

POSSIBILITY OF PREDICTING THE EXISTENCE OF A COMPLEX COMPOUND IN THE NaF-Na₂SO₄ SYSTEM

Milan MALINOVSKÝ^a and Jaroslava VRBENSKÁ^b

^a Department of Inorganic Technology,

^b Department of Electrotechnology,

Slovak Institute of Technology, 812 37 Bratislava

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A method of thermodynamic prediction of the existence of a complex compound in the NaF—Na₂SO₄ binary system is described. On the basis of the knowledge of a part of liquidus drawn in the vicinity of NaF melting point and coordinates of eutectic point, the conclusion was made that there exists the complex compound Na₃FSO₄ in the system. Its true and hypothetic melting points and the degree of its thermal dissociation were calculated. Further, the probable coordinates of a eutectic point in the Na₃FSO₄-Na₂SO₄ subsystem were found out. The calculated results were confronted with experimental determination; the agreement is very good. The method described can be useful for experimental studies of binary phase diagrams.

The question of existence of complex compounds is one of the most relevant problems when studying phase diagrams of condensed systems. Figurative points of these compounds make it possible to divide the original diagram into elementary parts, which is important both from the point of view of topological studies, and for the polyhedrization of diagrams¹ or when applying thermodynamic methods for calculating the course of liquidus curves or curves of monovariant phase equilibrium². However, in a number of cases, the experimental proof of the existence of complex compounds is difficult. It is especially in the case when the compound is chemically or thermally unstable, when exists only at higher pressures or only in a narrow temperature range³. In such a case it is very important to dispose of a method which makes it possible to predict existence of the compound. We shall show that thermodynamic analysis of the shape of phase equilibrium curves and coordinates of significant points in diagrams makes this prediction possible; moreover, it is possible to obtain some important information about this compound. This method will be illustrated by an example of the NaF-Na₂SO₄ system which has been thoroughly investigated experimentally⁴⁻⁶.

Let us assume that we know only a part of phase diagram of this system within 95-100 mol% NaF (*i.e.* part of NaF liquidus and part of isotherm of eutectic crystallization), which renders it possible to perform the cryometric analysis on the base of NaF, and the coordinates of eutectic point *E*, in the given case $x(\text{NaF}) =$

$= 0.59$, $x(\text{Na}_2\text{SO}_4) = 0.41$, $T(E) = 1\,054\text{ K}$. One of substances with which is the melt, corresponding to the point E , saturated at equilibrium is just NaF whose melting point is $1\,266.5\text{ K}$. For the activity of component i in the eutectic system in which solid solutions do not arise from the component i , the relation holds

$$\ln a(i) = \frac{\Delta H^f(i)}{R} \left[\frac{1}{T^f(i)} - \frac{1}{T} \right] + f[\Delta C_p(i)], \quad (1)$$

where $a(i)$ is the thermodynamic activity of the i -th component of given system in solution which is saturated at equilibrium with this component, and standard state chosen is the state of pure i -th liquid component at the system temperature and pressure. $\Delta H^f(i)$ is the molar enthalpy of fusion of the i -th component and $T^f(i)$ the temperature of fusion of the i -th component (in K). We assume that the component i does not thermally dissociate at the temperature of fusion, which is fulfilled *e.g.* for NaF (thermal dissociation of the type $\text{NaF} \rightarrow \text{Na} + \frac{1}{2}\text{F}_2$ does not take place during fusion).

With regard to the aim of this work, we neglect the term $f[\Delta C_p(i)]$ in Eq. (1); this simplification in the given case does not influence the conclusions which follow from the thermodynamic analysis.

Eq. (1) makes it possible to calculate the quantity $\Delta H^f(i)$ (in our case $i = \text{NaF}$) if we know the corresponding value of the quantity $a(i)$ for a temperature T in a solution saturated with sodium fluoride.

Let us set $a(i) = x(i)$ first. On inserting the coordinates of point E into Eq. (1) we find that $\Delta H^f(i) = 27\,504\text{ J mol}^{-1}$, which differs from the calorimetric value by JANAF (ref.⁷) equal to $7\,970\text{ cal mol}^{-1} = 33\,346\text{ J mol}^{-1}$ by $+17\%$ (the deviation is defined as $100[\Delta H^f(i) - \Delta H^f(i, \text{ph. d})]/\Delta H^f(i)$); $\Delta H^f(i)$ is the calorimetric quantity, $\Delta H^f(i, \text{ph. d})$ stands for the quantity calculated from Eq. (1).

