

Phase Diagrams of the Ternary System $\text{Na}_3\text{AlF}_6\text{—Na}_3\text{FSO}_4\text{—Na}_2\text{SO}_4$ and Its Thermodynamic Analysis

P. FELLNER, J. GABČOVÁ, V. DANIELIK, and M. LÁSKA

Department of Inorganic Technology, Faculty of Chemical Technology, Slovak Technical University, CS-812 37 Bratislava

Received 21 September 1992

Experimental data on solid—liquid phase equilibria in the binary systems $\text{Na}_3\text{AlF}_6\text{—Na}_3\text{FSO}_4$, $\text{Na}_3\text{AlF}_6\text{—Na}_2\text{SO}_4$, $\text{Na}_3\text{FSO}_4\text{—Na}_2\text{SO}_4$ and the ternary system $\text{Na}_3\text{AlF}_6\text{—Na}_3\text{FSO}_4\text{—Na}_2\text{SO}_4$ are presented. A model of molten salt mixtures based on the assumption of the existence of ionic pairs was applied to these systems. The temperatures of primary crystallization of Na_3AlF_6 , Na_3FSO_4 , and Na_2SO_4 were calculated. A good agreement between the experimental and calculated data was achieved.

The phase diagram of the ternary system $\text{Na}_3\text{AlF}_6\text{—Na}_3\text{FSO}_4\text{—Na}_2\text{SO}_4$ is presented. This system has not been published in literature. From the point of view of the phase diagram calculation this system is of interest because it contains two congruently melting compounds (Na_3AlF_6 and Na_3FSO_4) which partly thermally dissociate under melting.

EXPERIMENTAL

Solidus—liquidus equilibrium was determined by the method of thermal analysis (cooling curves method). The chemicals used were of anal. grade (Lachema, Brno). Sodium cryolite was synthesized from AlF_3 purified by sublimation. Temperature of the sample was measured by the PtRh10—Pt thermocouple. Comparing point (cool junction) of the thermocouple was kept at the temperature of (25.00 ± 0.01) °C. Mass of the sample in platinum crucible was 20 g, rate of cooling did not exceed 2 K min^{-1} . The thermocouple was calibrated using the melting points of pure salts: $\theta_{\text{fus}}(\text{NaF}) = 993.5$ °C (Monokrystaly Turnov); $\theta_{\text{fus}}(\text{BaCl}_2) = 955$ °C [1]; $\theta_{\text{fus}}(\text{Na}_2\text{SO}_4) = 884.8$ °C [2]; $\theta_{\text{fus}}(\text{LiF}) = 848.8$ °C [3]; $\theta_{\text{fus}}(\text{NaCl}) = 800.8$ °C [3]; $\theta_{\text{fus}}(\text{KCl}) = 771$ °C [3]; and the melting temperatures of eutectic mixtures: $\theta_{\text{eut}}(\text{NaCl—Na}_2\text{SO}_4) = 628$ °C [4]; $\theta_{\text{eut}}(\text{KCl—K}_2\text{SO}_4) = 685$ °C [5]. Repeated measurements of temperature of primary crystallization of the same sample were in the interval narrower than 1 K.

RESULTS AND DISCUSSION

Phase diagrams of the binary systems $\text{Na}_3\text{AlF}_6\text{—Na}_3\text{FSO}_4$, $\text{Na}_3\text{AlF}_6\text{—Na}_2\text{SO}_4$, and $\text{Na}_3\text{FSO}_4\text{—Na}_2\text{SO}_4$ have been published by Fellner and Gabčová [6],

Grjothheim, Halvorsen, and Urness [7], Matiašovský and Malinovský [8], and Koštenská and Malinovský [9], respectively. Our experimental data are in good agreement with the cited literature. The systems $\text{Na}_3\text{AlF}_6\text{—Na}_3\text{FSO}_4$ and $\text{Na}_3\text{FSO}_4\text{—Na}_2\text{SO}_4$ are simple eutectic mixtures (Figs. 1 and 2). In the system $\text{Na}_3\text{AlF}_6\text{—Na}_2\text{SO}_4$ there is a broad range of solid solutions of Na_2SO_4 in Na_3AlF_6 [7, 8] (Fig. 3).

At the experimental study of the phase equilibria in the ternary system $\text{Na}_3\text{AlF}_6\text{—Na}_3\text{FSO}_4\text{—Na}_2\text{SO}_4$, nine sections of the 1st order (constant ratio of two components) and ten sections of the 2nd order (constant content of one component) were investigated. Totally 90 mixtures were analyzed. The obtained data are summarized in Fig. 4a. Parameters of the ternary eutectic point are as follows (in mole %):

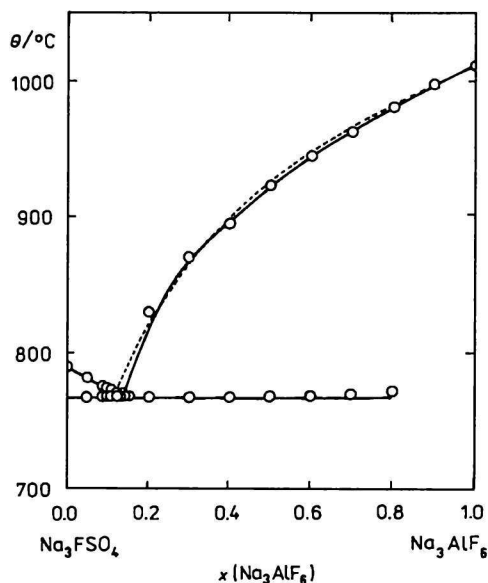


Fig. 1. Phase diagram of the system $\text{Na}_3\text{AlF}_6\text{—Na}_3\text{FSO}_4$. — Experimental; ---- calculated.

