Phase diagram of the system Li_3AlF_6—KCl. II.
Experimental results

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The phase diagram of the system Li_3AlF_6—KCl was studied using the TA method and x-ray phase analysis. The investigated system was found to be a simple eutectic quasi-binary system, the co-ordinates of the eutectic point being 25 mole % Li_3AlF_6 + 75 mole % KCl, $t_E = 620°C$. The Li_3AlF_6 liquidus curve is practically linear, whilst the liquidus curve of KCl is expressively convex with respect to the concentration axis. The course of the KCl liquidus curve enables one to assume a total destruction of Li_3AlF_6 molecules in the range of small concentrations of lithium cryolite.

In part I of this work [1] it was shown that the data on the phase diagram of the system Li_3AlF_6—KCl presented by *Matsushima* [2] are not consistent with the results of a thermodynamic analysis regarding the linear course of the KCl liquidus curve. These theoretic considerations were to be confirmed experimentally.

Experimental

In the study of the phase diagram of the system Li_3AlF_6—KCl the following reagencies were used:

LiF, for single crystals, m.p. 846 ± 1°C,
AlF_3, prepared by sublimation of a chemically pure product in a Pt apparatus according to *Matiašovský et al.* [3],
KCl, for single crystals, m.p. 772 ± 1°C.

Salts were fused in Pt crucibles in a normal atmosphere. The total weight of a sample was 20 g. The temperature was measured using a Pt/Pt10Rh thermocouple calibrated at the m.p. of Na_2SO_4 (885°C), NaCl (801°C), and the eutectic temperature NaCl—Na_2SO_4 (628°C), and registered by means of an automatic compensating recorder. The rate of cooling was 1—4°C/min. In the field of the primary crystallization of Li_3AlF_6, the cooling of 9 mixtures was registered whilst 14 samples were measured in the field of the primary crystallization of KCl. In most cases, the measurement was repeated 2 or 3 times.

The experimental results are presented graphically in Fig. 1. The values related to the KCl liquidus curve are plotted in Table 1.
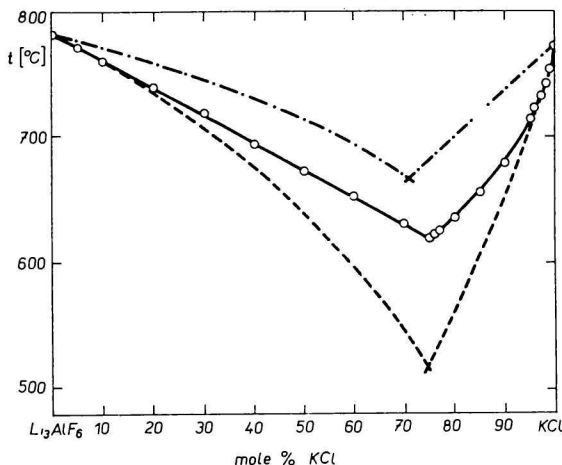
Fig. 1. The phase diagram of the quasi-binary system Li_3AlF_6-KCl.
$-\circ-\circ-$ experimental data; $-.-.-$ the data calculated according to the Le Chatelier—Schröder's equation; $---$ the data calculated with an assumption of the validity of the Temkin's model.

Discussion of results

The quasi-binary Li_3AlF_6-KCl system appears to be a simple eutectic system, the co-ordinates of the eutectic point E being: 25 ± 1 mole % Li_3AlF_6, 75 ± 1 mole % KCl, eutectic temperature $t_E = 620 \pm 1°C$.

The Li_3AlF_6 liquidus curve has practically a linear course from the m.p. of pure Li_3AlF_6 to the eutectic point E. On the other hand, the liquidus curve of KCl is expressively convex with respect to the concentration axis. This shape of the KCl liquidus curve principally differs from the one presented by *Matsushima* [2]; however, it is in a good agreement with the results of the thermodynamic analysis [1]. No real inflex point was found on the liquidus curve of KCl.

