

# Physicochemical properties of the molten system



## I. The temperature of primary crystallization

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*Dedicated to Professor L. Treindl, DrSc., in honour of his 60th birthday*

The results of investigation of the temperature of primary crystallization of the system  $\text{Na}_3\text{AlF}_6\text{—K}_3\text{AlF}_6\text{—Al}_2\text{O}_3$  are presented. The experimental data are compared with calculated temperatures of primary crystallization using the "universal model". It follows that alumina dissolved in molten  $\text{K}_3\text{AlF}_6$  forms another type of oxofluoride species than are those which have been reported for molten  $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3$  mixtures at comparable concentration.

Представлены результаты изучения температуры первичной кристаллизации системы  $\text{Na}_3\text{AlF}_6\text{—K}_3\text{AlF}_6\text{—Al}_2\text{O}_3$ . Экспериментально полученные величины сравниваются со значениями температур первичной кристаллизации, рассчитанными с помощью «универсальной модели». Сделан вывод, что трехокись алюминия, растворенная в расплавленном  $\text{K}_3\text{AlF}_6$  образует оксофторидные соединения иного типа, чем те, которые образуются в расплавленных смесях  $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3$  при сравнимых концентрациях.

For over more than 100 years, aluminium is produced by the electrolytic decomposition of alumina dissolved in molten cryolite at 950—970 °C. In spite of large improvements in recent years, the energy efficiency in this process nowadays approaches only 50 %. From an analysis of various factors which determine the energy consumption it follows that one of the fundamental premises for an increase of the current efficiency is a decreased operating temperature of the electrolysis [1]. The operating temperature essentially is determined by the temperature of primary crystallization ( $\theta_{pc}$ ) of the electrolyte. It is generally accepted that  $\theta_{pc}$  can be reduced by addition of suitable substances to the classical electrolyte and the effect of various additives, *viz.* alkali and alkaline earth fluorides and/or chlorides on the technologically important physi-

cochemical properties of the electrolyte has been extensively investigated with the aim to formulate a low-melting electrolyte [1].

In this research project, attention has been focused on  $K_3AlF_6$  as an additive which may be interesting from both technological and theoretical aspects. From the theoretical point of view it is of interest to compare physicochemical properties of the systems  $Na_3AlF_6-Al_2O_3$  and  $K_3AlF_6-Al_2O_3$ , which can help us to understand more deeply the behaviour of the classical cryolite-based electrolyte.

In this paper, the results of experimental investigation of solid—liquid equilibria in the ternary system  $Na_3AlF_6-K_3AlF_6-Al_2O_3$  are presented. Because of complex nature of this system [1], the treatment of the experimental data is based on formal models of molten salt mixtures. These models are also briefly discussed.

Solid—liquid phase equilibria in the system  $Na_3AlF_6-Al_2O_3$  have been studied extensively [1]. Much less reliable information has been published on the systems  $Na_3AlF_6-K_3AlF_6$  [2, 3] and especially on the system  $K_3AlF_6-Al_2O_3$  [4]. (One should be aware of misunderstanding in citation of this paper in [5] where mole and mass % of alumina have been confused.) More credible seem to be the data on the ternary system  $Na_3AlF_6-K_3AlF_6-Al_2O_3$  [3, 6] though they also need confirmation.

## Experimental

In this work the temperature of primary crystallization was measured using the "cooling curves method". Temperature was measured with PtRh10—Pt thermocouple. Used chemicals were of anal. grade except of aluminium fluoride which was purified by sublimation [7]. The temperature of primary crystallization was reproducible with a precision better than 1.5 K. The main experimental difficulties were caused by a high evaporation of samples with a high content of  $K_3AlF_6$ .

## Results and discussion

Experimental data were compared with calculated temperatures of primary crystallization. These temperatures of solid—liquid equilibria were calculated according to the Le Chatelier—Shreder equation

$$\ln \frac{a_l}{a_s} = \frac{\Delta H_{fus}^{\circ}}{R} \left( \frac{1}{T_{fus}} - \frac{1}{T} \right) \quad (1)$$

$a_l$  and  $a_s$  are the activities of the given component in liquid and solid phase, respectively,  $\Delta H_{fus}^{\circ}$  and  $T_{fus}$  are the enthalpy and temperature of fusion of pure

substance, respectively, and  $T$  is the corresponding temperature of solid—liquid equilibrium. The following data were used for calculation:

$$T_{\text{fus}}(\text{Na}_3\text{AlF}_6) = 1283 \text{ K}; \quad \Delta H_{\text{fus}}^\circ(\text{Na}_3\text{AlF}_6) = 107\,280 \text{ J mol}^{-1} \quad [1]$$

$$T_{\text{fus}}(\text{K}_3\text{AlF}_6) = 1269 \text{ K}; \quad \Delta H_{\text{fus}}^\circ(\text{K}_3\text{AlF}_6) = 122\,620 \text{ J mol}^{-1} \quad [8]$$

It is obvious that for calculation of the temperature of solid—liquid equilibrium at given composition of the system we need to know the ratio of activities of the given substance in the liquid and solid phases. Because of complex nature of the molten cryolite—alumina mixtures, formal models for calculation of this ratio have been employed.

