Thermochimica Acta 366 (2001) 79–87

thermochimica acta

www.elsevier.com/locate/tca

Phase diagram of the system Na_3AlF_6–NaF–Na_2SO_4

V. Danielik*, J. Gabová

Department of Inorganic Technology, Faculty of Chemical Technology, Slovak University of Technology,
SK-812 37 Bratislava, Slovak Republic

Received 29 March 2000; received in revised form 1 July 2000; accepted 4 September 2000

Abstract

In the phase diagram of the system NaF–Na_2SO_4, a binary compound Na_3FSO_4 exists. The compound allows to divide the ternary system Na_3AlF_6–NaF–Na_2SO_4 into the two subsystems Na_3AlF_6–NaF–Na_3FSO_4 and Na_3AlF_6–Na_2SO_4–Na_3FSO_4. Experimental coordinates of the eutectic point in the subsystem Na_3AlF_6–NaF–Na_3FSO_4 are: 7.6 mole%Na_3AlF_6 + 54.6 mole% NaF + 37.8 mole% Na_2SO_4, 761°C. Experimental coordinates of the eutectic point in the subsystem Na_3AlF_6–Na_2SO_4–Na_3FSO_4 are: 4.6 mole% Na_3AlF_6 + 26.3 mole% NaF + 69.1 mole% Na_2SO_4, 733°C.

Thermodynamic model for calculation of the system Na_3AlF_6–NaF–Na_2SO_4 is presented. The thermodynamic model describes well all available thermodynamic data of the system, viz. enthalpies of mixing and solid–liquid phase equilibria.

Keywords: Cryolite; Fluoride; Phase diagram; Ternary system; Solid–liquid equilibria

1. Introduction

Sodium sulphate is often present in small amounts in the cryolite-based electrolytes used for electrowinning of aluminium. The behavior of the sulfates in the electrolyte is not well understood [1]. Investigation of thermodynamic properties of systems containing both $AlF_6{}^{3-}$ and $SO_4{}^{2-}$ ions may help to clarify this problem. From this point of view, calculation of the phase diagram for the system Na_3AlF_6–NaF–Na_2SO_4 is interesting because it contains two congruently melting compounds, viz. Na_3AlF_6 and Na_3FSO_4.

In the system NaF–Na_2SO_4, the congruently melting compound Na_3FSO_4 exists [2]. Thus, the phase diagram Na_3AlF_6–NaF–Na_2SO_4 can be divided into the two subsystems Na_3AlF_6–NaF–Na_3FSO_4 and Na_3AlF_6–Na_2SO_4–Na_3FSO_4.

The subsystem Na_3AlF_6–NaF–Na_3FSO_4 has been investigated by Fellner et al. [3]. The cited authors calculated the phase diagram of the system assuming a partial thermal dissociation of the compounds Na_3AlF_6 and Na_3FSO_4 during melting. However, the agreement between the experimental and calculated phase diagram was unsatisfactory.

Results on the subsystem Na_3AlF_6–Na_2SO_4–Na_3FSO_4 have been published previously [4]. The authors calculated the phase diagram of the system using the same assumptions as in [3]. Agreement between experimental and calculated phase diagram was also unsatisfactory.

When the two experimental subsystems had been joined to the system Na_3AlF_6–NaF–Na_2SO_4 by transformation of composition coordinates, the obtained crystallization area of Na_3FSO_4 seems to be unlikely.

---

[*] Corresponding author. Fax: +421-7-52950171.
E-mail address: danielik@chtf.stuba.sk (V. Danielik).

PII: S0040-6031(00)00709-7

In this paper, we will present new data in the crystallization field of Na_3FSO_4 (20–65 mole% NaF; 0–20 mole% Na_3AlF_6 and 35–80 mole% Na_2SO_4) in order to clarify these discrepancies. A thermodynamic model is proposed which describes well the experimental phase diagram data.

2. Experimental

The temperatures of individual phase transitions (primary, secondary and eutectic crystallization) were determined by thermal analysis. Cooling runs of the mixtures under investigation were carried out at a rate of 1.2–2 K min^{-1}. The temperature was measured by a PtRh10–Pt thermocouple and its thermoelectric voltage was recorded at 2.5 s intervals and registered by a computer. The thermocouple was calibrated against reference melting temperatures of pure salts. The reproducibility in determination of equilibrium temperatures was about 2 K. Experimental details can be found in [5].

3. Thermodynamic model

Thermodynamic models of systems containing complex compounds are usually based on the assumptions of a partial dissociation of these compounds [2]. However, the structure of cryolite-based melts is not reliably known [6]. In the case of addition the compound Na_3FSO_4 the anion $FSO_4{}^{3-}$ does not exist in solid state [7]. Hence, it probably does not exist in the liquid state either. The model presented below is independent of the structure of the melt based on [8,9].

