Phase Diagram of the System Li_3AlF_6—KCl. I. Theory

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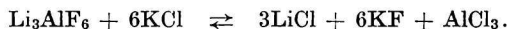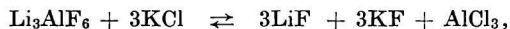*Bratislava 9*

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The thermodynamic analysis of the shape of the liquidus curves was carried out in the quasi-binary system Li_3AlF_6—KCl. It was proved that the liquidus curve for KCl would be convex with regard to the concentration axis. It is thus evident that the linear course of the KCl liquidus curve, which has been presented in literature, is incorrect.

General remarks

The system Li_3AlF_6—KCl can be considered to be a spacial linear section of the quaternary reciprocal system Li^+, K^+, $Al^{3+}||F^-$, Cl^- (Fig. 1). In the binary system, the following exchange reactions are possible:

$$Li_3AlF_6 + 3KCl \rightleftarrows 3LiCl + K_3AlF_6,$$

$$Li_3AlF_6 + 3KCl \rightleftarrows 3LiF + 3KF + AlCl_3,$$

$$Li_3AlF_6 + 6KCl \rightleftarrows 3LiCl + 6KF + AlCl_3.$$

However, by means of the X-ray analysis of the quenched samples only the characteristic lines of Li_3AlF_6 and KCl were determined. Thus it is evident that the exchange equilibrium is shifted completely to the left and that the examined system has a character of a quasi-binary system. Furthermore, the system Li_3AlF_6—KCl was found to be a simple eutectic system [1].

So far, two papers were published concerning the system Li_3AlF_6—KCl. *Malinovský* [1] studied a part of this system in the concentration range from 0 to 20 mole % KCl and on the basis of the measured values of the temperature of the primary crystallization he determined the enthalpy of melting of Li_3AlF_6 using the cryoscopic method. Recently, the phase equilibria in the system Li_3AlF_6—KCl were studied and thermodynamically interpreted by *Matsushima* [2] who also confirmed that this is a simple eutectic system with an eutectic point at 24.5 mole % Li_3AlF_6 and 75.5 mole % KCl, the eutectic temperature being 621°C. (It is to be mentioned, that the concentration data in [2] are reversed.) According to [2], the liquidus curves for both Li_3AlF_6 and KCl are linear.

With regard to the great importance of the study of this system for better understanding of the dissociation mechanism of lithium cryolite it was considered necessary to perform the thermodynamic analysis of the shape of the liquidus curves.

*The course of the liquidus curves in the proximity of the melting points
of pure components*

The fundamental thermodynamic differential equation for the activity of the first
component in a simple eutectic system $Q - Z$ along the corresponding liquidus curve is

$$\mathrm{d}\ln a_Q = \frac{\Delta H_Q^{\mathrm{l/s}}}{\boldsymbol{R}}\,\frac{\mathrm{d}T_Q}{T_Q^2}\,, \tag{1}$$

where $\Delta H_Q^{\mathrm{l/s}}$ is the molar enthalpy of melting of the component Q at the temperature T_Q,

$\boldsymbol{R}$ is the universal gas constant,

T_Q is the temperature of the primary crystallization of the substance Q from
a liquid solution $Q + Z$, in which the activity of the substance Q is equal
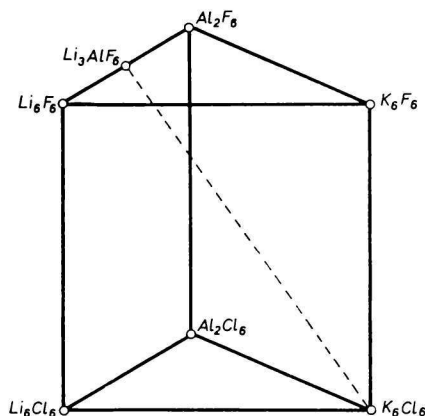to a_Q.

Fig. 1. The concentration triangular prism
of the quarternary reciprocal system Li⁺,
K⁺, Al³⁺||F⁻, Cl⁻

Fig. 1. The concentration triangular prism
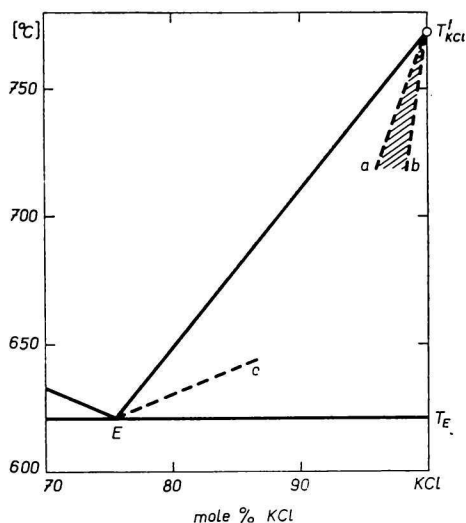of the quarternary reciprocal system Li+,
K+, Al3+||F−, Cl−

Fig. 2. Part of the phase diagram of the
system Li₃AlF₆—KCl.

