

Experimental determination and thermodynamic analysis of the phase diagrams of the systems NaCl—Na₂SO₄ and NaCl—NaF

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Phase diagrams of the systems NaCl—Na₂SO₄ and NaCl—NaF were experimentally investigated using the thermal analytical method. It was found that both systems probably have a simple eutectic character. However, in the case of the system NaCl—NaF existence of a narrow range of solid solutions formed on the base of NaCl cannot be excluded. Coordinates of the eutectic point in the system NaCl—Na₂SO₄ are following: 54.0 mole % NaCl, 46.0 mole % Na₂SO₄; $T(E) = 901$ K. Coordinates of the eutectic point in the system NaCl—NaF are: 66.0 mole % NaCl, 34.0 mole % NaF; $T(E) = 955$ K. Experimental data were treated by thermodynamic analysis. The 1st and the 2nd criterion of thermodynamic consistency were applied. The activity coefficients, the parameter b in the universal relationship, the parameter w in the relationship valid for true regular solutions and the excess Gibbs energies of components were determined.

Фазовые диаграммы систем NaCl—Na₂SO₄ и NaCl—NaF были экспериментально исследованы с использованием термоаналитического метода. Обнаружено, что обе системы относятся, вероятно, к простому эвтектическому типу. Однако, в случае системы NaCl—NaF не может быть исключена возможность существования узкого интервала твердых растворов, образующихся на основе NaCl. Координаты эвтектической точки в системе NaCl—Na₂SO₄ следующие: 54,0 мол. % NaCl, 46,0 мол. % Na₂SO₄; $T(E) = 901$ К. Координаты эвтектической точки в системе NaCl—NaF: 66,0 мол. % NaCl, 34,0 мол. % NaF; $T(E) = 955$ К. Экспериментальные данные были подвергнуты термодинамическому анализу. Были применены I и II критерии термодинамической согласуемости. Были определены также коэффициенты активности, параметр b в универсальном соотношении, параметр w в соотношении, действительном для истинных правильных растворов и избыточные энергии Гиббса для компонентов.

True binary systems NaCl—Na₂SO₄ and NaCl—NaF are interesting from the practical point of view. Their components are present in the electrolytes used in electrowinning of aluminium, in the melts used for thermal treatment of metals and in reaction media used for chemical reactions above 900 K.

In this paper these systems were experimentally reinvestigated. The results were treated using the criteria of thermodynamic consistency, the universal relationship [1] and the model of regular solutions [2].

The system NaCl—Na₂SO₄ has been investigated by many authors. Results of these studies are summarized in Table 1. All the authors claim that the system in

Table 1
Survey of eutectic data on the system NaCl—Na₂SO₄

$x(\text{NaCl, E})/\text{mole } \%$	$\frac{\theta(\text{E})}{^\circ\text{C}}$	Ref.
52	628	[3]
54	624	[4]
52	628	[5]
52	628	[6]
49	624	[7]
52	634	[8]
52	628	[9]
53	624	[10]
52	628	[11]
52	628	[12]
—	623	[13]
—	634	[14]
—	628	[15]
—	628	[16]
54	628	This paper

question is a simple eutectic one. Literature data on composition of the eutectic mixture are in satisfactory agreement. However, the data on the temperature of eutectic crystallization range from 896 to 907 K, which remarkably exceeds contemporarily acceptable experimental unaccuracy (max. ± 2 K).

Literature data on the system NaCl—NaF are summarized in Table 2. Also in this case we deal with a simple eutectic system. As can be seen from Table 2 the interval of concentration coordinate of the eutectic point is 31.2—41.0 mole % NaF and the interval of the temperature coordinate is 935.2—961.2 K. Thus these parameters also exceed an acceptable range of inaccuracy, *i.e.* ± 1 mole % in composition and ± 2 K in temperature of the eutectic point.

The aim of this work is to obtain reliable experimental data for both systems.

