The liquidus curves of lithium cryolite in the $Li_3AlF_6-CaF_2$, $Li_3AlF_6-SrF_2$, and $Li_3AlF_6-BaF_2$ systems and their thermodynamic analysis

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The liquidus curves of Li_3AlF_6 in the system $Li_3AlF_6-MeF_2$ (Me = Ca, Sr, Ba) were determined by means of the TA method and the x-ray phase analysis. All three investigated systems were found to be the simple eutectic systems, the co-ordinates of the corresponding eutectic points being: 40 ± 1 mole % CaF_2, 715 ± 2°C; 55 ± 1 mole % SrF_2, 620 ± 2°C and 45 ± 1 mole % BaF_2, 665 ± 2°C. In the temperature interval 782—720°C, the liquidus curves of Li_3AlF_6 in the systems $Li_3AlF_6-CaF_2$ and $Li_3AlF_6-SrF_2$ were found to correspond to the model of strictly regular (one-parameter) solutions whilst in the system $Li_3AlF_6-BaF_2$ it corresponded to the model of two-parameter regular solutions.

The consumption of electrolytically refined aluminium increases parallelly with the world production of aluminium. The most effective additive, mainly with regard to the increase in the electrical conductivity of the electrolyte both in the production of primary aluminium and in the electrolytic refining of aluminium appears to be lithium flouride [1, 2]. Since in the Al electrolyte free aluminium fluoride is usually present, the addition of LiF leads to the lithium cryolite (Li_3AlF_6) formation. The presence of LiF and Li_3AlF_6, besides increasing the electrical conductivity of the electrolyte, substantially decreases its temperature of the primary crystallization, thus rendering possible a decrease in the working temperature in the electrolysis. The lithium salts affect also favourably the density of the electrolyte [3].

The utilization of the lithium salts brings about the necessity of studying the influence of other additions on the basic physicochemical parameters of the Al electrolysis. In the present work, the influence of additions of CaF_2, SrF_2, and BaF_2 on the Li_3AlF_6 liquidus temperature was determined. The knowledge of the Li_3AlF_6 liquidus curves, besides being important with regard to the electrolytic process, is inevitable in the study of other important parameters, such as the density, electrical conductivity, viscosity, *etc.*

Experimental

The Li_3AlF_6 liquidus curves in the $Li_3AlF_6-MeF_2$ systems were determined by means of the thermal analysis method (TA) and the x-ray phase analysis. For the preparation of samples, lithium, calcium, strontium, and barium fluorides for single crystals (Research Institute of Single Crystals, Turnov, Czechoslovakia) produced and 1 hr calcinated at 600°C in an argon atmosphere were utilized. Aluminium fluoride was prepared by the sublimation of a chemically pure product in a Pt apparatus at appr.

1250°C according to *Matiašovský et al.* [4]. The sublimate contained appr. 99.5 wt % AlF_3 and 0.5 wt % Al_2O_3, the last compound not being considered in the preparation of samples.

The prepared mixtures were fused in Pt crucibles in a vertical silite furnace. The temperature was measured by means of a Pt/Pt10Rh thermocouple. With regard to the small thermal effects which were to be registered, no protection tube was used to protect the hot junction of the thermoelement. The temperature was indicated by means of a mirror mV-meter, accuracy class "1", as well as a compensating recorder EZ 11. The termocouple was calibrated on the m.p. of pure Na_2SO_4 (885°C), NaCl (800.8°C), KCl (772°C), and the eutectic temperature of the mixture $NaCl-Na_2SO_4$ (628°C).

In the study of the above mixtures, the losses resulting from the sublimation of AlF_3 which can occur before the melting of the weighed-in samples are to be eliminated. This can be attained either by a quick melting or by a high homogeneity and dispersity of the sample. The homogenization method of agitating in a nonpolar liquid according to *Holm* [5] was tested; however, the fine pulverizing in an agate dish with a following mixing of components proved to be fully satisfactory. The sample prepared in this way could be fused during 15 minutes at a temperature surpassing by appr. 50°C the respective temperature of the primary crystallization. After melting, the mixture in the crucible was homogenized by mixing using a Pt stirrer and the thermocouple was introduced through an opening in the Pt cover, the hot junction being placed appr. 4 mm above the bottom of the crucible. The rate of cooling was within 1—4°C/min. In some cases, in the first step the cooling curve was registered until reaching the temperature of the primary crystallization of Li_3AlF_6; then the mixture was overheated for appr. 30°C and the cooling curve was registered again, this time in full.

