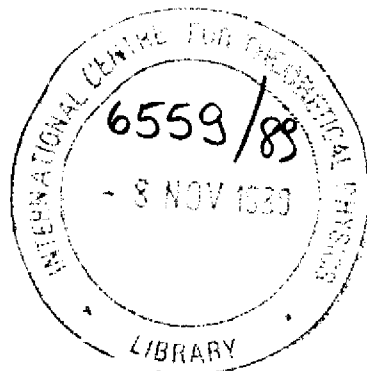


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**IONIC EQUILIBRIUM
BETWEEN OCTAHEDRAL AND TETRAHEDRAL COMPLEXES
IN LIQUID ALUMINIUM-SODIUM FLUORIDE MIXTURES**

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**INTERNATIONAL
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1989 MIRAMARE - TRIESTE



International Atomic Energy Agency
and
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**IONIC EQUILIBRIUM BETWEEN OCTAHEDRAL AND TETRAHEDRAL COMPLEXES
IN LIQUID ALUMINIUM-SODIUM FLUORIDE MIXTURES ***

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Abstract. An earlier statistical mechanical theory of complexing in molten mixtures of polyvalent metal halides and alkali halides is extended to situations in which an ionic equilibrium is established between two different types of complexes. The specific systems of interest are the mixtures of aluminium fluoride and sodium fluoride, in which early Raman scattering experiments by Gilbert, Mamantov and Begun have demonstrated coexistence of octahedral $(\text{AlF}_6)^{3-}$ units and tetrahedral $(\text{AlF}_4)^-$ units in the concentration range between 0.25 and 0.5 of AlF_3 . Our treatment is based on a simple ionic model and involves (i) an evaluation of binding free energies for the two units in vacuo, showing that $(\text{AlF}_6)^{3-}$ is strongly unstable against dissociation in this state, and (ii) a statistical mechanical theory of the liquid mixture, in which $(\text{AlF}_6)^{3-}$ is stabilized by ionic screening interactions. The resulting ionic equilibrium in the liquid involves, in excellent agreement with the Raman data, strong suppression of dissociation for $(\text{AlF}_6)^{3-}$, except near the composition corresponding to criolite ($\text{AlF}_3 \cdot 3\text{NaF}$). The temperature dependence of the ionic equilibrium is also evaluated, with special attention to molten criolite. Analogous calculations on aluminium-sodium chloride mixtures show that in these systems the equilibrium is completely shifted in favour of the $(\text{AlCl}_4)^-$ species, as a consequence of its stabilization by halogen polarizability.

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1. Introduction

A large number of liquid mixtures of polyvalent metal halides and alkali halides have been examined over the years by appropriate experimental probes, involving diffraction experiments in a few systems but mostly Raman scattering, infrared emission and absorption, optical absorption from electronic transitions and thermodynamic measurements. The alkali halide acts as a halogen donor to break the structure of the pure polyvalent metal halide melt, and the local coordination of the polyvalent ions in the mixture is of primary interest. A critical discussion of the evidence, with a full list of references, has been recently given¹. The local coordination of the polyvalent ion in the various systems can be classified by means of appropriate structural coordinates into three main classes of behaviour, namely (i) relatively long-lived fourfold coordination of tetrahedral or distorted tetrahedral type, (ii) relatively long-lived sixfold coordination of octahedral or distorted octahedral type, and (iii) more or less rapid fluctuations between different coordination states. In the former two cases the word "complex" is often used to denote a molecular-ion unit having in the liquid a lifetime which is of the order of, or even appreciably longer than, typical translational and rotational diffusion times.

