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The AlF_3–BaF_2–NaF molten salt system: calorimetric investigations and modelling

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Abstract

The enthalpies of formation of liquid AlF_3–BaF_2–NaF ternary mixtures were measured by high-temperature calorimetry. The "direct drop" mixing procedure was applied in accordance with the physico-chemical properties of the system. The heat of mixing, referred to the liquid state, requires a knowledge of the enthalpy change between room temperature and the experimental temperature of the samples added to the melt. This term is not well known for AlF_3, because it sublimes under normal conditions. Therefore, in this paper we used a new method to analyse raw experimental data based on the use of a thermodynamic model which evaluates the excess functions of the liquid. The results obtained are compared with literature values.

Keywords: Calorimetry; Direct drop mixing; Ternary system

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1. Introduction

Molten salt mixtures of chlorides and fluorides of aluminium, barium and sodium are used for electrolytic production and purification of aluminium [1].

A basic knowledge of the thermodynamics of the the quaternary reciprocal mixture {Al, Ba, Na//Cl, F} is needed to improve industrial processes and to minimise some drawbacks. The first step in this work was a thermodynamic study of the AlF_3–BaF_2–NaF ternary system.

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A knowledge of the thermodynamic properties of the liquid phase are important in order to derive the phase diagram of this ternary system. We have, therefore, using calorimetry at high temperature, measured the enthalpy of formation of some pseudo-binary sections of this ternary system.

The "drop method" [2] was used to study the mixing of the liquids. This method requires a knowledge of the enthalpy change, relative to the sample dropped, between room temperature and the experimental temperature. Unfortunately, one major difficulty lies in the fact that experimental thermodynamic data are not available for AlF_3 at high temperature as this salt sublimes under normal conditions [3]. Therefore, in the present work, we have analysed experimental data using a method that is different from that generally used in this kind of experiment [4, 5]. It is based on the use of a thermodynamic model which provides the excess functions of the liquid.

2. Experimental

2.1. Chemicals

Purification and synthesis of the reagents used in this study were carried out at the Institut of Inorganic Chemistry of Trondheim (Norway). AlF_3 was obtained from Ardal and Sunndal Verk, "Suprapur reagent". Before it was used in the calorimeter it was purified by sublimation. AlF_3 was placed in a graphite crucible and distilled under reduced pressure on heating to 1273 K. Two successive sublimations were necessary to obtain clear crystals. BaF_2 was synthesized from BaO (Merck Suprapur). The main steps of this preparation are

$$BaO + 2NH_4F \cdot HF \longrightarrow (NH_4)_2BaF_4 + H_2O\,(T = 423\ K)$$

$$(NH_4)_2BaF_4 \longrightarrow (NH_4)BaF_3 + NH_4F\,(T = 573\ K)$$

$$(NH_4)BaF_3 \longrightarrow BaF_2 + NH_4F\,(T = 632\ K)$$

Finally, excess BaO was removed from the melt by recrystallization of BaF_2.

The NaF used was Merck "zur Analyse" reagent. This salt was purified and treated by progressive heating up to 15 K above its melting point and cooled down at 3 K min^{-1}. After solidification clear crystals were selected for the experiments.

The reagents were handled in an argon glove box with a measured mass fraction of water of about 5×10^{-6} and continuous gas purification by forced recirculation through external molecular sieves.

2.2. Procedure

The calorimetric apparatus (a very-high-temperature enthalpimeter), the mixing device and the experimental method adopted have all been described in detail elsewhere [6, 7].

The crucibles used in these experiments were made of graphite and the calorimeter was calibrated by dropping platinum samples into the laboratory crucible during the experimental run.

The enthalpy of formation of some mixtures of this ternary system were obtained either by adding solid AlF_3 at room temperature T_0 to the initial BaF_2–NaF binary liquid mixture at the experimental temperature T, or by adding solid BaF_2 at room temperature T_0 to the initial AlF_3–NaF binary liquid mixture at the experimental temperature T.