The reproducibility of the applied method was determined by repeated measurements using the same sample as well as several samples of the same composition.

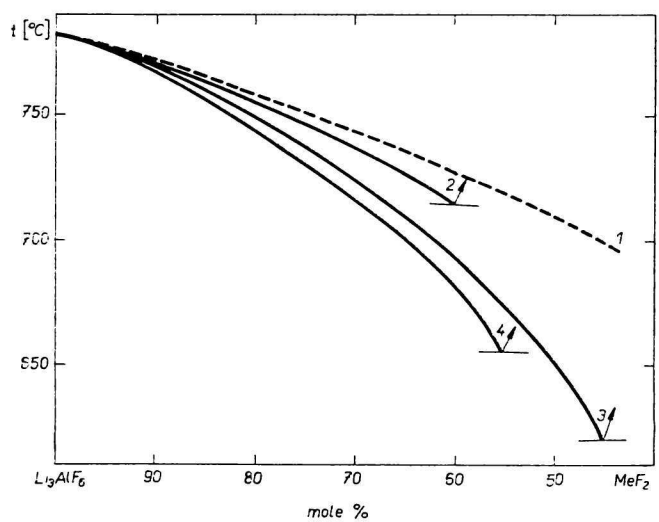

Fig. 1. Liquidus curves of Li_3AlF_6 in the $Li_3AlF_6-MeF_2$ systems.
1. calculated curve according to Le Chatelier—Schröder; *2.* experimental curve in the system $Li_3AlF_6-CaF_2$; *3.* experimental curve in the system $Li_3AlF_6-SrF_2$; *4.* experimental curve in the system $Li_3AlF_6-BaF_2$.

For the preparation of lithium cryolite, a mixture of LiF and AlF_3 was used. It is to be pointed out that no principal difference in the mechanism of cooling was found between the $3LiF-AlF_3-MeF_2$ and the $Li_3AlF_6-MeF_2$ mixtures.

In the systems containing SrF_2 and BaF_2, the possible influence of the hygroscopicity of these substances on the temperature of the primary crystallization of Li_3AlF_6 was to be determined. Therefore the measurements in these two systems were repeated whilst weighing-in the components in a dry-box with a filling consisting of synthetic zeolite Nalsit 4. It was found that in this case, the Li_3AlF_6 liquidus curve in the system $Li_3AlF_6-SrF_2$ is shifted upwards by max. 20°C and in the system $Li_3AlF_6-BaF_2$ by max. 25°C as compared to the values which were obtained without using the dry-box. In the diagram, the values obtained with the dry-box were plotted.

The x-ray phase analysis which was carried out using the difractograph UR-S-50 I with the above samples indicated that there are no solid solutions or chemical compounds present in the studied mixtures. The suitability of the used method was confirmed by the x-ray analysis of the 3 times remelted samples, where no principal changes in the chemical composition were determined. Besides, it was found that under the given conditions, the reaction $3LiF + AlF_3 = Li_3AlF_6$ is shifted completely to the right side, which indicates the stability of the complex AlF_6^{3-} ions and simultaneously confirms that Li_3AlF_6 appears to be an independent component of the investigated systems. The experimental results are presented graphically in Fig. 1.

Discussion of results

The investigated quasi-binary systems of the type $Li_3AlF_6-MeF_2$ appear to be the simple eutectic systems with the co-ordinates as presented in Table 1.

Table 1

Co-ordinates of the eutectic points in the $Li_3AlF_6-MeF_2$ systems

System	Composition of the eutectic point [mole %]		Temperature of the eutectic crystallization [°C]
	Li_3AlF_6	MeF_2	
$Li_3AlF_6-CaF_2$	60 ± 1	40 ± 1	715 ± 2
$Li_3AlF_6-SrF_2$	45 ± 1	55 ± 1	620 ± 2
$Li_3AlF_6-BaF_2$	55 ± 1	45 ± 1	655 ± 2

In order to determine the deviation of the experimentally established liquidus curves of Li_3AlF_6 from their theoretical course, the ideal liquidus curve was calculated using the Le Chatelier–Schröder equation [6] in the form

$$T_i = \frac{\Delta H_i^f}{\Delta S_i^f - RT \ln x_i}.$$

For calculation, the following values were selected: $t^f = 782$°C and $\Delta H^f = 20.5$ kcal mol^{-1} with regard to the results of the calorimetric measurement presented by *Björge* and *Jenssen* [7] and to the cryoscopic measurements carried out by *Malinovský* [8].