Reasons for this difference which substantially exceeds the possible experimental inaccuracy in determining the quantities ΔH^f , might be:

- inaccurate coordinates of the eutectic point E in the given phase diagram,
- considerably nonideal course of NaF liquidus,
- existence of a complex compound in the NaF–Na₂SO₄ system.

Under the present conditions of experimental technique, the maximum inaccuracy in determining the eutectic temperature $T(E)$ does not exceed $\pm 2\text{ K}$; this scattering causes a deviation of calculated value of the quantity $\Delta H^f(i, \text{ph. d})$ equal approximately 1.1% . The maximum inaccuracy of experimental determination of composition of point E , *i.e.* $\pm 2\text{ mol } \%$ brings about a deviation in the value of $\Delta H^f(i, \text{ph. d})$ equal approximately 6% . Thus, it is evident that the reason sub *a*) does not enable one to explain satisfactorily the given difference between $\Delta H^f(i)$ and $\Delta H^f(i, \text{ph. d})$.

Likewise it is not probable that differences in the values of enthalpies of fusion would be caused by a considerable deviation of NaF liquidus from an ideal course. It is well-known that in simple eutectic systems with a common univalent alkali cation, the course of liquidus curves differs only slightly from ideality. For instance, for the NaCl-Na₂SO₄ system which is very similar to the NaF-Na₂SO₄ system from the chemical point of view, it holds true that the activity coefficient $\gamma(\text{NaCl}) = 1.02$ in a melt corresponding to the eutectic point, which therefore means an insignificant positive deviation from ideality. However, if we insert the quantities for eutectic point in the NaF-Na₂SO₄ system (and, naturally, the calorimetric quantity $\Delta H^f(i)$) into Eq. (1) we find that $a(i) = 0.5281$, and then $\gamma(i) = a(i)/x(i) = 0.8951$. This expressive negative deviation from ideality is absolutely improbable.

Therefore the assumption sub c) is altogether justified, namely, that a complex compound Z of a general composition $(\text{NaF})_p(\text{Na}_2\text{SO}_4)_q$ is formed in the NaF-Na₂SO₄ system. Now we will postulate some properties of this compound, and investigate how they will reflect on the course of NaF liquidus, on the coordinates of point E and on the value of $\Delta H^f(i, \text{ph. d.})$.

Compound Z Does not Absolutely Dissociate

The composition coordinates of the eutectic point E are to be converted from the NaF-Na₂SO₄ system into the NaF-(NaF)_p.(Na₂SO₄)_q system. From the material balance it holds for the mole fraction $y(i)$ in the NaF-Z system ($i = \text{NaF}$)

$$y(i) = \frac{x(i)q - [1 - x(i)]p}{x(i)q - [1 - x(i)](p - 1)} \quad (2)$$

Some limitation for the ratio of stoichiometric coefficients p and q follows from the value $x(i) = 0.59$ at the point E. It is easily proved that $x(i) < p/(p + q)$ must hold, and when $x_1 = 0.59 \approx 0.60$,

$$3/2 > p/q \quad (3)$$

The coefficients p and q are small integers, whose ratio must satisfy inequality (3). This circumstance was taken into account in making up Table I in which the mole fraction $y(i)$ at the point E for chosen pairs of values of p and q and also the values of $\Delta H^f(i, \text{ph. d.})$ calculated from Eq. (1) are given. Here we state considerable sensitivity of values $\Delta H^f(i, \text{ph. d.})$ to the magnitude of $y(i)$. The value $\Delta H^f(i, \text{ph. d.}) = 29\,448 \text{ J mol}^{-1}$ which results from $p = q = 3$, is the nearest value to the calorimetric value $\Delta H^f(i) = 33\,346 \text{ J mol}^{-1}$; the corresponding compound is then $Z = (\text{NaF})_3 \cdot (\text{Na}_2\text{SO}_4)_3 = \text{Na}_9[\text{F}_3(\text{SO}_4)_3]$.

Let us estimate the heat of fusion of compound Z. It holds approximately that $\Delta H^f(Z) = 3 \Delta H^f(\text{NaF}) + 3 \Delta H^f(\text{Na}_2\text{SO}_4) = 169\,074 \text{ J mol}^{-1}$ (data on $\Delta H^f(\text{NaF})$)

and $\Delta H^f(\text{Na}_2\text{SO}_4)$ by JANAF (ref.⁷); as well $\Delta S^f(Z) \approx 3 \Delta S^f(\text{NaF}) + 3 \Delta S^f(\text{Na}_2\text{SO}_4) = 138.7 \text{ J mol}^{-1} \text{ K}^{-1}$. Then $T^f(Z) = \Delta H^f(Z)/\Delta S^f(Z) = 1219 \text{ K}$. On inserting this value into Eq. (1), we find that $a(Z) = y(Z) = 0.0734$ holds for the eutectic point. However, for $p = q = 3$ we will calculate from Eq. (2) that $y(i) = 0.5684$ and therefore $y(Z) = 1 - y(i) = 0.4316$, which differs rather strikingly from the value of 0.0734; the corresponding activity coefficient of compound Z, $\gamma(Z)$, would equal to 0.17. Existence of the thermally absolutely undissociated complex compound Z in the phase diagram of the NaF–Na₂SO₄ system is consequently altogether improbable.

