Thermodynamic analysis of the two-component systems LiF—NaF and NaF—NaCl*

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The phase diagrams of the systems LiF—NaF and NaF—NaCl have been investigated using the classical TA method. It has been found that the system LiF—NaF is a eutectic system with limited solid solutions of LiF in NaF, the extent of which is approx. 8 mole % LiF. The coordinates of the eutectic point are 60.5 mole % LiF, 39.5 mole % NaF, $t_{\rm e} = 652^{\circ}$ C. The system NaF—NaCl is a simple eutectic system with the eutectic point of the following coordinates: 66 mole % NaF, 34 mole % NaCl, $t_{\rm E} = 688.5^{\circ}$ C. The thermodynamic analysis of the systems LiF—NaF and NaF—NaCl has been performed on the basis of the experimental results.

Фазовые диаграммы систем LiF—NaF и NaF—NaCl были изучены методом термического анализа. Было найдено, что система LiF—NaF является эвтектической системой с областью ограниченных твердых растворов LiF в NaF, которые достигают приблизительно 8 мол.% LiF. Точка состава эвтектики имеет координаты 60,5 мол.% LiF и 39,5 мол.% NaF, $t_e = 652^{\circ}$ C. Система NaF—NaCl является простой эвтектической системой, эвтектика которой имеет состав 66 мол.% NaF и 34 мол.% NaCl, $t_e = 688,5^{\circ}$ C. На основании экспериментальных данных рассмотрены системы LiF—NaF и NaF—NaCl с точки зрения термодинамического анализа.

The system LiF—NaF was studied by several authors. The results of their measurements are presented in Table 1. The majority of the authors agree that LiF—NaF is a simple eutectic system. In 1965 Holm [8, 9] and at the same time Matiašovský et al. [10] have shown that on the NaF side there exists a narrow region of limited solid solutions up to approx. 4 mole % LiF at the eutectic temperature. In subsequent papers Short and Roy [13] and Holm [12] confirm the existence of the solid solutions in this system, but they denote a wider extent of them, up to 8 mole % LiF in NaF.

The results of measurements of the phase diagram of NaF—NaCl system are collected in Table 2. All the authors state that NaF—NaCl is a simple eutectic system.

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The system LiF—NaF The comparison of the referred data

t ^f _{LiF} ℃	l ^f _{NaF} °C	E		Def	Neder	
		mole % LiF	t _E , °C	Kel.	Notes	
848.0	990.0	61.0	652	[1]	SES	
_	_	61.5	646	[2]	SES	
845.0	990.0	60.0	652	[3]	SES	
845.0	990.0	60.0	652	[4]	SES	
845.0	990.0	60.0	650	[5]	Read from the graph	
846.0	990.0	61.5	645	[6]	SES	
846.0	990.0	61.0	650	[7]	Read from the graph	
846.3	994.5	61.0	649	[8, 9]	Es with lim. SS	
846.0	993.0	60.4	659	[10]	Es with lim. SS	
848.0	990.0	60.0	652	[11]	Read from the graph	
848.0	995.0	61.0	649	[12]	Es with lim. SS	

ES — eutectic system,

SES — simple eutectic system,

SS - solid solution.

The data concerning the composition of the eutectic mixtures of the systems LiF—NaF and NaF—NaCl are in good accordance. Greater differences can be found in the value $t_{\rm E}$ in the case of the system LiF—NaF: 645—659°C and NaF—NaCl: 662—682°C. To obtain these $t_{\rm E}$ values and the courses of liquidus lines with better accuracy and to get the data enabling to take a standpoint to the extent of the solid solution in the system LiF—NaF, both systems, LiF—NaF and NaF—NaCl have been re-investigated in the whole concentration range. Although the mentioned systems were experimentally studied many times, the detailed thermodynamic analysis has not been made till now.

