

# Two Approaches to the Calculation of the Phase Diagrams Containing Congruently Melting Compounds Systems NaF—Na<sub>2</sub>SO<sub>4</sub> and NaF—NaAlF<sub>4</sub>

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Phase diagrams of the systems NaF—Na<sub>2</sub>SO<sub>4</sub> and NaF—NaAlF<sub>4</sub> (the systems containing compounds Na<sub>3</sub>FSO<sub>4</sub> and/or Na<sub>3</sub>AlF<sub>6</sub>) were calculated using two different assumptions: i) The congruently melting compound (Na<sub>3</sub>FSO<sub>4</sub> or Na<sub>3</sub>AlF<sub>6</sub>) completely dissociates. ii) The compound dissociates only partially. It is shown that both models are formal and as far as solidus—liquidus equilibria are concerned they yield approximately the same results. The model based on partial dissociation of the complex compound assuming the ideal behaviour of liquid phase is improper for description of the thermodynamic behaviour of the system.

In this work the calculations of some properties of molten salt systems NaF—Na<sub>2</sub>SO<sub>4</sub> and NaF—NaAlF<sub>4</sub> are presented. The agreement between experimental data and calculated phase diagrams will be discussed.

Phase diagrams of the discussed systems have been presented in papers [1–5]. From Figs. 1 and 4 it can be seen that the systems NaF—Na<sub>2</sub>SO<sub>4</sub> and NaF—NaAlF<sub>4</sub> contain congruently melting compounds Na<sub>3</sub>FSO<sub>4</sub> and Na<sub>3</sub>AlF<sub>6</sub>, respectively. There is no doubt about the existence of the anion AlF<sub>6</sub><sup>3-</sup> [6]. However, as it follows from the structure of the compound Na<sub>3</sub>FSO<sub>4</sub> [7] the anion FSO<sub>4</sub><sup>3-</sup> does not exist in solid state. Regardless of that the phase diagrams of the systems NaF—Na<sub>2</sub>SO<sub>4</sub> and NaF—AlF<sub>3</sub> resemble each other because both systems contain a congruently melting compound.

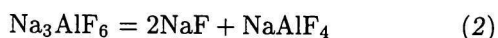
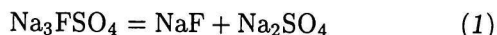
## THEORETICAL

The calculations of the phase diagrams of both systems were realized under two different assumptions:

i) The congruently melting compound completely dissociates (the degree of dissociation  $b = 1$ ).

ii) The compound dissociates only partially ( $b < 1$ ).

The basic principles of both approaches are described in the papers [8, 9]. In this work we will assume that the compounds dissociate according to the schemes (1) and (2)



## The Model Based on a Partial Dissociation of the Compound

This model was described in numerous papers in literature. It has been applied to the system NaF—Na<sub>2</sub>SO<sub>4</sub> in the work [9]. The model assumes that the anion partly dissociates under melting. Thus the melt contains both nondissociated compound  $m\text{AX} \cdot n\text{BX}$  and the products of dissociation AX and BX. For example, in the case of the system NaF—Na<sub>2</sub>SO<sub>4</sub> it holds [9]



$$K = 1.123 = \frac{y(\text{NaF}) \cdot y(\text{Na}_2\text{SO}_4)}{y(\text{Na}_3\text{FSO}_4)} \quad (4)$$

where  $y$  denotes the equilibrium mole fraction of the species in the melt after dissociation.

The equilibrium temperature of primary crystallization can be calculated according to the Le Chatelier—Shreder equation [10, 11]

$$\frac{d \ln a_i}{dT} = \frac{\Delta_{\text{fus}} H_i^\ominus}{RT^2} \quad (5)$$

where  $a_i$  is the activity of substance “i” and  $\Delta_{\text{fus}} H_i^\ominus$  is the enthalpy of fusion of pure substance “i”

