Phase diagram of the system $NaF—Na_2SO_4$

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Phase diagram of the system $NaF—Na_2SO_4$ was investigated using the method of registration of cooling curves. It was found that the system contains no solid solutions. There is here a chemical compound $NaF \cdot Na_2SO_4 = Na_3FSO_4$ which melts congruently at 1060 K (787°C). This compound forms with NaF and also with Na_2SO_4 simple eutectic systems. Coordinates of eutectic points in these systems are following: E_1: 59.0 mole % NaF, 41.0 mole % Na_2SO_4, $T(E_1) = 1054$ K (781°C), solid phases being NaF, Na_3FSO_4; E_2: 27.5 mole % NaF, 72.5 mole % Na_2SO_4, $T(E_2) = 1024$ K (751°C), solid phases being Na_3FSO_4, Na_2SO_4. It was found that the remarkable thermal dissociation of Na_3FSO_4 influences the course of liquidus curves of both pure components, NaF and Na_2SO_4. The degree of thermal dissociation of the compound was estimated using the "method of liquidus of the second component".

Методом регистрации кривых охлаждения была исследована фазовая диаграмма бинарной системы $NaF—Na_2SO_4$. Она представляет собой систему без твердых растворов, в которой находится соединение $NaF \cdot Na_2SO_4 = Na_3FSO_4$ с конгруэнтной точкой плавления при 1060 K (787°C). Это соединение образует как с NaF, так и с Na_2SO_4 простые эвтектические системы. Координаты эвтектических точек, следующие: $E_1 = 59,0$ моль. % NaF, 41,0 моль. % Na_2SO_4, $T(E_1) = 1054$ K (781 °C); твердые фазы NaF, Na_3FSO_4, E_2 = 27,5 моль. % NaF, 72,5 моль. % Na_2SO_4, $T(E_2)$ = 1024 K (751°C); твердые фазы Na_3FSO_4, Na_2SO_4. Было найдено, что значительная термическая диссоциация соединения Na_3FSO_4 выразительно влияет на ход кривых ликвидуса NaF и Na_2SO_4. Применением "метода ликвидуса второго компонента" была оценена степень термической диссоциации Na_3FSO_4.

Sodium sulfate, which is almost always present in different amounts in cryolite-based electrolytes, influences negatively current efficiency of aluminium electrolysis. This negative influence could be diminished if we were able to bound the SO_4^{2-} anion into a complex, which would result in diminishing its activity. The study of interactions of Na_2SO_4 with components of electrolyte (Na_3AlF_6, NaF, CaF_2) and with possible additives to this electrolyte (LiF, NaCl, *etc.*) can be therefore of theoretical and practical interest.

Phase diagram of the system Na_3AlF_6—Na_2SO_4 has been recently investigated and analyzed [1]. This paper deals with the phase diagram of the system NaF—Na_2SO_4. There are several papers dealing with the phase diagram of the system NaF—Na_2SO_4 [2—7]. All authors came to the same conclusion that there are no solid solutions in this system and that the system contains the chemical compound Na_3FSO_4 which melts congruently. The main parameters characterizing the system as they were obtained by different authors are summarized in Table 1.

Table 1

Literature data on the phase diagram of the system NaF—Na_2SO_4

Ref.	E_1			E_2			Na_3FSO_4	
	c_{NaF} mole %	$T(E_1)$ K	$t(E_1)$ °C	c_{NaF} mole %	$T(E_2)$ K	$t(E_2)$ °C	T/K	$t/°C$
[2, 3]	61.0	1046	773	30.0	1016	743	1054	781
[4]	65.5	1053	780	29.5	1023	750	1059	786
[6]		1045	772		1020	747	1057	784
[7]	59.0	1054	781	29.0	1022	749	1060	787
This paper	59.0	1054	781	27.5	1024	751	1060	787

Unfortunately, differences between the data exceed acceptable deviations which could originate from experimental inaccuracy. Number of experimentally studied mixtures is too small and it does not allow to make a reliable analysis of the course of liquidus curves in this system. In order to make it possible it was necessary to reinvestigate the phase diagram of the system more thoroughly.