Let us consider the system AX–BX, in which a compound exists in the solid state, where m, n denote numbers of moles of AX and BX, respectively. In the model we assume that the compound $m\mathrm{AX}\cdot n\mathrm{BX}$ completely dissociates under melting to the species AX and BX.

It is convenient to change composition of the compound $m\mathrm{AX}\cdot n\mathrm{BX}$ into compound $(\mathrm{AX})_p\cdot(\mathrm{BX})_q$ where

$$p=\frac{m}{m+n},\qquad q=\frac{n}{m+n} \tag{1}$$

It is obvious that $p+q=1$. Thus, by melting 1 mole of the compound $(\mathrm{AX})_p\cdot(\mathrm{BX})_q$, which completely dissociates to AX and BX, we will get 1 mole of the melt containing species AX and BX.The molar enthalpy of fusion of $(\mathrm{AX})_p\cdot(\mathrm{BX})_q$ equals to

$$\Delta_{\mathrm{fus}}H^0_{\mathrm{m}}[(\mathrm{AX})_p\cdot(\mathrm{BX})_q]=\frac{\Delta_{\mathrm{fus}}H^0_{\mathrm{m}}(m\mathrm{AX}\cdot n\mathrm{BX})}{m+n} \tag{2}$$

The activities of AX and BX are (standard state corresponds to pure component at the temperature and pressure of the melt)

$$a(\mathrm{AX})=x(\mathrm{AX})\cdot\gamma(\mathrm{AX}),\qquad a(\mathrm{BX})=x(\mathrm{BX})\cdot\gamma(\mathrm{BX}) \tag{3}$$

Activity coefficients of AX and BX could be obtained from the molar excess Gibbs energy:

$$RT\ln\gamma_i=\left[\frac{\partial\left(\sum n_i\Delta G^{\mathrm{E}}_i\right)}{\partial n_i}\right]_{T,p,n_{j\neq i}} \tag{4}$$

We may choose a new standard state in order to calculate hypothetic activity of $(\mathrm{AX})_p\cdot(\mathrm{BX})_q$. The new standard state means the melt with the composition of the pure compound $(\mathrm{AX})_p\cdot(\mathrm{BX})_q$ at the temperature and the pressure of the melt.

Formally, the compound $(\mathrm{AX})_p\cdot(\mathrm{BX})_q$ divides the system AX–BX into two subsystems AX–$(\mathrm{AX})_p\cdot(\mathrm{BX})_q$ and $(\mathrm{AX})_p\cdot(\mathrm{BX})_q$–BX. Then the molar Gibbs energy of a subsystem ΔG^*_{m} [i.e. AX–$(\mathrm{AX})_p\cdot(\mathrm{BX})_q$] is

$$\Delta G^*_{\mathrm{m}}=\Delta G_{\mathrm{m}}-(1-x^*_i)\Delta G^0_{\mathrm{m}} \tag{5}$$

where ΔG_{m} denotes the molar Gibbs energy of the system AX–BX; x^*_i is mole fraction of a component "i" in the subsystem [i.e. mole fraction AX in the subsystem AX–$(\mathrm{AX})_p\cdot(\mathrm{BX})_q$]; ΔG^0_{m} denotes the value of the molar Gibbs energy of the system AX–BX at the composition of the pure compound $(\mathrm{AX})_p\cdot(\mathrm{BX})_q$.

When we assume that the chemical potential of the compound $(\mathrm{AX})_p\cdot(\mathrm{BX})_q$ corresponding to its standard state is

$$\mu[(\mathrm{AX})_p\cdot(\mathrm{BX})_q]=p\mu(\mathrm{AX})+q\mu(\mathrm{BX}) \tag{6}$$

then for the activity of $(\mathrm{AX})_p\cdot(\mathrm{BX})_q$ it holds

$$\begin{aligned}a[(\mathrm{AX})_p(\mathrm{BX})_q]&=x[(\mathrm{AX})_p(\mathrm{BX})_q]\cdot\gamma[(\mathrm{AX})_p(\mathrm{BX})_q]\\&=\frac{x(\mathrm{AX})^p\cdot x(\mathrm{BX})^q}{x(\mathrm{AX})^p_0\cdot x(\mathrm{BX})^q_0}\\&\quad\times\frac{\gamma(\mathrm{AX})^p\cdot\gamma(\mathrm{BX})^q}{\gamma(\mathrm{AX})^p_0\cdot\gamma(\mathrm{BX})^q_0}\end{aligned} \tag{7}$$

where $x(i)_0$ and $\gamma(i)_0$ are the mole fractions and activity coefficients of AX and BX in the melt with the composition of the pure compound $(AX)_p \cdot (BX)_q$, respectively.