## The Model Based on the Complete Dissociation of the Compound

Let us consider the system AX—BX, in which a compound  $m\text{AX} \cdot n\text{BX}$  exists in the solid state. According to [8] we may write  $(\text{AX})_p \cdot (\text{BX})_q$  where

$$p = \frac{m}{m+n}, \quad q = \frac{n}{m+n} \quad (6)$$

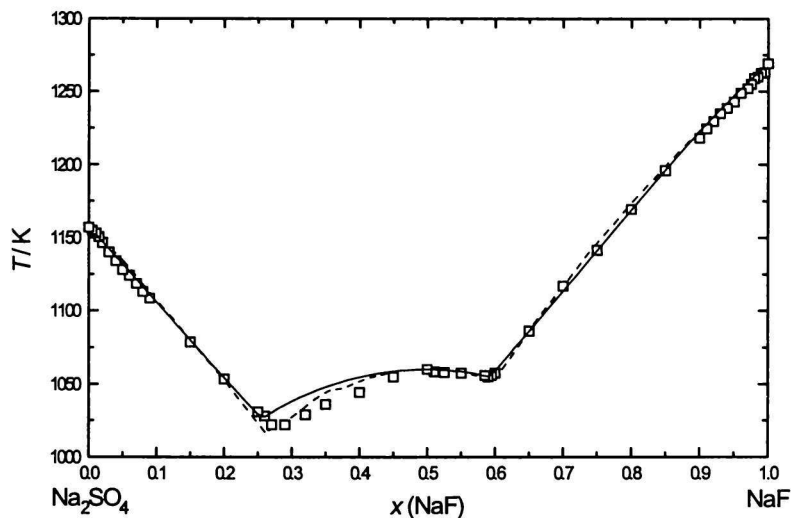


Fig. 1. Phase diagram of the system NaF—Na<sub>2</sub>SO<sub>4</sub> according to *Koštenská* and *Malinovský* [13] (□); model based on complete dissociation of the compound (—); model based on partial dissociation of the compound (---).

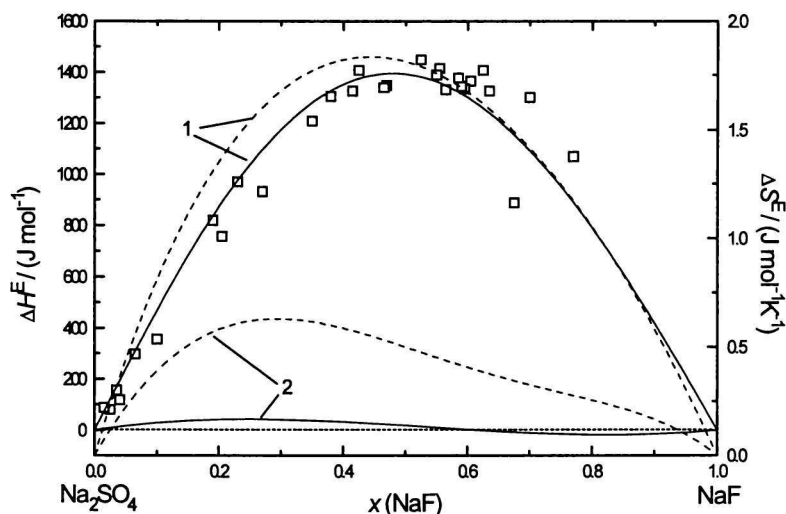


Fig. 2. Molar enthalpy of mixing of the system NaF—Na<sub>2</sub>SO<sub>4</sub> according to *Hatem* and *Gaune-Escard* [14] (□); calculated enthalpy of mixing (—) (based on paper by *Hatem* and *Gaune-Escard* [14] (1); on paper by *Kleppa* and *Julsrud* [15] (2)); excess entropy (---) (based on paper by *Hatem* and *Gaune-Escard* [14] (1); on paper by *Kleppa* and *Julsrud* [15] (2)).

and the enthalpy of fusion of (AX)<sub>p</sub>·(BX)<sub>q</sub> equals

$$a(\text{BX}) = x(\text{BX}) \cdot \gamma(\text{BX}) \quad (9)$$

$$\Delta_{\text{fus}} H^{\ominus}((\text{AX})_p \cdot (\text{BX})_q) = \frac{\Delta_{\text{fus}} H^{\ominus}(m\text{AX} \cdot n\text{BX})}{m+n} \quad (7)$$