Full line: Matsushima's experimental
data [2].

Dotted lines: *a)* calculated slope of the
tangent to the KCl liquidus curve for
$x_{\mathrm{KCl}} \to 1$ and $k_{\mathrm{KCl}}^{\mathrm{St}} = 4$; *b)* the same for
$k_{\mathrm{KCl}}^{\mathrm{St}} = 10$; *c)* calculated slope of the
tangent to the KCl liquidus curve in the
eutectic point.

Since for $x_Q \to 1$, $a_Q \to x_Q$ (x_Q being the mole fraction of the substance Q in the solution
$Q + Z$ saturated at T_Q with respect to Q), we may write

$$\lim_{x_Q \to 1} \frac{\mathrm{d}T_Q}{\mathrm{d}x_Q} = \frac{\boldsymbol{R}(T_Q^{\mathrm{f}})^2}{\Delta H_Q^{\mathrm{f}}} = K_Q^{\mathrm{td}}. \tag{2}$$

The validity of the equation (2) is limited to the case when each molecule of the substance Z introduces only one new particle into the molten substance Q. If the number of new particles is greater than 1, then the right side of the equation (2) is to be multiplied by the Stortenbeker's correction factor $k_{Z/Q}^{St}$, which is numerically equal to the number of new particles. Then, according to [3]

$$\lim_{x_Q \to 1} \frac{dT_Q}{dx_Q} = K_Q^{td} \cdot k_{Z/Q}^{St}. \tag{3}$$

Hence it is inevitable to know the dissociation scheme of the substance Z, which is present in minor concentrations in the substance Q.

Let us assume that $Q = Li_3AlF_6$ and $Z = KCl$. In this case we may assume that KCl dissociates into K^+ and Cl^- Then $k_{Z/Q}^{St} = 2$ and we may write

$$\lim_{x_Q \to 1} \frac{dT_Q}{dx_Q} = \frac{R(T_Q^f)^2}{\Delta H_Q^f} \cdot 2 = 215.5°C. \tag{4}$$

For this calculation the data presented by [2] have been accepted: $T_Q^f = T_{Li_3AlF_6}^f = 1056$ K, and $\Delta H_Q^f = \Delta H_{Li_3AlF_6}^f = 20.7 \times 10^3$ cal mole^{-1}.

From the data presented by *Matsushima* [2] and with regard to the linear character of liquidus curves it follows that

$$\lim_{x_Q \to 1} \frac{dT_Q}{dx_Q} = \frac{\Delta T_Q}{\Delta x_Q} = \frac{783° - 621°}{0.755} = 214.6°C. \tag{5}$$

Since the possible inaccuracy is $5-10\%$, the agreement between the values calculated using the equations (4) and (5) may be regarded as very good.

The same calculation for the liquidus curve of KCl is stipulated by the knowledge of the dissociation scheme of Li_3AlF_6 dissolved in molten KCl at low concentrations. In this case several possibilities are to be taken into account

$$a) \quad Li_3AlF_6 \to 3Li^+ + AlF_6^{3-}; \quad k_{Q/Z}^{St} = 4.$$
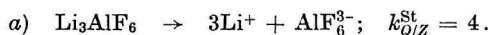
In this scheme, the complex anion AlF_6^{3-} is assumed to be stable in the diluted solutions of Li_3AlF_6 in KCl, what is very improbable.

$$b) \quad Li_3AlF_6 \to 3Li^+ + (1 - \beta) AlF_6^{3-} + \beta AlF_4^- + 2\beta F^-.$$
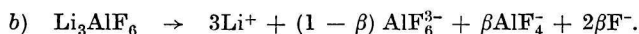
Here the equilibrium constant of dissociation of the anion AlF_6^{3-} is given by the equation

$$K = \frac{[AlF_4^-][F^-]^2}{[AlF_6^{3-}]}.$$

If the mole fraction for Li_3AlF_6, $x_Q \to 0$, the dissociation degree $\beta \to 1$. Therefore, in this case $k_{Q/Z}^{St} \to 6$. An analogical scheme was proposed by *Grjotheim* [4] and by *Frank* and *Foster* [5] for the dissociation of Na_3AlF_6