If A, B, C represent the three pure salts, x_A, x_B, x_C the corresponding ternary mole fractions and x_A^*, x_B^* the mole fraction of A and B in the initial binary system with $(x_A^*/x_B^* = x_A/x_B = \theta)$ then the measured ternary molar enthalpy change $\Delta_{mix}H_{S-l}$, is the algebraic sum of the following terms

$$\Delta_{mix}H_{S-l} = \Delta_{mix}H(x_A A + x_B B + x_C C) - (1 - x_C)\Delta_{mix}H(x_A^* A + x_B^* B) + x_C[H(C, l, T) - H(C, s, T_0)] \quad (1)$$

where $\Delta_{mix}H(x_A A + x_B B + x_C C)$ and $\Delta_{mix}H(x_A^* A + x_B^* B)$ are the molar enthalpy changes corresponding respectively to the reactions

$$x_A A(l, T) + x_B B(l, T) + x_C C(l, T) = (A_{x(A)}, B_{x(B)}, C_{x(C)})(l, T)$$

$$x_A^* A(l, T) + x_B^* B(l, T) = (A_{x^*(A)}, B_{x^*(B)})(l, T).$$

$H(C, l, T) - H(C, s, T_0)$ is the enthalpy increment of C between T_0 and T.

$\Delta_{mix}H_{S-l}$ was deduced from experimental data. Due to the vapor pressure of AlF_3, the term, $H(C, l, T) - H(C, s, T_0)$, cannot be obtained accurately from thermodynamic tables: the values of the enthalpy of melting given in the literature, 47.27 kJ mol^{-1} [8] or 112.01 kJ mol^{-1} [9], differ considerably. In both cases the enthalpy values were obtained by estimation either from solubility data using a thermodynamic cycle based on many approximations [8], or by extrapolation over a wide composition range of calorimetric data obtained by dissolution of AlF_3 in alkali fluorides.

The thermodynamic Hoch–Arpshofen model [10] was used to represent the experimental data obtained in this study. The model, originally developed for metallic solutions, was applied to different systems: metal–salt [11], metal–oxide [12], silicate [13], and ionic systems [14]. For this last systems, the model is particularly well-adapted when salts are partially ionic, i.e. ZrF_4, $BiCl_3$, etc.

For a solution containing components (A, B, C), the contribution of the A–B binary system to the solution is

$$\Delta_{mix}H_{AB} = n_{AB}W_{AB}x_A(1 - (1 - x_B)^{n_{AB}-1})$$

where W_{AB} is the interaction parameter and n_{AB} is an integer (≥ 2) corresponding to the size of the complexes formed in the melt: for example, for $n_{AB} = 3$ the complexes are made up of two moles of A and one mole of B (A_2B) or 2 moles of B and one mole of A (AB_2).

The total enthalpy of mixing of the ternary system, is the sum of each contribution: A–B, A–C and B–C

$$\Delta_{mix}H(x_A A + x_B B + x_C C) = \Delta_{mix}H_{AB} + \Delta_{mix}H_{AC} + \Delta_{mix}H_{BC}$$

Finally, Eq. (1) becomes

$$\begin{aligned}\Delta_{\text{mix}} H_{\text{S}-\text{l}} = {} & n_{\text{AB}} W_{\text{AB}} x_{\text{A}}(1-(1-x_{\text{B}})^{n_{\text{AB}}-1}) + n_{\text{AC}} W_{\text{AC}} x_{\text{A}}(1-(1-x_{\text{C}})^{n_{\text{AC}}-1}) \\ & + n_{\text{BC}} W_{\text{BC}} x_{\text{B}}(1-(1-x_{\text{C}})^{n_{\text{AB}}-1}) \\ & -(1-x_{\text{C}}) n_{\text{AB}} W_{\text{AB}} x_{\text{A}}^{*}(1-(1-x_{\text{B}}^{*})^{n_{\text{AB}}-1} \\ & + x_{\text{C}}[H(\text{C},\text{l},T) - H(\text{C},\text{s},T_0)] \end{aligned} \qquad (2)$$

In this equation, W_{AB}, $W_{\text{AC}}, \ldots$, n_{AB}, $n_{\text{AC}} \ldots$, $H(\text{C},\text{l},T) - H(\text{C},\text{s},T_0)$, are unkonwn terms. Relation (2) can be written for each of the N experimental points. We have therefore a system with N equations and seven unknowns. At the beginning of our procedure, we fix the values of n and we apply a method of multiple regression. We calculate in this way, the three values of $W$and the term $H(\text{C},\text{l},T) - H(\text{C},\text{s},T_0)$. This calculation is done for different values of n, the best set of results is the one which gives a correlation coefficient closest to 1.