Table 2

Survey of eutectic data on the system NaCl—NaF

$x(\text{NaCl, E})/\text{mole } \%$	$\frac{\theta(\text{E})}{^\circ\text{C}}$	Ref.
66.0	675	[17]
65.5	675	[18]
65.5	675	[7]
66.0	676	[19]
66.5	675	[20]
66.0	675	[21]
63.0	680	[22]
65.0	680	[23]
66.0	675	[24]
66.0	678	[25]
66.0	675	[26]
66.0	678	[27]
68.8	—	[28]
65.0	675	[29]
66.0	681	[30]
67.7	682	[31]
59.0	662	[32]
66.5	680	[33]
66.0	688	[34]
66.0	682	This paper

Experimental

For experimental investigation of the phase diagrams of the systems NaCl— Na_2SO_4 and NaCl—NaF the classical method of thermal analysis was used. The temperature was measured by the PtRh10—Pt thermocouple. Cool junction was kept at constant temperature (± 0.01 K) in ultrathermostat U 10 (Mechanik Prüfgeräte Medingen). EMF of the thermocouple was recorded on the recorder EZ-11 (Laboratorní přístroje, Prague). Speed of shift of paper was 40 mm/h, rate of cooling the sample did not exceed 2 K/min. The used chemicals were of anal. grade.

In the system NaCl— Na_2SO_4 14 mixtures in the region of primary crystallization of NaCl and 16 mixtures in the region of primary crystallization of Na_2SO_4 were investigated. Following coordinates of the eutectic point were found: (54.0 ± 0.5) mole % NaCl, (46.0 ± 0.5) mole % Na_2SO_4 ; $T(\text{E}) = (901 \pm 1)$ K ((628 ± 1) °C).

In the system NaCl—NaF 12 mixtures in the region of primary crystallization of NaCl and 19 mixtures in the region of primary crystallization of NaF were investigated. The coordinates of the eutectic point in this system are: ($66.0 \pm$

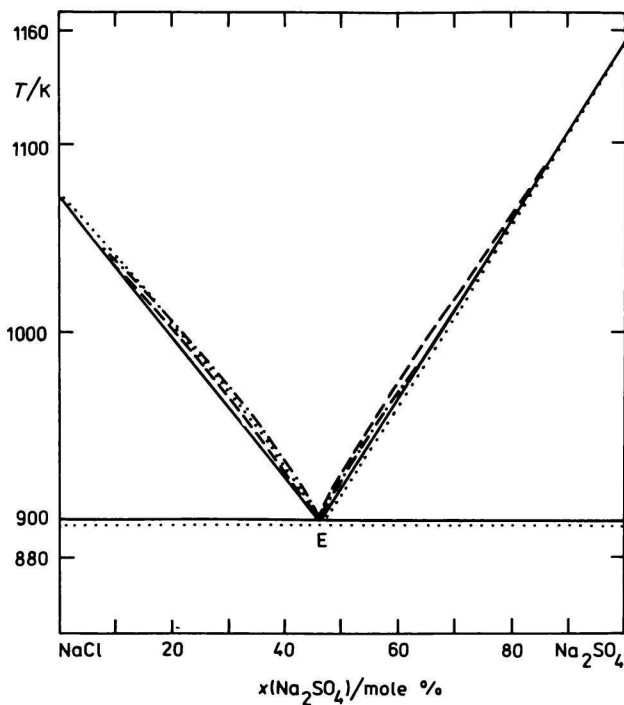


Fig. 1. Phase diagram of the system NaCl—Na₂SO₄.

— Experiment; ···· $a(i) = x(i)$; ---- universal relationship; - · - · - regular solutions.

± 0.5 mole % NaCl, (34.0 ± 0.5) mole % NaF; $T(E) = (955 \pm 1)$ K $((682 \pm 1)^\circ\text{C})$. Phase diagrams of both systems are presented in Figs. 1 and 2, respectively. The obtained results confirmed that both systems have a simple eutectic character.