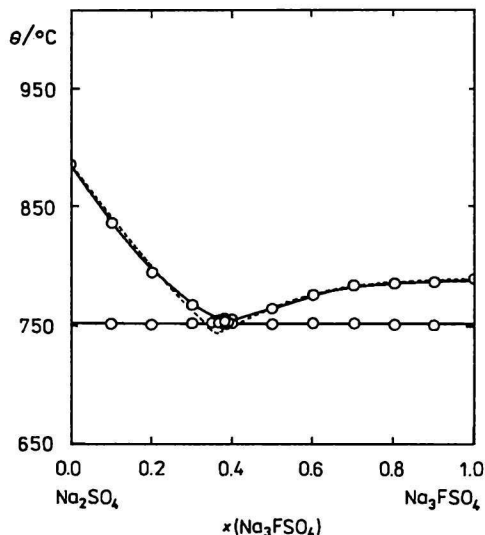


Fig. 2. Phase diagram of the system $\text{Na}_3\text{FSO}_4\text{--Na}_2\text{SO}_4$. — Experimental; ---- calculated.

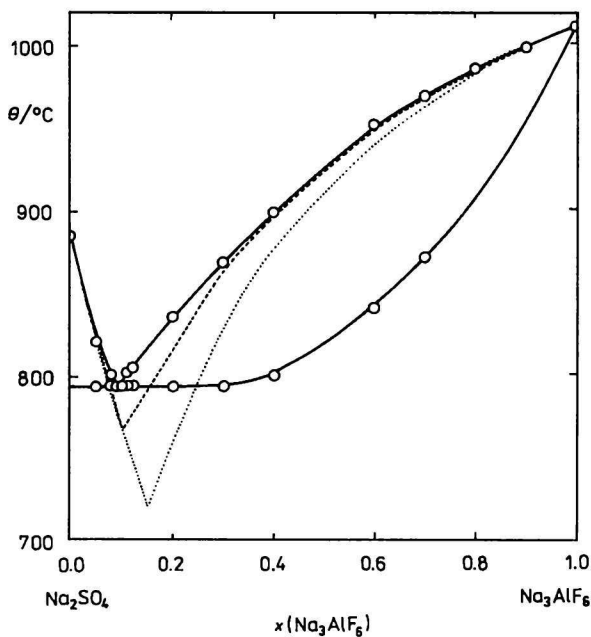


Fig. 3. Phase diagram of the system $\text{Na}_3\text{AlF}_6\text{--Na}_2\text{SO}_4$. — Experimental; ---- calculated (solid solutions were taken into account); calculated (solid solutions were not taken into account).

$\theta_{\text{out}}(7\% \text{ Na}_3\text{AlF}_6, 36\% \text{ Na}_3\text{FSO}_4, 57\% \text{ Na}_2\text{SO}_4) = 743\text{ }^\circ\text{C}$. (Detailed numerical data on the phase diagram will be supplied by the authors on request.)

Calculation of the Phase Diagram of the System $\text{Na}_3\text{AlF}_6\text{--Na}_3\text{FSO}_4\text{--Na}_2\text{SO}_4$

The temperature of primary crystallization can be calculated according to the Le Chatelier—Shreder equation

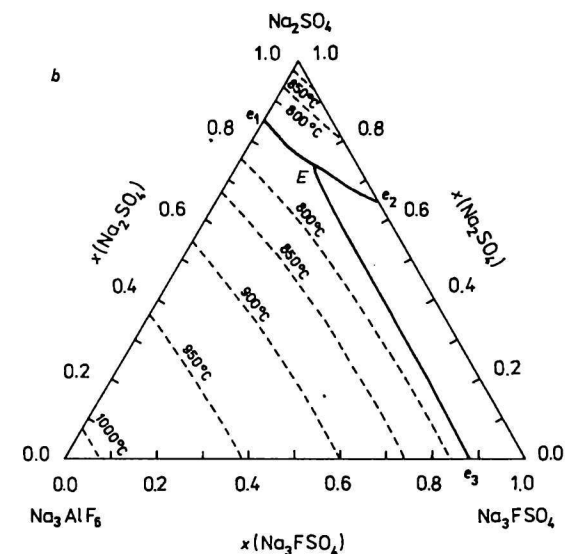
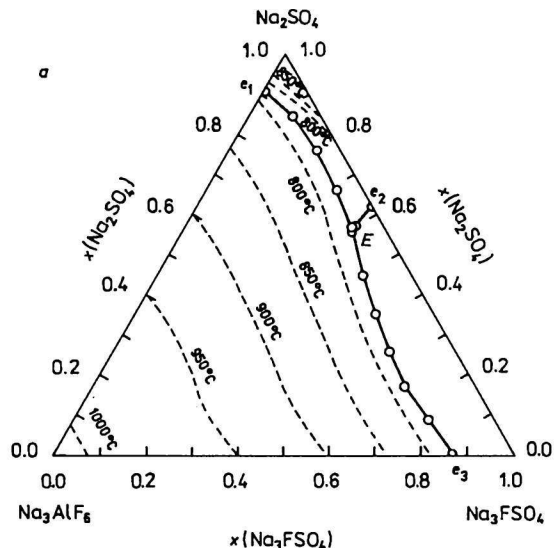


