Calculation of surfaces of liquidus and of isotherms in the phase diagrams of the ternary systems NaCl—NaF—Na$_3$FSO$_4$ and NaCl—Na$_2$SO$_4$—Na$_3$FSO$_4$

J. GABČOVÁ, +M. MALINOVSKÝ, and P. KOTTÁŠ

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

Phase diagrams of the ternary systems NaCl—NaF—Na$_3$FSO$_4$ and NaCl—Na$_2$SO$_4$—Na$_3$FSO$_4$ were investigated by the thermal analytical method. It was found that both systems are of simple eutectic type with one eutectic point. Coordinates of the eutectic points are following:

The system NaCl—NaF—Na$_3$FSO$_4$: 62.0 mole % NaCl, 11.4 mole % NaF, 26.6 mole % Na$_3$FSO$_4$; $T(E) = 898.2$ K (625 °C).

The system NaCl—Na$_2$SO$_4$—Na$_3$FSO$_4$: 54.6 mole % NaCl, 31.8 mole % Na$_2$SO$_4$, 13.6 mole % Na$_3$FSO$_4$; $T(E) = 869.2$ K (596 °C).

Calculation of the surfaces of liquidus and of the isotherms of the phase diagrams was carried out under the assumption that the compound Na$_3$FSO$_4$ partly thermally dissociates under melting.

Исследованы фазовые диаграммы тройных систем NaCl—NaF—Na$_3$FSO$_4$ и NaCl—Na$_2$SO$_4$—Na$_3$FSO$_4$ с помощью термоаналитического метода. Обнаружено, что обе системы представляют собой простой эвтектический тип с одной точкой эвтектики. Координаты точек эвтектики следующие:

Система NaCl—NaF—Na$_3$FSO$_4$: 62,0 мол. % NaCl, 11,4 мол. % NaF, 26,6 мол. % Na$_3$FSO$_4$; $T(E) = 898,2$ K (625 °C).

Система NaCl—Na$_2$SO$_4$—Na$_3$FSO$_4$: 54,6 мол. % NaCl, 31,8 мол. % Na$_2$SO$_4$, 13,6 мол. % Na$_3$FSO$_4$; $T(E) = 869,2$ K (596 °C).

Расчет поверхностей ликвидуса и изотерм фазовых диаграмм был проведен в предположении, что соединение Na$_3$FSO$_4$ частично термически диссоциирует при плавлении.

The systems NaCl—NaF—Na$_3$FSO$_4$ and NaCl—Na$_2$SO$_4$—Na$_3$FSO$_4$ are of a simple eutectic type having one ternary eutectic point. Literature data on experimentally found coordinates of the eutectic points are summarized in Table 1.

The congruently melting compound Na$_3$FSO$_4$ partly thermally dissociates under melting. According to a very flat maximum on the liquidus curve of Na$_3$FSO$_4$ in the

Table 1

Literature eutectic data on the systems $NaCl—NaF—Na_3FSO_4$ and $NaCl—Na_2SO_4—Na_3FSO_4$

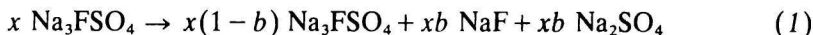| System	$x(i, \dot{E})$/mole %				$T(E)$	$T(E)$	Ref.
	NaCl	NaF	Na_2SO_4	Na_3FSO_4	K	°C	
$NaCl—NaF—Na_3FSO_4$	62.30	14.20	—	23.50	893.2	620	[1]
	60.30	16.10	—	23.60	897.2	624	[2]
	62.00	11.40	—	26.60	898.2	625	[3]
$NaCl—Na_2SO_4—Na_3FSO_4$	51.70	—	35.90	12.40	867.2	594	[1]
	50.00	—	38.70	11.30	875.2	602	[2]
	54.60	—	31.80	13.60	869.2	596	[3]

system NaF—Na_2SO_4 [4] one can estimate that the degree of dissociation of this compound is rather high. From the analysis of liquidus curve and from the coordinates of the eutectic point E in the system NaF—Na_3FSO_4 it was found that the degree of thermal dissociation b_0 of the pure compound Na_3FSO_4 equals 0.73—0.75 [4]. Uncertainty of this parameter was estimated to be ± 0.1. Thus one can conclude that the value of the parameter b_0 lies in the interval 0.63—0.85.