3. Results

3.1. AlF_3 addition

Ternary mixtures were obtained by addition of AlF_3 to BaF_2–NaF mixtures of different compositions.

Calorimetric experiments were carried out at 1290 K. Due to the vapor pressure of AlF_3 at this temperature (1.13 kPa), we limited the concentration range to $0 < x(AlF_3) < 0.7$. Experiments were performed for several initial compositions of the binary system BaF_2–NaF, corresponding to

$$\theta = x^*(\text{NaF})/x^*(\text{BaF}_2) = x(\text{NaF})/x(\text{BaF}_2) = 17/3;\ 3;\ 9/11;\ 13/7;\ 11/9;\ 7/13$$

Results are shown in Fig. 1. Good reproductibility is observed within experimental uncertainty (± 5%).

The curves representing excess molar enthalpies against $x(AlF_3)$ show a break at around $x(AlF_3) = 0.6$ ($\theta = 13/7; 3; 9/11; 7/13$). These discontinuities can be attributed to the solubility limit of AlF_3 in the melt. The phase diagram of this ternary system has been measured by thermal analysis [15], but due to the vaporization of the melt, in this composition range ($x(AlF_3) > 0.6$), it was possible to measure only a few experimental points and it was difficult to determine the liquidus temperature at the composition corresponding to the discontinuities.

3.2. BaF_2 addition

Ternary mixtures were obtained by adding BaF_2 to AlF_3–NaF mixtures of different compositions.