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

The activity of (AX)<sub>p</sub>·(BX)<sub>q</sub> is

$$RT \ln \gamma(i) = \left[ \frac{\partial (\sum n_i G_i^{\text{E}})}{\partial n_i} \right]_{T,p,n_{j,i}} \quad (10)$$

$$a((\text{AX})_p \cdot (\text{BX})_q) =$$

$$= x((\text{AX})_p \cdot (\text{BX})_q) \cdot \gamma((\text{AX})_p \cdot (\text{BX})_q) \quad (8)$$

We may choose a new standard state at the temperature and the pressure of the system at the composition of the compound. Then it holds [8, 12]

and the activities of AX and BX are

$$G^* = G - G_0 \quad (11)$$

$$a(\text{AX}) = x(\text{AX}) \cdot \gamma(\text{AX}),$$

where  $G_0$  and  $G^*$  denote the molar Gibbs energy of the system at the composition of the compound and the

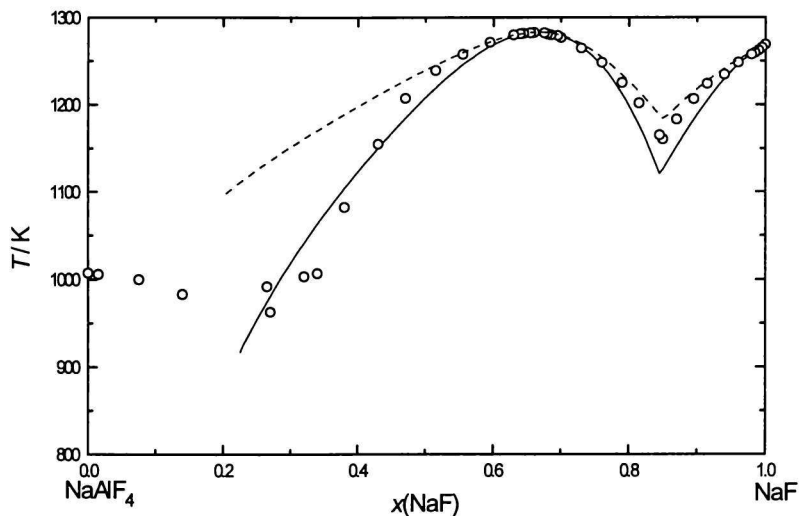


Fig. 3. Phase diagram of the system NaF—NaAlF<sub>4</sub> according to *Holm* [16] (O); model based on complete dissociation of the compound (—); model based on partial dissociation of the compound (---).

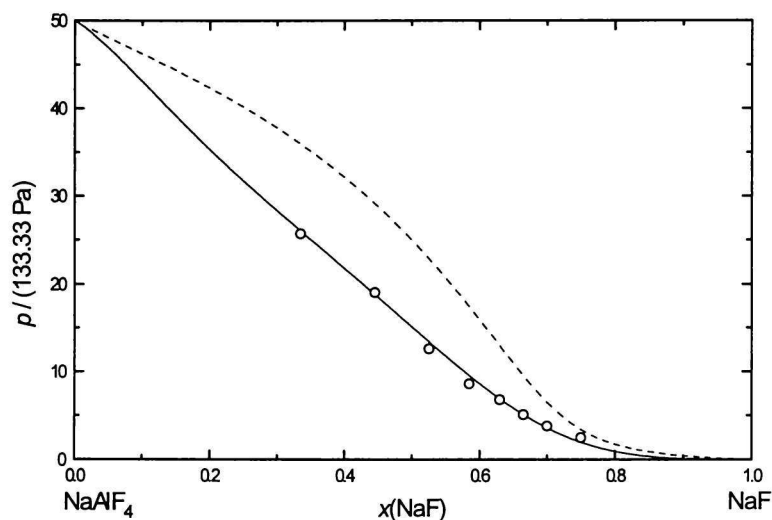


Fig. 4. Vapour pressure over the melt of the system NaF—NaAlF<sub>4</sub> according to *Guzman et al.* [17] (O); model based on complete dissociation of the compound (—); model based on partial dissociation of the compound (---).

molar Gibbs energy of the melt in the new standard state, respectively. Then for the activity of (AX)<sub>p</sub> · (BX)<sub>q</sub> it holds

$$\begin{aligned} a((AX)_p (BX)_q) &= \\ &= x((AX)_p (BX)_q) \cdot \gamma((AX)_p \cdot (BX)_q) \\ &= \frac{x(AX)^p \cdot x(BX)^q}{x(AX)_0^p \cdot x(BX)_0^q} \frac{\gamma(AX)^p \cdot \gamma(BX)^q}{\gamma(AX)_0^p \cdot \gamma(BX)_0^q} \end{aligned} \quad (12)$$

where  $x_{i,0}$  and  $\gamma_{i,0}$  are the mole fractions and activity coefficients of AX and BX at the composition of the compound, respectively.