We focus in this work on the mixtures of AlF_3 and NaF in the range of concentration $c \leq 1/2$ of AlF_3 . This appears to be, out of the 140 or so liquid halide mixtures that have so far been experimentally examined, the only system in which very clear evidence for coexistence between octahedral and tetrahedral complexes in the concentration range $1/4 \leq c < 1/2$ has been reported². Such coexistence in the above composition range clearly indicates that the stability of the octahedral complex against dissociation into the tetrahedral one is appreciable in this particular system, but not overwhelmingly strong. In the latter case halogen sharing between octahedral complexes would already be present, as was reported for mixtures of YCl_3 and alkali chlorides from Raman scattering experiments³. The further possibility, i. e. instability of sixfold coordination in the melt against long-lived fourfold coordination, is instead quite common. It is thus of interest to investigate theoretically what are the microscopic system parameters that determine the relative stability of the two complexes in the system where they are known to be competitive.

The evidence for the ionic equilibrium between the two complexes in Al-Na fluoride mixtures comes from their Raman scattering spectra². These show peaks associated with both $(\text{AlF}_6)^{3-}$ and $(\text{AlF}_4)^-$ units. The relative concentration of the two species, at temperature $T \cong$

1053 K and composition in the range $0.375 \leq c \leq 0.462$, is derived from the relative intensities of their breathing modes, under the assumption that the dissociation constant governing the equilibrium between the two species is not greatly different in mixtures of neighbouring compositions. The conclusion of the analysis is that the fractional concentration x of $(\text{AlF}_6)^{3-}$ units in the above composition range is close to the ideal upper limit $x_{\text{max}} = (1 - 2c)/2c$ allowed for $c \geq 1/4$ by the available number of fluorine ions in the mixture. However, at the composition corresponding to criolite ($\text{AlF}_3 \cdot 3\text{NaF}$, or $c = 1/4$ and $x_{\text{max}} = 1$) and a somewhat higher temperature ($T = 1288$ K), the $(\text{AlF}_4)^-$ species still appears as a spectral shoulder, indicating a degree of dissociation of approximately 20+25 % for $(\text{AlF}_6)^{3-}$. There is a special interest in understanding the behaviour of molten criolite, in view of its use as a solvent for alumina in the industrial electrolytic process for the production of aluminium metal.

Our approach is a direct extension of the theory that we have given earlier⁴ for the stability of tetrahedral complexes in molten calcium-alkali halide mixtures. The "dissociation constant" for the reaction



in the liquid mixture is evaluated from the balance between two free energy contributions. These are (i) the difference in binding free energy for the two species in vacuo, and (ii) the change in the excess free energy of the ionic melt on dissociation of an octahedral unit. We calculate the first of these free energy contributions in section 2 by means of ionic models that have been previously used for various tetrahedral complexes⁵ and tested by comparison of calculated vibrational frequencies with Raman spectroscopy data. Not surprisingly, we find that the $(\text{AlF}_6)^{3-}$ unit in vacuo would be completely unstable against the dissociation process in eqn (1). However, the ionic screening interactions in the melt, which are primarily due to the free Na^+ ions, stabilize the triply charged $(\text{AlF}_6)^{3-}$ units relatively to the singly charged $(\text{AlF}_4)^-$ units. The corresponding free energy is evaluated in section 3 by a statistical mechanical approach based on the mean spherical approximation (MSA) for charged hard spheres. Our results for the ionic equilibrium between the two species in the melt and for its temperature dependence, with special attention to molten criolite, are presented and compared with the Raman spectroscopy evidence in this section. For further insight in the ionic equilibrium of present interest, we then give and discuss in section 4 similar calculations on Al-Na chloride mixtures. Finally, a summary of the main results and further discussion of molten criolite, in relation to the structural changes that may be expected in this melt on exposure to electron donors, are given in section 5.

2. Binding in isolated complexes

The predictions of simple ionic models in regard to binding, bond length and Raman frequencies of various isolated tetrahedral complexes, including $(\text{AlF}_4)^-$ and $(\text{AlCl}_4)^-$, have been recently presented by Wang Li and Tosi⁵. We only need here to extend their treatment to octahedral complexes and to evaluate their binding and bond length with the same interionic force parameters.