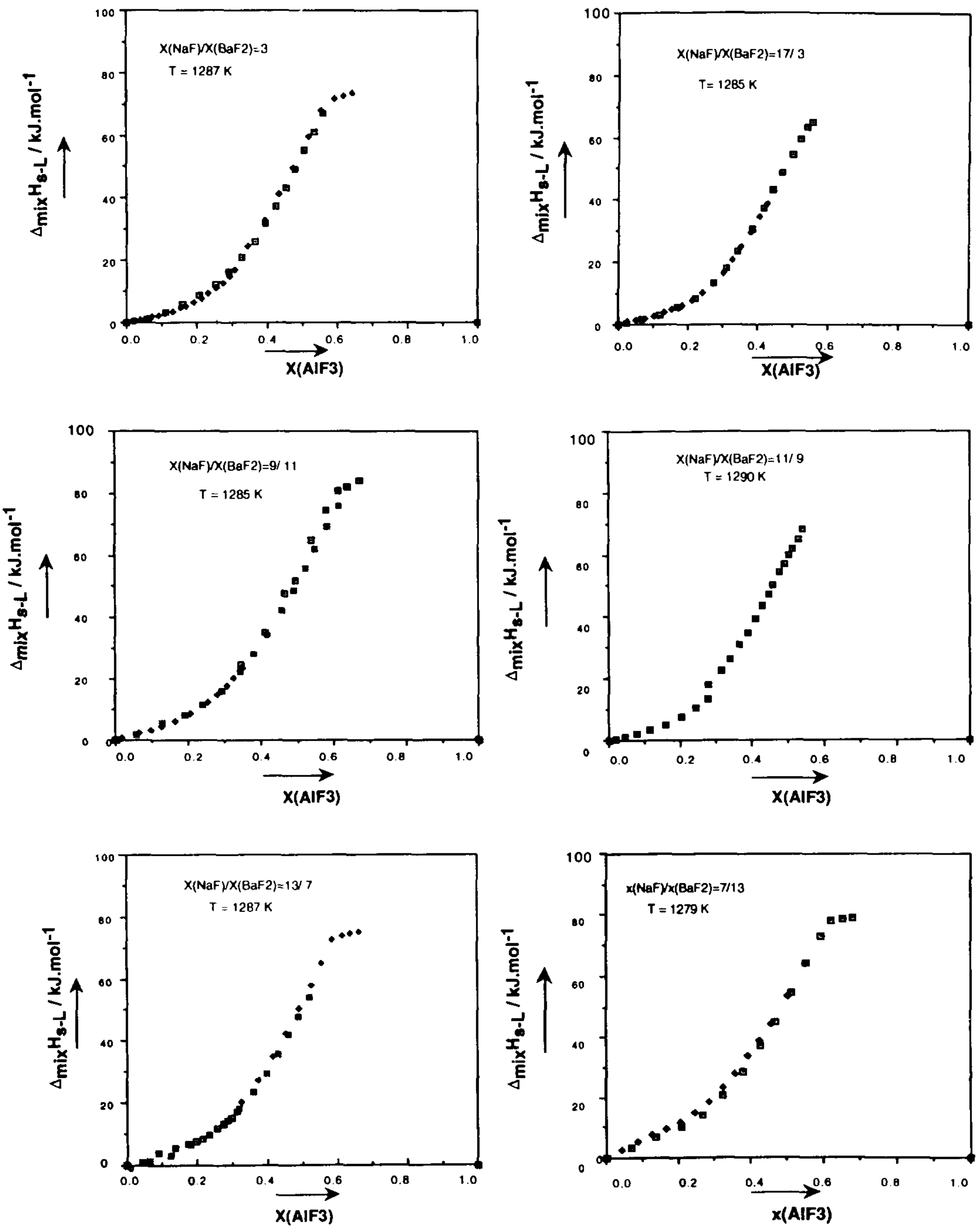

Fig. 1. Excess molar enthalpy, $\Delta_{\mathrm{mix}}H_{\mathrm{s-l}}$, plotted against $x(\mathrm{AlF_3})$ for the ternary mixtures obtained from additions of $\mathrm{AlF_3}$ solid samples to several initial binary mixtures of $\mathrm{BaF_2}$–NaF that were liquid at the experimental temperature.

The enthalpy of formation of the mixtures was measured at 1308 K in the composition range $0 < x(\mathrm{BaF_2}) < 0.7$. The initial compositions of the binary system $\mathrm{AlF_3}$–NaF correspond to

$$\theta = x^*(\mathrm{NaF})/x^*(\mathrm{AlF_3}) = 4;\ 7/3;\ 13/7;\ 3/2;\ 11/9;\ 9.$$

The excess molar enthalpies, $\Delta_{\mathrm{mix}}H_{\mathrm{S\text{-}l}}$, are plotted against $x(\mathrm{BaF_2})$ in Fig. 2. Good reproductibility is again observed within the experimental uncertainty (± 5%). As mentioned above some curves representing the excess molar enthalpies against $x(\mathrm{BaF_2})$ show a discontinuity around $x(\mathrm{BaF_2}) = 0.6$, for the ratio $x(\mathrm{NaF})/x(\mathrm{AlF_3})$ equal to 13/7, 3/2, and 11/9. These discontinuities are related to the formation of a solid phase inside the melt.

Comparison between the ternary phase diagram given in the literature and the limit solubilities deduced from these curves indicates a difference of about 80 K. Little experimental information is available for this phase diagram, but it is possible to compare the results deduced from the section $(x(0.25\mathrm{AlF_3} + 0.75\mathrm{NaF}) + (1-x)\mathrm{BaF_2})$ [15] with the phase diagram of the $(x\mathrm{Na_3AlF_6} + (1-x)\mathrm{BaF_2})$ binary system [16]. From the binary system the limit solubility of $\mathrm{BaF_2}$ at 1280 K is obtained at $x(\mathrm{BaF_2}) = 0.8$. However, from the ternary system, this limit is found for $x(\mathrm{BaF_2}) = 0.65$. Therefore, there is considerable difference between the two sets of experimental data.

4. Modelling and discussion

For all mixtures, a knowledge of the heat of mixing referred to the liquid state, i.e. corrected for the enthalpy increment of the added compound, is of great importance in understanding the behaviour of ions in the melt.

In the first step of the calculation, we used 195 experimental values of $\Delta_{\mathrm{mix}}H_{\mathrm{S\text{-}l}}$ obtained by adding $\mathrm{AlF_3}$ to the initial binary mixtures, $x^*\mathrm{BaF_2} + (1-x^*)\mathrm{NaF}$. Eq. (2) was applied to these experimental points and a system of 195 equations obtained. The heat of mixing of the $\mathrm{BaF_2}$–NaF binary system has been measured [17]. The minimum is equal to $-0.75\ \mathrm{kJ\ mol^{-1}}$ for $x(\mathrm{BaF_2}) = 0.5$. Therefore, in our calculation we considered that the interaction between $\mathrm{BaF_2}$ and NaF is negligible and $W(\mathrm{BaF_2}\text{–}\mathrm{NaF}) = 0$. Thus, there are five unknown terms. A numerical solution was found by least-squares minimization and the results are given in Table 1.