Experimental

The phase diagrams of the systems LiF—NaF and NaF—NaCl were investigated by the TA method. These salts were used: LiF "pure" (Lachema, Brno) m.p. 848.3°C [32], NaF "anal. grade" (Lachema, Brno) m.p. 993.5°C — this value was found in the Laboratory of Molten Salts, Institute of Inorganic Chemistry, Slovak Academy of Sciences — NaCl "anal. grade" (Lachema, Brno) m.p. 800.8°C [32]. The individual salts were calcinated and stored in wide mouth bottles in an exsiccator. The salts were weighed in a Pt-crucible, the whole amount being 20 g. The sample was melted in a silite furnace in an open atmosphere. The temperature was measured with a PtRh10—Pt thermocouple. The test junction of the thermocouple was inserted in the axis of the crucible always in the same depth in the measured melt; the reference junction was maintained at the constant temperature with a precision $\pm 0.01^{\circ}$ C using the ultrathermostat. The calibration of the thermocouple was performed by means of the melting

The comparison of the referred data						
1 NaF	I NaCI	E		Pof	Notos	
°C	°C	mole % NaF	t _E , °C	Kei.	Notes	
992.0	804.0	34.0	675	[14]	SES	
986.0	797.0	34.5	675	[15]	SES	
	_	34.5	675	[16]	SES	
990.0	800.0	34.0	676	[17]	SES	
996.0	800.0	33.5	675	[18]	SES	
990.0	800.0	34.0	675	[19]	SES	
986.0	801.0	37.0	680	[20]	Read from the graph	
992.0	800.0	35.0	680	[21]	SES	
990.0	800.0	34.0	675	[22]	SES	
990.0	800.0	34.0	678	[23]	SES	
990.0	800.0	34.0	675	[24]	SES	
990.0	800.0	34.0	678	[25]	Read from the graph	
_	_	31.2		[26]	SES	
986.0	797.0	35.0	675	[27]	SES	
997.0	800.0	34.0	681.0	[28]	SES	
996.0	800.0	33.3	682.0	[29]	SES	
		41.0	662.0	[30]	SES	
994.5	800.5	33.5	680.0	[31]	SES	

The system NaF—NaCl The comparison of the referred data

points of the pure substances: NaF (m.p. 993.5°C), Na₂SO₄ (m.p. 884.8°C [33]), LiF (m.p. 848.3°C [32]), NaCl (m.p. 800.8°C [32]), KCl (m.p. 771°C [32]) and by means of the eutectic points of the mixtures, which form simple eutectic systems: *e.g.* KCl—K₂SO₄ (73.4 mole % KCl+26.6 mole % K₂SO₄), $t_{\rm E}$ = 690°C [34]; NaCl—Na₂SO₄ (51.85 mole % NaCl+48.15 mole % Na₂SO₄), $t_{\rm E}$ = 628°C [35]. The data of thermocouple were recorded with a line recorder, type EZ 11 (Czechoslovak production). The rate of cooling did not exceed 2°C/min. The stability of the recorder was checked by the source of referential voltage, constructed at the Institute of Inorganic Chemistry, Slovak Academy of Sciences.

Experimental results

In the case of the system LiF—NaF, in the range of primary crystallization of LiF 15 mixtures, in the range of NaF 26 mixtures were investigated. The found values are given in Table 3. According to our measurements LiF—NaF is a eutectic system with limited solid solutions of LiF in NaF, the extent of which is approx. 8 mole % LiF in NaF at the eutectic temperature. Thus the results of *Holm* [12] and *Short* and *Roy* [13] were confirmed. The coordinates of the eutectic point of the system are: 60.5 ± 0.5 mole % LiF, 39.5 ± 0.5 mole % NaF, $t_{\rm E} = 652 \pm 1^{\circ}$ C.