The potential energy $U(r)$ for the octahedral $(\text{AlX}_6)^{3-}$ unit formed by Al^{3+} with six X^- halogens, relative to the state of free ions and as a function of the Al-X bond length r , is

$$U(r) = -3 \left(6 - 2\sqrt{2} - \frac{1}{2} \right) \frac{e^2}{r} - 3 p_0(r) [E(r) - B(r)] + 6 \left[\Phi_{\text{AlX}}(r) + 2 \Phi_{\text{XX}}(\sqrt{2}r) + \frac{1}{2} \Phi_{\text{XX}}(2r) \right] \quad (2)$$

The three terms in eqn (2) give the interactions between the ionic charges, the contribution from electronic polarization dipoles of magnitude $p_0(r)$ on each halogen, and the short-range interaction energies. The halogen polarization is treated by the deformation dipole model⁶, yielding

$$p_0(r) = \alpha_X \frac{E(r) - B(r)}{1 + (3\sqrt{2} + 1/2) \alpha_X / (2r^3)} \quad (3)$$

Here, α_X is the halogen polarizability, $E(r)$ is the magnitude of the electric field created by the ionic charges on a halogen, i. e.

$$E(r) = (3 - \sqrt{2} - 1/4) e/r^2 \quad (4)$$

and $B(r)$ accounts for the deformation dipole from short-range overlap between the Al^{3+} ion and each halogen. It is given by

$$B(r) = \frac{|Y|}{\alpha_X K} \left| \frac{d\Phi_{\text{AlX}}(r)}{dr} \right| \quad (5)$$

where Y and K are the halogen effective shell charge and the halogen shell-core force constant, respectively, while $\Phi_{\text{AlX}}(r)$ is the overlap repulsive contribution to the Al-X short-range interactions. Finally, the short-range interactions have the form proposed by Busing⁷,

$$\Phi_{ij}(r_{ij}) = -c_i c_j / r_{ij}^6 + \phi_{ij}(r_{ij}) \quad (6)$$

with

$$\phi_{ij}(r_{ij}) = f(\rho_i + \rho_j) \exp \left[(R_i + R_j - r_{ij}) / (\rho_i + \rho_j) \right] \quad (7)$$

the first term in eqn (6) being due to van der Waals interactions and the second to overlap repulsions.

Minimization of eqn (2) with respect to r yields the equilibrium value r_0 of the Al-X bond length and the corresponding contribution $U(r_0) \equiv U_0$ of the potential energy of the molecular ion to its binding. The results are shown in Table 1 for both $(\text{AlX}_4)^-$ and $(\text{AlX}_6)^{3-}$ units, with $\text{X} = \text{F}$ or Cl , under the label PX (polarizable halogens). We also give the results obtained under the assumption $\alpha_X = 0$ for the halogen polarizability (under the label NPX), since this is a system parameter whose role we shall wish to discuss. The difference between the potential energies of the two isolated units, $U_0^{(6)} - U_0^{(4)}$, is also shown in the Table.

Clearly, the octahedral unit has a bond length which is larger by about 0.2 Å, as a consequence of the halogen-halogen Coulombic repulsions, and is unstable against dissociation by a huge energy difference, of the order of 200 kcal/mole. We also see that, while the bond length is insensitive to the inclusion of halogen polarizability, the calculated potential energy strongly depends on it. The important fact, however, is that the role of halogen polarizability is much more important in the binding energy of the tetrahedral unit than for the octahedral one. Specific reference to the rows giving our results for the energy difference $U_0^{(6)} - U_0^{(4)}$ allows one to separately visualize the role of size differences (by comparison of the NPX values for the fluoride and the chloride) and the role of halogen polarization (by comparison between the PX and NPX values in each halide). As we shall see in the following, the ionic screening interactions in the molten mixtures are also size-dependent and could overcompensate the difference $U_0^{(6)} - U_0^{(4)}$ in both the fluoride and the chloride, if the tetrahedral $(\text{AlCl}_4)^-$ unit were not so strongly stabilized by chlorine polarization.

