

Study of the binary systems LiF—NaCl and LiF—KCl*

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The phase diagrams of the binary systems LiF—NaCl and LiF—KCl have been investigated using the method of thermal analysis. The system LiF—NaCl is a simple eutectic system with real inflection points on the both liquidus curves. The coordinates of the eutectic point were found to be: 41.5 mole % LiF, 58.5 mole % NaCl, $t_E = 686.5^\circ\text{C}$. The system LiF—KCl is also a simple eutectic system with a real inflection point on the LiF liquidus curve, the coordinates of the eutectic point being 20.0 mole % LiF, 80.0 mole % KCl, $t_E = 719^\circ\text{C}$. In both systems the course of the liquidus curves was calculated using different relations, and the values of activity coefficients as well as the coordinates of the inflection points were determined. In both systems there is a large deviation from an ideal behaviour.

Методом термического анализа были исследованы фазовые диаграммы двухкомпонентных систем LiF—NaCl и LiF—KCl. Система LiF—NaCl является простой эвтектической системой. На обеих ветвях ликвидуса имеются реальные точки перегиба. Координаты точки эвтектики: 41,5 мол.% LiF, 58,5 мол.% NaCl, $t_E = 686,5^\circ\text{C}$. Система LiF—KCl также является простой эвтектической системой с реальной точкой перегиба на кривой ликвидуса LiF. Эвтектика имеет состав 20,0 мол.% LiF, 80,0 мол.% KCl, $t_E = 719^\circ\text{C}$. Сделан расчет линии ликвидуса для обеих систем при использовании различных схем расчета, определены значения коэффициентов активности и координаты точек перегиба. Обе системы значительно отклоняются от идеальности.

The data published on the systems LiF—NaCl and LiF—KCl are presented in Tables 1 and 2, respectively. As to the eutectic composition, there is a fair agreement between the published data, however, there are large discrepancies concerning the eutectic temperature. Therefore both systems have been experimentally re-examined and the course of the liquidus curves has been analyzed thermodynamically.

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Table 1

System LiF—NaCl
Comparison of the published data

| t_{LiF}^f °C | t_{NaCl}^f °C | E (eutectic point) | | Ref. | Notes |
|-------------------|--------------------|--------------------|------------|------|----------------------|
| | | mole % LiF | t_E , °C | | |
| 848.0 | 802.0 | 41.5 | 680.0 | [1] | SES |
| 848.0 | 800.0 | 43.0 | 684.0 | [2] | Taken from the graph |
| 846.0 | 800.0 | 40.5 | 668.0 | [3] | Liquidus given |
| 848.0 | 800.0 | 42.0 | 678.0 | [4] | Phase diagram given |
| 848.0 | 800.0 | 43.0 | 684.0 | [5] | Taken from the graph |
| 848.0 | 800.0 | 41.5 | 670.0 | [6] | SES |
| 848.0 | 800.0 | 41.5 | 670.0 | [7] | SES |
| 848.0 | 800.0 | 42.0 | 672.0 | [8] | Taken from the graph |

SES — simple eutectic system.

Table 2

System LiF—KCl
Comparison of the published data

| t_{LiF}^f °C | t_{KCl}^f °C | E (eutectic point) | | Ref. | Notes |
|-------------------|-------------------|--------------------|------------|------|----------------------|
| | | mole % LiF | t_E , °C | | |
| 846 | 765 | 18.0 | 716 | [9] | Taken from the graph |
| 848 | 772 | 20.0 | 715 | [1] | SES |
| 848 | 772 | 19.0 | 710 | [10] | Liquidus given |
| 846 | 772 | 19.0 | 710 | [3] | Liquidus given |
| 847 | 774 | 20.0 | 710 | [11] | Taken from the graph |

SES — simple eutectic system.

Experimental

The phase diagrams of the systems LiF—NaCl and LiF—KCl were studied by means of thermal analysis as described in [12].

In the system LiF—NaCl 16 and 17 samples were examined in the field of the primary crystallization of LiF and NaCl, respectively. The simple eutectic system LiF—NaCl is a quasi-binary system being a stable diagonal section of the ternary reciprocal system Li^+ , $Na^+ \parallel F^-$, Cl^- . There are real inflection points on the both liquidus curves and the coordinates of the eutectic point are: 41.5 ± 0.5 mole % LiF, 58.5 ± 0.5 mole % NaCl, $t_E = 686.5 \pm 1^\circ C$ (Table 3).