Mole %		Wei	ght %	ТРС	ľ _E
LiF	NaF	LiF	NaF	°C	°Ĉ
0.0	100.0	0.000	100.000	993.5	
0.5	99.5	0.310	99.690	991.5	
1.0	99.0	0.620	99.380	990.0	—
1.5	98.5	0.932	99.068	987.5	_
2.0	98.0	1.245	98.755	986.0	_
2.5	97.5	1.559	98.441	984.5	
3.0	97.0	1.875	98.125	982.0	
3.5	96.5	2.191	97.809	980.0	
4.0	96.0	2.509	97.491	978.0	_
4.5	95.5	2.828	97.172	976.0	<u> </u>
5.0	95.0	3.149	96.851	974.0	_
6.0	94.0	3.793	96.207	970.0	
7.0	93.0	4.443	95.557	965.5	
8.0	92.0	5.098	94.902	962.0	646.0
9.0	91.0	5.758	94.242	958.0	_
10.0	90.0	6.423	93.577	953.0	644.0
20.0	80.0	13.377	86.623	908.0	652.0
30.0	70.0	20.932	79.068	854.0	653.0
40.0	60.0	29.170	70.830	797.0	653.0
50.0	50.0	38.185	61.815	735.0	652.0
55.0	45.0	43.020	56.980	700.5	651.5
56.0	44.0	44.015	55.985	691.0	652.0
57.0	43.0	45.020	54.980	683.5	651.5
58.0	42.0	46.035	53.965	674.5	652.0
59.0	41.0	47.060	52.940	664.5	652.0
59.5	40.5	47.576	52.424	661.0	652.0
60.0	40.0	48.095	51.905	656.0	652.0
60.5	39.5	48.616	51.384	_	652.0
61.0	39.0	49.140	50.860	654.5	652.0
61.5	38.5	49.667	50.333	656.0	651.5
62.0	38.0	50.196	49.804	660.5	652.0
63.0	37.0	51.263	48.737	666.0	652.0
64.0	36.0	52.340	47.660	674.0	652.0
65.0	35.0	53.428	46.572	680.0	652.0
70.0	30.0	59.039	40.961	709.5	651.0
80.0	20.0	71.189	28.811	759.5	652.0
90.0	10.0	84.755	15.245	803.5	650.5
95.0	5.0	92.149	7.851	826.0	650.0
96.0	4.0	93.681	6.319	833.0	650.0
97.0	3.0	95.232	4.768	837.0	650.0

The composition, temperature of primary crystallization TPC, temperature of the eutectic point $(t_{\rm E})$ of the system LiF—NaF

Mole %		Weight %		TPC	l _E
LiF	NaF	LiF	NaF	°C	°C
98.0	2.0	96.802	3.198	841.0	654.0
99.0	1.0	98.391	1.609	844.0	655.0
99.5	0.5	99.193	0.807	846.0	654.0
100.0	0.0	100.000	0.000	848.3	

Table 3 (Continued)

In the system NaF—NaCl in the range of primary crystallization of NaF 19 mixtures and in the range of primary crystallization of NaCl 12 mixtures were investigated. The measured values are in Table 4. According to our investigation NaF—NaCl is a simple eutectic system. The coordinates of the eutectic point are: 34 ± 1 mole % NaF, 66 ± 1 mole % NaCl, $t_{\rm E} = 688 \pm 1^{\circ}$ C.

Theoretical

The experimentally obtained liquidus curves of the individual systems are compared with the calculated curves. It has been considered that the components form:

1. the classical ideal solution [36-38],

2. the regular ionic solution [39],

3. the "universal" solution [40].

1. The classical ideal solution

 $a_i = x_i;$

 a_i — the activity of the *i*-th substance,

 x_i — mole fraction of the substance *i*.

LeChatelier-Schröder equation was applied in the calculation [36-38].