In the molten mixtures containing Na_3FSO_4 the degree of thermal dissociation of this compound changes from the value b_0 (which is valid for the pure substance Na_3FSO_4) to a value b, which generally differs from b_0. When we add NaF or Na_2SO_4 to the melt of Na_3FSO_4 the degree of thermal dissociation of Na_3FSO_4 decreases, $b < b_0$. In the limit, in an infinitively diluted solution of Na_3FSO_4 in NaF ($x(NaF) \rightarrow 1$) or in Na_2SO_4 ($x(Na_2SO_4) \rightarrow 1$) it holds $b_\infty = b_0^2$. When we add to the melt of Na_3FSO_4 sodium chloride, which obviously is not the product of the partial thermal dissociation of Na_3FSO_4, the degree of thermal dissociation increases and at limiting dilution it holds $b_\infty = 1$. Thus the addition of NaF or Na_2SO_4 to molten Na_3FSO_4 influences the quantity b in opposite sense than the addition of $NaCl$.

The temperature of liquidus of the ternary mixture is a function of concentration of all three components of the melt and formally it is also a function of the parameter b. Thus if we know the temperature of liquidus of ternary mixtures we can (assuming that the melt behaves ideally) calculate the quantity b. As b_0 is a function of b ($b_0 = f(b)$) we can calculate on the basis of knowledge of b the most probable value of the degree of thermal dissociation b_0 of the pure compound Na_3FSO_4 and compare the result with that obtained on the basis of the analysis of the binary system NaF—Na_2SO_4.

However, at the analysis of phase diagrams we usually use an opposite approach which is more simple. We choose b_0 (from an interval having physical meaning) and we calculate for each composition the parameter b and the temperature of liquidus. From the fitness of the experimental and calculated liquidus temperature we judge on the plausibility of made assumptions. The method of calculation will be demonstrated on an example of the system $NaCl$—NaF—Na_3FSO_4.

Let the system consist of x mol of Na_3FSO_4, y mol of NaF, and z mol of $NaCl$. $x + y + z = d$. (In our case $d = 1$ mol.) The material balance of substances with respect to the partial thermal dissociation of Na_3FSO_4 is as follows

$$x \ Na_3FSO_4 \rightarrow x(1-b) \ Na_3FSO_4 + xb \ NaF + xb \ Na_2SO_4 \tag{1}$$

$$y \ NaF \rightarrow y \ NaF \tag{2}$$

$$z \ NaCl \rightarrow z \ NaCl \tag{3}$$

Because all components of the system have the same cation there is no need for using a special model for activity of ideal melt. The analysis of the systems

NaF—Na$_3$FSO$_4$ [5], NaCl—Na$_3$FSO$_4$ [5], NaF—NaCl [6], and NaCl—Na$_2$SO$_4$ [6] has shown that all the systems behave practically ideally. Thus we can assume that also behaviour of these components in a ternary mixture will be ideal. Then the activities of the components equal to their mole fractions in the melt. Numerical value of the sum of the amount of substances in the melt is then given by the expression

$$x(1-b) + xb + xb + y + z = 1 + xb \qquad (4)$$

and it holds

$$a(\text{Na}_3\text{FSO}_4) = \frac{x(1-b)}{1+xb} \qquad (5)$$

$$a(\text{NaF}) = \frac{xb+y}{1+xb} \qquad (6)$$

$$a(\text{NaCl}) = \frac{z}{1+xb} \qquad (7)$$

$$K_{\text{dis}}(\text{Na}_3\text{FSO}_4) = \frac{a(\text{NaF}) \cdot a(\text{Na}_2\text{SO}_4)}{a(\text{Na}_3\text{FSO}_4)} = \frac{(xb+y)b}{(1-b)(1+xb)} \qquad (8)$$

For the equilibrium constant of thermal dissociation K_{dis}^0 of pure substance Na$_3$FSO$_4$ it holds [4]

$$K_{\text{dis}}^0 = \frac{b_0^2}{1-b_0^2} \qquad (9)$$

where $b_0 = \lim\limits_{x \to 1} b$.