The system LiF—KCl is a stable diagonal section of the ternary reciprocal system Li^+ , $K^+ \parallel F^-$, Cl^- . It

Table 3
Composition, TPC, and t_E of the system LiF—NaCl

| Mole % | | Weight % | | TPC °C | t_E °C |
|--------|------|----------|---------|-----------|-------------|
| LiF | NaCl | LiF | NaCl | | |
| 100 | 0 | 100.000 | 0.000 | 848.3 | — |
| 99 | 1 | 97.775 | 2.225 | 838.0 | 668.0 |
| 98 | 2 | 95.604 | 4.396 | 830.5 | 678.0 |
| 97 | 3 | 93.485 | 6.515 | 823.5 | 680.0 |
| 96 | 4 | 91.417 | 8.583 | 818.0 | 681.0 |
| 95 | 5 | 89.398 | 10.602 | 812.0 | 684.5 |
| 90 | 10 | 79.975 | 20.025 | 788.0 | 685.0 |
| 80 | 20 | 63.965 | 36.035 | 756.5 | 686.0 |
| 70 | 30 | 50.873 | 49.127 | 737.0 | 685.5 |
| 65 | 35 | 45.182 | 54.818 | 729.0 | 686.0 |
| 60 | 40 | 39.966 | 60.034 | 719.0 | 685.5 |
| 55 | 45 | 35.167 | 64.833 | 710.0 | 686.5 |
| 50 | 50 | 30.739 | 69.261 | 702.0 | 686.5 |
| 47 | 53 | 28.242 | 71.758 | 697.5 | 686.5 |
| 43 | 57 | 25.083 | 74.917 | 688.0 | 686.5 |
| 42 | 58 | 24.322 | 75.678 | — | 686.5 |
| 41 | 59 | 23.571 | 76.429 | — | 686.5 |
| 40 | 60 | 22.832 | 77.168 | 688.0 | 686.5 |
| 39 | 61 | 22.103 | 77.897 | 690.0 | 686.5 |
| 38 | 62 | 21.384 | 78.616 | 692.0 | 686.5 |
| 37 | 63 | 20.676 | 79.324 | 694.0 | 686.5 |
| 36 | 64 | 19.977 | 80.023 | 696.0 | 686.5 |
| 35 | 65 | 19.288 | 80.712 | 697.0 | 686.0 |
| 30 | 70 | 15.981 | 84.019 | 706.0 | 686.0 |
| 25 | 75 | 12.885 | 87.115 | 714.0 | 686.0 |
| 20 | 80 | 9.985 | 90.015 | 723.5 | 685.5 |
| 15 | 85 | 7.265 | 92.735 | 741.0 | 685.5 |
| 10 | 90 | 4.700 | 95.300 | 756.5 | 685.0 |
| 5 | 95 | 2.283 | 97.717 | 777.0 | 683.0 |
| 4 | 96 | 1.816 | 98.184 | 781.0 | 681.0 |
| 3 | 97 | 1.354 | 98.646 | 785.5 | 679.0 |
| 2 | 98 | 0.898 | 99.102 | 790.0 | 675.5 |
| 1 | 99 | 0.446 | 99.554 | 795.5 | — |
| 0 | 100 | 0.000 | 100.000 | 800.8 | — |

is a simple eutectic system with a real inflection point on the liquidus curve of LiF. 19 and 10 samples were examined in the field of the primary crystallization of LiF and KCl, respectively. The coordinates of the eutectic point are: 20.0 ± 0.5 mole % LiF, 80.0 ± 0.5 mole % KCl, $t_E = 719.0 \pm 1^\circ\text{C}$ (Table 4).

Theoretical

The liquidus curves in both systems were calculated by means of the LeChatelier—Schröder equation [13—15] under the presumptions:

Table 4
Composition, TPC, and t_E of the system LiF—KCl

| Mole % | | Weight % | | TPC °C | t_E °C |
|--------|-------|----------|---------|-----------|-------------|
| LiF | KCl | LiF | KCl | | |
| 100.0 | 0.0 | 100.000 | 0.000 | 848.3 | — |
| 99.5 | 0.5 | 98.576 | 1.424 | 843.0 | — |
| 99.0 | 1.0 | 97.178 | 2.822 | 841.0 | 710.0 |
| 98.0 | 2.0 | 94.459 | 5.541 | 832.0 | 714.0 |
| 97.0 | 3.0 | 91.836 | 8.164 | 829.0 | 715.5 |
| 96.0 | 4.0 | 89.304 | 10.696 | 823.0 | 715.5 |
| 95.0 | 5.0 | 86.859 | 13.141 | 818.0 | 717.0 |
| 90.0 | 10.0 | 75.793 | 24.207 | 804.0 | 716.5 |
| 80.0 | 20.0 | 58.187 | 41.813 | 793.0 | 717.5 |
| 75.0 | 25.0 | 51.069 | 48.931 | 789.0 | 719.0 |
| 70.0 | 30.0 | 44.805 | 55.195 | 786.0 | 718.5 |
| 65.0 | 35.0 | 39.250 | 60.750 | 783.0 | 720.0 |
| 60.0 | 40.0 | 34.290 | 65.710 | 779.5 | 718.0 |
| 55.0 | 45.0 | 29.835 | 70.165 | 776.5 | 719.0 |
| 50.0 | 50.0 | 25.810 | 74.190 | 773.0 | 719.0 |
| 40.0 | 60.0 | 18.827 | 81.173 | 758.5 | 719.0 |
| 30.0 | 70.0 | 12.975 | 87.025 | 743.0 | 719.5 |
| 25.0 | 75.0 | 10.392 | 89.608 | 734.0 | 719.0 |
| 22.0 | 78.0 | 8.936 | 91.064 | 726.0 | 719.0 |
| 21.0 | 79.0 | 8.465 | 91.535 | 721.5 | 719.0 |
| 20.0 | 80.0 | 8.002 | 91.998 | — | 719.5 |
| 19.0 | 81.0 | 7.545 | 92.455 | — | 719.0 |
| 18.0 | 82.0 | 7.095 | 92.905 | 721.0 | 719.0 |
| 15.0 | 85.0 | 5.784 | 94.216 | 724.0 | 719.0 |
| 10.0 | 90.0 | 3.722 | 96.278 | 735.5 | 719.0 |
| 5.0 | 95.0 | 1.798 | 98.202 | 747.5 | 716.5 |
| 4.0 | 96.0 | 1.429 | 98.571 | 752.0 | 717.0 |
| 3.0 | 97.0 | 1.064 | 98.936 | 756.5 | 717.0 |
| 2.0 | 98.0 | 0.705 | 99.295 | 760.5 | 717.0 |
| 1.0 | 99.0 | 0.350 | 99.650 | 765.0 | 715.5 |
| 0.5 | 99.5 | 0.174 | 99.826 | 768.5 | 716.5 |
| 0.0 | 100.0 | 0.000 | 100.000 | 771.0 | — |

TPC — temperature of primary crystallization,

t_E — temperature of eutectic crystallization.

1. $a_i = x_i$ (the components form an ideal solution); a_i is the activity and x_i is the mole fraction of the i -th component.
2. The components form an ideal ionic solution according to *Temkin's* model [16]. In this case $a_i = x_i^2$.
3. Activity was expressed by means of the universal relationship [17],

Table 5

Comparison of the experimental and calculated coordinates of the inflection points

| Inflection point | LiF—NaCl | | LiF—KCl |
|------------------------------------|-----------|------------|-----------|
| | LiF curve | NaCl curve | LiF curve |
| $x_{\text{inf}}^{\text{exp}}$ | 0.655 | 0.675 | 0.585 |
| $x_{\text{inf}}^{\text{calc}}$ | 0.578 | 0.655 | 0.578 |
| $T_{\text{inf}}^{\text{exp}}$ (K) | 1003 | 975 | 1051 |
| $T_{\text{inf}}^{\text{calc}}$ (K) | 943.45 | 946.80 | 943.45 |

Table 6

Activity coefficients for the liquidus curves of the systems LiF—NaCl and LiF—KCl

a) System LiF—NaCl

| t , °C | T , K | x_{LiF} | γ_{LiF} |
|----------|---------|------------------|-----------------------|
| 840 | 1113 | 0.990 | 0.990 |
| 820 | 1093 | 0.965 | 0.961 |
| 800 | 1073 | 0.930 | 0.943 |
| 780 | 1053 | 0.880 | 0.940 |
| 760 | 1033 | 0.815 | 0.957 |
| 740 | 1013 | 0.715 | 1.026 |
| 720 | 993 | 0.600 | 1.136 |
| 700 | 973 | 0.490 | 1.310 |
| 686.5 | 959.5 | 0.415 | 1.477 |

| t , °C | T , K | x_{NaCl} | γ_{NaCl} |
|----------|---------|-------------------|------------------------|
| 780 | 1053 | 0.955 | 0.977 |
| 760 | 1033 | 0.910 | 0.970 |
| 740 | 1013 | 0.850 | 0.974 |
| 720 | 993 | 0.775 | 0.998 |
| 700 | 973 | 0.665 | 1.084 |
| 686.5 | 959.5 | 0.585 | 1.174 |

b) System LiF—KCl

| t , °C | T , K | x_{LiF} | γ_{LiF} |
|----------|---------|------------------|-----------------------|
| 840 | 1113 | 0.990 | 0.990 |
| 820 | 1093 | 0.955 | 0.971 |
| 800 | 1073 | 0.870 | 1.003 |
| 780 | 1053 | 0.625 | 1.345 |
| 760 | 1033 | 0.400 | 1.950 |
| 740 | 1013 | 0.280 | 2.620 |
| 720 | 993 | 0.205 | 3.354 |
| 719 | 992 | 0.200 | 3.348 |