In the LiF—NaF system there are limited solid solutions on the NaF side. The calculation of the liquidus curve of NaF was realized with respect to the existence of the solid solutions as follows

$$\ln a_i^s = \ln x_i^s = \frac{\Delta H_i^s}{R} \left(\frac{1}{T_i} - \frac{1}{T_i} \right) \tag{1}$$

This ΔH_i^* value is calculated from eqn (1) using the value $T_i = T_E$ and $x_i^s = x_E^s$ (the extent of the solid solution at the eutectic temperature). Then using the obtained ΔH_i^* value we calculate the corresponding a_i^s (x_i^s) for the individual values of T_i . The course of the liquidus line of NaF is calculated from the equation for systems with limited solid solutions

Mole %		Weight %		TPC	t _E
NaF	NaCl	NaF	NaCl	°C	°C
100.0	0.0	100.000	0.000	993.5	a ar
99.5	0.5	99.305	0.695	992.0	_
99.0	1.0	98.614	1.386	991.0	
98.5	1.5	97.924	2.076	988.0	680.0
98.0	2.0	97.238	2.762	985.5	678.5
97.0	3.0	95.873	4.127	981.5	681.0
96.0	4.0	94.518	5.482	978.0	683.0
95.0	5.0	93.174	6.826	974.0	684.0
90.0	10.0	86.685	13.315	954.0	685.0
80.0	20.0	74.186	25.814	915.0	686.0
70.0	30.0	62.636	37.364	875.0	686.5
60.0	40.0	51.869	48.131	828.5	687.0
55.0	45.0	46.755	53.245	804.0	688.0
50.0	50.0	41.808	58.192	778.0	688.0
45.0	55.0	37.021	62.979	751.0	688.0
40.0	60.0	32.385	67.615	719.5	687.0
38.0	62.0	30.572	69.428	709.5	688.5
37.0	63.0	29.674	70.326	704.0	688.0
36.0	64.0	28.781	71.219	697.5	688.5
35.0	65.0	27.894	72.106	691.0	688.5
34.0	66.0	27.013	72.987	_	688.5
33.0	67.0	26.137	73.863	690 ¹ 0	687.5
32.0	68.0	25.267	74.733	694.0	688.0
31.0	69.0	24.402	75.598	696.5	688.5
30.0	70.0	23.542	76.458	699.0	686.5
20.0	80.0	15.226	84.774	734.5	687.0
10.0	90.0	7.393	92.607	768.5	686.5
5.0	95.0	3.644	96.356	785.0	685.5
4.0	96.0	2.906	97.094	789.0	685.5
3.0	97.0	2.174	97.826	792.0	685.5
2.0	98.0	1.445	98.555	795.0	684.5
1.0	99.0	0.720	99.280	798.0	683.0
0.5	99.5	0.360	99.640	799.0	
0.0	100.0	0.000	100.000	800.8	

The composition, temperature of primary crystallization, temperature of the eutectic point of the system NaF—NaCl

$$\ln \frac{a_{i}^{l}}{a_{i}^{s}} = \frac{\Delta H_{i}^{t}}{R} \left(\frac{1}{T_{i}^{t}} - \frac{1}{T_{i}} \right) + \frac{1}{R} \int_{\tau_{i}}^{\tau_{i}^{t}} \left[\frac{1}{T^{2}} \int_{\tau_{i}}^{\tau_{i}^{t}} \Delta C_{P_{i}}^{l/s} \, \mathrm{d}T \right] \mathrm{d}T$$
(2)

where ΔH_i^{t} — the melting enthalpy of the pure substance *i* (J mol⁻¹), *R* — gas constant (J K⁻¹ mol⁻¹),

- T_i the melting point of the pure substance *i* (K),
- T_i the temperature of primary crystallization of the substance i (K),
- $C_{P_i}^{Vs}$ the change of molar heat capacity at P = const for the reaction "solidus—liquidus" (J K⁻¹ mol⁻¹).

In eqn (2) we insert for a_i^s the values calculated from eqn (1). The course of the liquidus LiF in the system LiF—NaF as well as the liquidus lines NaF and NaCl in the system NaF—NaCl is calculated using the LeChatelier—Schröder equation.