Thermodynamic analysis

Comparison of the enthalpies of fusion of pure components $\Delta H(\text{fus}, i)$ obtained from cryometry with calorimetric data

The enthalpy of fusion of pure components in both investigated systems was determined by the cryometric method (application of the 1st criterion of thermodynamic consistency [35]). The following relationship was used

$$k^0(i) = \frac{R(T(\text{fus}, i))^2}{\Delta H(\text{fus}, i)} \cdot k_{\text{st}}(j/i) \quad (1)$$

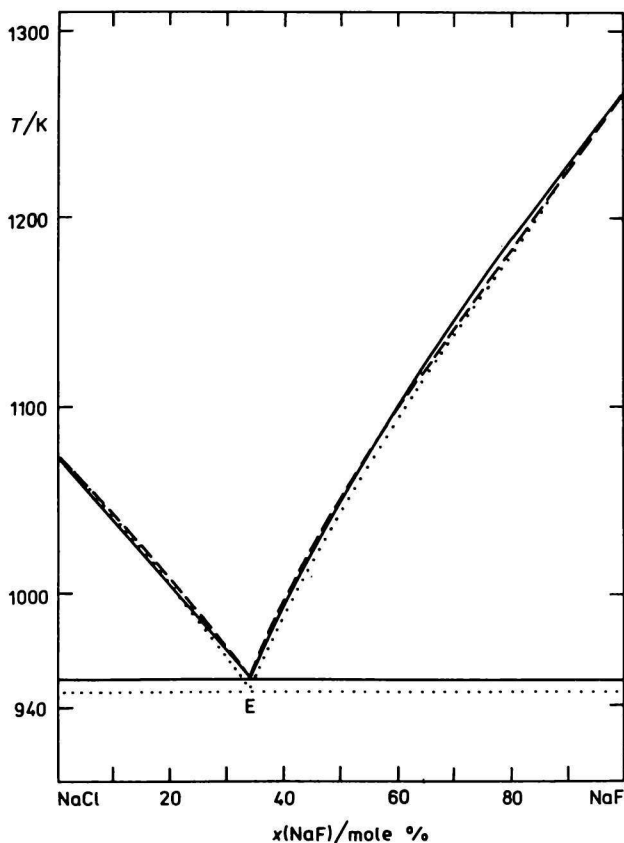


Fig. 2. Phase diagram of the system NaCl—NaF.

———— Experiment; ···· $a(i) = x(i)$; - - - - universal relationship; regular solutions coincide with liquidus curves.

$k^0(i)$ is the slope of tangent to the liquidus curve of the component i for $x(i) \rightarrow 1$, R is the gas constant, $T(\text{fus}, i)$ is the temperature of fusion of pure component i and $k_{\text{st}}(j/i)$ is the Stortenbecker correction factor which equals the number of new species formed when one molecule of the substance j is brought in pure molten substance i .

The calculation gave the following results:

The system NaCl—Na₂SO₄: $\Delta H(\text{fus}, \text{NaCl}) = 27\,004 \text{ J mol}^{-1}$;
 $\Delta H(\text{fus}, \text{Na}_2\text{SO}_4) = 23\,464 \text{ J mol}^{-1}$.

The system NaCl—NaF: $\Delta H(\text{fus}, \text{NaCl}) = 29\,580 \text{ J mol}^{-1}$;
 $\Delta H(\text{fus}, \text{NaF}) = 34\,367 \text{ J mol}^{-1}$.

