Thermodynamic Modelling of Fluoride Molten Salts Using the Cell Model

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ABSTRACT

The thermodynamic modelling of fluoride based melts was undertaken as part of studies on the physico-chemical properties of low temperature electrolytes suitable for use in the Hall-Heroult process. The IRSID adaption of Kapoor and Frohberg's cell model and the compound energy model were used for describing the behaviour of the liquid and solid phases of interest.

The cell model was used to calculate the liquidus temperatures and activities of species in the LiF-AlF_3, NaF-AlF_3, LiF-NaF binary systems. Model parameters (cell formation and cell interaction energies) for each of these binary systems were obtained through optimisation procedures using the Thermo-Calc computational package to fit literature data. Composition dependent terms for the model parameters were used and a good fit was obtained between model calculations and the literature data.

For the LiF-NaF binary system published experimental data were used in conjuction with the compound energy model to describe the limit of LiF solubility in the NaF matrix.

In the present work model parameters obtained from the NaF-AlF_3, LiF-AlF_3 and LiF-NaF binary systems have been used to calculate phase diagrams in the Li_3AlF_6-Na_3AlF_6, Na_3AlF_6-LiF and Na_3AlF_6-AlF_3-(5%LiF) pseudo binary systems. The calculated liquidus curves for these systems were found to agree well with literature data. The cell model is able to calculate ternary and higher order phase diagrams using model parameters obtained from the binary sub-systems.

The calculated entropy of mixing in the above binary systems is discussed with respect to their thermodynamic solution behaviour.

1. INTRODUCTION

The cell model was originally developed by Kapoor and Frohberg[1] and was applied to binary and ternary melts in the system CaO-SiO_2-FeO. This model was later extended by Gaye and Welfringer[2] to represent thermodynamic properties of complex slags. Gaye and co-workers[2-4] have also extended the applicability of the cell model to slags containing sulphide and fluoride anions as well as oxygen. Recent thermodynamic modelling work at the G K Williams Centre[5] has replicated Gaye's work and has shown that the cell model is able to accommodate sulphide and fluoride anions in a range of silicate and aluminate based slags as well as in oxy-sulphide and oxy-halide melts over an entire composition range.

In the present work the application of this model has been extended to fluoride based molten salts. This modelling work is part of an initiative of the Melt Chemistry Group at the CSIRO Division of Minerals to determine some of the physio-chemical properties of low temperature electrolytes suitable for use in the Hall-Heroult process for aluminium production. Results obtained for the binary systems AlF_3-NaF, AlF_3-LiF and LiF-NaF and the ternary system AlF_3-LiF-NaF are presented.

2. MODELLING PROCEDURE

The liquid phase has been modelled using Kapoor and Frohberg's cell model. The solid phase has been modelled using the compound energy model[6].

According to Gaye[3], the basic tenet of the cell model is two sub lattices, one containing anions, the other containing cations in decreasing order of their charge. The structure of the melt is described in terms of cells which consist of a central anion surrounded by two cations, e.g. Al-F-Al or Na-F-Na or Al-F-Na in the NaF-AlF_3 system. The free energy of mixing of the system is then associated with two energy parameters:

1. W_{ij} - the energy associated with the formation of an asymmetric cell from two symmetric cells, e.g. $2W_{Al\text{-}Na}$ is the energy required for the reaction: Al-F-Al + Na-F-Na = 2 Al-F-Na [1]

2. E_{ij} - the energy associated with the interaction between a symmetric and an asymmetric cell, e.g. $E_{Al\text{-}Na}$ is the interaction energy between the cells Al-F-Al and Al-F-Na. The interaction between symmetric cells are considered in a series of additivity rules which reduces such interactions to the form E_{ij}

These two parameters, E_{ij} and W_{ij}, can be used as single variables or as functions of composition. In the present work linear compositional dependent parameters have been used, e.g.:

$$W_{Al\text{-}Na} = W_0 + W_1 X_{Al} \qquad [2]$$

$$E_{Al\text{-}Na} = E_0 + E_1 X_{AlF} \qquad [3]$$

The cells are assumed to be randomly distributed in the melt. The interaction and formation parameters are assumed independent of temperature.

The cell formation and cell interaction energies are used in the expression of the free energy of mixing for the system. Other thermodynamic properties such as activity of species and phase boundaries (phase diagrams) can be calculated from the free energy of mixing expression.