Experimental

Phase diagram of the system NaF—Na_2SO_4 was studied by the method of registration of cooling curves. Sodium fluoride and sodium sulfate of anal. grade were used, their melting points being T(NaF) = 1266.5 K (993.5°C); T(Na_2SO_4) = 1157.8 K (884.8°C). Temperature was measured by means of PtRh10—Pt thermocouple which was calibrated according to melting points of series of salts: NaF (1266.5 K = 993.5°C), Na_2SO_4 (1157.8 K = 884.8°C), LiF (1121 K = 848°C), NaCl (1073.8 K = 800.8°C), KCl (1044 K = 771°C).

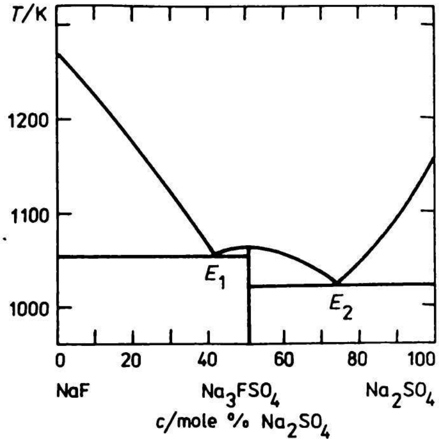

Fig. 1. Phase diagram of the system $NaF—Na_2SO_4$.

As the last point the eutectic temperature of the system $NaCl—Na_2SO_4$ (901 K = 628°C) was used. Liquidus curves were plotted on recorders eKBT 1 EN and EZ 11. Samples of mass 20 g were used, cooling rate being (1—2) K min^{-1}. 50 binary mixtures of the system were investigated. The phase diagram constructed on the basis of obtained TA data is presented in Fig. 1.

Results and discussion

It was confirmed that in the system $NaF—Na_2SO_4$ exists the compound Na_3FSO_4 which melts congruently at $T^{\mathrm{f}} = (1060 \pm 1)$ K (787 ± 1)°C. In agreement with other authors no solid solutions were found in this system. The eutectic temperature could be registered even in mixtures having composition 99 mole % NaF + 1 mole % Na_2SO_4 and 0.5 mole % NaF + 99.5 mole % Na_2SO_4.

The compound Na_3FSO_4 forms both with NaF and Na_2SO_4 simple eutectic systems. Coordinates of eutectic points in these systems are characterized by the following data:

E_1: 59.0 mole % NaF, 41.0 mole % Na_2SO_4 (= 30.5 mole % NaF, 69.5 mole % Na_3FSO_4), $T(E_1)$ = 1054 K = 781°C, solid phases being NaF and Na_3FSO_4;

E_2: 27.5 mole % NaF, 72.5 mole % Na_2SO_4 (= 38.0 mole % Na_3FSO_4, 62.0 mole % Na_2SO_4), $T(E_2)$ = 1024 K = 751°C, solid phases being Na_3FSO_4 and Na_2SO_4.

The system is interesting by the fact that the melting point of the compound Na_3FSO_4 is substantially lower than melting points of the basic components: $T^{\mathrm{f}}(NaF) - T^{\mathrm{f}}(Na_3FSO_4) = 206.5$ K; $T^{\mathrm{f}}(Na_2SO_4) - T^{\mathrm{f}}(Na_3FSO_4) = 97.8$ K.

Strongly rounded maximum on the liquidus curve of the compound Na_3FSO_4 gives evidence about high degree of its thermal dissociation. As no other compound was found in the $NaF—Na_2SO_4$ system it can be expected that the thermal dissociation proceeds according to the scheme

$$Na_3FSO_4 \rightleftharpoons NaF + Na_2SO_4 \qquad (A)$$

Cooling curves recorded in both subsystems showed that the temperature of eutectic crystallization manifests very distinctly. Also the temperature of primary crystallization of NaF could be registered practically in the whole interval of the existence of liquidus curve of this component. In the case of the compound Na_3FSO_4 its temperature of primary crystallization on the side of NaF, where the difference between temperature of primary crystallization and eutectic temperature is only 6 K, could not be clearly observed because both "stops" merged. In the region of liquidus of Na_2SO_4 an undercooling was observed, especially in the vicinity of eutectic point. The undercooling was observed even at cooling rate 1 K min^{-1}.