The value of $\Delta H(\text{fus, NaCl})$ calculated from cryometric data obtained in the system $\text{NaCl—Na}_2\text{SO}_4$ is lower than the calorimetric one ($28\,660\text{ J mol}^{-1}$ [36]; $28\,158\text{ J mol}^{-1}$ [37]; $27\,991\text{ J mol}^{-1}$ [38]). It is quite usual that the values of $\Delta H(\text{fus, i})$ calculated from cryometric data are lower in comparison with calorimetric values. This can be explained by that the dynamic methods (thermal analysis being one of them) used for determination of liquidus curves are accompanied by certain undercooling which results in the fact that $\Delta H(\text{fus, i, cryom}) < \Delta H(\text{fus, i, calor})$. When the cryometric measurements are carried out in a correct way the undercooling can be limited to an acceptable extent and the value of $\Delta H(\text{fus, i, cryom})$ will not differ from $\Delta H(\text{fus, i, calor})$ more than about 5 %. In many cases this difference is even smaller. Thus, e.g. the calculated value of $\Delta H(\text{fus, Na}_2\text{SO}_4)$ in the system $\text{NaCl—Na}_2\text{SO}_4$ agrees well with calorimetric value ($23\,723\text{ J mol}^{-1}$ [36]; $23\,012\text{ J mol}^{-1}$ [37]). The deviation in this case is $\pm 1.1\%$.

The value of $\Delta H(\text{fus, NaCl})$ obtained from cryometric data in the system NaCl—NaF is about 3.2—5.6 % higher than the calorimetric value of enthalpy of fusion of sodium chloride given above. Also the cryometric value of $\Delta H(\text{fus, NaF, cryom})$ exceeds the calorimetric data ($33\,346\text{ J mol}^{-1}$ [37]; $33\,890\text{ J mol}^{-1}$ [39]) by 1.4—3.0 %. As we pointed out the maximum inaccuracy of cryometric method does not exceed 5 %. Thus one cannot exclude that the cryometric value of $\Delta H(\text{fus, NaCl, cryom})$ obtained in this work indicates the existence of a narrow range of solid solutions formed on the base of NaCl. Thermodynamic analysis of liquidus and solidus curves in the systems of eutectic type allows to estimate the extent of the assumed solid solutions at the eutectic temperature $T(E)$.

The relation between $\Delta H(\text{fus, i})$ and $k^0(i)$ is given by eqn (1). In the case of the system NaCl—NaF ($\text{NaCl} = i, \text{NaF} = j$) obviously $k_s(j/i) = 1$. We may write the relationship for the liquidus of NaCl and formally also for the curve of monovariant equilibrium which determines the region of saturated solutions of NaF in NaCl (this curve starts at the point $T(\text{fus, NaCl})$) as follows

$$k^0(\text{liquidus, NaCl}/j) = \frac{R(T(\text{fus, NaCl}))^2}{\Delta H^*(\text{liquidus, NaCl}/j)} \quad (2)$$

$$k^0(\text{solidus, NaCl}/j) = \frac{R(T(\text{fus, NaCl}))^2}{\Delta H^*(\text{solidus, NaCl}/j)} \quad (3)$$

where ΔH^* is the quantity formally resembling the enthalpy of fusion. (When no solid solutions occur $\Delta H^*(\text{liquidus, NaCl}/j) \equiv \Delta H(\text{fus, NaCl, cryom})$). When the quantity $\Delta H(\text{fus, i, cryom})$ is remarkably greater than $\Delta H(\text{fus, i, calor})$ we may assume that it holds

$$\Delta H(\text{fus, i, cryom}) = \Delta H(\text{fus, i, calor}) + \Delta H^*(\text{solidus, i}/j) \quad (4)$$

From eqns (2) and (3) it follows

$$\begin{aligned} k^0(\text{solidus, NaCl}/j) \cdot \Delta H^*(\text{solidus, NaCl}/j) &= \\ = k^0(\text{liquidus, NaCl}/j) \cdot \Delta H(\text{fus, NaCl, cryom}) &\quad (5) \end{aligned}$$

and further

$$k^0(\text{solidus, NaCl}/j) = \frac{k^0(\text{liquidus, NaCl}/j) \cdot \Delta H(\text{fus, NaCl, cryom})}{\Delta H^*(\text{solidus, NaCl}/j)} \quad (6)$$