The cell formation and cell interaction energies (or parameters) were optimised using published phase diagram data. In the present work all the data handling required to determine the model parameters was performed using the Parrot module of the Thermo-Calc computational package[7].

Other thermodynamic data required by the Thermo-Calc package includes the free energy of fusion of the end components of a binary system and the free energy of formation of any intermediate compounds which form in the system.

The compound energy model for solid solutions assumes cations and anions are randomly distributed on their own sublattice. Nearest neighbours are located on the other sublattice and the bond energies of nearest neighbours are constant. The free energy of the solid phase is then given by equation 4[7].

$$G^m = G^{ref} - TS^{ideal} + G_m^{ex} \qquad [4]$$

where: $G^{ref} = \sum X_i G_i^0$ for the components of the solid phase, and G_i^0 is the free energy of formation of component '*i*',

$$TS^{ideal} = -RT \sum X_i \, Ln X_i \qquad [5]$$

and $G_m^{ex} = X_1 X_2 \sum A_n (X_1 - X_2)^n$ [6]

is the excess free energy for a binary system. The exponent 'n' in Equation 6 indicates the degree of complexity of the model, e.g. n = 0 for an regular solution, n = 1 for a sub-regular solution and so on. For an ideal solution the constant A_n=0.

3. RESULTS

3.1 NaF-AlF_3 system

The NaF-AlF_3 binary system contains two compounds. The first compound cryolite (Na_3AlF_6) melts congruently at about 1010°C[8-10]. A second compound chiolite ($Na_5Al_3F_{14}$) melts incongruently at 738 °C[8-10,12]. The cryolite compound divides the binary system into two pseudo binary systems. The NaF-Na_3AlF_6 system forms a simple eutectic with no solid solubility. The eutectic occurs at about 888 °C and 13.6 mole % AlF_3[8,10,14]. The Na_3AlF_6-AlF_3 system contains a peritectic point at 738 °C and 40.9 mole % AlF_3[8-10,12,13]. A eutectic occurs at 693 °C and 47.1 mole % AlF_3[8-10,12,13].

The calculated liquidus boundaries from the cell model for the NaF-AlF_3 system together with some experimental data from the literature[13-15] are presented in Figure 1. These results show that the cell model is capable of representing all the features of the binary system. There is good agreement between the calculated and the measured liquidus in all the phase fields.

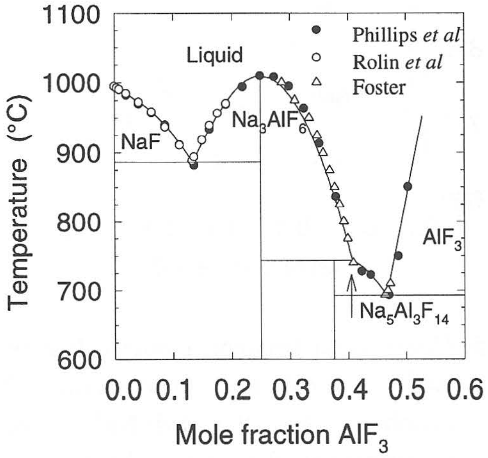

Figure 1: Comparison between model calculations (line) and experimental data (symbols) from Phillips et al.[13], Rolin and Rey[14], and Foster[15] of the liquidus boundary for the NaF-AlF_3 binary system.

The cell model was also used to calculate the activity of NaF and AlF_3 in the liquid phase at a given temperature. Figure 2 compares the calculated activity of NaF(l) and AlF_3(s) at 1020 °C, with measured data from Dewing[16]. The activity of NaF(l) has been measured using an EMF method in a solid electrolyte cell. The activity of AlF_3(s) has then been calculated using a Gibbs-Duham integration.

There is good agreement between calculated and measured activities of NaF over most of the composition range. The calculated activity of AlF_3 is higher than measured data between 25 and 50 mole % AlF_3.

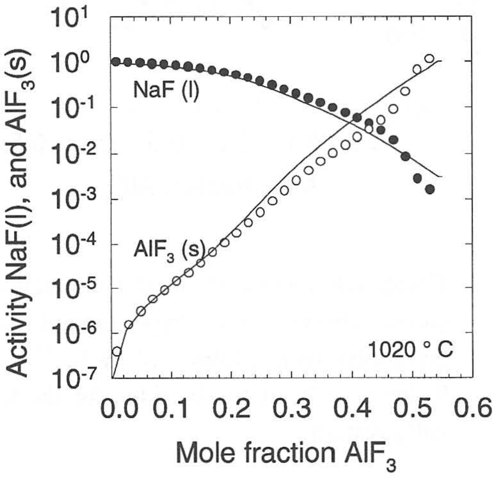

Figure 2:Calculated (curves) and measured[16] (symbols) activity from Dewing of NaF(l) and AlF_3(s) at 1020 °C.