Error in the determination of eutectic temperature does not exceed 1 K. Error in eutectic composition of the point E_1 was estimated to be in limits 0.5—1.0 mole %. This point was determined as a cross section of liquidus curve of NaF with the eutectic isotherm. Error in determination of composition of the eutectic point E_2 is estimated to be ± 2.0 mole %.

Thermodynamic analysis of liquidus of NaF *and* Na_2SO_4

Analysis of the course of liquidus curves can be done in the most convenient way in such subsystem which has a character of a simple eutectic system. Therefore

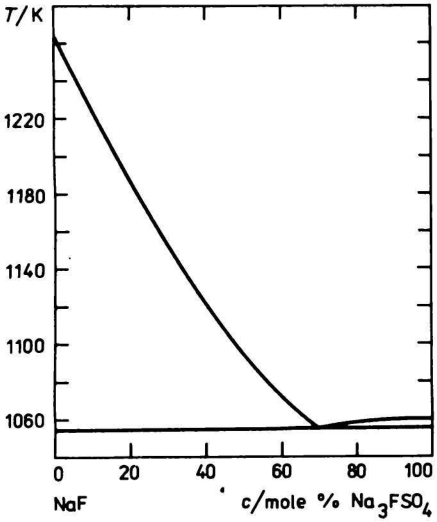

Fig. 2. Phase diagram of the subsystem NaF—Na_3FSO_4 of the system NaF—Na_2SO_4.

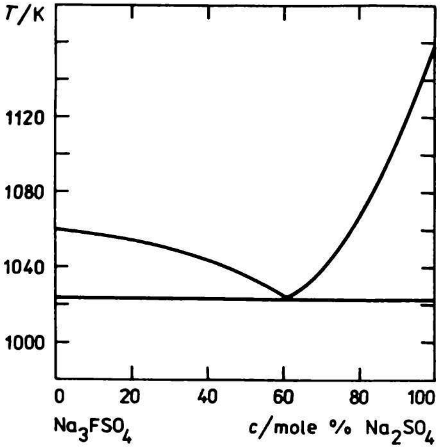

Fig. 3. Phase diagram of the subsystem Na_3FSO_4—Na_2SO_4 of the system NaF—Na_2SO_4.

liquidus curves of all substances presented in the phase diagram of the basic system NaF—Na_2SO_4 were transformed to new concentration coordinates in the subsystems NaF—Na_3FSO_4 and Na_3FSO_4—Na_2SO_4 (Figs. 2 and 3). At the transformation all curves in the phase diagram (except horizontal and vertical lines) are deformed. *E.g.* if we compare Fig. 1 with Fig. 2 it follows that a concave course of liquidus of NaF in the system NaF—Na_2SO_4 changes to convex in the phase diagram of the subsystem NaF—Na_3FSO_4. (The expressions "convex" and "concave" are considered with respect to the concentration axis.)

Cryometric determination of the enthalpy of fusion of NaF *and* Na_2SO_4

The cryometric determination of the enthalpy of fusion of NaF is based on the liquidus temperature of mixtures laying in the concentration interval 0—5 mole % Na_3FSO_4. The data were treated according to the relation $\Delta T(\mathrm{NaF})/x(\mathrm{Na_3FSO_4}) = \mathrm{f}[x(\mathrm{Na_3FSO_4})]$. The limit of this function, $k^0(\mathrm{NaF})/\mathrm{K}$, was determined for $x(\mathrm{Na_3FSO_4}) \rightarrow 0$ in a graphical way. It was found that its value is $k^0(\mathrm{NaF})/\mathrm{K} = 395$.