We further assume that in the limits of accuracy of the experiment it holds

$$K_{\text{dis}}^0 = K_{\text{dis}} \qquad (10)$$

Then we obtain from eqns (8) and (10)

$$b = \frac{-y + (1-x)K_{\text{dis}}^0}{2x(1+K_{\text{dis}}^0)} + \left[\left(\frac{y(1-x)K_{\text{dis}}^0}{2x(1+K_{\text{dis}}^0)} \right)^2 + \frac{K_{\text{dis}}^0}{x(1+K_{\text{dis}}^0)} \right]^{1/2} \qquad (11)$$

Using b calculated from eqn (11) we can determine the activities defined by relationships (5), (6), and (7). Inserting these activities in the Le Chatelier—Shreder equation we can calculate isotherms in the ternary system NaCl—NaF—Na$_3$FSO$_4$ and determine the lines of monovariant equilibrium.

We chose the following set of b_0 values: 0.65, 0.70, 0.75, 0.80, 0.85. The values of $\Delta H(\text{fus, NaCl})$, $\Delta H(\text{fus, NaF})$, $\Delta H(\text{fus, Na}_2\text{SO}_4)$, $T(\text{fus, NaCl})$, $T(\text{fus, NaF})$, $T(\text{fus, Na}_2\text{SO}_4)$, $\Delta C_p(\text{l}^0/\text{s}^0, \text{NaCl})$, $\Delta C_p(\text{l}^0/\text{s}^0, \text{NaF})$, $\Delta C_p(\text{l}^0/\text{s}^0, \text{Na}_2\text{SO}_4)$ were taken from tables [7]; $\Delta H(\text{fus, Na}_3\text{FSO}_4)$ and $T(\text{fus, Na}_3\text{FSO}_4)$ were taken from [4]. The

calculations were done for compositions corresponding both to the sections of the first order [8] and the second order [9]. Numerical calculations were done on the computer Siemens 4004 at the Computing Centre of the Universities of Bratislava. Simplified procedure of computation is outlined in the last paragraph of this paper.