2. The components form an ionic regular solution [39] (the existence of the solid solutions in the system LiF—NaF has been neglected). It holds

$$RT_{i} \ln x_{i} + (1 - x_{i})^{2} w = \Delta H_{i}^{t} \left(\frac{T_{i}}{T'} - 1 \right), \qquad (3)$$

where w is the interaction parameter (J mol⁻¹). To determine its value, the method described in [41] can be used.

For ΔH_i^t one obtains from eqn (3)

$$-\frac{RT_{i}\ln x_{i}}{1-\frac{T_{i}}{T_{i}^{t}}} = \Delta H_{i}^{t} + w \frac{(1-x_{i})^{2}}{1-\frac{T_{i}}{T_{i}^{t}}}$$

	The value of the parameter w in the systems LiF—NaF and NaF—NaCl					
Ĺ.	r	<i>W</i> LIF	$w_{ m NaF}$			
LiF	NaF	J mol⁻	J mol⁻			
0.595	0.405	-4.560×10^{3}	-5.705×10^{3}			
0.605	0.395	-5.619×10^{3}	-4.997×10^{3}			
0.615	0.385	-6.760×10^{3}	-4.310×10^{3}			
	x	$w_{ m NaF}$	W _{NaCl}			
NaF	NaCl	J mol ⁻¹	J mol ⁻¹			
0.330	0.670	18.903×10^{2}	23.581×10^{2}			
0.340	0.660	13.963×10^2	33.561×10^2			
0.350	0.650	$*8.958 \times 10^{2}$	40.721×10^2			

 Table 5

 The value of the parameter w in the systems LiF—NaF and NaF—NaCl

It is the straight line equation which intersects the axis of the coordinates at the value ΔH_i and has the slope w. As we have found, this way of the determination of the parameter w in the systems LiF—NaF and NaF—NaCl is so sensitive to the experimental inaccuracies, that it cannot be used with success. Thus the parameter



Fig. 1. The dependence w = f(x) for the system LiF—NaF. ---- for the liquidus LiF, --- for the liquidus NaF.

w was calculated from eqn (3) using the data of the eutectic point as well as of two points shifted by 1 mole % in both directions from the experimentally found eutectic point (Table 5). This ± 1 mole % interval corresponds approximately to the inaccuracy in measurement. These values have been plotted in the graph





(Figs. 1 and 2) and the value w, determined as the point of intersection, was used for the calculation of the liquidus curves according to eqn (3). The mentioned point of intersection corresponds to the point, the temperature of which is equal to the eutectic one. The composition of this point differs in the case of LiF—NaF by 0.35 mole % from the experimental composition; this deviation is substantially less than the permitted inaccuracy of the measurement. In the case of the system NaF—NaCl This difference is 1.25 mole %, which is also satisfactory.

3. The activity has been expressed by means of the universal relationship [40], for which it holds $a_i = x_i^k$, where

$$k = \frac{k_{j/i}^{\mathrm{St}}}{1 + b(1 - x_i)}$$

- $k_{j/i}^{st}$ the Stortenbeker correction factor which is equal to the number of new particles, inserted by one molecule of the substance *j* into the pure substance *i*,
- b the parameter found on the basis of the eutectic point data from the eqn (4)

$$\ln a_i = \ln x_i^k = \frac{k_{iii}^{\text{st}}}{1 + b(1 - x_i)} \ln x_i = \frac{\Delta H_i^t}{R} \left(\frac{1}{T_i} - \frac{1}{T_i}\right)$$
(4)



Fig. 3. The phase diagram of the system LiF—NaF. The comparison of the calculated liquidus curves with the experiment.

the experimental curve, $---a_i = x_i$, --- the regular solution, -- the universal relationship (for the liquidus curve LiF it fuses with the experimental curve).

for LiF—NaF:
$$b_{\text{LiF}} = -0.4685$$
 for NaF—NaCl: $b_{\text{NaF}} = 0.1151$
 $b_{\text{NaF}} = -0.3372$ $b_{\text{NaCl}} = 0.3761$

Then, from eqn (4), the courses of the liquidus curves have been calculated. The values ΔH_i^t , T_i^t , and $\Delta C_{P_i}^{Us}$ are taken from [32]. The calculated liquidus curves are compared with the experimental ones in Figs. 3 and 4. It is evident, that the curves calculated from the theory of ionic regular solutions, as well as the curves calculated from the universal relationship are in the best agreement with the experiment.