Table 6 (Continued)

| $t, ^\circ\text{C}$ | T, K | x_{KCl} | y_{KCl} |
|---------------------|---------------|------------------|------------------|
| 760 | 1033 | 0.980 | 0.988 |
| 740 | 1013 | 0.925 | 0.986 |
| 720 | 993 | 0.815 | 1.052 |
| 719 | 992 | 0.800 | 1.067 |

$$a_i = x_i^k \quad (1)$$

where

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

$k_{j/i}^{\text{St}}$ — the Stortenbeker correction factor which is numerically equal to the number of new particles introduced by one molecule of the substance j into the pure substance i :

$$k_{\text{NaCl/LiF}}^{\text{St}} = k_{\text{LiF/NaCl}}^{\text{St}} = k_{\text{KCl/LiF}}^{\text{St}} = k_{\text{LiF/KCl}}^{\text{St}} = 2;$$

b — a parameter calculated from the experimental data of the eutectic point:

$$\text{LiF—NaCl: } b_{\text{LiF}} = 2.2135, b_{\text{NaCl}} = 2.2334$$

$$\text{LiF—KCl: } b_{\text{LiF}} = 9.3795, b_{\text{KCl}} = 9.0624$$

The calculated and experimental liquidus curves are compared in Figs. 1 and 2. In both systems there are large deviations from ideality in the entire range of concentrations. The system LiF—NaCl suits the Temkin's model up to 4 mole % NaCl and 2 mole % LiF only, the system LiF—KCl up to 2 mole % KCl and 2 mole % LiF. The universal relationship was found to be the best suited to a mathematical description of the liquidus curves in the systems investigated.

The position of the inflection points on the liquidus curves was calculated by means of the relation

$$\ln x_{i,\text{infl}} = \frac{\Delta S_i^f}{R(p+q)} - 2 \quad (2)$$

which holds for systems without a common ion of the type $M_pA_q\text{—}N_pB_q$.

ΔS_i^f — the molar entropy of melting of pure substance i ($\text{J mol}^{-1} \text{K}^{-1}$),

$x_{i,\text{infl}}$ — the mole fraction of the substance i in the inflection point,

R — the gas constant ($\text{J mol}^{-1} \text{K}^{-1}$),

p, q — the number of the given ionic species in the molecule ($p = q = 1$).

Subsequently, the value of $T_{i,\text{infl}}$ (Table 5) was calculated by means of equation

$$\ln x_{i,\text{infl}} = \frac{\Delta H_i^r}{R} \left(\frac{1}{T^r} - \frac{1}{T_{i,\text{infl}}} \right) \quad (3)$$

Compared with the relatively small differences between the experimental and calculated values of the concentration coordinate which range from 0.7 mole % (LiF curve in the system LiF—KCl) up to 7.7 mole % (LiF curve in the system LiF—NaCl), there is a substantial difference between the experimental and calculated temperature coordinates ranging from 28.2 K (NaCl curve in the system LiF—NaCl) up to 107.6 K (LiF curve in the system LiF—KCl). A similar regularity may be frequently observed also with the eutectic points of this type of systems. Formally, it is a consequence of a certain symmetry in the dependence of the values of activity coefficients on the concentration.

Further we have calculated the activity coefficients for the liquidus curves of both systems by means of the relation

$$\ln a_i = \ln x_i + \ln \gamma_i = \frac{\Delta H_i^r}{R} \left(\frac{1}{T_i^r} - \frac{1}{T_i} \right) \quad (4)$$

or

$$\ln \gamma_i = \frac{\Delta H_i^r}{R} \left(\frac{1}{T^r} - \frac{1}{T_i} \right) - \ln x_i \quad (5)$$