3.2 LiF-AlF_3 system

The LiF-AlF_3 system contains one intermediate compound, namely lithium cryolite (Li_3AlF_6) which melts congruently at 782 °C[17]. This compound divides the binary system into two pseudo-binaries, simple eutectic systems. The LiF-Li_3AlF_6 system has a eutectic at about 711 °C and 15 mole % AlF_3[17]. The Li_3AlF_6-AlF_3 system has a eutectic at about 709 °C and 36 mole % AlF_3[17].

The results from the cell model together with literature data[17,18] on the liquidus are shown in Figure 3. This figure shows that the cell model is also able to represent the main features of this binary system. There is good agreement between the measured and the calculated liquidus particularly in the LiF- Li_3AlF_6 half of the system. The calculated boundary of the AlF_3 primary field is higher than the data from Holm and Holm[17].

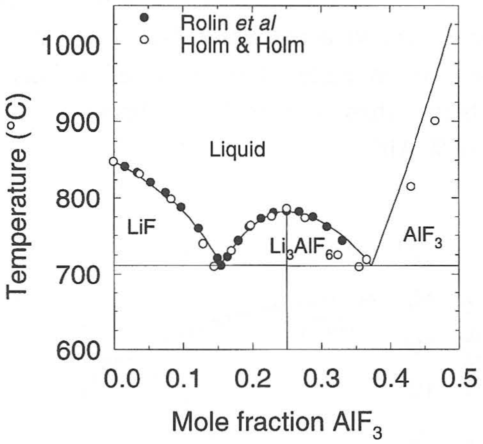

Figure 3: Comparison between model calculations (solid curves) and experimental data (symbols) from Holm and Holm,[17] and Rolin et al.[18], of the liquidus for the LiF-AlF_3 system.

Figure 4 compares the calculated activities of LiF(l) and AlF_3(s) with measured data from Dewing[19] at 800° C. There is a very good agreement between the calculated and the measured activity of LiF and AlF_3 in this system.

3.3 LiF-NaF system

The LiF-NaF system forms a eutectic with limited solid solubility of LiF in NaF. The eutectic point occurs at 649 °C and 0.61 mole fraction LiF. The maximum solubility of LiF in solid NaF is 0.08 mole fraction at the eutectic temperature[17].

The calculated phase diagram using the cell model (for liquid) and compound energy model (for solid) is shown in Figure 5 in comparison with measured literature data from Holm and Holm[17]. Clearly there is a very good agreement between the calculated and the measured phase diagram.

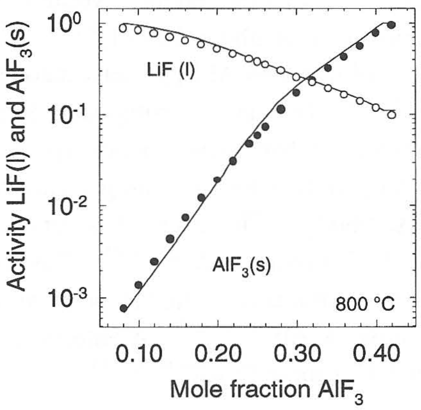

Figure 4: Calculated (curves) and measured activities (symbols) of LiF(l) and AlF_3(s) at 800°C. Experimental data was obtained from Dewing[19].

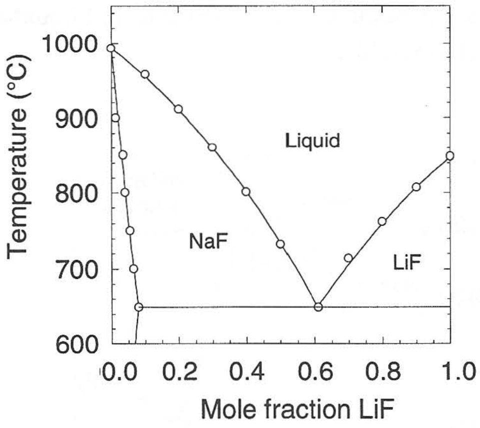

Figure 5: Comparison between model calculations (solid curves) and experimental data (symbols) for the LiF-NaF system. Experimental data was obtained from Holm and Holm[17].