From comparison of the experimental and calculated data it follows that the best fit for the system $NaCl—NaF—Na_3FSO_4$ is obtained with $b_0 = 0.80$ and 0.85, respectively. For the system $NaCl—Na_2SO_4—Na_3FSO_4$ the best fit is obtained with $b_0 = 0.65$. The corresponding curves of monovariant equilibrium and isotherms in the system $NaCl—NaF—Na_3FSO_4$ calculated with $b_0 = 0.80$ ($b = 0.85$ gave practically the same results), are plotted in Fig. 1. The same data for the system $NaCl—Na_2SO_4—Na_3FSO_4$ ($b_0 = 0.65$) are given in Fig. 2. Experimental and calculated coordinates of the ternary eutectic points are compared in Tables 2 and 3.
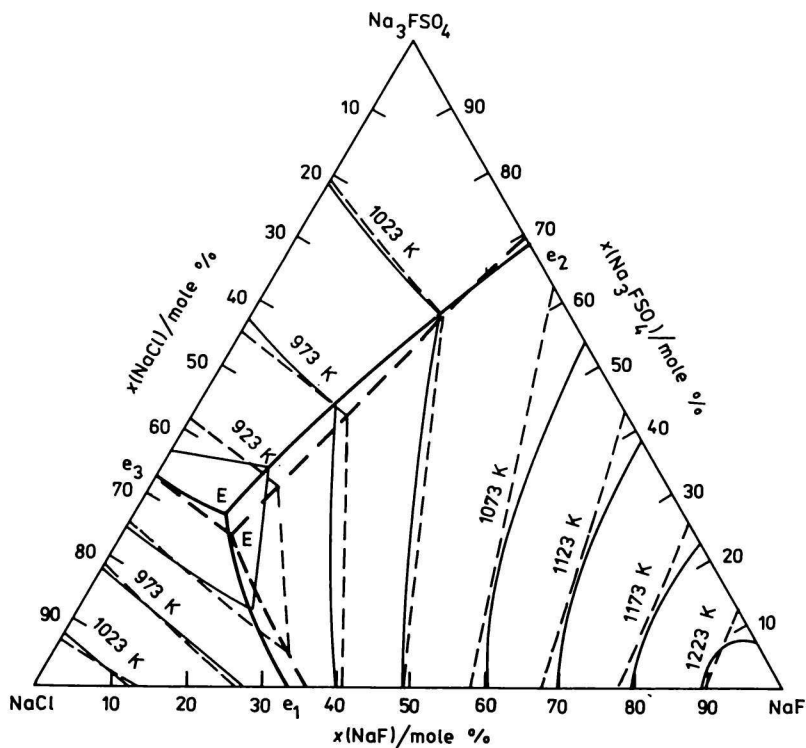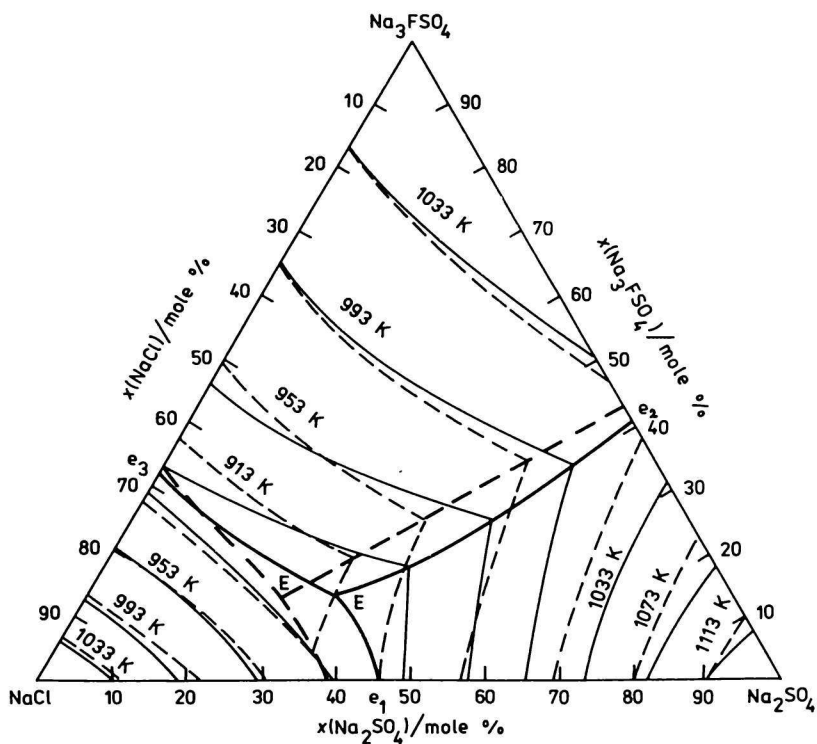

Fig. 1. Phase diagram of the system $NaCl—NaF—Na_3FSO_4$. The experimental and calculated lines of monovariant equilibrium and isotherms (K) are compared.
———— Experiment; —————— calculated with $b_0 = 0.80$.

Fig. 2. Phase diagram of the system NaCl—Na$_2$SO$_4$—Na$_3$FSO$_4$. The experimental and calculated lines of monovariant equilibrium and isotherms (K) are compared.
———— Experiment; — — — — — calculated with $b_0 = 0.65$.

Table 2

Comparison of the experimental and calculated data on the ternary eutectic point of the system
NaCl—NaF—Na$_3$FSO$_4$

	$x(i, E)$ mole %			$T(E)$	$T(E)$
	NaCl	NaF	Na$_3$FSO$_4$	K	°C
Experiment	62.00	11.40	26.60	898.2	625.0
$b_0 = 0.65$	60.36	18.00	21.64	886.4	613.2
$b_0 = 0.70$	61.02	16.75	22.23	885.6	612.4
$b_0 = 0.75$	61.63	15.50	22.87	884.8	611.6
$b_0 = 0.80$	62.22	14.24	23.54	883.9	610.7
$b_0 = 0.85$	62.79	13.00	24.21	882.9	609.7

Table 3

Comparison of the experimental and calculated data on the ternary eutectic point of the system
$NaCl-Na_2SO_4-Na_3FSO_4$

	$x(i, E)$ mole %			$T(E)$	$T(E)$
	NaCl	Na_2SO_4	Na_3FSO_4	K	°C
Experiment	54.60	31.80	13.60	869.2	596.0
$b_0 = 0.65$	61.27	25.96	12.77	904.8	631.6
$b_0 = 0.70$	61.70	33.61	4.69	919.9	646.7
$b_0 = 0.75$	62.00	34.46	3.54	922.8	649.6
$b_0 = 0.80$	62.04	33.41	4.55	920.4	647.2
$b_0 = 0.85$	63.00	31.61	5.39	922.0	648.8