Compound Z Thermally Partly Dissociates

Let Z be partly decomposed on melting into its original components; the degree of this decomposition of the pure compounds Z let be b_0 , the degree of decomposition (thermal dissociation) of Z in the solution with NaF of final dilution let be b and at infinite dilution for $x(Z) \rightarrow 0$ let be b_∞ (it can be proved that it holds $0 < b_\infty < 1$). Then one molecule of Z brings $(1 - b_\infty)$ molecules of Z, pb_∞ molecules of NaF and qb_∞ molecules of Na₂SO₄ into the pure melt of NaF after melting. The course of NaF liquidus for $y(Z) \rightarrow 0$ is influenced only by these particles which do not occur in fused NaF, *i.e.* Z and Na₂SO₄; altogether they amount to $1 - b_\infty + qb_\infty$. By treating the experimental data for NaF liquidus in the NaF–Na₂SO₄ system it was found that the slope of tangent $k^0(i)$ to the liquidus line of NaF for $x(i) \rightarrow 1$

TABLE I

The values of $y(i)$ of NaF mole fraction at the eutectic point *E* of the NaF–(NaF)_{*p*}–(Na₂SO₄)_{*q*} system and the corresponding calculated values of $\Delta H^f(i, \text{ph. d})$ (J mol⁻¹)

| <i>p</i> | <i>q</i> | $y(i)$ | $\Delta H^f(i, \text{f. d})$ |
|----------|----------|--------|------------------------------|
| 1 | 1 | 0.3051 | 61 881 |
| 2 | 2 | 0.4675 | 39 635 |
| 1 | 2 | 0.6525 | 22 255 |
| 4 | 3 | 0.2407 | 74 240 |
| 3 | 3 | 0.5684 | 29 448 |
| 2 | 3 | 0.6985 | 18 704 |
| 5 | 4 | 0.4306 | 43 921 |
| 4 | 4 | 0.6372 | 23 492 |
| 3 | 4 | 0.7338 | 16 134 |

is equal to 395 K. It is well-known that the cryometric relation

$$\Delta H^f(i) = \frac{R[T^f(i)]^2}{k^0(i)} k^{st}(Z/i), \quad (4)$$

holds, where $k^{st}(Z/i)$ is the Stortenbeker correction factor equal to the number of new species which arise in pure molten NaF as a result of introducing one molecule of Z. After inserting the respective quantities ($i = \text{NaF}$) we find from Eq. (4) $k^{st}(Z/i) = 1.01 \approx 1$. Thus, $k^{st}(Z/i) = 1 = 1 - b_\infty + qb_\infty$; from it $q = 1$. Therefore, the compound $(\text{NaF})_p \cdot \text{Na}_2\text{SO}_4$ is referred to. With regard to Eq. (3) also $p = 1$ holds. Thus, $Z = \text{NaF} \cdot \text{Na}_2\text{SO}_4 = \text{Na}_3\text{FSO}_4$. For this compound it is found in Table 1 $y(i) = 0.3051$ and $\Delta H^f(i, \text{ph. d}) = 61\,881 \text{ J mol}^{-1}$. The last value is much higher than the calorimetric value of $\Delta H^f(i)$. The reason for it is the fact that in case of thermal dissociation of Z, the actual NaF concentration, $c(i)$, differs considerably from $y(i)$. Let the degree of thermal dissociation of compound Z in solution with NaF be b ; then y moles of NaF weighed-in and $(1 - y)$ moles of Z will yield $(y + (1 - y)b)$ moles of NaF, $(1 - y)(1 - b)$ moles of Z and $(1 - y)b$ moles of Na₂SO₄ in the melt. The actual concentration of NaF, $c(i)$, is then given by the relation

$$c(i) = \frac{y + (1 - y)b}{1 + (1 - y)b}. \quad (5)$$

We shall easily make sure that

$$c(i) = \frac{y + (1 - y)b}{1 + (1 - y)b} < y,$$

holds as far as $0 < b < 1$. The physical reason is simple: the NaF concentration is higher than the originally weighed-in amount (*i.e.* y moles of NaF) because an additional amount of NaF originates from thermal dissociation of the compound Z.