As we will show later the liquid solution of NaCl—NaF behaves almost ideally. Thus it is justified to assume that also for the limited solid solubility of NaF in NaCl (only several mole %) the system will approach the ideal behaviour. Then we may write

$$\ln x(\text{solidus, NaCl, E}) = \frac{\Delta H^*(\text{solidus, NaCl}/j)}{R} \left[\frac{1}{T(\text{fus, NaCl})} - \frac{1}{T(E)} \right] \quad (7)$$

The value of $\Delta H^*(\text{solidus, NaCl}/j)$ can be obtained from eqn (4). For $\Delta H(\text{fus, NaCl, calor})$ the newest value recommended by JANAF [37] was chosen, viz. $28\,158 \text{ J mol}^{-1}$. $\Delta H^*(\text{solidus, NaCl}/j) = 1427 \text{ J mol}^{-1}$. After inserting into eqn (6) we find $k^0(\text{solidus, NaCl}) = 6720.8$. This value of the slope of tangent characterizes the region of partial solid solutions in the vicinity of the point $T(\text{fus, NaCl})$. After inserting the value of $\Delta H^*(\text{solidus, NaCl}/j)$ into eqn (7) we obtain $x(\text{solidus, NaCl, E})$, i.e. the expected range of solid solutions formed on the base of NaCl at the temperature of eutectic crystallization $T(E)$. It was found that $x(\text{solidus, NaCl, E}) = 0.9803$.

Application of the 2nd criterion of thermodynamic consistency

Composition of the eutectic points in the systems NaCl—Na₂SO₄ and NaCl—NaF was checked by the application of the 2nd criterion of thermodynamic consistency [35]

$$\begin{aligned} x(i, E) \cdot \Delta \bar{H}(l/s^0, i, E) \cdot k(i, E) &= \\ = x(j, E) \cdot \Delta \bar{H}(l/s^0, j, E) \cdot k(j, E) &\quad (8) \end{aligned}$$

where $x(i, j, E)$ are the mole fraction of components i and j , respectively, at the eutectic point, $\Delta \bar{H}(l/s^0, i, j, E)$ are the partial molar enthalpies of fusion of substances i and j at the eutectic point, $k(i, j, E)$ are the slopes of tangents to the liquidus curves of the components i and j , respectively, at the eutectic point.

When we assume that the systems are ideal, the relationship (8) can be simplified. Obviously it holds

$$\begin{aligned}\Delta\bar{H}(l/s^0, i) &= \Delta\bar{H}(l, i) - H(s^0, i) = \bar{H}(l, i) - H(l^0, i) + \\ &+ H(l^0, i) - H(s^0, i) = \Delta\bar{H}(l/l^0, i, \text{mix}) + \Delta H(l^0/s^0, i)\end{aligned}$$

If behaviour of the solutions is not far from ideality, $\Delta H(l/l^0, i, \text{mix}) = 0$. Because the temperature dependence of the quantity $\Delta H(l^0/s^0, i)$, $i = \text{NaCl}, \text{Na}_2\text{SO}_4, \text{NaF}$, is not very remarkable, we can write

$$\Delta H(l^0/s^0, i) = \Delta H(\text{fus}, i)$$

Thus finally we obtain for ideal system

$$\Delta\bar{H}(l/s^0, i) = \Delta H(\text{fus}, i) \quad (9)$$

Using these simplifying assumptions we got the following results:

In the system $\text{NaCl}-\text{Na}_2\text{SO}_4$ we have on the left-hand side of the equation the value $30\,411 \text{ J K mol}^{-1}$ and on the right-hand side the value $29\,464 \text{ J K mol}^{-1}$. In the system $\text{NaCl}-\text{NaF}$ we have on the left-hand side the value $34\,381 \text{ J K mol}^{-1}$ and on the right-hand side the value $36\,339 \text{ J K mol}^{-1}$. These results confirm correctness of the experimentally determined coordinates of the eutectic points in the studied systems.