It is known that for the systems "i—j" of this type it holds

$$\Delta H_i^{\mathrm{f}}(\mathrm{cryom}) = \frac{R(T_i^{\mathrm{f}})^2}{k_i^0} k_{j/i}^{\mathrm{St}} \qquad (1)$$

For calculation of $\Delta H_i^{\mathrm{f}}(\mathrm{cryom})$ we need to know the Stortenbeker correction factor $k_{j/i}^{\mathrm{St}}$. It can be easy proved that it holds (without respect to the character of dissociation of Na_3FSO_4) that $k_{j/i}^{\mathrm{St}} = 1$ ($j = \mathrm{Na_3FSO_4}$, $i = \mathrm{NaF}$).

After setting numerical values in eqn (*1*) we obtain $\Delta H^{\mathrm{f}}(\mathrm{NaF})(\mathrm{cryom}) = 33.79\ \mathrm{kJ\ mol^{-1}}$. This value differs only about 1.3% from the calorimetric value which is $33.35\ \mathrm{kJ\ mol^{-1}}$ [8]. This agreement confirms that the measurement of liquidus curve of NaF was carried out practically at equilibrium conditions and that no limited solid solutions on the base of NaF are present.

The same method of determination of the slope to liquidus curve of Na_2SO_4 in the system Na_3FSO_4—Na_2SO_4 for $x(\mathrm{Na_2SO_4}) \rightarrow 1$ as in the above case was applied. It was found that $k^0(\mathrm{Na_2SO_4})/\mathrm{K} = 600$. It is easy to show that also in this case it holds that $k_{j/i}^{\mathrm{St}} = 1$ ($j = \mathrm{Na_3FSO_4}$, $i = \mathrm{Na_2SO_4}$). Putting numerical values in eqn (*1*) we obtain $\Delta H^{\mathrm{f}}(\mathrm{Na_2SO_4})(\mathrm{cryom}) = 18.58\ \mathrm{kJ\ mol^{-1}}$. Calorimetric value [8] is given as $\Delta H^{\mathrm{f}}(\mathrm{Na_2SO_4})(\mathrm{calor}) = 23.01\ \mathrm{kJ\ mol^{-1}}$. The deviation between the calorimetric and cryometric values is 19.3%, which exceeds errors which could originate from experimental inaccuracy of the calorimetric and cryometric methods.*

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* The deviation of both values is defined by the relation $|\delta| = 100(\Delta H_i^{\mathrm{f}}(\mathrm{calor}) - \Delta H_i^{\mathrm{f}}(\mathrm{cryom})/ / \Delta H_i^{\mathrm{f}}(\mathrm{calor}))$.

The explanation is that the determination of liquidus curve of Na_2SO_4 was not carried out in conditions close to thermodynamic equilibrium. This assumption is supported by the tendency of Na_2SO_4 rich melts to undercooling. However, also kinetics of formation of anion FSO_4^{3-} can play a role in this respect. Since $\Delta H^f(Na_2SO_4)(\text{cryom}) < \Delta H^f(Na_2SO_4)(\text{calor})$ the existence of limited solid solutions formed on the base of Na_2SO_4 is unprobable [9].

Analysis of reasons of convex course of liquidus curve of NaF *and* Na_2SO_4

From Figs. 2 and 3 it follows that the liquidus of both basic components in the subsystems NaF—Na_3FSO_4 and Na_3FSO_4—Na_2SO_4 is remarkably convex with respect to concentration axis. Inflex points are in both cases irrational (*i.e.* they are covered by the liquidus curve of the second component). It is known that for the existence of an inflex point (which is equivalent to the phenomenon of convex orientation of part of the liquidus curve with respect to concentration axis) it must hold $\mathrm{d}^2T/\mathrm{d}x_i^2 \cdot 1/\mathrm{K} = 0$. Applying this condition to the equation of liquidus curve

$$T_i = \frac{\Delta H_i^f}{\Delta S_i^f - R \ln a_i} \tag{2}$$

and assuming that it holds $a_i = x_i$ and $\Delta H_i^f \neq f(T)$ we obtain the relation

$$\ln a_i^{\text{inflex}} = \frac{\Delta S_i^f}{R} - 2 \tag{3}$$

where ΔH_i^f, ΔS_i^f are the molar enthalpy and entropy of fusion of the i-th component, a_i is its activity.