Finally, the bottom rows of Table 1 report for completeness the values of the Helmholtz free energy difference $f_6 - f_4$ between octahedral and tetrahedral complexes, that will be used for calculations on molten mixtures in the following sections. These values were obtained by supplementing $U_0^{(6)} - U_0^{(4)}$ with the rotational and vibrational free energy contributions, the latter being evaluated in the harmonic approximation from the measured vibrational frequencies for $(\text{AlF}_4)^-$ tetrahedra², $(\text{AlF}_6)^{3-}$ octahedra^{2, 8} and $(\text{AlCl}_4)^-$ tetrahedra⁹ in the solid or liquid state, and estimated for $(\text{AlCl}_6)^{3-}$ octahedra.

3. Ionic equilibrium in Al-Na fluoride mixtures

We regard a liquid Al-Na fluoride mixture of composition $(\text{AlF}_3)_c(\text{NaF})_{1-c}$, with $c \leq 1/2$, as a four-component fluid consisting of $(\text{AlF}_6)^{3-}$ complexes in molar fraction xc , $(\text{AlF}_4)^-$ complexes in molar fraction $(1-x)c$, F^- ions in molar fraction $(1-2c-2xc)$ and Na^+ ions in molar fraction $(1-c)$. Evidently, we are not allowing for any free Al^{3+} ions nor for the possibility that complexes may form higher bound states by joining through fluorine sharing. The maximum allowed value of x , from the molar fraction of free fluorine ions, is $x_{\text{max}} = 1$ for $c \leq 1/4$ and $x_{\text{max}} = (1-2c)/2c$ for $1/4 \leq c \leq 1/2$. We calculate below the Helmholtz free energy of such a model and determine the equilibrium value of x as a function of concentration c by minimization at fixed temperature T and molecular volume v , the latter being obtained or estimated as a function of c and T from the density data reported by Grjotheim et al.¹⁰. The roles of composition and temperature in the ionic equilibrium between the two types of complexes will be separated by repeating the calculations at two different temperatures (1053 K and 1288 K) over the whole range of concentration up to $c = 1/2$. Although the calculations should strictly be carried out at constant pressure P , we anticipate that Pv never exceeded a magnitude of a few $k_B T$ in our calculations.

The Helmholtz free energy F , aside from an irrelevant additive constant, can be written as

$$F = xcf_6 + (1-x)cf_4 - TS_m(x) + F_t(x) + F_{\text{ex}}(x) \quad (8)$$

where f_6 and f_4 are the binding free energies already introduced in section 2, S_m is the ideal entropy of mixing, F_t is the ideal translational free energy and F_{ex} is the excess free energy arising from the interactions between all the components of the liquid. From the expression

$$S_m(x) = -k_B \left[xc \ln(xc) + (c-cx) \ln(c-cx) + (1-c) \ln(1-c) + (1-2c-2xc) \ln(1-2c-2xc) \right] \quad (9)$$

we find upon minimization that the equilibrium value of x is determined by the equation

$$\frac{x}{(1-x)(1-2c-2xc)^2} = \left[\frac{h^2}{2\pi k_B T v^{2/3}} \right]^3 \left[\frac{m_{\text{Al}} + 6m_{\text{F}}}{(m_{\text{Al}} + 4m_{\text{F}})m_{\text{F}}^2} \right]^{3/2} \exp\left[-\frac{f(x)}{k_B T}\right] \quad (10)$$

where the m 's are the atomic masses and

$$f(x) = f_6 - f_4 + \frac{1}{c} \left(\frac{\partial F_{\text{ex}}(x)}{\partial x} \right)_{T,v,c} \quad (11)$$

Clearly, eqn (10) has the form of the law of mass action for the dissociation reaction in eqn (1),

although its activation free energy acquires a dependence on x , according to eqn (11), from the fact that the reaction is taking place in a dense medium.