In the binary system the composition dependence of the molar excess Gibbs energy can be described by

$$\Delta G_\mathrm{m}^\mathrm{E} = x_1 x_2 (g_0 + g_1 x_2 + g_2 x_2^2 + g_3 x_2^3) \tag{8}$$

When the data on the enthalpy of mixing are available (which is the case of the systems NaF–Na_2SO_4, Na_3AlF_6–NaF), we can express the molar excess Gibbs energy from the classical relationship

$$\Delta G_\mathrm{m}^\mathrm{E} = \Delta H_\mathrm{m,mix} - T\,\Delta S_\mathrm{m}^\mathrm{E} \tag{9}$$

where $\Delta H_\mathrm{m,mix}$ and $\Delta S_\mathrm{m}^\mathrm{E}$ were assumed to be independent on temperature and may be described by equations

$$\Delta H_\mathrm{m,mix} = x_1 x_2 (h_0 + h_1 x_2 + h_2 x_2^2 + h_3 x_2^3) \tag{10}$$

$$\Delta S_\mathrm{m}^\mathrm{E} = x_1 x_2 (s_0 + s_1 x_2 + s_2 x_2^2 + s_3 x_2^3) \tag{11}$$

In the Eqs. (9)–(12) g_i, h_i, s_i are the polynomial parameters.

In the case of the ternary system the molar excess Gibbs energy of the system can be described by the relationship

$$\Delta G_\mathrm{m}^\mathrm{E} = \sum \Delta G_\mathrm{m,binary}^\mathrm{E} + \sum g_{ijk} x_1^i x_2^j x_3^k \tag{12}$$

where i, j, k are integer values.

4. Results and discussion

New experimental data were obtained in the concentration range 2–10 mole% Na_3AlF_6; 23–61 mole% NaF and 31–73 mole% Na_2SO_4. The experimental results are summarized in Table 1. The coordinates of eutectic points were determined as follows: 4.6 mole% Na_3AlF_6 + 26.3 mole% NaF+ 69.1 mole% Na_2SO_4, 733°C and 7.6 mole% Na_3AlF_6 +54.6 mole% NaF + 37.8 mole% Na_2SO_4, 761°C.

According to Fellner et al. [3] there are solid solutions of Na_2SO_4 in Na_3AlF_6 up to 80 mole% Na_2SO_4 in the binary system Na_3AlF_6–Na_2SO_4 [3]. In the composition range mentioned above no solid solutions were determined.

Phase diagram of the system Na_3AlF_6–NaF–Na_2SO_4 was calculated using the thermodynamic model described above. Molar enthalpies and temperatures of fusion of pure components used in the calculation are listed in Table 2. The model is based on the following assumptions and approximations:

1. In the first step the composition co-ordinates of the system NaF–Na_3AlF_6 are transformed to the system NaF–$NaAlF_4$. This transformation does not reflect the real ionic composition of the melt, but it is suitable to describe the thermodynamic properties. Therefore, the calculated ternary system is NaF–$NaAlF_4$–Na_2SO_4.
2. The excess Gibbs energy (J mol^{-1}) of the system NaF–$NaAlF_4$ is expressed by the equation

   $$\Delta G_\mathrm{m}^\mathrm{E} = x(\mathrm{NaF})x(\mathrm{NaAlF_4})\,\{a_0 + a_1 x(\mathrm{NaAlF_4}) + a_2[x(\mathrm{NaAlF_4})]^2 + a_3[x(\mathrm{NaAlF_4})]^3\}$$

   The parameters of the above equation were determined by a non-linear regression analysis (the criterion of the least squares, confidence level 99%) using the available experimental data for the content of sodium in aluminium in contact with cryolite-based melt [10–14], the vapour pressure of $NaAlF_4$ [15] and the solid–liquid equilibrium of NaF with the melt [16]. For the molar enthalpy of mixing of the system NaF–$NaAlF_4$ the data by Holm [17] and by Hong and Kleppa [18] were used. Model parameters of the molar excess Gibbs energy of the system NaF–$NaAlF_4$ are listed in Table 3.