Table 1
Calculated parameters obtained on adding $\mathrm{AlF_3}$

Mixtures or compound	n	W/kJ mol^{-1}	H(l, 1290 K)-H(s, 298 K) kJ mol^{-1}
$\mathrm{AlF_3}$–$\mathrm{BaF_2}$	2	-77.54 ± 2.64	
$\mathrm{AlF_3}$–NaF	3	-34.15 ± 0.76	
$\mathrm{AlF_3}$			180.97 ± 2.00
Correlation coefficient		0.987	

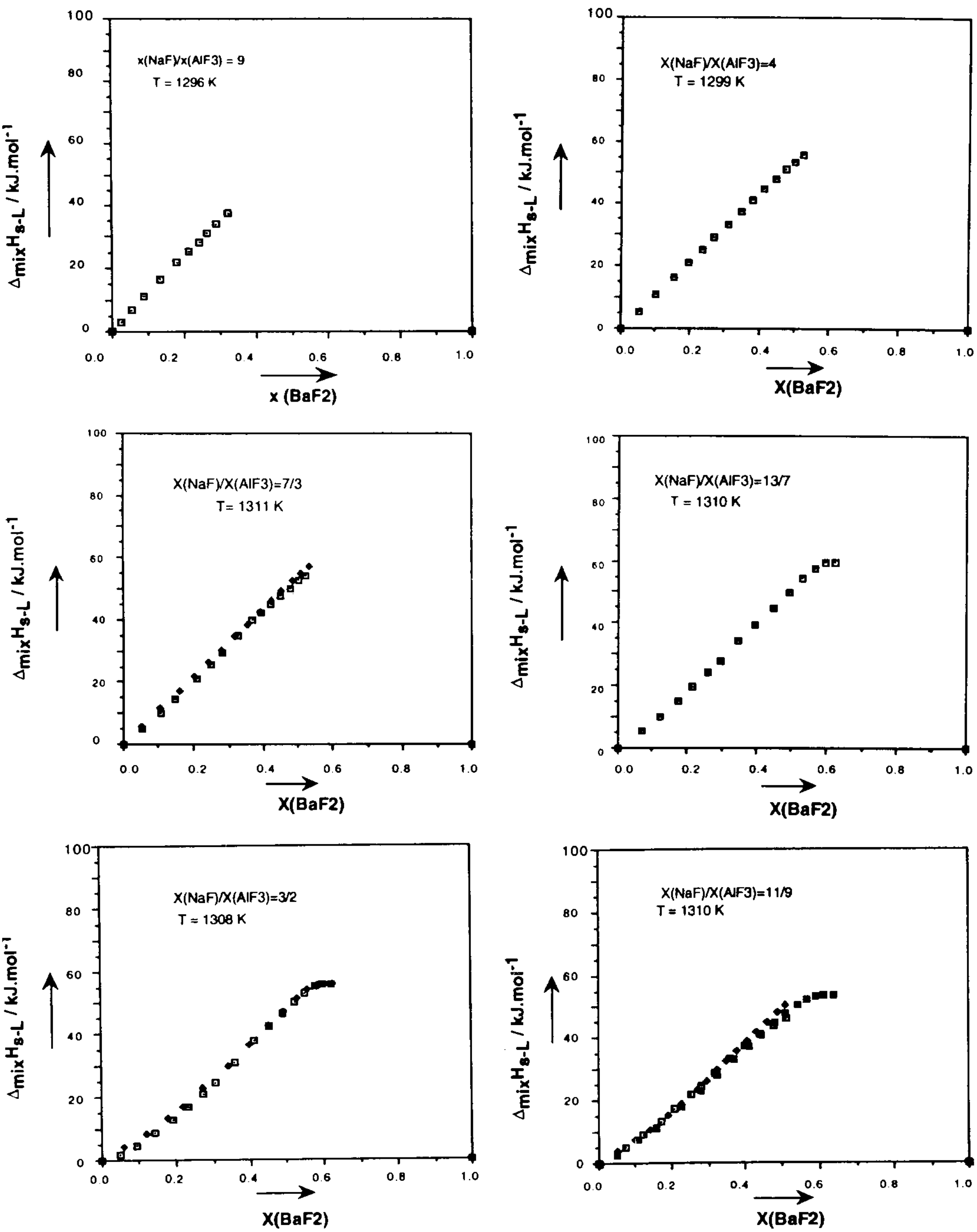

Fig. 2. Excess molar enthalpy, $\Delta_{\mathrm{mix}}H_{\mathrm{s-l}}$, plotted against $x(\mathrm{BaF_2})$ for the ternary mixtures obtained from additions of $\mathrm{BaF_2}$ solid samples to several initial binary mixtures of $\mathrm{AlF_3}$–NaF that were liquid at the experimental temperature.

The enthalpy increment, $H(\mathrm{AlF_3,l,1290\,K}) - H(\mathrm{AlF_3,s,298\,K})$, is the sum of two terms

$$H(\mathrm{AlF_3,l,1290\,K}) - H(\mathrm{AlF_3,s,298\,K}) = H(\mathrm{AlF_3,s,1290\,K}) - H(\mathrm{AlF_3,s,298\,K}) + \Delta_{\mathrm{fus}}H(\mathrm{AlF_3,1290\,K}) \quad (3)$$

The same procedure was applied to the experimental data of Hong and Kleppa [18] and Holm [8] for the binary mixtures AlF_3–Na_3AlF_6 [8], AlF_3–Li_3AlF_6 [8], AlF_3–ZnF_2 [18], AlF_3–KF [18], AlF_3–LiF [18], and AlF_3–NaF [18]. We calculated the enthalpy of melting of AlF_3 at 1290 K. The enthalpy of mixing of these mixtures was obtained by adding samples of solid AlF_3 at 1290 K. A total of 196 experimental points was used in the calculation.