We proceed to estimate the last term on the rhs of eqn (11) by modelling the fluid as a four-component mixture of charged hard spheres, to be treated in the MSA¹¹. The essential equations of this statistical mechanical treatment have already been given in our earlier work on the stability of tetrahedral complexes⁴ and are immediately adapted to the present calculations with only trivial changes in notation. We only need to specify the hard sphere diameters for the various components of the liquid and these are collected in Table 2. We have used for Na^+ and X^- the diameters reported by Senatore et al.¹² from work on molten alkali halides, while for the diameters σ_6 of $(\text{AlX}_6)^{3-}$ and σ_4 of $(\text{AlX}_4)^-$ we have followed our earlier work in the choice $\sigma_i = \sigma_X + r_{\text{Xi}}$, where r_{Xi} is the X-X bond length in a complex (given by $r_0\sqrt{2}$ for octahedra and by $r_0\sqrt{8/3}$ for tetrahedra). This choice is somewhat less than for a freely rotating unit. Our results, to be given immediately below, are quite insensitive to the precise choice of the diameters of the two types of complexes, within a few tenths of an Ångström.

Our main results for the ionic equilibrium between octahedral and tetrahedral complexes in Al-Na fluoride mixtures at two different temperatures are shown in Figure 1 and Table 3. These have been obtained with the PX values for the binding free energies and hard sphere sizes. Figure 1 gives the equilibrium values of the fractional concentrations x of octahedra (full curves) and $(1-x)$ of tetrahedra (dashed curves). A quantitative comparison with the values derived from their Raman scattering data by Gilbert et al.² at $T \cong 1053$ K is given in Table 3. The Table also reports the calculated values for the activation free energy $f(x)$ at the equilibrium value of x . It is evident from its sign and magnitude that the ionic screening interactions in the liquid mixture amply overcompensate the difference in binding free energy for the two complexes in the isolated state.

It is clear from Table 3 that the agreement between theory and experiment in the concentration range above $c = 0.375$ is excellent. More importantly, theory and experiment agree in yielding the number of free F^- ions as essentially zero in this concentration range at $T \cong 1053$ K, so that the equilibrium fractional concentration of octahedral complexes is very close to x_{max} . This qualitative feature of the theoretical results remains essentially unchanged when the PX values for the system parameters are replaced by the NPX values.

For deeper insight into the relevant system parameters we have to turn to the concen-

tration range close to criolite and to the temperature dependence of the ionic equilibrium. It is seen from Figure 1 that in the vicinity of $c = 1/4$ the theory based on PX parameters predicts deviations of the equilibrium concentration x of octahedra from its ideal upper limit x_{\max} , which assumes the value 1 at $c \leq 1/4$ with a discontinuity in its derivative at $c = 1/4$. As a matter of fact, at the composition of criolite the theory predicts $x = 0.96$ at $T = 1053$ K and $x = 0.85$ at $T = 1288$ K, the latter value being comparable with the estimate of a degree of dissociation for octahedral complexes of the order of 20+25 % that Gilbert *et al.*² derived from their Raman spectra. Such partial dissociation of the octahedral complexes in the vicinity of the special composition corresponding to criolite is instead missed when the NPX values of the system parameters are used.

4. Role of halogen polarization in Al-Na chloride mixtures

We have just seen that the temperature dependence of the ionic equilibrium in Al-Na fluoride mixtures, and its behaviour in the vicinity of the composition corresponding to criolite, indicate that the electronic polarizability of the halogen is playing a major role. We stress again that this is due to the stabilization that it induces for the tetrahedral unit relative to the octahedral unit, as already pointed out in section 2. Transcending the present simple models, the same effect would appear in quantal calculations as incipient covalent bonding, which would be more important in the tetrahedral unit than in the octahedral one.

We shall here give the results of similar calculations that we have carried out on the ionic equilibrium between $(\text{AlCl}_6)^{3-}$ units and $(\text{AlCl}_4)^-$ units in molten Al-Na chloride mixtures, using the parameters already reported in Tables 1 and 2. According to the discussion in section 2, these will allow us to separate the size effects from the halogen polarizability effects in determining the relative stability of octahedral units and tetrahedral units in liquid mixtures. The relevant results are shown in Table 4, together with the corresponding results for Al-Na fluoride mixtures that we have already discussed in section 3.