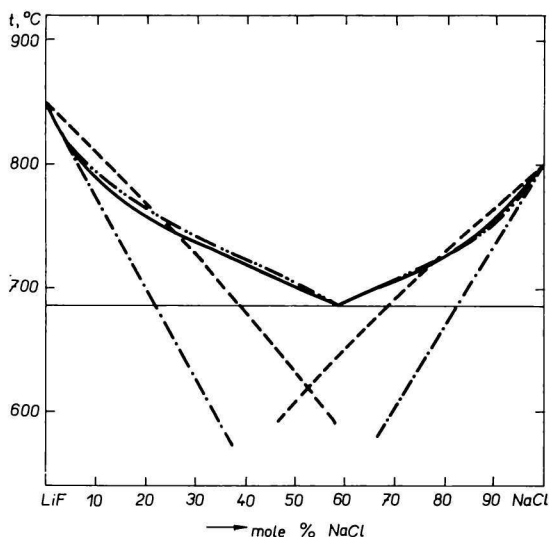


Fig. 1. Phase diagram of the system LiF—NaCl. Comparison of the calculated and experimental data.
 — experimental, - - - $a_i = x_i$, - · - Temkin's model, - - - universal relationship.

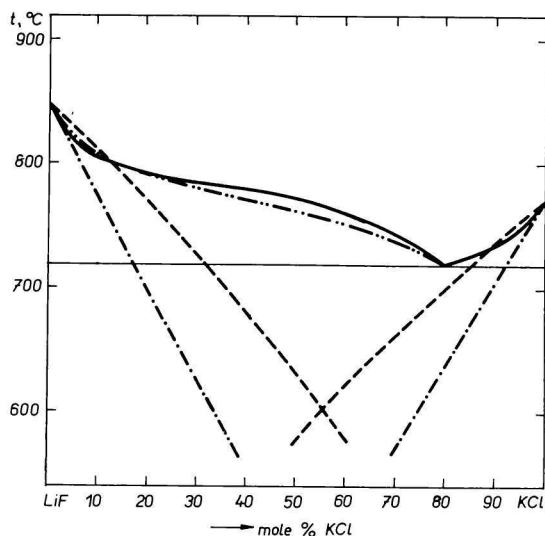


Fig. 2. Phase diagram of the system LiF—KCl. Comparison of the calculated and experimental data.
 — experimental, - - - $a_i = x_i$, - · - · - Temkin's model, - - - universal relationship (the KCl curve fuses with the experimental one).

The calculation has been carried out under the simplifying presumption that $\Delta H_i^{l/s} = \Delta H_i^f$. This simplification produces only an insignificant error which does not affect the general tendency of the calculated parameters.

γ_i — the activity coefficient of the component i at temperature T_i ,

ΔH_i^f — the molar enthalpy of fusion of the substance i (J mol^{-1}),

T^f — the melting temperature of the substance i (K),

x_i — the mole fraction of the substance i at the temperature T_i (experimental value).

The values required for calculations are taken from [18]:

$$T_{\text{LiF}}^f = 1121.3 \text{ K}, \quad T_{\text{NaCl}}^f = 1073.8 \text{ K}, \quad T_{\text{KCl}}^f = 1044 \text{ K},$$

$$\Delta H_{\text{LiF}}^f = 6.474 \times 10^3 \text{ cal mol}^{-1} = (27.105 \times 10^3 \text{ J mol}^{-1}),$$

$$\Delta H_{\text{NaCl}}^f = 6.730 \times 10^3 \text{ cal mol}^{-1} = (28.177 \times 10^3 \text{ J mol}^{-1}),$$

$$\Delta H_{\text{KCl}}^f = 6.282 \times 10^3 \text{ cal mol}^{-1} = (26.259 \times 10^3 \text{ J mol}^{-1})$$

The calculated activity coefficients are summarized in Table 6. From the calculated activity coefficients as well as from the experimental course of the liquidus curves (Figs. 1 and 2) it follows that the systems LiF—NaCl and LiF—KCl exhibit both negative and positive deviation from an ideal liquidus course (Table 7).

Table 7

Deviations from ideality

| | LiF—NaCl | | LiF—KCl | |
|------------|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|
| | Negative deviation (mole fraction) | Positive deviation (mole fraction) | Negative deviation (mole fraction) | Positive deviation (mole fraction) |
| LiF curve | 1.00—0.745 | 0.745—0.615 | 1.00—0.880 | 0.880—0.200 |
| NaCl curve | 1.00—0.765 | 0.765—0.585 | | |
| KCl curve | | | 1.00—0.885 | 0.885—0.800 |

In the range of high concentration of the substance *i* a negative deviation from ideality was observed. In this concentration interval the colligative regulation dominates, which is expressed by the fact that in all cases the component *j* introduces into pure component *i* two new particles. In the range of lower concentrations of the substance *i* specific interactions of ions in the solution predominate. From Table 7 it follows that the replacement of Na⁺ for K⁺ results in a twofold decrease of the region of the negative deviation from ideality.

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