For the description of the molar excess Gibbs energy of the system the following relationship was used

$$\Delta G^E = \Delta H^E - \Delta TS^E =$$

$$\begin{aligned} &= x_1 x_2 (h_0 + h_1 x_2 + h_2 x_2^2 + h_3 x_2^3) - \\ &- T x_1 x_2 (s_0 + s_1 x_2 + s_2 x_2^2 + s_3 x_2^3) \end{aligned} \quad (13)$$

$\Delta H^E$  and  $\Delta S^E$  were assumed to be independent of temperature.  $x_i$  is mole fraction of "i" and  $h_i$  and  $s_i$  for  $i = 1-4$  are empirical coefficients.

## CALCULATIONS

### The System NaF—Na<sub>2</sub>SO<sub>4</sub>

#### The Model Based on a Partial Dissociation of the Compound

The calculation is similar to that in the work [13]. The equilibrium constant of reaction (1) was assumed to be independent of temperature. The calculated

phase diagram is compared with experimental data in Fig. 1.

### The Model Based on Complete Dissociation of the Compound

The empirical coefficients of eqn (13) were determined on the basis of experimental data on the temperature of primary crystallization and the enthalpy of mixing using the simplex method. Criterion of the least-squares method was used. For the enthalpy of mixing we used the data by *Hatem* and *Gaune-Escard* [14] and by *Kleppa* and *Julsrud* [15], respectively. Even if the enthalpy of mixing in both cited papers is different, the calculated liquidus curves are almost identical.

From the data presented in paper [14] it follows

$$\begin{aligned} \Delta H^E = & x(\text{NaF}) \cdot x(\text{Na}_2\text{SO}_4) (4314 + \\ & + 3363 \cdot x(\text{Na}_2\text{SO}_4) - 562 \cdot x(\text{Na}_2\text{SO}_4)^2 - \\ & - 2311 \cdot x(\text{Na}_2\text{SO}_4)^3) \end{aligned} \quad (14)$$

$$\begin{aligned} \Delta S^E = & x(\text{NaF}) \cdot x(\text{Na}_2\text{SO}_4) \cdot (9.6 - \\ & - 6.4 \cdot x(\text{Na}_2\text{SO}_4) + 3.6 \cdot x(\text{Na}_2\text{SO}_4)^2 - \\ & - 0.4 \cdot x(\text{Na}_2\text{SO}_4)^3) \end{aligned} \quad (15)$$

From the data presented in paper [15] it follows

$$\begin{aligned} \Delta H^E = & x(\text{NaF}) \cdot x(\text{Na}_2\text{SO}_4) \cdot (-237.5 + \\ & + 619.4 \cdot x(\text{Na}_2\text{SO}_4)) \end{aligned} \quad (16)$$

$$\begin{aligned} \Delta S^E = & x(\text{NaF}) \cdot x(\text{Na}_2\text{SO}_4) \cdot (5.04 - \\ & - 7.21 \cdot x(\text{Na}_2\text{SO}_4) + 4.53 \cdot x(\text{Na}_2\text{SO}_4)^3) \end{aligned} \quad (17)$$

The calculated phase diagram is compared with experimental data in Fig. 1. The quantities  $\Delta H^E$  and  $\Delta S^E$  are plotted in Fig. 2.

From Fig. 1 it follows that also the model based on a partial dissociation of the compound describes the liquidus data well despite of the fact that it assumes ideal thermodynamic behaviour of the melt. This is not true because the mixing of components is not ideal (Fig. 2). This means that the deviations from ideality are hidden in the formal "equilibrium constant"

The model based on the complete dissociation of the compound describes the data on the temperature of primary crystallization as well as the enthalpy of mixing. Thus, in this case the deviations from ideality are included in the model.