3.4 Liquidus in the AlF_3-LiF-NaF ternary system

Some pseudo binary phase diagrams in the AlF_3-LiF-NaF ternary system have been calculated using optimised cell parameters from the binary sub-systems. For these systems the stability of the solid phase affects the position of the liquidus boundary. The relative stability of the cryolite solid phase (solid solution between Na_3AlF_6 and Li_3AlF_6) can be adjusted through the compound energy model parameters. Saboungi et al.[20] indicated that Na_3AlF_6 and Li_3AlF_6 formed a regular solid solution. They calculated a regular solution parameter of 33.89 kJ/mol. In the present work regular solution behaviour in the solid phase was also assumed to occur between Na and Li cations on their sub-lattice. However, a parameter of 40 kJ/mol was required in order to obtain a satisfactory fit to the liquidus in the ternary system.

Figures 6 to 8 show a comparison between calculated liquidus boundary and measured data for the Na_3AlF_6-Li_3AlF_6 system, the Na_3AlF_6-LiF system and the Na_3AlF_6-5wt% LiF-AlF_3 system respectively. All three calculated pseudo binary systems show satisfactory agreement with literature data.

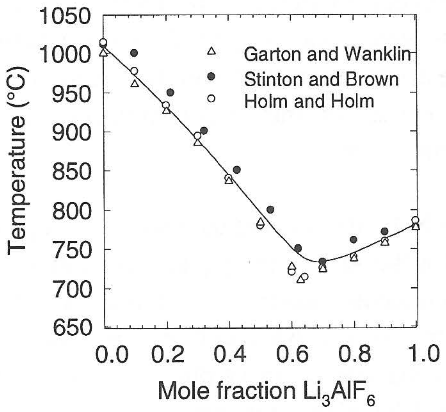

Figure 6:Comparision between calculated (solid line) and literature data (symbols), from Garton and Wanklin[21], Stinton and Brown[22] and Holm and Holm[23], of the liquidus for the Na_3AlF_6-Li_3AlF_6 pseudo binary system.

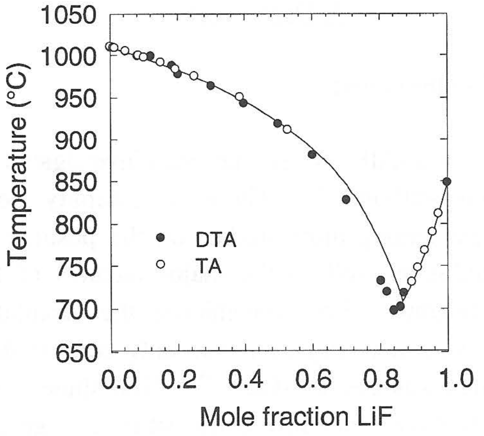

Figure 7: Comparison between calculated (solid lines) and literature data (symbols) from Holm and Holm[17], of the liquidus for the Na_3AlF_6-LiF pseudo binary system. The literature data are from both differential thermal analysis (DTA) and thermal analysis(TA) techniques.

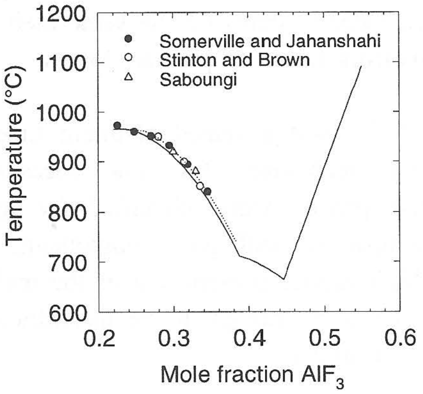

Figure 8:Comparison between calculated (solid lines) and literature data (symbols) of the liquidus boundary for the Na_3AlF_6-5Wt % LiF-AlF_3 pseudo binary system. The literature data were obtained from Stinton and Brown[24], Saboungi[20] and Somerville and Jahanshahi[25]. Also shown are predicted liquidus boundary from the linear correlation of Rostum et al. [26](dashed line).

4. Discussion

4.1 NaF-AlF_3 system

The NaF-AlF_3 system has been investigated by numerous authors[8-15]. There is generally good agreement among most studies on the position of the liquidus as well as the major features of the phase diagram. For convenience the calculated liquidus shown in Figure 1 was only compared to only three sources of data[13-15]. The three were chosen to cover the entire compositional range and also to represent data obtained using a variety of experimental techniques.