Fig. 4. a) Experimental and b) calculated phase diagrams of the system $\text{Na}_3\text{AlF}_6\text{--Na}_3\text{FSO}_4\text{--Na}_2\text{SO}_4$.

$$\ln a_i = \frac{\Delta H_{\text{fus},i}}{R} \left[\frac{1}{T_{\text{fus},i}} - \frac{1}{T_i} \right] \quad (1)$$

where a_i is the activity of the i -th component in molten mixture, $\Delta H_{\text{fus},i}$ and $T_{\text{fus},i}$ are the enthalpy and temperature of fusion, respectively, and T_i is the temperature of solid—liquid equilibrium (the temperature of primary crystallization) at given composition of the mixture.

When we know the enthalpy and temperature of fusion of a given component as well as its activity in the molten mixture, we can calculate its temperature of primary crystallization. The calculations presented in this work are based on the assumptions that the activity of a component in the molten mixture equals its mole fraction. As this mole fraction is

calculated according to the thermodynamic model, it will be called a model mole fraction. Definition of the activity of thermally dissociating compounds will be discussed later.

The thermodynamic model used in this work is based on two assumptions:

- i) the complex anions AlF_6^{3-} and FSO_4^{3-} partly thermally dissociate under melting;
- ii) the ions in the molten mixture mix randomly.

The thermal dissociation of the complex anions can be estimated if we assume that the reactions of the complex species in the liquid phase can be described by the following reaction schemes



The equilibrium constants were taken from literature [9, 10]. The dissociation scheme of cryolite anion is an oversimplification of the real situation [10]. However, in neutral melts with the ratio $n(\text{NaF})/n(\text{AlF}_3)$ equal to 3 the use of this model is justified.

At the calculations it was assumed that the equilibrium constants K_I , K_{II} do not depend on temperature. This is identical with the assumption that the dissociation enthalpies of both substances equal zero. The other assumption is that the enthalpies of fusion of Na_3AlF_6 and Na_3FSO_4 equal the hypothetical enthalpies of fusion of these substances [11]. Usually there is not a great difference between the hypothetical and the real (calorimetric) enthalpy of fusion of the substance which partly dissociates under melting.

It can be shown [12] that eqn (1) can be used for calculation of the liquidus temperature also in the case of the compound which partly dissociates under melting when the activity of undissociated substance in liquid phase is defined as

$$a_i = x_i/x_i^* \quad (2)$$

where x_i^* is the mole fraction of thermally non-dissociated substance in the melt which is in equilibrium with the pure solid substance. Because the constants K_I and K_{II} were obtained by comparison of the calculated and experimental data in the way similar to that discussed here they should be considered as adjustable parameters which include partly also the deviation of the molten mixture from ideality.

The experimental and calculated temperatures of primary crystallization for binary systems are compared in Figs. 1–3. It can be seen that the systems Na_3AlF_6 — Na_3FSO_4 and Na_3FSO_4 — Na_2SO_4 are simple eutectic mixtures. From the results it follows that

the used thermodynamic model describes the phase diagrams of these systems very well.

There are limited solid solutions of sodium sulfate in Na_3AlF_6 . Thus at the calculation of the phase diagram according to eqn (1) the ratio of activities of given substance in the liquid and solid phases has to be used. In this work it was assumed that the activity of Na_3AlF_6 in solid solution equals its mole fraction (ideal solid solution). As it follows from Fig. 3 this approximation gives good agreement between the calculated and experimental data in broad composition range.

The phase diagram of the system Na_3AlF_6 — Na_3FSO_4 — Na_2SO_4 was calculated in a similar way as the phase diagrams of the binary systems. The experimental and calculated phase diagrams are compared in Figs. 4a and 4b. It follows that the agreement between the experimental and calculated liquidus surfaces is good. Deviation between the experimental and calculated temperatures of primary crystallization of Na_3AlF_6 at the temperatures lower than 900 °C may be influenced by the existence of solid solutions of Na_2SO_4 in cryolite. Experimentally, however, the formation of solid solution has not been detected and therefore it has not been taken into account in the calculations. A good agreement between the experimental and calculated phase diagrams suggests that the used model describes properly the thermodynamic behaviour of the studied system.

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Translated by P. Fellner