   Calculated and experimental data on the phase diagram and molar enthalpy of mixing of the system NaF–$NaAlF_4$ are compared in Figs. 1 and 2. It can be seen that agreement between experimental and calculated data is good.
3. The excess Gibbs energy (J mol^{-1}) of the system NaF–Na_2SO_4 is expressed by the equation:

   $$\Delta G_\mathrm{m}^\mathrm{E} = x(\mathrm{NaF})x(\mathrm{Na_2SO_4})\{b_0 + b_1 x(\mathrm{Na_2SO_4}) + b_2[x(\mathrm{Na_2SO_4})]^2 + b_3[x(\mathrm{Na_2SO_4})]^3\}$$

   For the molar enthalpy of mixing of the system NaF–Na_2SO_4, experimental data has been published by Hatem and Gaune-Escard [19]. Kleppa and Julsrud [20] were reported their data in the form of an equation. However, the published data

Table 1
Experimental temperatures of the primary crystallization ($t_{pc,exp}$), of the secondary crystallization ($t_{sc,exp}$), and the eutectic temperatures ($t_{e,exp}$) in the system Na_3AlF_6–NaF–Na_2SO_4[a]

$x(Na_3AlF_6)$	x(NaF)	$x(Na_2SO_4)$	$t_{pc,exp}$ (°C)	$t_{sc,exp}$ (°C)	$t_{e,exp}$ (°C)	Equilibrium solid phase
0.020	0.245	0.735	741	–	733	Na_2SO_4
0.040	0.240	0.720	735	–	–	Na_2SO_4
0.060	0.235	0.705	768	746	733	Na_3AlF_6
0.020	0.294	0.686	752	741	733	Na_3FSO_4
0.040	0.288	0.672	755	–	733	Na_3FSO_4
0.060	0.282	0.658	769	743	733	Na_3AlF_6
0.020	0.343	0.637	763	753	732	Na_3FSO_4
0.040	0.336	0.624	758	752	734	Na_3FSO_4
0.060	0.329	0.611	755	–	733	Na_3AlF_6
0.080	0.322	0.598	798	752	734	Na_3AlF_6
0.040	0.384	0.576	769	758	734	Na_3FSO_4
0.060	0.376	0.564	763	–	732	Na_3AlF_6
0.080	0.368	0.552	788	760	731	Na_3AlF_6
0.040	0.432	0.528	775	766	733	Na_3FSO_4
0.060	0.423	0.517	767	–	733	Na_3FSO_4
0.080	0.414	0.506	783	766	731	Na_3AlF_6
0.040	0.480	0.480	780	767	–	Na_3FSO_4
0.060	0.470	0.470	776	767	–	Na_3FSO_4
0.080	0.460	0.460	778	768	–	Na_3AlF_6
0.040	0.528	0.432	779	766	764	Na_3FSO_4
0.060	0.517	0.423	772	765	762	Na_3FSO_4
0.080	0.506	0.414	771	–	761	Na_3AlF_6
0.100	0.495	0.405	793	765	764	Na_3AlF_6
0.040	0.576	0.384	770	–	763	NaF
0.060	0.564	0.376	766	–	762	Na_3FSO_4
0.080	0.552	0.368	764	–	761	Na_3AlF_6
0.100	0.540	0.360	792	–	760	Na_3AlF_6
0.060	0.611	0.329	788	765	760	NaF
0.080	0.598	0.322	775	766	761	NaF
0.100	0.585	0.315	786	–	761	Na_3AlF_6

[a] In the last column the solid phase, which crystallizes first, is presented.

are in disagreement. Data on the molar enthalpy of mixing measured by high temperature calorimetry used by Kleppa and Julsrud [20] are considered more accurate than the data measured by drop calorimetry used by Hatem and Gaune Escard [19]. However, on the basis of data presented in this work it cannot be decided which experimental data should be preferred. Therefore, the parameters in the above equations were determined by a non-linear regression analysis (given above) for

Table 2
Enthalpies and temperatures of fusion of components used for the calculation

Component	ΔH_i^{fus} (kJ mol^{-1})	T_i^{fus} (K)	Reference
NaF	33137	1269	[21]
Na_3AlF_6	107280	1284	[1]
Na_2SO_4	23012	1157	[21]
Na_3FSO_4	69000	1060	[2]

Table 3
The parameters of the equation of molar excess Gibbs energy[a] of the system NaF–$NaAlF_4$

Parameter	Calculated value
a_0	$-(95.6 \pm 3.5) \times 10^3 + (43.97 \pm 0.72)T$
a_1	$-(249 \pm 25) \times 10^3 + (202.3 \pm 3.2)T$
a_2	$(659 \pm 56) \times 10^3 - (502.1 \pm 6.7)T$
a_3	$-(457 \pm 40) \times 10^3 + (347.9 \pm 5.0)T$

[a] Temperature is calculated in K.