Phillips et al.[13] used a cooling curve method for the determination. A crucible of slowly cooled melt was carefully watched and the temperature where crystals first appeared was noted. This point corresponded to a break in the cooling curve of the melt and represented the liquidus temperature. Repeated measurements on the same melt showed minimal errors due to evaporative losses.

Foster[15] used a sealed platinum tube and a quenching technique for his measurements. Quenched phases were identified by refractive index comparison with pure components. Errors due to high vapour pressures over the melt in the sealed tube were thought to be insignificant (less than 0.03 °C/atm.).

The close agreement between the results of these two studies shown in Figure 1, and also with Rolin et al.[14] indicated the precision of the results. To date no direct comparison with the results of Phillips et al. in the AlF_3 primary phase field has been found. The visual inspection method used by Phillips et al. may experience increased evaporation losses of AlF_3 for melts with compositions high in AlF_3. Hence there may be an overestimation of the AlF_3 content of the melt especially near AlF_3 saturation.

4.2 LiF-AlF_3 system

Only two sources of liquidus data on the LiF-AlF_3 have been found. Holm and Holm[17] used a combination of DTA and TA techniques. For DTA measurements samples were held in a platinum crucible which was inserted inside a nickel container with a lid. It is not clear what precautions were made to minimise evaporative loss of AlF_3 from the melt surface. Some DTA measurements were made on a heating cycle. This practice may add some error to the measurements due to segregation and uneven composition of the starting material. DTA techniques were mainly used for melts in the Li_3AlF_6 and AlF_3 primary fields. TA techniques were used for melts in the LiF and Li_3AlF_6 phase field.

Figure 3 shows close agreement between the results of Rolin and Rey[14] and Holm and Holm[17] over the LiF and Li_3AlF_6 phase fields up to the lithium cryolite composition. After the cryolite composition, the points from Holm and Holm's results show some spread and generally lower results compared to Rolin. The measurement for these points were made using DTA during a heating cycle. The errors associated with this technique are the likely cause for this underestimation of the liquidus temperature.

In the NaF-AlF_3 system the calculated liquidus boundary for the AlF_3 primary phase coincides with the measurements made by Phillips et al.[13]. However in the LiF-AlF_3 system the calculated liquidus for the AlF_3 primary phase over estimates the measured liquidus temperature for a given AlF_3 content. This is despite using consistent free energy of fusion data for AlF_3. However a compromise may be made to better reproduce the AlF_3 saturation in the choice of the fusion data. This difference could also be due to the loss of AlF_3 from the melt surface during the DTA measurements of Holm and Holm. Hence the AlF_3 content of the melt may be over estimated. The calculation was therefore considered to be within the experimental uncertainty.

4.3 Liquidus lines in the ternary NaF-AlF_3-LiF system

The selection of the regular solution parameter for the Na_3AlF_6-Li_3AlF_6 solid solution (40 kJ/mol) represents a compromise between the Na_3AlF_6-Li_3AlF_6 and the Na_3AlF_6-LiF systems on one hand (Figures 6 and 7) and the Na_3AlF_6-5 wt % LiF-AlF_3 system (Figure 8) on the other hand. A better fit would be possible for the Na_3AlF_6-Li_3AlF_6 and the Na_3AlF_6-LiF systems if a slightly higher parameter was used. Also a better fit would be possible for the Na_3AlF_6-5 wt % LiF-AlF_3 system if a slightly lower parameter was used. Therefore for the two systems involving increasing LiF contents there is a increased positive departure from ideality. This indicates that at increasing Li_3AlF_6 (or LiF) content in the melt there is an increasing tendency for the species to repel each other.

4.4 Free energy of mixing

The primary information produced by the cell model is the free energy of mixing. Additional thermodynamic information such as activities of species and liquidus boundaries are derived from the free energy of mixing curves. The close agreement between the literature data and calculated phase diagrams illustrated in Figures 1, 3 and 5 suggest the free energy of mixing calculated by the cell model was reasonable close to reality for the binary systems investigated.

A comparison between the calculated free energy of mixing for the two binary systems NaF(l)-AlF_3(l) and LiF(l)-AlF_3(l) is shown in Figure 9. The NaF-AlF_3 system shows lower free energy of mixing compared with the LiF-AlF_3 system. This indicates stronger interactions between the NaF and AlF_3 species in the melt compared to LiF-AlF_3 interactions.