In order to determine the deviation of the course of liquidus curves in the investigated system from an ideal course, in Fig. 1 beside the experimental values also the liquidus curves calculated according to two different assumptions were presented.

A. The molten mixture represents a classical ideal system.

Then for the temperature of the primary crystallization of the substance i the Le Chatelier—Schröder equation is valid [4]

$$T_i = \frac{\Delta H_i^f}{\Delta S_i^f - R \ln x_i},$$

where ΔH_i^f and ΔS_i^f are the enthalpy and entropy of fusion, respectively, of the substance i, x_i is the molar ratio of the substance i in the melt.

In the calculation, the following values were accepted:
Li_3AlF_6: $T^f = 782°C = 1055$ K (value measured by the authors), $\Delta H^f = 21.0$ kcal mol^{-1}, this being the average of the values presented by *Malinovský* [5] (21.1 kcal mol^{-1}), *Björge* and *Jenssen* [6] (20.2 kcal mol^{-1}), *Latreille* and co-workers [7, 8]

(21.5 kcal mol⁻¹), *Matsushima* [2] (20.7 kcal mol⁻¹) and by *Holm* and *Holm-Jenssen* [9] (20.9 kcal mol⁻¹).

KCl: According to *Janz* [10], $T^t = 770°C = 1043$ K, $\Delta H^t = 6.34$ kcal mol⁻¹. According to the authors' measurement, $T^t = 772°C$. Therefore, the value of ΔH^t was also recalculated with respect to this temperature [11]. For the final calculation, the values $T^t = 1045$ K and $\Delta H^t = 6.352$ kcal mol⁻¹ were used.

B. The molten mixture represents an ideal ionic system where the activities of components can be expressed according to the Temkin model [12, 13].

It is assumed that both Li_3AlF_6 and KCl dissociate according to simple dissociation schemes

$$Li_3AlF_6 \rightarrow 3Li^+ + AlF_6^{3-}$$

and

$$KCl \rightarrow K^+ + Cl^-$$
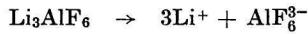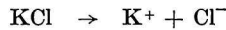
If in a given mixture, the molar ratio of Li_3AlF_6 equals x and that of KCl y $(x + y = 1)$, then for the activities of both components the following equations are valid

$$a_{Li_3AlF_6} = \frac{27\,x^4}{(1 + 2\,x)^3},$$

Table 1

The dependence of the temperature of the primary crystallization (TPC)
of KCl on the composition

mole % KCl	TPC [°C]	mole % KCl	TPC [°C]
100	772	96	723
99.9	768.5	95	714
99.8	766	90	680
99.7	764	85	656
99.5	761	80	637
99.0	753.5	77	626
98.0	742.5	76	622
97.0	732.5	75	620

Table 2

The dependence of the Stortenbeker's correction factor $k_{Q/Z}^{St}$ on the concentration
of Li_3AlF_6 in molten KCl

Composition [mole %]		ΔT_Z	$\dfrac{\Delta T_Z}{\Delta x_Q}$	$k_{Q/Z}^{St}$
Li_3AlF_6 (Q)	KCl (Z)			
1.0	99.0	18.5	1850°	5.4
0.5	99.5	11	2200°	6.5
0.3	99.7	8	2888°	7.8
0.2	99.8	6	3000°	8.8
0.1	99.9	3.5	3500°	10.0

$$a_{KCl} = \frac{y^2}{3 - 2y} .$$

The temperature of the primary crystallization can be calculated from the relation

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

In all calculations, ΔH_i^f was assumed to be temperature independent.

From Fig. 1 it is evident that the experimentally determined liquidus curves in the system Li_3AlF_6—KCl are situated between the liquidus curves calculated for a classical ideal system and those corresponding to an ideal ionic system. The ideal ionic model, however, suits better the real course of the liquidus curves in the proximity of pure components.