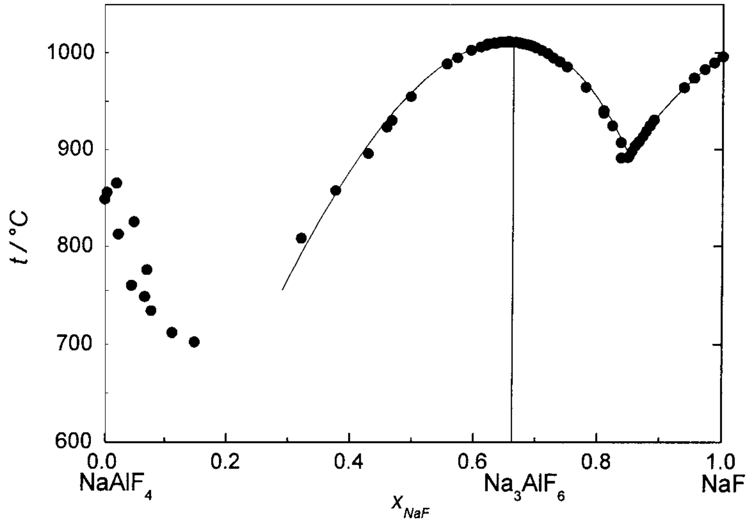

Fig. 1. Phase diagram of the system NaF–NaAlF$_4$: (●) data by Solheim and Sterten [16]; (—) calculated.

each set of data [19,20]. Evaluation of the molar excess entropy of the system NaF–Na$_2$SO$_4$ was conducted from the solidus–liquidus equilibrium data reported by Koštenská and Malinovský [2]. Model parameters of the molar excess Gibbs energy of the system NaF–Na$_2$SO$_4$ are listed in Table 4. Model A uses experimental enthalpy data published by Hatem and Gaune-Escard [19]; model B uses those from the equation reported by Kleppa and Julsrud [20].

The molar enthalpy of mixing and molar excess entropy of the system NaF–Na$_2$SO$_4$ is given in Fig. 3. It can be seen that even the mixing data by Hatem and Gaune-Escard [19] and Kleppa and Julsrud [20] are very different, the calculated curves of solidus–liquidus equilibria according to these data are almost identical (see Fig. 4). It follows that the calculation of phase diagram is not suitable for verification of the data on enthalpy of mixing.

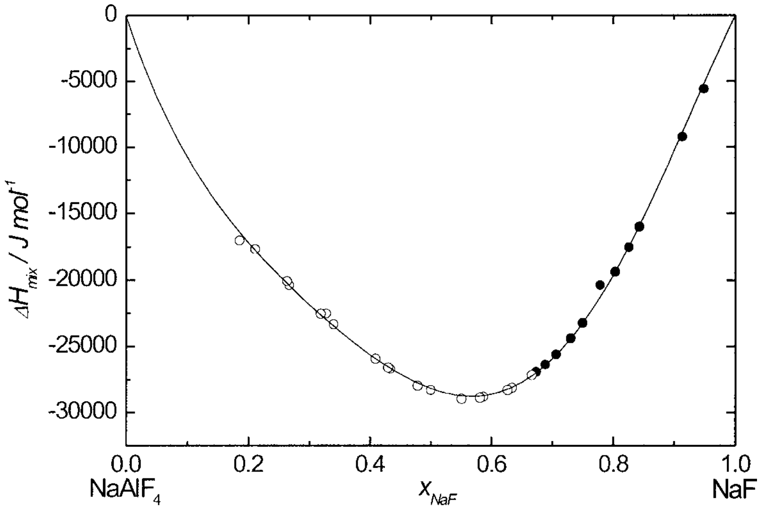

Fig. 2. Molar enthalpy of mixing of the system NaF–NaAlF$_4$: (○) data by Hong and Kleppa [18]; (●) data by Holm [17]; (—) calculated.

Table 4
The parameters of the equation of molar excess Gibbs energy[a] of the system NaF–Na_2SO_4 by using both models

Parameter	Model A	Model B
b_0	$(5720 \pm 120) - (11.66 \pm 0.39)T$	$-2375 - (6.02 \pm 0.64)T$
b_1	0	$619.4 - (-12.1 \pm 4.0)T$
b_2	0	$-(29.6 \pm 8.4)T$
b_3	$(-1450 \pm 540) + (3.94 \pm 0.54)T$	$-(21.9 \pm 5.6)T$

[a] Temperature is calculated in K.