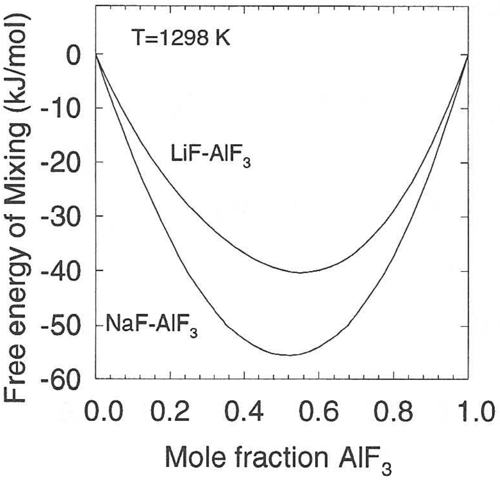

Figure 9: Calculated free energy of mixing for the systems NaF(l)-AlF_3(l) and LiF(l)-AlF_3(l) at 1298 K.

4.5 Entropy and enthalpy of mixing

Figure 10 shows the calculated entropy of mixing for the systems NaF(l)-AlF_3(l) and LiF(l)-AlF_3(l). Both systems show a M shaped curve for the entropy of mixing with a minimum at the cryolite composition (25 mole % AlF_3). This minimun shows there is an ordering of components in the melt and indicates a departure from ideal behaviour.

Figure 11 shows a comparison between the calculated and the ideal entropy of mixing in the NaF(l)-LiF(l) system. The entropy of mixing for the NaF(l)-LiF(l) system shows behaviour very close to being ideal. The ideal entropy is slightly higher at the maximum position.

Enthalpy of mixing for both the NaF-AlF_3 and LiF-AlF_3 systems was derived for the liquid phase using the cell model. Compared to literature data, good agreement was obtained for low AlF_3 regions. Significant and gradually increasing deviation was observed for AlF_3 mole fractions above 0.25. The cause of these observed deviations will be determined in future work.

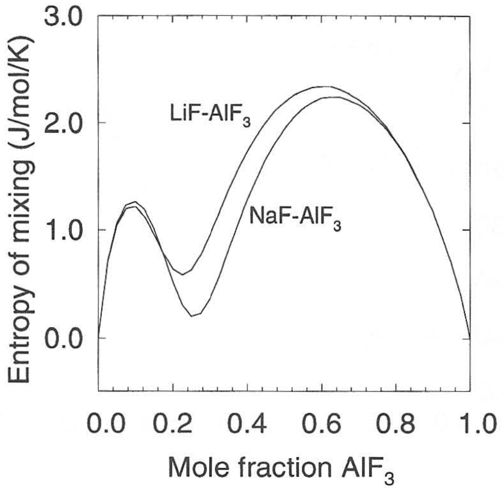

Figure 10:Calculated entropy of mixing for the systems NaF(l)-AlF_3(l) and LiF(l)-AlF_3(l) at 1298 K.

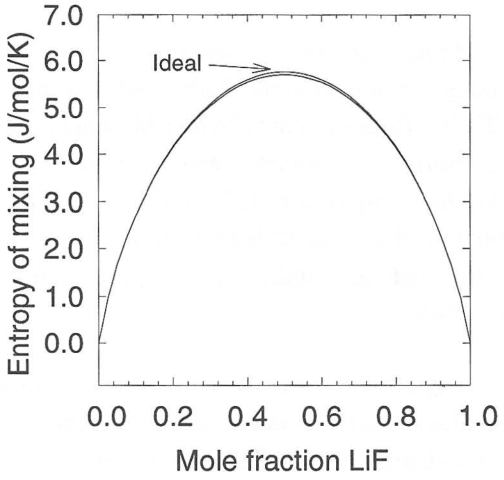

Figure 11:Calculated entropy of mixing for the system LiF(l)-NaF(l) at 1298 K, compared to ideal entropy of mixing.

5. CONCLUSIONS

The cell model is able to reproduce the phase diagram and activities of species in the three binary systems NaF-AlF_3, LiF-AlF_3 and LiF-NaF. The model is also able to calculate liquidus boundaries in the ternary system NaF-LiF-AlF_3 using optimised binary model parameters and a regular solution model for the solid phase.

The calculated free energy of mixing curves show stronger interactions between NaF-AlF_3 than between LiF-AlF_3 species. The calculated entropy of mixing for the LiF-NaF system shows close to ideal behaviour.

FUTURE WORK

The present work represents the first stage in the planned thermodynamic work. In future work the mixing of fluoride and oxide species will be examined when alumina is introduced into the AlF_3-NaF-LiF system.

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