The results are presented in Table 2. The interaction parameter obtained in this case for the binary AlF_3–NaF system ($W(\mathrm{AlF_3{-}NaF}) = -34.07 \pm 0.7\ \mathrm{kJ\ mol^{-1}}$) is in very good agreement with that calculated from the ternary system ($W(\mathrm{AlF_3{-}NaF}) = -34.15 \pm 0.76\ \mathrm{kJ\ mol^{-1}}$). By taking the average of these values ($W(\mathrm{AlF_3{-}NaF}) = -34.11\ \mathrm{kJ\ mol^{-1}}$), the heat of mixing against the composition of the melt was calculated and compared with the values from the experimental results of Hong and Kleppa [18]. The minimum of the curve (Fig. 3) was found for $x(\mathrm{AlF_3}) = 0.42$ ($\Delta_{\mathrm{mix}}H = -40\ \mathrm{kJ\ mol^{-1}}$) and $x(\mathrm{AlF_3}) = 0.35$ ($\Delta_{\mathrm{mix}}H = -45\ \mathrm{kJ\ mol^{-1}}$) respectively for the calculated and experimental series. The difference, about 12%, can be attributed to the heat of melting of AlF_3. Indeed if we correct the raw experimental values of Hong and Kleppa with the heat of melting obtained in this work, we obtain similar results.

Using the enthalpy of melting calculated above, we also calculated the enthalpy increment of solid AlF_3 between 1290 and 298 K from Eq. (3). We obtain $H(\mathrm{AlF_3,s,1290\,K}) - H(\mathrm{AlF_3,s,298\,K}) = 83.4\ \mathrm{kJ\ mol^{-1}}$. This value was compared with the one given in the literature, 96.5 kJ mol^{-1} [19]. The sublimation of AlF_3 during the measurements can explain the difference between these values; indeed it represents 3% of the enthalpy of sublimation of this salt.