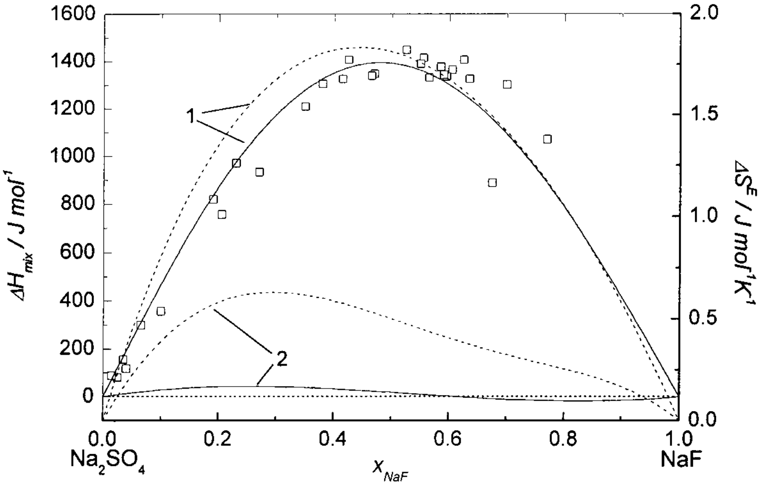

Fig. 3. Molar enthalpy of mixing and molar excess entropy of the system NaF–Na_2SO_4: (☐) data by Hatem and Gaune-Escard [19]; (—) (1), calculated molar enthalpy of mixing based on the paper by Hatem and Gaune-Escard [19]; (···) (1), calculated molar excess entropy based on the paper by Hatem and Gaune-Escard [19]; (—) (2), equation published by Kleppa and Julsrud [20]; (···) (2), calculated molar excess entropy based on the paper by Kleppa and Julsrud [20].

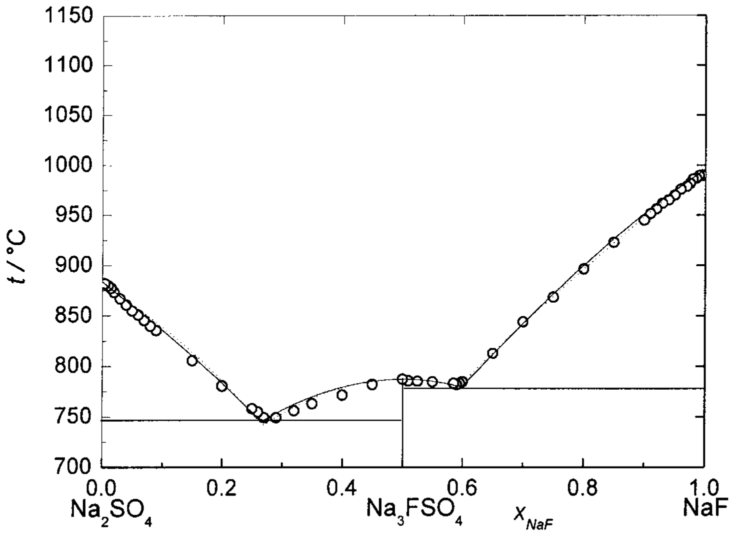

Fig. 4. Phase diagram of the system NaF–Na_2SO_4: (○) experimental data by Koštenská and Malinovský [2]; (—) calculated data based on the paper by Hatem and Gaune-Escard [19]; (···) calculated data based on the paper by Kleppa and Julsrud [20].

4. Molar excess Gibbs energy (J mol^{-1}) of the system NaF–$NaAlF_4$–Na_2SO_4 is expressed by the equation

$$\Delta G_{\mathrm{m}}^{\mathrm{E}} = \sum \Delta G_{\mathrm{m,binary}}^{\mathrm{E}} + d_1 x_1 x_2^2 x_3 + d_2 x_1 x_2^3 x_3^2 + d_3 x_1^2 x_2^2 x_3^2 + d_4 x_1^3 x_2 x_3 + d_5 x_1^3 x_2 x_3^2 + d_6 x_1^3 x_2^3 x_3^2$$

where x_1, x_2, x_3 are mole fractions of NaF, $NaAlF_4$ and Na_2SO_4, respectively.

The molar excess Gibbs energy (J mol^{-1}) of the system $NaAlF_4$–Na_2SO_4 had to be calculated from the ternary system since no data on the binary system were available. The model equation of molar excess Gibbs energy of this binary system was determined as

$$\Delta G_{\mathrm{m}}^{\mathrm{E}} = x(\mathrm{NaAlF_4})x(\mathrm{Na_2SO_4})\{c_0 + c_2[x(\mathrm{Na_2SO_4})]^2 + c_3[x(\mathrm{Na_2SO_4})]^3\}$$

The parameters of above equations were determined by a non-linear regression analysis (given above) using experimental data on solidus–liquidus equilibria of the system Na_3AlF_6–NaF–Na_2SO_4 ([3,4], this work) which were transformated to the system NaF–$NaAlF_4$–Na_2SO_4. The parameters of the above equations and probable inaccuracy of the system NaF–$NaAlF_4$–Na_2SO_4 are listed in Table 5 for both models. It can be seen that the agreement between calculated and the experimental data from this work is better than the agreement between calculated and previously published data [3,4]. The crystallization area of Na_3FSO_4 seems to be unlikely according to the previously published experimental data [3,4].

