the heat of dissociation of cryolite was found to be $\Delta H^{Diss} = 22\,000$ cal $mol^{-1}$.[4,6] By adopting this value on the $AlF_3$ side too, and using the experimental $\Delta H^M$ values, the degree of dissociation, $\alpha_1$, was calculated. The results are given in Table 1.

*Discussion.* From the $\Delta H^M$ values given in Table 1 it is clear that the interactions between $F^-$ and $AlF_3$ in a 1:1 NaF-$AlF_3$ mixture are weak, with $\Delta H^M$ for a mixture of $0.5NaF + 0.5AlF_3$ equal to $-1700$ cal $mol^{-1}$.[6] The present author has shown [5,6] that the equilibrium

(III) $Na_3AlF_{6(l)} + 2AlF_{3(l)} = 3NaAlF_{4(l)}$

is shifted to the left, with $\Delta H = 12$ kcal $mol^{-1}$, $\Delta S \simeq 0$ cal $K^{-1}$ $mol^{-1}$.

Hence, when the $AlF_3$ content in the melt is increased beyond the cryolite composition, the result will be an increased dissociation of $AlF_6^{3-}$ to "$AlF_3$" and $F^-$ according to

$$AlF_6^{3-} \rightarrow "AlF_3" + 3F^-$$

and not any formation of a strong $AlF_4^-$ complex. A melt of the $NaAlF_4$ composition consists of 0.02 mol $Na_3AlF_6$, 0.51 mol "$AlF_3$", and 0.47 mol NaF (Table 1). In this melt the solvated aluminium fluoride, "$AlF_3$," can formally be treated as an $AlF_4^-$ complex. The bond between the solvated $AlF_3$ and the fourth fluoride ion must, however, be a weak one as the low $\Delta H^M$ indicates. The $AlF_4^-$-complex can be illustrated by $^-F\ldots\ldots AlF_3$. From this one can conclude that in a melt of the $NaAlF_4$ composition, "$AlF_3$" exists in a weak distorted *tetrahedral* field:

$AlF_4^- = (AlF_3)F^-$(distorted tetrahedral)

This is different from a pure cryolite melt, where, as it has previously been shown,[5] "$AlF_3$" most probably will be present in a somewhat distorted *octahedral* field:

$AlF_6^{3-} = (AlF_3)3F^-$( distorted octahedral)

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# The Crystal and Molecular Structure of Methyl 3,6-Anhydro-α-D-glucopyranoside

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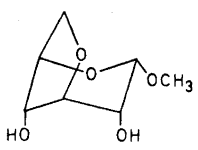
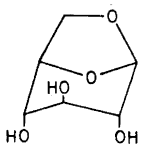
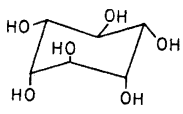
The pyranose rings in methyl 3,6-anhydro-α-D-glucopyranoside (I) and 1,6-anhydro-β-D-glucopyranose (II) are forced into the $^1C_4$ conformation and should be considerably distorted as a result of the strain caused by the *cis*-fused 5-membered ring. The distance between the axial oxygen atoms, O-2 and O-4, should therefore be longer in (II) and shorter in (I) than in a corresponding unstrained system. A recent X-ray diffraction study of II [1] demonstrated, *inter alia*, that the distance between O-2 and O-4 was 3.30 Å. A similar study of methyl 3,6-anhydro-α-D-galactopyranoside [2] demonstrated the distortion of the pyranose ring.




I




II




III

That the distance between O-2 and O-4 in I is exceptionally short was indicated by two observations. Firstly the β-anomer of I, which should have a similar structure, showed unexpectedly high mobilities on paper electrophoresis in borate and sulphonated phenyl boronic acid buffers.[3] The complex formation with boron, which requires an O–O distance of approximately 2.4 Å,[4] can only take place between the axially disposed oxygen atoms O-2 and O-4.

Secondly Schwarz and Totty [5,6] observed that I was a considerably stronger acid ($K_a$ $62.3 \times 10^{-14}$) than, *e.g.*, the unstrained *muco*-inositol (III, $K_a$ $7.10 \times 10^{-14}$). 1,6-Anhydro-β-D-glucopyranose is even weaker ($K_a$ $2.96 \times 10^{-14}$). These results were explained in terms of a hydrogen bridge between O-2 and O-4 in the corresponding anions. The distance between these atoms in III is about 2.89 Å and should consequently be considerably smaller in I.

We now report an X-ray diffraction study of I. The compound crystallized in space group $P2_12_12_1$; **a** = 8.210 (1), **b** = 17.764 (3), **c** = 5.555 (1), $Z = 4$. The crystals decomposed on X-ray irradiation. From equi-inclination Weissenberg photographs, taken using Cu$K\alpha$ radiation, 335 data were collected. The phase determinations were carried out by a computerized application

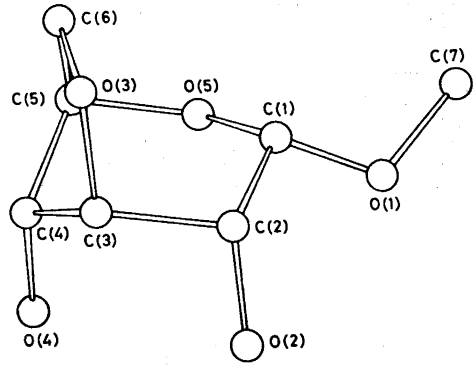



*Fig. 1.* The molecular structure of methyl 3,6-anhydro-α-D-glucopyranoside.