Because at chosen standard state $a_i \leqq 1$ a part of liquidus curve can be convex if it holds $\Delta S_i^f \leqq 2R = 16.63\ \mathrm{J\ K^{-1}\ mol^{-1}}$. In the case of NaF $\Delta S^f(\mathrm{NaF}) = \Delta H^f(\mathrm{NaF})/T^f(\mathrm{NaF}) = 26.33\ \mathrm{J\ K^{-1}\ mol^{-1}}$. Nevertheless the liquidus of NaF is remarkably convex with respect to concentration axis. This paradox can be caused by two reasons:

1. Liquidus of NaF deviates strongly from ideality.
2. Liquidus of NaF is influenced by thermal dissociation of Na_3FSO_4.

The first assumption apparently does not correspond to reality. The only acceptable explanation of the course of liquidus of NaF can be based on the assumption of thermal dissociation of Na_3FSO_4 to NaF and Na_2SO_4. We shall try to estimate the degree of the dissociation.

Determination of the degree of thermal dissociation of the compound Na_3FSO_4

In thermodynamics there are several possibilities how to determine the degree of thermal dissociation b_0 of pure component Z. The most familiar is the method described by *Glasstone* [10] which requires knowledge of ΔH^f_Z. As we do not know the value of this quantity we cannot use the method. From other methods the most frequently used is the "method of liquidus of the second component" which was proposed by *Grjotheim et al.* [11]. The method is based on the study of liquidus of component C in the system Z—C which is chosen so that the component C is not product of thermal dissociation of the complex compound Z. However, it is possible to prove that the method of liquidus of the second component can be used also for the analysis of the course of liquidus of substances which are product of thermal dissociation of the complex compound Z. This variant of the method has not been described in literature yet. It is suitable for the analysis of liquidus of NaF and Na_2SO_4 which are products of dissociation of the complex compound Na_3FSO_4.

If the thermal dissociation of this compound proceeds according to scheme (A) the following material balance is to be fulfilled. We weight-in x moles of NaF and $(1-x)$ moles of Na_3FSO_4. After melting we have in equilibrium melt x original moles of NaF, $(1-x)(1-b)$ moles of thermally undissociated Na_3FSO_4 plus products of dissociation, *viz.* $(1-x)b$ moles of NaF and $(1-x)b$ moles of Na_2SO_4. b is the degree of dissociation of Na_3FSO_4 in mixture with NaF. The real mole fraction of NaF in this mixture equals

$$y=\frac{x+b-bx}{1+b-bx} \tag{4}$$

In all considerations we shall assume that the system NaF—Na_3FSO_4 is ideal. It is obvious that the quantity b depends (at constant temperature) on b_0 and on mole fraction of NaF in the mixture. The relationship among these quantities can be determined from the expression for equilibrium constant of the reaction of thermal dissociation (A) calculated for pure component Na_3FSO_4 $(x=0)$ and for its mixture with NaF $(x>0)$.

In the first case it holds

$$K^0_{\text{dis}}=\frac{b_0^2}{1-b_0^2} \tag{5}$$

and in the second case

$$K_{\text{dis}}=\frac{[x+(1-x)\,b]\,b}{(1-b)[1+(1-x)\,b]} \tag{6}$$

If the temperature interval is not too broad we can assume that $K^0_{\mathrm{dis}} \doteq K_{\mathrm{dis}}$. It follows that

$$b = -\frac{x}{2(1-x)} + \left[\frac{x^2}{4(1-x)^2} + \frac{b_0^2}{1-x}\right]^{1/2} \tag{7}$$