Table 5
The parameters of the molar excess Gibbs energy[a] and probable inaccuracy of the system NaF–$NaAlF_4$–Na_2SO_4 for both models[b]

Parameter	Model A	Model B
c_0	$-(24.1 \pm 1.8) \times 10^3$	0
c_2	0	$(58 \pm 11) \times 10^3$
c_3	2950 ± 690	$-(78.6 \pm 7.8) \times 10^3$
d_1	$(157 \pm 20) \times 10^3$	0
d_2	0	$(5.81 \pm 0.21) \times 10^6$
d_3	0	$-(3.14 \pm 0.13) \times 10^6$
d_4	$-(173 \pm 11) \times 10^3$	0
d_5	0	$(275 \pm 19) \times 10^3$
d_6	$(2.86 \pm 0.30) \times 10^6$	0
σ_1 (°C)	11.6	13.7
σ_2 (°C)	6.7	7.4

[a] Temperature is calculated in K.

[b] σ_1 denotes the probable inaccuracy of the all experimental data on the ternary system ([3,4], this work); σ_2 denotes the probable inaccuracy of the data published in this work.

Comparison of the experimental and calculated data is shown in Figs. 5 and 6. Experimental and

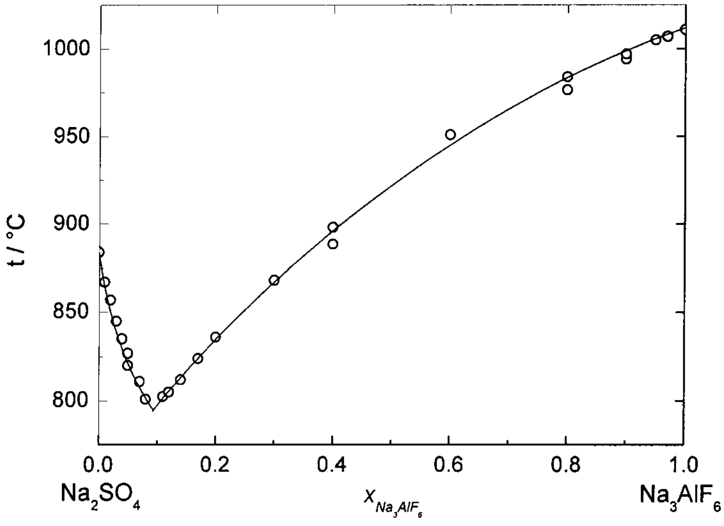

Fig. 5. Phase diagram of the system Na_3AlF_6–Na_2SO_4: (○) experimental [3]; (—) calculated (both models based on the papers by Hatem and Gaune-Escard [19] and Kleppa and Julsrud [20] give identical values).