### The System NaF—NaAlF<sub>4</sub>

Calculation procedure is similar to that described above. However, while in the former case any complex anions do not exist in the melt, in this case the existence of anion has been proved experimentally [6].

### The Model Based on a Partial Dissociation of the Compound

In this work we assumed the simplest dissociation scheme [13]



Comparison of the experimental and calculated temperatures of primary crystallization [16] is shown in Fig. 3. Comparison of the experimental [17] and calculated vapour pressure over the melt is shown in Fig. 4.

### The Model Based on the Complete Dissociation of the Compound

In this case we can introduce into the model the data on enthalpy of mixing [18, 19]. Coefficients of the excess Gibbs energy were obtained in a similar way as in the case of the system NaF—Na<sub>2</sub>SO<sub>4</sub>. In this case, however, also the vapour pressure data over the melt were taken into account.

The excess Gibbs energy was described by relationships

$$\begin{aligned} \Delta H^E = & x(\text{NaF}) \cdot x(\text{NaAlF}_4) \cdot (-104810 - \\ & - 195235 \cdot x(\text{NaAlF}_4) + 568372 \cdot x(\text{NaAlF}_4)^2 - \\ & - 412538 \cdot x(\text{NaAlF}_4)^3) \end{aligned} \quad (19)$$

$$\begin{aligned} \Delta S^E = & x(\text{NaF}) \cdot x(\text{NaAlF}_4) \cdot (-34.1 - \\ & - 198.7 \cdot x(\text{NaAlF}_4) + 453.1 \cdot x(\text{NaAlF}_4)^2 - \\ & - 305.5 \cdot x(\text{NaAlF}_4)^3) \end{aligned} \quad (20)$$

The results of calculations are shown in Figs. 3—5.

From Figs. 3 and 4 it follows that the model based on a partial dissociation of the compound describes reasonably well the liquidus curves of the phase diagram but does not describe the data on vapour pressure above the melt satisfactorily. Enthalpy of mixing is not included in this model.

The model based on the complete dissociation of the compound well describes both solidus—liquidus equilibrium and vapour pressure over the melt.

## CONCLUSION

Suitability of the models for the description of behaviour of thermodynamic properties of molten mixtures was tested by comparing the experimental and calculated data on solid—liquid equilibria, enthalpy of mixing, and vapour pressure of the studied systems.

As it follows from the presented results the model based on a partial dissociation of the compound is not able to describe all those results. Its suitability for the description of liquidus curves is only limited. Besides, the data on vapour pressure above the system NaF—NaAlF<sub>4</sub> and enthalpy of mixing (Figs. 2 and 3) cannot

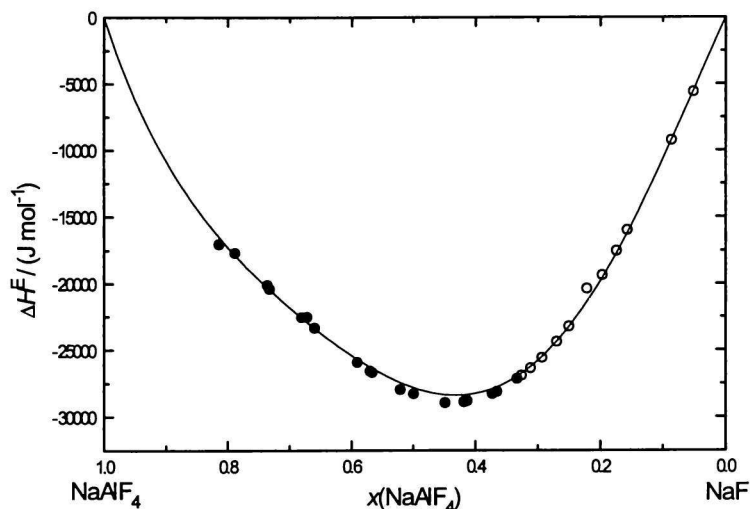


Fig. 5. Molar enthalpy of mixing of the system NaF—NaAlF<sub>4</sub> according to Holm [19] (○); Hong and Kleppa [18] (●); model based on complete dissociation of the compound (—).

be described by this model because of assuming ideal behaviour.

The model based on the complete dissociation of the compound well describes all the discussed data.

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