The same procedure was used for the mixtures obtained by dropping BaF_2 into the initial AlF_3–NaF melt. Eq. (2) was applied to the 79 experimental points. In this calculation, the value of $W(\mathrm{AlF_3{-}NaF})$ was fixed to the average of the two above-

Table 2
Calculated parameters obtained from literature data

Mixtures or compound	W/kJ mol^{-1}	$\Delta_{\mathrm{fus}}H$(1290 K)/kJ mol^{-1}
AlF_3–Na_3AlF_6	-20.35 ± 0.77	
AlF_3–Li_3AlF_6	-9.33 ± 0.81	
AlF_3–ZnF_2	-8.72 ± 0.84	
AlF_3–KF	-43.17 ± 0.76	
AlF_3–LiF	-19.28 ± 0.67	
AlF_3–NaF	-34.07 ± 0.7	
AlF_3		97.77 ± 1.91
correlation coefficient	0.991	

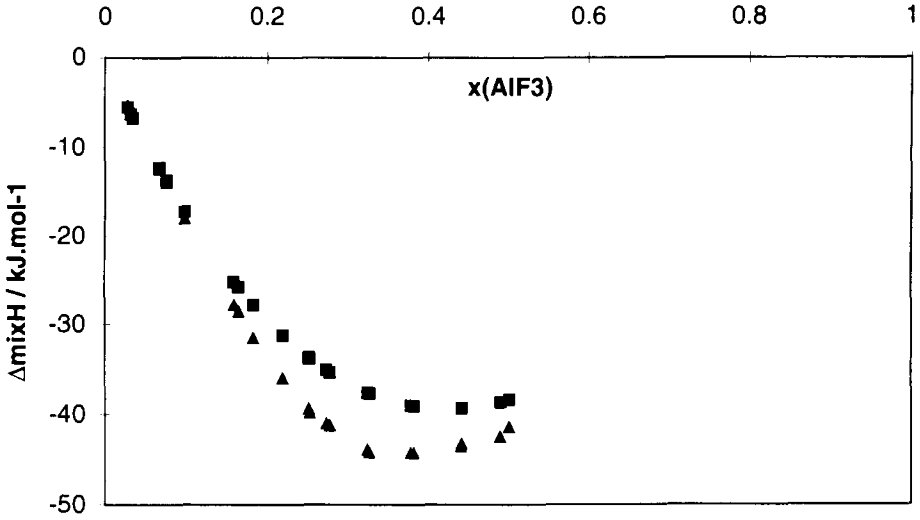

Fig. 3. Excess molar enthalpies, $\Delta_{mix}H$, for the liquid AlF_3–NaF mixtures plotted against $x(AlF_3)$: ▲, from Ref. [18]; ■, calculated.

Table 3
Calculated parameters obtained on adding BaF_2

Mixtures or compound	n	W/kJ mol^{-1}	H(l, 1290 K) – H(s, 298 K) kJ mol^{-1}
AlF_3–BaF_2	2	-82.56 ± 3.06	
AlF_3–NaF (fixed)	3	-34.11	
BaF_2			115.01 ± 1.47
Correlation coefficient		0.989	

mentioned values, and $W(BaF_2–NaF)$ set to zero, as previously indicated. The results are given in Table 3.

The values of $W(AlF_3–BaF_2)$ obtained from these two calculations, -77.54 ± 2.64 (Table 1) and -82.56 ± 3.06 kJ mol^{-1} (Table 3), are in agreement within the uncertainity.

The enthalpy increment of BaF_2 between 1290 and 298 K was determined as $H(BaF_2, l, 1290\,K) - H(BaF_2, s, 298\,K) = 115.01 \pm 1.47$ kJ mol^{-1}, which is in agreement with the literature value [20], 123 kJ mol^{-1}. The values of n and Wcalculated for the AlF_3–NaF binary system suggest:

(a) The formation of complex anions inside the melt. Indeed the heat of mixing (about -40 kJ mol^{-1} at the minimum) is very negative and cannot be explained only by the variation in the local environment of each ion.

(b) The stoichiometry of these complex anions. Indeed $n = 3$ corresponds to $2NaF \cdot AlF_3$, $(2Na^+AlF_5^{2-})$ and $NaF \cdot 2AlF_3$, $(Na^+Al_2F_7^-)$. Recently the structure and thermodynamics of AlF_3–MF (M is Li, Na, K) melts have been determined by quantitative Raman spectroscopy and vapour pressure measurements [21, 22]. The main conclusion is that the AlF_5^{2-} is a major anionic species together with F^- and AlF_4^-. This conclusion is in accordance with our results as $Al_2F_7^-$ is a dimerized form of AlF_4^-.

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