Concerning the small temperature interval, $\Delta H^{1/s}$ was considered to be temperature independent. The calculated liquidus curve is presented in Fig. 1.

The experimentally determined values of the temperature of the primary crystallization were utilized for the determination of the "classical" activity coefficients in the temperature interval from 720 to 780°C where it was possible to compare all the three investigated systems. The calculated activity coefficients indicate a negative deviation from the ideality.

In similar systems, the model of regular solutions was successfully applied, by *Holm* [9]; therefore an attempt was done to apply the same model also to the studied systems. The results calculated for the studied temperature interval according to the relationship

$$RT \ln \gamma_A = x_B^2 \omega ,$$

where γ is the activity coefficient and ω the interaction parameter, are presented in Table 2, together with the activity coefficients. The dependence of the activity coefficients on the temperature and composition as well as an analogous dependence of the interaction parameter ω for the Li_3AlF_6 liquidus in all three studied systems are presented in Figs. 2 and 3.

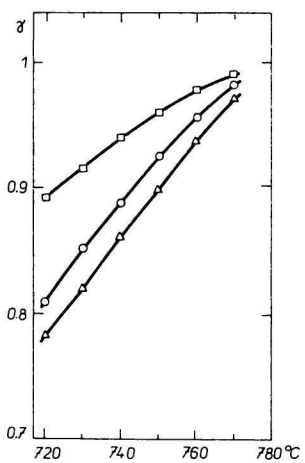

Fig. 2. The dependence of the activity coefficients on the temperature.
□ in the system $Li_3AlF_6-CaF_2$;
○ in the system $Li_3AlF_6-SrF_2$;
△ in the system $Li_3AlF_6-BaF_2$.

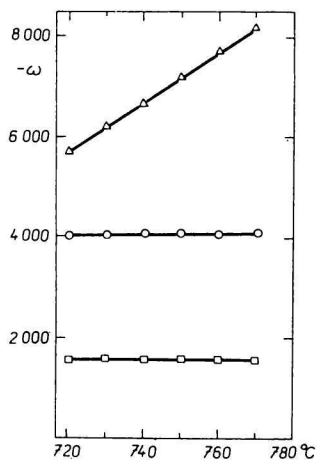

Fig. 3. The dependence of the interaction parameter on the temperature.
□ in the system $Li_3AlF_6-CaF_2$;
○ in the system $Li_3AlF_6-SrF_2$;
△ in the system $Li_3AlF_6-BaF_2$.

From the data which are plotted in Table 2 it follows that the $Li_3AlF_6-CaF_2$ mixtures up to 38 mole % CaF_2, and the $Li_3AlF_6-SrF_2$ mixtures up to 32 mole % SrF_2 suit the model of the strictly regular solutions.

The melts of the system $Li_3AlF_6-BaF_2$ in the concentration range 0–30 mole % BaF_2 suit the model of the two-parameter regular solutions for which a linear temperature dependence of the interaction parameter is valid

Table 2

Coefficients of activity and parameters of interaction in the $Li_3AlF_6-MeF_2$ systems

t	$Li_3AlF_6-CaF_2$			$Li_3AlF_6-SrF_2$			$Li_3AlF_6-BaF_2$		
[°C]	x	γ	$-\omega$	x	γ	$-\omega$	x	γ	$-\omega$
770	0.897	0.992	1 556	0.906	0.983	4 030	0.915	0.972	8 160
760	0.832	0.979	1 545	0.850	0.956	4 110	0.868	0.937	7 690
750	0.773	0.961	1 567	0.803	0.925	4 080	0.826	0.899	7 150
740	0.718	0.940	1 564	0.760	0.888	4 150	0.786	0.860	6 630
730	0.668	0.916	1 580	0.720	0.852	4 070	0.747	0.820	6 170
720	0.621	0.893	1 560	0.685	0.810	4 170	0.708	0.783	5 680

$$\omega = \omega_0 + \alpha T$$

For the $Li_3AlF_6-BaF_2$ mixtures, in the studied concentration range the interaction parameter can be expressed by the equation

$$\omega = 44\,000 - 50\,T$$

The assumption on the similarity of characters of the systems containing sodium or lithium cryolite beside the alkaline earth fluorides was demonstrated by a successful utilization of the model of regular solutions. This was confirmed by a small oscillation of the interaction parameter (± 2%) in the systems containing CaF_2 and SrF_2 as well as by a small deviation of the temperature dependence of the interaction parameter from the linearity (± 1%) in the system $Li_3AlF_6-BaF_2$.

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