We draw attention, first of all, to the values of $f(x)$ in the NPX calculations in Table 4. These are similar in the fluoride and in the chloride, showing that the size dependence of ionic screening in the liquid mixture is largely cancelling the size dependence of the difference in binding free energies for the isolated complexes. The result is that, contrary to all expectations,

the $(\text{AlCl}_6)^{3-}$ units would be predicted to be stable in the Al-Na chloride mixtures.

On the other hand, the PX calculations lead to qualitatively correct predictions for the chloride mixtures as well. Ionic screening in the chloride melts is unable to overcome the extra stability that a tetrahedral unit acquires from chlorine polarization. Hence, $(\text{AlCl}_6)^{3-}$ units are totally unstable in the liquid chloride mixtures as well as in the isolated state.

5. Summary and discussion

Our theoretical approach has allowed us to obtain a satisfactory description of the ionic equilibrium between octahedral and tetrahedral complexes in molten Al-Na fluoride mixtures and to recognize that the relevant system parameter for the relative stability of the two complexes in the melt is the halogen polarizability (or incipient covalent bonding) leading to relative stabilization of the tetrahedral unit. The role of ionic sizes can be expected to be less important in such a relative stability problem, in view of strong cancellation between their effect in the binding of complexes and in the ionic screening by the liquid medium. We also wish to stress that in our approach essentially quantitative agreement has been achieved with the available Raman spectroscopy data without adjustment of parameters to the melt under consideration. In a broader view, our statistical mechanical treatment could be applied to other similar melts with the simple expedient of treating the binding free energies of complexes as adjustable parameters.

It seems worth emphasizing at this point that we have obtained a good theoretical description for the ionic structure of molten criolite as a function of temperature. Clearly, at this particular composition and in its immediate neighbourhood, partial dissociation of the $(\text{AlF}_6)^{3-}$ species is taking place even at the lowest temperature in the melt. Viewing, therefore, the ionic structure of this melt as a mixture of $(\text{AlF}_6)^{3-}$ and $(\text{AlF}_4)^-$ species in a medium of free Na^+ and F^- ions, it becomes interesting to theoretically enquire about the structural changes that would occur under exposure to electron donors. We have specifically in mind an experiment by Grjotheim¹³, in which molten criolite was exposed to sodium vapour in an effort to clarify the respective roles of Al and Na in the electrolytic process for the production of Al metal. We expect that the sodium vapour upon ionization will lead to a decrease in the screening length of the melt, thus enhancing the dissociation of the $(\text{AlF}_6)^{3-}$ species and promoting the dissociation of the $(\text{AlF}_4)^-$ species as well. In the event, neutralization of Al^{3+} by the available electrons, rather than by fluorine ions, would result.

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Table 1. Bond length and binding in isolated $(AlX_4)^-$ and $(AlX_6)^{3-}$ units

| | | $(AlF_4)^-$ | $(AlF_6)^{3-}$ | $(AlCl_4)^-$ | $(AlCl_6)^{3-}$ |
|----------------------------------|--------------------|-------------|----------------|--------------|-----------------|
| r_o (Å) | PX | 1.71 | 1.90 | 2.15 | 2.39 |
| | NPX | 1.66 | 1.88 | 2.15 | 2.39 |
| $-U_o$ (kcal/mole) | PX | 1476 | 1247 | 1294 | 1055 |
| | NPX | 1394 | 1210 | 1117 | 984 |
| $U_o(6) - U_o(4)$ (kcal/mole) | PX | | 229 | | 239 |
| | NPX | | 184 | | 133 |
| $f_6 - f_4$ (kcal/mole) | PX ^(a) | | 216 | | 224 |
| | NPX ^(a) | | 170 | | 119 |
| | PX ^(b) | | 211 | | -- |

(a) At T = 1053 K.