Calculation of the liquidus curves

Liquidus curves in the systems $\text{NaCl}-\text{Na}_2\text{SO}_4$ and $\text{NaCl}-\text{NaF}$ were calculated using the Le Chatelier—Shreder equation [40—42] under assumption that both systems are ideal from the thermodynamic point of view. ($a(i) = x(i)$.) The calculated curves are compared with experimental data in Figs. 1 and 2. It is seen that there is only small difference between the calculated and experimental data.

Determination of the activity coefficients of components of the studied systems at the eutectic point

For classically ideal solution it holds $a(i) = x(i)$.

For real solutions

$$a(i) = \gamma(i) \cdot x(i) \quad (10)$$

$a(i)$ is the activity, $x(i)$ is the mole fraction and $\gamma(i)$ is the activity coefficient of the component i .

It holds

$$\gamma(i) = \frac{a(i)}{x(i)} = \frac{x(\text{id}, i)}{x(\text{real}, i)} \neq 1 \quad (11)$$

$x(\text{id}, i)$ denotes mole fraction of the i -th component obtained from the Le Chatelier—Shreder equation [40—42] (assuming $a(i) = x(i)$) and $x(\text{real}, i)$ is the experimentally obtained mole fraction.

From numerical value of activity coefficient of the component in given system one can estimate how the behaviour of this system differs from ideality.

At the determination of activity coefficient at the eutectic point we proceed in such a way that one calculates the data for liquidus curves in the vicinity of the eutectic temperature. One may determine the value $a(\text{id}, i) = x(\text{id}, i)$ and from eqn (11) calculate the activity coefficients. Using this procedure the following data were obtained:

a) The system NaCl—Na₂SO₄:

$$\begin{array}{ll} x(\text{id}, \text{NaCl}) = 0.54499 & \\ x(\text{real}, \text{NaCl}) = 0.54 & \gamma(\text{NaCl}, E) = 1.0092 \\ x(\text{id}, \text{Na}_2\text{SO}_4) = 0.47408 & \\ x(\text{real}, \text{Na}_2\text{SO}_4) = 0.46 & \gamma(\text{Na}_2\text{SO}_4, E) = 1.0306 \end{array}$$

b) The system NaCl—NaF:

$$\begin{array}{ll} x(\text{id}, \text{NaCl}) = 0.67313 & \\ x(\text{real}, \text{NaCl}) = 0.66 & \gamma(\text{NaCl}, E) = 1.0199 \\ x(\text{id}, \text{NaF}) = 0.35593 & \\ x(\text{real}, \text{NaF}) = 0.340 & \gamma(\text{NaF}, E) = 1.0468 \end{array}$$

Taking into account unaccuracy of experimental data we may state that the values of the activity coefficients are close to unit and, therefore, we can consider the behaviour of both systems as ideal.

Determination of the parameter b in the universal relationship

For description of the deviation of behaviour of given component from ideality also the universal relationship [1] can be used according to which it holds

$$a(i) = x(i)^{k(j/i)} \quad (12)$$

where

$$k(j/i) = \frac{k_{st}(j/i)}{1 + b(1 - x(i))} \quad (13)$$

b is the parameter calculated *e.g.* on the basis of the concentration coordinate of the eutectic point. The parameter b is rather sensitive to this coordinate. Shift of

the eutectic point about 0.5 mole % changes in the studied systems the value of b at least by 18 % (Tables 3 and 4). Thus reliable determination of the parameter b requires precise experimental data. Using the Le Chatelier—Shreder equation [40—42] and assuming validity of eqns (12) and (13) we may calculate the liquidus curves of components in both systems. The results of the calculation are presented in Figs. 1 and 2.