Furthermore, the experimental results were examined with respect to the thermodynamic consistency. According to *Malinovský* [4], for the system $Q - Z$, the relation is valid

$$k_Q^0 = \lim_{x_Q \to 1} \frac{dT}{dx_Q} = \frac{R(T_Q^f)^2}{\Delta H_Q^f} \cdot k_{Z/Q}^{St} ,$$

where $k_{Z/Q}^{St}$ is the Stortenbeker's correction factor for the substance Z dissolved in a large excess of the substance Q. If $Z = $ KCl, then $k^{St} = 2$ and for k_Q^0 the value 210.6°C is obtained.

As it was shown above, the Li_3AlF_6 liquidus curve is practically linear and hence

$$k_Q^0 = \frac{\Delta T_Q}{\Delta x_Q} = \frac{162}{0.75} = 216.0° .$$

The calculated value differs from the theoretic one by $\frac{216.0 - 210.6}{210.6} \cdot 100 =$ = 2.6%, this being a fairly good agreement.

In the case of the strongly curved KCl liquidus, the ratios $\Delta T_Z/(1 - y_Z)$ were calculated and their limit for $y_Z \to 1$ was determined (Table 2). The value of the Stortenbeker's correction factor $k_{Q/Z}^{St}$ ($Q = Li_3AlF_6$, $Z = $ KCl) was calculated according to the equation

$$k_{Q/Z}^{St} = \lim_{y_Z \to 1} \frac{\Delta T_Z}{1 - y_Z} \quad \frac{\Delta H_Z^f}{R(T_Z^f)^2} .$$

Physically, $k_{Q/Z}^{St}$ is equal to the number of new particles which are introduced into a large excess of molten KCl by one Li_3AlF_6 molecule.

From Table 2 it follows that at very low concentrations of Li_3AlF_6 in KCl, the molecules of lithium cryolite entirely disintegrate with the formation of 10 new particles in molten KCl: $3Li^+$, $6F^-$ and one particle containing Al^{3+} (see [1]). With increasing concentration, the total dissociation of Li_3AlF_6 is strongly suppressed.

As it was shown in Part I of this work [1], according to *Dodé* and *Hag ge* [14, 15] for a liquidus curve in the proximity of the eutectic point E the relation is valid

$$(x_A \Delta \overline{H}_A^{1/8} k_A)_E = (x_B \Delta \overline{H}_B^{1/8} k_B)_E ,$$

where x_A, x_B — the co-ordinates of the eutectic point E,

$\Delta \bar{H}^{l/s}_{A(B)}$ — the partial molar change of the enthalpy for the reaction $A^0_{sol} \to A_{liq}$ and $B^0_{sol} \to B_{liq}$, respectively, at the eutectic composition and temperature,

$k_{A(B)}$ — the slopes of the tangents to liquidus curves of A and B in the eutectic point E.

For the KCl liquidus curve, this relation can be applied in the form

$$(k_{KCl})_{E,theor} = \frac{0.25 \cdot 21 \quad 10^3 \cdot 216}{0.75 \cdot 6.352 \cdot 10^3} = 238 \text{ K.}$$

For simplification, in this calculation the identity $\Delta \bar{H}^{l/s}_i = \Delta H^f_i$ is assumed.

On the basis of the experimentally determined values of the temperature of the primary crystallization of KCl in the proximity of the eutectic point E it was found that

$$(k_{KCl})_{E,exp} = \lim_{(x - x_E) \to 0} \frac{T - T_E}{x - x_E} = 260 \text{ K.}$$

This value differs from the theoretic one by less than 10%. Considering the above simplification in the calculation of $(k_{KCl})_{E,theor}$ and the rather complicated determination of an exact course of the liquidus curve in the proximity of the eutectic point E, this agreement can be considered to be very good.

It can be concluded that in this work, the data presented by *Matsushima* [2] have been confirmed regarding the general character of the system $Li_3AlF_6 - KCl$ and the co-ordinates of the eutectic point E; however, the KCl liquidus curve was determined to be convex with respect to the concentration axis and its course in the proximity of both the melting point of pure KCl and the eutectic point E was found to be in agreement with the theoretic assumptions.

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