The position of the eutectic point in the case of NaF-NaCl system has been verified using the *Dodé-Hagège* [42] relationship

$$(x_i)_{\rm E} (\Delta \bar{H}_i^{1/s})_{\rm E} (k_i)_{\rm E} = (x_i)_{\rm E} (\Delta \bar{H}_i^{1/s})_{\rm E} (k_i)_{\rm E}, \qquad (5)$$

where $(x_i, x_j)_{\rm E}$ — mole fractions of substances *i* and *j* in the eutectic point, $(\Delta \bar{H}_i^{1/s}, \Delta \bar{H}_i^{1/s})_{\rm E}$ — the partial molar melting enthalpy of the substance *i* and *j* in the eutectic point.

These values have been calculated in a simplified way using the relation



Fig. 4. The phase diagram of the system NaF—NaCl. The comparison of the calculated liquidus curves with the experiment.

the experimental curve, $---a_i = x_i$, -- the regular solution, - the universal relationship (for the liquidus curve NaCl it fuses with the experimental curve).

$$\Delta \bar{H}_{i}^{\nu_{s}} = \Delta H_{i}^{t} - \int_{T_{i}}^{T_{i}^{t}} \Delta C_{P_{i}}^{\nu_{s}} \,\mathrm{d}T \tag{6}$$

 $(k_i, k_j)_{\rm E}$ are the slopes of the tangent to the liquidus curves of the substances *i* and *j* in the eutectic point.

The product on the left side of eqn (5): 59.5×10^5 J K mol⁻¹ The product on the right side of eqn (5): 55.1×10^5 J K mol⁻¹ Consequently the agreement is very good.

The position of the eutectic point in the LiF—NaF system has been verified using the *Hagège* relation [43] in the form

$$\begin{aligned} x_{i}^{l} \quad k_{i}^{l} \quad \Delta \bar{H}_{i}^{l's} \bigg[1 + \frac{RT_{E}^{2}}{k_{i}^{s} \ \Delta \bar{H}_{i}^{l's}} \left(\frac{\partial \ln a_{i}^{s}}{\partial x_{i}^{s}} \right) \bigg] = \\ &= x_{i}^{l} \cdot k_{i}^{l} \cdot \Delta \bar{H}_{i}^{l's} \bigg[1 + \frac{RT_{E}^{2}}{k_{i}^{s} \cdot \Delta \bar{H}_{i}^{l's}} \left(\frac{\partial \ln a_{i}^{s}}{\partial x_{i}^{s}} \right) \bigg] \end{aligned}$$

$$(7)$$

This relation takes into consideration the existence of solid solutions. The calculation has been realized under the assumption that solid solution is an ideal one, *i.e.*, $a^s = x^s$ and the liquid solution is strictly regular.

 x_i^{i}, x_j^{i} — mole fraction of the substance *i* and *j* in the eutectic point, x_i^{s}, x_j^{s} — mole fraction of the substance *i* and *j* in the solid solution at the eutectic

temperature

$$\Delta \bar{H}_{i}^{1/s} = \bar{H}_{i}^{1} - \bar{H}_{i}^{s} = \bar{H}_{i}^{1} - H_{i}^{0.1} + H_{i}^{0.1} - (\bar{H}_{i}^{s} - H_{i}^{0.s} + H_{i}^{0.s}) =$$
$$= \Delta \bar{H}_{i,\text{mix}}^{1} - \Delta \bar{H}_{i,\text{mix}}^{s} + \Delta H_{i}^{0.1/0,s}$$
(8)