Table 3
Values of the parameter b in the system NaCl—Na₂SO₄

$x(\text{NaCl})/\text{mole \%}$	$b(\text{NaCl})$	$x(\text{Na}_2\text{SO}_4)/\text{mole \%}$	$b(\text{Na}_2\text{SO}_4)$
54.0(E)	0.04068	46.0(E)	0.19545
54.5	0.00758	46.5	0.16910
53.5	0.07326	45.5	0.22280

Table 4
Values of the parameter b in the system NaCl—NaF

$x(\text{NaCl})/\text{mole \%}$	$b(\text{NaCl})$	$x(\text{NaF})/\text{mole \%}$	$b(\text{NaF})$
66.0(E)	0.17371	34.0(E)	0.06757
66.5	0.12017	34.5	0.04651
65.5	0.22867	33.5	0.08864

Determination of the interaction parameter w in the relationship for strictly regular solutions

The liquidus curves were calculated under the assumption that the components form a strictly regular solutions [2]. This approach is correct when one deals with the systems of the 1st kind [43, 44], which is also our case.

It holds

$$RT(i) \cdot \ln(x(i)) + [1 - x(i)]^2 \cdot w = \Delta H(\text{fus}, i) \left[\frac{T(i)}{T(\text{fus}, i)} - 1 \right] \quad (14)$$

where w is the interaction parameter.

The relationship (14) holds under the assumption that the quantity $\Delta H(10^3/s^0, i)$ depends only negligibly on temperature. In our case ($i = \text{NaCl}, \text{Na}_2\text{SO}_4, \text{NaF}$) this assumption is satisfactorily fulfilled. The parameter w can be determined either by the method described in the monograph by *Grjothheim* [45] or by the pro-

cedure described in paper [34]. It was found that in the system NaCl—Na₂SO₄ $w = 1.225 \times 10^3 \text{ J mol}^{-1}$ and in the system NaCl—NaF $w = 1.080 \times 10^3 \text{ J mol}^{-1}$.

Calculated liquidus curves are compared with experimental data in Figs. 1 and 2. It is seen that the experimental and calculated data are in good agreement regardless of the model (universal or regular relationship) used in calculation.

Determination of the excess Gibbs energies of components

The excess Gibbs energies of components in the solutions corresponding to the eutectic points were determined according to the equation published by Førlund [46]

$$\begin{aligned} \Delta \bar{G}(\text{ex}, i) = & \Delta H(\text{fus}, i) \left[\frac{T(i)}{T(\text{fus}, i)} - 1 \right] + \Delta a(i) \left[T(\text{fus}, i) - \right. \\ & \left. - T(i) - T(i) \ln \frac{T(\text{fus}, i)}{T(i)} \right] + \frac{\Delta b(i)}{2} \left[T(\text{fus}, i) - T(i) \right]^2 + \\ & + \frac{\Delta c(i)}{2} \left[\frac{1}{T(i)} - \frac{1}{T(\text{fus}, i)} \right]^2 \cdot T(i) - RT(i) \ln x(i) \end{aligned} \quad (15)$$

$\Delta \bar{G}(\text{ex}, i)$ is the excess partial molar Gibbs energy, $T(i)$ is the temperature of eutectic crystallization (experimental), a , b , c are the coefficients of the molar heat capacities. The data for $\Delta H(\text{fus}, i)$, $T(\text{fus}, i)$, $\Delta a(i)$, $\Delta b(i)$, and $\Delta c(i)$ were taken from literature [36]. Results of the calculations are summarized in Table 5.

Table 5
Excess partial molar Gibbs energies in the systems
NaCl—Na₂SO₄ and NaCl—NaF

System	Component	$\frac{\Delta \bar{G}(\text{ex})}{\text{J mol}^{-1}}$
NaCl—Na ₂ SO ₄	NaCl	86.3
NaCl—Na ₂ SO ₄	Na ₂ SO ₄	281.4
NaCl—NaF	NaCl	174.9
NaCl—NaF	NaF	221.6

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