Above we have determined the NaF activity $a(i)$ at the point E from Eq. (1), $a(i) = 0.5281$. For ideal or practically ideal solutions, the activity and the actual concentration are identical. On inserting the value 0.5281 into Eq. (5), we find that the degree of thermal dissociation b of component Z is 0.6803 for the melt at the composition of eutectic point E, *i.e.* if $y(i)$ is equal 0.3051 in the system NaF-Z.

Determination of the Degree of Thermal Dissociation of Pure Compound Z

The most probable scheme of thermal dissociation of Z is obviously



This case occurs when in the system investigated there exists only one complex compound. In the liquid mixture formed by melting one weighed-in mole of pure compound Z at its melting point there coexist $(1 - b_0)$ moles of undissociated compound Z, b_0 moles of NaF and b_0 moles of Na_2SO_4 ; for mole fractions of these substances it holds

$$y(\text{Z}) = \frac{1 - b_0}{1 + b_0}; \quad y(\text{NaF}) = y(\text{Na}_2\text{SO}_4) = \frac{b_0}{1 + b_0}.$$

For the equilibrium thermodynamic constant of dissociation it is valid

$$K^0(\text{dis}) = \frac{y(\text{NaF}) y(\text{Na}_2\text{SO}_4)}{y(\text{Z})} = \frac{b_0^2}{1 - b_0^2}. \quad (6)$$

For a mixture of weighed-in y moles of NaF and $(1 - y)$ moles of Z, it holds that on melting there coexist $(y + (1 - y)b)$ moles of NaF, $(1 - y)(1 - b)$ moles of Z and $(1 - y)b$ moles of Na_2SO_4 in it at equilibrium. Therefore

$$Y(\text{NaF}) = \frac{y + (1 - y)b}{1 + (1 - y)b}, \quad Y(\text{Z}) = \frac{(1 - y)(1 - b)}{1 + (1 - y)b},$$

$$Y(\text{Na}_2\text{SO}_4) = \frac{(1 - y)b}{1 + (1 - y)b},$$

where $Y(i)$ are the actual mole fractions of all substances present in the melt, considering the partial thermal dissociation of compound Z.

For the equilibrium constant of thermal dissociation, $K(\text{dis})$, of component Z in the mixture with NaF it holds

$$K(\text{dis}) = \frac{[y + (1 - y)b] b}{(1 - b) [1 + (1 - y)b]}. \quad (7)$$

The mole fraction of NaF at the eutectic point of the NaF-Z system, *i.e.* $y = 0.3051$ and the respective value of b , *i.e.* 0.6803 are inserted into Eq. (7). Then $K(\text{dis}) = 1.12368$ and since for ideal systems $K(\text{dis}) \approx K^0(\text{dis})$ (the temperature dependence of equilibrium constants is neglected), $b_0 = 0.7274$ is calculated from Eq. (6). The quantity b_0 is comparatively high. Therefore the liquidus of Z will be characterized by a flat maximum.

Determination of Melting Point of Compound Z

It approximately holds true that $\Delta H^f(\text{Z}) = \Delta H^f(\text{NaF}) + \Delta H^f(\text{Na}_2\text{SO}_4) = 56\,484 \text{ J}$.

• mol⁻¹. For the activity of Z it is valid

$$\ln a(Z) = \frac{\Delta H^f(Z)}{R} \left[\frac{1}{T^f(Z, \text{hyp})} - \frac{1}{T} \right], \quad (8)$$

where $T^f(Z, \text{hyp})$ is the hypothetical melting point of absolutely undissociated compound Z.

Eq. (8) is applied partly to the pure compound Z [$a^0(Z)$, $T^f(Z)$], partly to the compound Z in a saturated solution with composition and temperature of the eutectic point E, [$a^E(Z)$, $T(E)$]. Then the quantity $T^f(Z, \text{hyp})$ can be eliminated, and

$$T^f(Z) = \Delta H^f(Z) \left[\frac{\Delta H^f(Z)}{T(E)} + R \ln \frac{a^E(Z)}{a^0(Z)} \right]^{-1} \quad (9)$$

is valid. Since $a^0(Z) = (1 - b_0)/(1 + b_0) = 0.1578$, $(1 - y) = 0.695$ and $b = 0.6803$, we get

$$a^E(Z) = \frac{(1 - y)(1 - b)}{1 + (1 - y)b} = 0.1509. \quad (10)$$

Then we find from Eq. (9) that $T^f(Z) = 1061.4$ K. The calculated melting point of the compound Z is therefore only 7.4 K higher than the measured temperature $T(E)$ of eutectic point in the NaF-Z system.