In the system $NaCl-NaF-Na_3FSO_4$ the calculated composition of the ternary eutectic point (for $b_0 = 0.80$) differs from the experimental one by 0.22—3.06 mole %. Experimental temperature of the eutectic point is by 14.3 K (*i.e.* 1.6 %) higher than the calculated one. For $b_0 = 0.85$ the composition differs by 0.79—2.39 mole % and the corresponding temperature is higher by 15.3 K (*i.e.* 1.7 %).

For the system $NaCl-Na_2SO_4-Na_3FSO_4$ the experimental and calculated composition of the eutectic point differs by 0.8—6.7 mole % and the experimental temperature of the eutectic point is by 35.6 K (*i.e.* 3.9 %) lower than the calculated one. As it follows from Table 3 the parameters of the eutectic point are very sensitive to the value of the parameter b_0, which may be caused by the deviation of the eutectic melt from ideal behaviour.

From comparison of the calculated and experimental surfaces of liquidus and isotherms in both studied systems it follows that the calculated data for the system $NaCl-NaF-Na_3FSO_4$ are closer to experimental values. Greater differences between experimental and calculated data in the system $NaCl-Na_2SO_4-Na_3FSO_4$ may be explained by the presence of the compound Na_2SO_4 in this system.

Simplified procedure of calculations

The program for computation of the surfaces of liquidus and isotherms in the systems $NaCl-NaF-Na_3FSO_4$ and $NaCl-Na_2SO_4-Na_3FSO_4$ consists of three parts. In the first part composition of the points lying on the sections of the second order were generated with the step of 10 mole % for each component (NaCl, NaF, Na_3FSO_4 or NaCl, Na_2SO_4, Na_3FSO_4) in the range from 0 to 100 mole %. The

points on the sections of the first order were generated as the cross-sections of the sections with constant ratios of NaF/Na_3FSO_4, $NaCl/Na_3FSO_4$, and $Na_2SO_4/ /Na_3FSO_4$, respectively. These ratios changed from 0.1 to 0.9 with the step of 0.1. For given composition and the degree of dissociation of Na_3FSO_4 the activities and the temperature of primary crystallization of each component were calculated (using the Le Chatelier—Shreder equation). This calculation assumes that the solidus—liquidus equilibria of the components are independent and thus the liquidus temperature of an arbitrary component may be calculated in the whole concentration range of the ternary system. The real interval of the temperature of primary crystallization extends from the melting point of pure component i to the cross-section of its liquidus curve with the liquidus curve of another component. Behind this point the liquidus of the i-th component corresponds to a metastable state. Thus for given composition of the ternary system we can calculate the temperatures of primary crystallization of all three components. The highest temperature has a real physical meaning and it determines the component which crystallizes as the first.

The second part of the program was used for calculation of the ternary eutectic point and the lines of monovariant equilibrium (*i.e.* the lines corresponding to simultaneous crystallization of two components: $NaCl—NaF$, $NaCl—Na_3FSO_4$, $NaF—Na_3FSO_4$, $NaCl—Na_2SO_4$, $Na_2SO_4—Na_3FSO_4$). The ternary eutectic point was sought in such a way that at chosen concentration the temperatures of primary crystallization of all three components were calculated. The concentrations of components were generated so that the differences between the temperatures of primary crystallization of the components diminished until the difference was less than 0.1 K. The procedure for calculation of the lines of simultaneous crystalliza-tion was similar as that used for determination of the eutectic point. In this case, however, the content of the third component was changed with the step of 2 mole % starting at 0 mole % of this component. Again the calculation was carried out until the difference between the temperatures of primary crystallization was less than 0.1 K.

The third part of the program was used for calculation of isotherms of the system. In this work the difference of 50 K between isotherms was chosen. Composition of the system was changed along the sections of the second order and the calculated temperature of primary crystallization was compared with multiples of 50 K. As in the previous cases the calculation was done with precision 0.1 K.

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Translated by P. Fellner