$$c) \quad Li_3AlF_6 \to 3Li^+ + 3F^- + AlF_3; \quad k_{Q/Z}^{St} = 7.$$
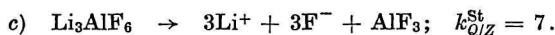
An analogical scheme for the dissociation of Na_3AlF_6 was presented by *Rolin* [6]

$$d) \quad Li_3AlF_6 \to 3Li^+ + Al^{3+} + 6F^-$$
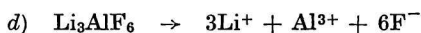
Here $k_{Q/Z}^{St} = 10$; though, in this case the formation of complexes $AlCl_4^-$ and $AlCl_6^{3-}$, respectively, seems to take place. An analogical scheme of dissociation of Na_3AlF_6 was experimentally demonstrated by *Zarzycki* [7] in the system $Na_3AlF_6-LiBO_2$ and by *Petit* and *Ngo Tuang* [8] in the system $Na_3AlF_6-BaCl_2$. Thus, the value of the constant $k_{Q/Z}^{St}$ is evidently within the limits

$$4 \leqslant k_{Q/Z}^{St} \leqslant 10$$

and for the slope of a tangent to the liquidus curve of KCl we obtain

$$1344°C \leqslant \lim_{x_z \to 1} \frac{dT_z}{dx_z} \leqslant 3360°C.$$

According to *Matsushima* [2]

$$\lim_{x_z \to 1} \frac{dT_z}{dx_z} = \frac{\Delta T_z}{\Delta x_z} = \frac{772° - 621°}{0.245} = 616.33°C.$$

To this value corresponds the value $k_{Q/Z}^{St} = 1.83 \approx 2$ (if a possible inaccuracy of the measurement is considered). This value is evidently unreal since it indicates that in molten KCl one molecule Li_3AlF_6 dissociates under the formation of only two new particles.

The course of the liquidus curves in the proximity of the eutectic point

According to *Dodé* and *Hagège* [9], in the proximity of the eutectic point the following relation is valid

$$x_Q \, \Delta \bar{H}_Q^{l/s} \, k_Q = x_Z \, \Delta \bar{H}_Z^{l/s} \, k_Z, \tag{6}$$

where x_Q and $x_Z = 1 - x_Q$ are the co-ordinates of the eutectic point E,

$\Delta \bar{H}_Q^{l/s}$ and $\Delta \bar{H}_Z^{l/s}$ are the partial molar enthalpies of the substances Q and Z, respectively, for the process "solidus → liquidus" at the temperature of the eutectic crystallization T_E,

k_Q and k_Z are the slopes of the tangents to the liquidus curves of the substances Q and Z in the eutectic point E and, therefore

$$k_Q = \left(\frac{dT_Q}{dx_Q} \right)_E \quad \text{and} \quad k_Z = \left(\frac{dT_Z}{dx_Z} \right)_E$$

The relation (6) can be used for checking the consistency of the course of the liquidus curve in a system of a given type.

The linear course of the liquidus curve of Li_3AlF_6 in the investigated system was confirmed by two different authors [1, 2] and thus it can be regarded as determined reliably. Therefore we shall use the relation (6) for a control of the course of the liquidus curve of KCl in the proximity of the eutectic point E. For this purpose the value of k_Z ($Z = KCl$) is to be determined. For simplification, we assume $\Delta \bar{H}_Q^{l/s} \cong \Delta H_{Li_3AlF_6}^f = 20.7$ kcal mole^{-1} and $\Delta \bar{H}_Z^{l/s} \cong \Delta H_{KCl}^f = 6.5$ kcal mole^{-1}. This approximation affects only a minor error in the final result. Introducing the above values into the relation (6), we obtain

$$k_Z \cong \frac{0.245 \times 20.7 \times 10^3 \times 214.6}{0.755 \times 6.5 \times 10^3} = 221.8°C.$$

However, according to Matsushima's results $k_Z = 616.3°C$.

It is evident that the difference in these results surpasses many times the possible experimental error. Hence the course of the liquidus curve of KCl in the proximity of the eutectic point, as presented by *Matsushima* [2], is improbable.

From the thermodynamic analysis it ensues that the course of the liquidus line of KCl is not a linear one, since the slopes of the tangents to the liquidus curve for $x_{KCl} \to 1$ and $x_{KCl} = x_E$ are substantially different. Regarding the values of both slopes, the liquidus curve of KCl is to be convex towards the concentration axis (Fig. 2). The linear course of the liquidus presented by Matsushima seems, therefore, to be open to criticism.

In order to confirm the conclusions of the thermodynamic analysis, it is necessary to reexamine the phase diagram Li_3AlF_6-KCl experimentally. The experimental data will be presented in Part II of this paper.

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