Estimation of the Concentration Coordinates of Eutectic Point E in the Z-Na₂SO₄ Subsystem*

Let us assume that this subsystem is, as the NaF-Z subsystem, a simple eutectic system. Since we have established the quantities $\Delta H^f(Z)$ and b_0 , we can calculate from Eq. (8) that $T^f(Z, \text{hyp}) = 1491.7$ K. For the temperature of liquidus of component Z,

$$T = \Delta H^f(Z) \left[\frac{\Delta H^f(Z)}{T^f(Z, \text{hyp})} - R \ln y^*(Z) \right]^{-1} \quad (11)$$

is valid. To determine the quantity $y^*(Z)$, let us assume a fused mixture of y moles of Z and $(1 - y)$ moles of Na₂SO₄. There coexist $y(1 - b)$ moles of Z, yb moles of NaF and $(yb + 1 - y)$ moles of Na₂SO₄ in it at equilibrium. Then

$$y^*(Z) = \frac{y(1 - b)}{1 + yb}, \quad (12)$$

$$(1 - y^*(Z))(\text{Na}_2\text{SO}_4) = \frac{1 + yb - y}{1 + yb} \quad (13)$$

apply. From the equality $K(\text{dis}) = K^0(\text{dis})$ we find the relation

$$b = -\frac{1-y}{2y} + \left[\left(\frac{1-y}{2y} \right)^2 + \frac{b_0^2}{y} \right]^{1/2} \quad (14)$$

for the quantity b . The knowledge of the quantity b makes it possible to determine the actual mole fraction $y^*(Z)$ of the compound Z and $(1 - y^*(Z))(\text{Na}_2\text{SO}_4)$ in the

TABLE II

The calculated temperature (K) of liquidus of the complex compound $Z = \text{Na}_3\text{FSO}_4$ and of the component Na_2SO_4 in the Z - Na_2SO_4 system in dependence on the weighed-in mole fraction of compound Z

| $x(Z)$ | $T^f(Z)$ | $T^f(\text{Na}_2\text{SO}_4)$ |
|--------|----------|-------------------------------|
| 1.0 | 1 061.40 | — |
| 0.9 | 1 060.76 | — |
| 0.8 | 1 058.58 | — |
| 0.7 | 1 054.28 | — |
| 0.6 | 1 047.08 | — |
| 0.5 | 1 035.82 | 965.95 |
| 0.45 | 1 028.15 | 981.07 |
| 0.40 | 1 018.72 | 997.00 |
| 0.35 | 1 007.13 | 1 013.78 |
| 0.3 | 992.79 | 1 031.45 |
| 0.2 | — | 1 069.59 |
| 0.1 | — | 1 111.70 |
| 0.0 | — | 1 158.00 |

TABLE III

The confrontation of predicted and experimentally found data in the NaF - Na_2SO_4 system

| Value | Predicted | Found |
|--------------------------------------|---------------------------|---------------------------|
| Type of compound Z | Na_3FSO_4 | Na_3FSO_4 |
| $T^f(Z)$, K | 1 061.4 | 1 060 \pm 1 |
| b_0 | 0.73 | 0.70—0.75 |
| $T(E^*)$, K | 1 011 | 1 024 |
| $x(\text{Na}_2\text{SO}_4)$ at E^* | 0.635 | 0.62 |

given liquid mixture. For the temperature of Na₂SO₄ liquidus, the relation holds

$$T = \frac{\Delta H^f(j)}{\Delta S^f(j) - R \ln(1 - y^*(Z))}, \quad (15)$$

where $\Delta S^f(j)$ is the entropy of fusion of $j = \text{Na}_2\text{SO}_4$, $T^f(j) = 1\,158\text{ K}$, $\Delta H^f(j) = 23\,012\text{ J mol}^{-1}$ by JANAF (ref.⁷). The results of calculations of the liquidus curves of Z and Na₂SO₄ are given in Table II.

The essential data, estimated and measured in work⁶, on the NaF-Na₂SO₄ system are confronted in Table III. It follows from this table that there is very good agreement between the theoretically predicted and experimentally found values of basic quantities of the phase diagram of NaF-Na₂SO₄. The experimental determinations proved as well the above-mentioned assumption on a flat maximum on the liquidus curve of the complex compound in the system investigated.

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