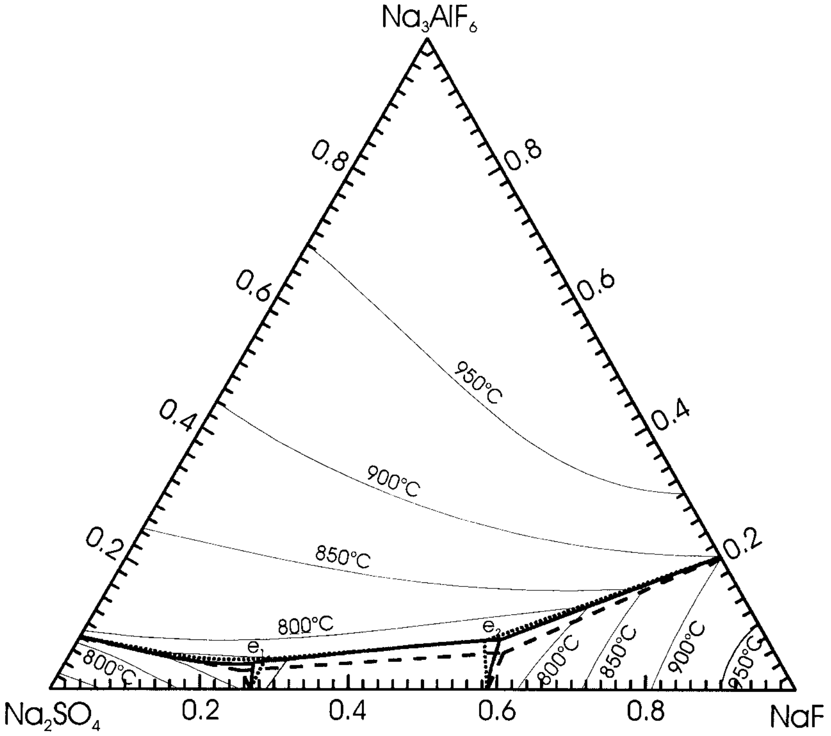

Fig. 6. Phase diagram of the system Na_3AlF_6–NaF–Na_2SO_4: (···) experimental (this work); (—) calculated curves based on the paper by Hatem and Gaune-Escard [19]; (- - -) calculated curves based on the paper by Kleppa and Julsrud [20]; isothermes are calculated according to the paper published by Hatem and Gaune-Escard [19].

Table 6
Experimental and calculated ternary eutectic points

	Experimental		Model A		Model B	
	e_1	e_2	e_1	e_2	e_1	e_2
x(Na_3AlF_6)	0.046	0.076	0.041	0.077	0.033	0.056
x(NaF)	0.263	0.546	0.251	0.565	0.236	0.578
x(Na_2SO_4)	0.691	0.378	0.708	0.358	0.731	0.366
t (°C)	733	761	729.8	756.6	737.5	777.3

calculated ternary eutectic points are listed in Table 6. It can be seen that the model using the molar enthalpy of mixing by Hatem and Gaune-Escard [19] describes experimental data better than the model using for the molar enthalpy of mixing the equation by Kleppa and Julsrud [20]. However, the difference between these two models is too small to allow to make any further conclusions. Both models describe all experimental data ([3,4], this work) on solid–liquid equilibria well within the range of experimental error.

Acknowledgements

This work was supported by the Research grant no. 1/6250/99 of the Slovak Grant Agency (VEGA 1/6250/99).

References

[1] K. Grjotheim, C. Krohn, M. Malinovský, K. Matiašovský, J. Thonstad, Aluminium Electrolysis — Fundamentals of the Hall — Héroult Process, 2nd Edition, Aluminium — Verlag, Düsseldorf, 1982.

[2] I. Koštenská, M. Malinovský, Chem. Zvesti 36 (1982) 159.

[3] P. Fellner, J. Gabová, V. Danielik, Thermochim. Acta 242 (1994) 243.

[4] P. Fellner, J. Gabová, V. Danielik, M. Láska, Chem. Papers 47 (1993) 215.

[5] P. Fellner, J. Gabová, Thermochim. Acta 206 (1992) 321.

[6] B. Gilbert, E. Robert, E. Tixhon, J.E. Olsen, T. Østvold, Inorg. Chem. 35 (1996) 4198.

[7] A. Pabst, Am. Mineral AMMIA 58 (1973) 116.

[8] T. Foosnes, T. Østvold, H. Øye, Acta Chem. Scand. A32 (1978) 973.

[9] W.Ch. Bale, A.D. Pelton, Met. Trans. B14 (1983) 77.

[10] W.H. Tingle, J. Petit, W.B. Frank, Aluminium 57 (1981) 286.

[11] R.D. Peterson, A.T. Tabereaux, Light Met. (1986) 491.

[12] V. Danielik, P. Fellner, Chem. Papers 52 (1998) 195.

[13] E.W. Dewing, M.J. Gilbert, Light Met. (1980) 221.

[14] P. Fellner, Ž. Lubyová, Chem. Papers 40 (1986) 145.

[15] J. Guzman, K. Grjotheim, T. Østvold, Light Met. (1986) 425.

[16] A. Solheim, Å. Sterten, in: Proceedings of the Ninth International Symposium On Light Metals Production, Tromsø–Trondheim, Norway, 19–21 August 1997, p. 225.

[17] J.L. Holm, Thermodynamic properties of molten cryolite and other fluoride mixtures, Thesis, Institute of Inorganic Chemistry, NTH, Trondheim, Norway, 1971.

[18] K.C. Hong, O.J. Kleppa, High Temp. Sci. 8 (1976) 299.

[19] G. Hatem, M. Gaune-Escard, J. Phys. Chem. 86 (1982) 3039.

[20] O.J. Kleppa, S. Julsrud, Acta Chem. Scand. A34 (1980) 655.

[21] D.R. Stull, H. Prophet, JANAF Thermochemical Tables, 2nd Edition, Nat. Bur. Stand. (USA), Coden NSRDA, 1971.