 $\Delta \bar{H}_{i,\text{mix}}^{\text{t/s}} = RT \ln \gamma_i^{\text{t}}$; because there is the assumption of the strictly regular liquid solution, $RT \ln \gamma_i^{\text{t}} = (1 - x_i)^2 w$ [39]: $\Delta H_i^{0,1/0,s} = \Delta H_i^{\text{t}}$; $\Delta \bar{H}_{i,\text{mix}}^{s} = 0$, then after inserting into eqn (8) we obtain

$$\Delta \bar{H}_i^{1/s} = (1 - x_i)^2 w + \Delta H_i^t \tag{9}$$

From the relation (9) $\Delta \bar{H}_i^{Vs}$ and $\Delta \bar{H}_i^{Vs}$ were calculated.

- k_i^{i}, k_j^{i} the slopes of the tangents of the liquidus curves of the components *i* and *j* in the eutectic point,
- $k_{i}^{s}, \dot{k}_{j}^{s}$ the slopes of the tangents to the solidus curves at the eutectic temperature.

The product on the left side of eqn (7): 99.8×10^5 J K mol⁻¹. The product on the right side of eqn (7): 106.6×10^5 J K mol⁻¹ A good agreement of the results confirms the correctness in determining the positions of the eutectic points in LiF—NaF and NaF—NaCl systems. It has been found that in the case of the

systems with common anions the coefficient b in eqn (4) is negative, which means a negative deviation from ideality, both for LiF and NaF. In the case of NaF this deviation is more expressive, because of the existence of the limited solid solution at the NaF side. On the contrary, in the system with common cations we observe that b is positive and the NaF—NaCl system exhibits a weak positive deviation from ideality. This difference is to be attributed to the different kind of the interaction $Li^+ \leftrightarrow Na^+$ and $F^- \leftrightarrow Cl^-$