For calculation of the liquidus curve we can use the following procedure. We choose a value of b_0. Then for each mole fraction x we can calculate (using eqn *(7)*) the degree of dissociation b and further from eqn (*4*) also the true mole fraction of NaF in molten mixture. For the relation between the true mole fraction of NaF, y and temperature of liquidus it holds

$$\ln y(\mathrm{NaF}) = \frac{\Delta H^{\mathrm{f}}(\mathrm{NaF})}{R}\,\frac{T - T^{\mathrm{f}}(\mathrm{NaF})}{T\,T^{\mathrm{f}}(\mathrm{NaF})} + \mathrm{f}[\Delta C_p(\mathrm{NaF})] \tag{8}$$

Value of b_0 was estimated from coordinates of the eutectic point E_1. If we assume that $\Delta C_p^{0,l/0,s}(\mathrm{NaF}) = 0\ \mathrm{J\ K^{-1}\ mol^{-1}}$, $y(\mathrm{NaF}) = 0.52810$. From the composition of eutectic point $x(\mathrm{NaF}) = 0.305$ we obtain that $K_{\mathrm{dis}} = 1.12347$ and $b_0 = 0.7274$.

Taking into account the influence of temperature on activity of NaF we obtained the following data: $y(\mathrm{NaF}) = 0.53478$, $b = 0.71067$, $K_{\mathrm{dis}} = 1.31358$, and the following data: $y(\mathrm{NaF}) = 0.53478$, $b = 0.71067$, $K_{\mathrm{dis}} = 1.31358$, and $b_0 = 0.7535$. This set of data was obtained with $\Delta C_p^{0,l/0,s}(\mathrm{NaF})$ which was taken from Kelley's thermodynamic tables [12].

Thus it follows that the degree of dissociation b_0 of pure complex compound $\mathrm{Na_3FSO_4}$ calculated from coordinates of eutectic point E_1 in the phase diagram NaF—$\mathrm{Na_3FSO_4}$ can be estimated to be 0.73—0.75. It follows further that the phenomenon of partial thermal dissociation of $\mathrm{Na_3FSO_4}$ can rationally explain the convex course of liquidus curve of NaF in the system NaF—$\mathrm{Na_3FSO_4}$. In the case of liquidus of $\mathrm{Na_2SO_4}$ this explanation is not satisfactory. For obtaining a reasonable agreement with experiment it would be necessary to assume also deviation of the system from ideality. However, it is not possible to exclude that the experimental data on liquidus of $\mathrm{Na_2SO_4}$ do not correspond to equilibrium conditions.

References

1. Koštenská, I. and Malinovský, M., *Chem. Zvesti 32,* 821 (1978).
2. Wolters, A., *Neues Jahrb. Mineral., Geol., Paläontol. Beil. 30,* 55 (1910).
3. Mukimov, S., *Izv. Sektora Fiz.-Khim. Analiza 12,* 37 (1940).
4. Rea, R. F., *J. Amer. Ceram. Soc. 21,* 98 (1938).
5. Schmitz-Dumont, O. and Heckmann, I., *Z. Anorg. Allg. Chem. 260,* 49 (1949).
6. Gladushchenko, V. A. and Bergman, A. G., *Zh. Obshch. Khim. 25,* 1651 (1955).
7. Griba, M., *Thesis.* Slovak Technical University, Bratislava, 1977.

8. Stull, D. R. and Prophet, H., *JANAF Thermochemical Tables,* 2nd Edition. Natl. Bur. Stand., Washington, 1971.
9. Malinovský, M., *Chem. Zvesti 30,* 737 (1976).
10. Glasstone, S., *Textbook of Physical Chemistry,* 2nd Edition, p. 757. Van Nostrand, New York, 1947.
11. Grjotheim, K., Halvorsen, T., and Urnes, S., *Can. J. Chem. 37,* 1170 (1959).
12. Kelley, K. K., *Contributions to the Data on Theoretical Metallurgy,* p. 171. Bull 584, U.S. Bureau of Mines, Washington, 1960.

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