(b) At T = 1288 K.

Table 2. Values of hard sphere diameters (Å)

| σ_{Na} | σ_F | σ_{Cl} | $\sigma_6(F)$ | | $\sigma_4(F)$ | | $\sigma_6(Cl)$ | $\sigma_4(Cl)$ |
|---------------|------------|---------------|---------------|------|---------------|------|----------------|----------------|
| | | | PX | NPX | PX | NPX | | |
| 2.24 | 2.27 | 3.04 | 4.96 | 4.92 | 5.06 | 4.98 | 6.42 | 6.55 |

Table 3. Ionic equilibrium in Al-Na fluoride mixtures at T = 1053 K

| | | | | |
|--------------------|----------------------|----------------------|----------------------|----------------------|
| c | 0.375 | 0.406 | 0.425 | 0.462 |
| $n_6 = xc$ | 0.124 | 0.093 | 0.074 | 0.038 |
| | 0.116 ^(a) | 0.101 ^(a) | 0.079 ^(a) | 0.041 ^(a) |
| $n_4 = (1-x)c$ | 0.251 | 0.313 | 0.351 | 0.425 |
| | 0.258 ^(a) | 0.304 ^(a) | 0.346 ^(a) | 0.420 ^(a) |
| $f(x)$ (kcal/mole) | - 67 | - 66 | - 66 | - 65 |

(a) From the analysis of Raman scattering spectra by Gilbert et al, ref. 2.

Table 4. Comparison between Al-Na chloride and Al-Na fluoride mixtures at T = 1053 K.

| | | Al-Na(Cl) | | Al-Na(F) | |
|------------|--------------------|--------------------|--------------------|----------|-------|
| | | PX | NPX | PX | NPX |
| c = 1/4: | $f(x)$ (kcal/mole) | 0.1 | - 90 | - 64 | - 109 |
| | n_6 | 2×10^{-8} | 0.249 | 0.24 | 0.249 |
| | n_4 | 0.25 | 5×10^{-4} | 0.01 | 0.001 |
| c = 0.406: | $f(x)$ (kcal/mole) | - 1.2 | - 100 | - 66 | - 109 |
| | n_6 | 4×10^{-8} | 0.09 | 0.09 | 0.09 |
| | n_4 | 0.406 | 0.31 | 0.31 | 0.31 |

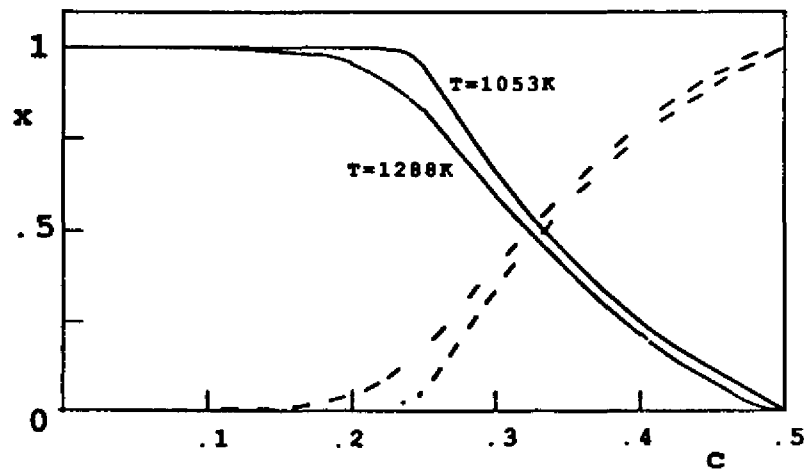


Fig.1

Equilibrium value of the fractional concentration x of $(\text{AlF}_6)^{3-}$ units in molten AlF_3 - NaF mixtures as a function of the concentration c of AlF_3 at two different temperatures (full curves). The dashed curves show the corresponding values of $(1-x)$, i. e. the fractional concentration of $(\text{AlF}_4)^-$ units.



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