References

- 1. Bergman, A. G. and Dergunov, E. P., Dokl. Akad. Nauk SSSR 31, 752 (1941).
- 2. Volkov, N. N. and Shwab, T. F., Izv. Fiz. Khim. Nauch.-Issled. Inst. Irkutsk. Gos. Univ. 2 (1), 60 (1953).
- 3. Barton, C. J., Bratcher, L. M., and Grimes, W. R., Oak Ridge Nat. Lab., ORNL-2548, 1959.
- 4. Thoma, R. E., Sturm, B. J., and Guinn, E. H., Oak Ridge Nat. Lab., ORNL-3594, 1964.
- 5. Blankenship, F. F., Thoma, R. E., and Bredig, M. A., Fused Salts Phase Equilibria, Encyclopedia of Science and Technology. McGraw-Hill, New York, 1960.
- 6. Belyaev, I. N. and Revina, O. Y., Fiziko-khimicheskii analiz solevykh sistem. (Physicochemical Analysis of Salt Systems.) Izd. RGU, Rostov, 1962.
- 7. Bukhalova, G. A. and Sementsova, D. V., Zh. Neorg. Khim. 10, 1881 (1965).
- 8. Holm, J. L., Acta Chem. Scand. 19, 638 (1965).
- 9. Holm, J. L., Electrochim. Acta 11, 351 (1966).
- 10. Matiašovský, K., Čakajdová, I., and Malinovský, M., Chem. Zvesti 19, 513 (1965).
- 11. Kuvakin, M. A., Zh. Neorg. Khim. 14, 282 (1969).
- 12. Holm, J. L., Dr. Thesis. NTH, Trondheim, 1971.
- 13. Short, J. M. and Roy, R., J. Amer. Ceram. Soc. 47, 149 (1964).
- 14. Plato, W., Z. Phys. Chem. 58, 364 (1907).
- 15. Wolters, L. A., Neues Jahrbuch Min. Geol. Beilage 30, 83 (1910).
- 16. Rea, R. F., J. Amer. Ceram. Soc. 21, 98 (1938).
- 17. Polyakov, V. D., Izv. SFCHA Akad. Nauk SSSR 11, 208 (1938).
- 18. Rassonskaya, I. S. and Bergman, A. G., Dokl. Akad. Nauk SSSR 38, 7, 238 (1943).
- 19. Bergman, A. G. and Banashek, E. I., Izv. SFCHA Akad. Nauk SSSR 22, 196 (1953).
- 20. Ishaque, M., Bull. Soc. Chim. Fr. 1952, 130.
- 21. Sauerwald, F. and Dombois, H. E., Z. Anorg. Allg. Chem. 227, 60 (1954).
- 22. Bukhalova, G. A., Izv. SFCHA Akad. Nauk SSSR 26, 138 (1955).
- 23. Bukhalova, G. A., Zh. Neorg. Khim. 4, 117 (1959).
- 24. Mateyko, Z. A. and Bukhalova, G. A., Zh. Neorg. Khim. 8, 715 (1963).
- 25. Maltsev, V. I. and Bukhalova, G. A., Zh. Neorg. Khim. 10, 1464 (1965).
- 26. Doucet, J., Bizouard, M., and Netzer, Ch., C. R. Acad. Sci. 76, 4826 (1954).
- 27. Belyaev, A. I., Zhemchuzhina, E. A., and Firsanova, L. A., Fizicheskaya khimiya rasplavlennykh solei. (Physical Chemistry of Molten Salts.) P. 49. Metallurgizdat, Moscow, 1957.
- Abramov, G. A. and Malinovský, M., *Elektrometallurghiya tsvetnykh metallov, Trudy LPI.* (Electrometallurgy of Non-Ferrous Metals, Proc. LPI.) No. 188, 82. Metallurgizdat, Leningrad, 1957.
- 29. Kuvakin, M. A. and Kusakin, P. S., Zh. Neorg. Khim. 4, 2577 (1959).
- 30. Litvinova, G. N., *Diagrammy rastvorimosti nekotorykh solevykh sistem*. (The Solubility Diagrams of Some Salt Systems.) Izd. Rostov. Univ., Rostov, 1964.

- 31. Grjotheim, K., Halvorsen, T., and Holm, J. L., Acta Chem. Scand. 21, 2300 (1967).
- 32. Stull, D. R. and Prophet, H., JANAF Thermodynamical Tables, 2nd Ed., Natl. Bur. Stand. (USA); Coden: NSRDA, 1971.
- 33. Foster, P. A., Jr., J. Amer. Ceram. Soc. 53, 598 (1970).
- 34. Bergman, A. G., Kislova, A. I., and Posypayko, V. I., Zh. Obshch. Khim. 24, 1722 (1954).
- 35. Bergman, A. G. and Bakumskaya, E. L., Zh. Neorg. Khim. 25, 2405 (1955).
- 36. LeChatelier, H., C. R. Acad. Sci. (Paris) 100, 50, 441 (1885).
- 37. Schröder, I., Z. Phys. Chem. 11, 449 (1893).
- 38. Van Laar, J. J., according to: Prigogine, I. and Defay, R., *Chemische Thermodynamik*, p. 328. VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1962.
- 39. Hildebrand, J. H., Proc. Nat. Acad. Sci. USA 13, 267 (1927); according to: Guggenheim, E. A., Thermodynamics, 3rd Ed. North-Holland, Amsterdam, 1957.
- 40. Malinovský, M. and Koštenská, I., Chem. Zvesti 28, 493 (1974).
- Grjotheim, K., Contribution to the Theory of the Aluminium Electrolysis. Kgl. Norske Vidensk. Selsk. Skr., No 5. F. Bruns, Trondheim, 1956.
- 42. Dodé, M. and Hagège, R., C. R. Acad. Sci. 248, 2339 (1959).
- 43. Hagège, R., C. R. Acad. Sci. 249, 956 (1959).

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