### *The system $\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3$*

Our data on the phase equilibria in this system are in agreement with literature [9]. It is well known that alumina dissolves in molten cryolite under the formation of oxofluoride anions [1]. Stoichiometry of these species depends on composition of the system. In this work, the activity of sodium cryolite in the melt was described by the “universal” model [10]. Because alumina at infinite dilution in cryolite melt yields three new particles [9], it follows that at the first approximation we can write

$$a(\text{Na}_3\text{AlF}_6, \text{l}) = x^3(\text{Na}_3\text{AlF}_6)$$

As the melt is in equilibrium with pure solid sodium cryolite it holds

$$a(\text{Na}_3\text{AlF}_6, \text{s}) = 1$$

This model is not well suited for description of the thermodynamic behaviour of this system. Only for very diluted solutions of alumina in molten  $\text{Na}_3\text{AlF}_6$  there is a satisfactory agreement between the calculated values of the temperature of primary crystallization and experimental  $\theta_{\text{pc}}$  values determined in this work which agree with the literature data [9]. Nevertheless this approach may be useful for planning the experiments in ternary systems and for the treatment of experimental data. Its advantage consists in the fact that it does not require any adjustable parameters.

### *The system $\text{K}_3\text{AlF}_6\text{—Al}_2\text{O}_3$*

There are no reliable data on this binary system in literature. They can only be estimated from the phase diagram of the ternary system  $\text{Na}_3\text{AlF}_6\text{—K}_3\text{AlF}_6\text{—Al}_2\text{O}_3$  [6]. Experimental data on the  $\theta_{\text{pc}}$  obtained in this work for the system

$K_3AlF_6-Al_2O_3$  are shown in Fig. 1. They are compared with the calculated liquidus curve of  $K_3AlF_6$ . In the case of this system it was assumed that

$$a(K_3AlF_6, l) = x^2(K_3AlF_6) \quad a(K_3AlF_6, s) = 1$$

We did not succeed in the experimental determination of the eutectic temperature in the mixtures containing less than 10 mole % of alumina. Nevertheless in the calculation a unit activity of  $K_3AlF_6$  in the whole composition range has been assumed (*i.e.* no solid solutions of alumina in  $K_3AlF_6$  were considered).

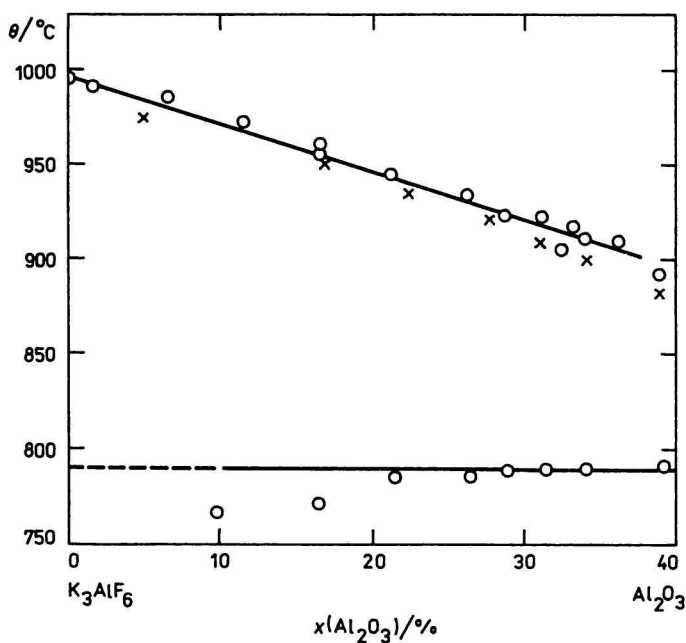


Fig. 1. Phase diagram of the system  $K_3AlF_6-Al_2O_3$ .

○ This paper, × according to [6], — calculated ( $a(K_3AlF_6) = x^2(K_3AlF_6)$ ).

As can be seen from Fig. 1, the assumption that alumina brings only two new particles into the potassium cryolite melt gives reasonable fit with experiment.

It can be assumed that in this case species with the bond  $Al \begin{array}{c} \diagup O \diagdown \\ \diagdown O \diagup \end{array} Al$  are formed even at low content of alumina in contrast to the system  $Na_3AlF_6-Al_2O_3$  [11].

The system  $\text{Na}_3\text{AlF}_6\text{--K}_3\text{AlF}_6$ 

Experimental temperatures of primary crystallization obtained in this work are compared with literature data in Fig. 2. Differences can be explained mainly by experimental difficulties caused by a high evaporation of the melt with a high content of  $\text{K}_3\text{AlF}_6$ . In the present work no special attention was paid to this binary system as it has been discussed in detail by *Grjotheim et al.* [2]. Formation of solid solutions and/or compounds has been reported in this system [2]. The quoted paper [2] contained also a detailed analysis of preceding works devoted to the study of phase equilibria in this system. Because of these uncertainties, liquidus curves in this system cannot be calculated. For the following discussion it was assumed according to the universal model that it holds

$$a(\text{Na}_3\text{AlF}_6, l) = x^3(\text{Na}_3\text{AlF}_6) \quad a(\text{K}_3\text{AlF}_6, l) = x^3(\text{K}_3\text{AlF}_6)$$

This follows from the assumption that  $\text{K}_3\text{AlF}_6$  brings three new particles into the melt and *vice versa*.

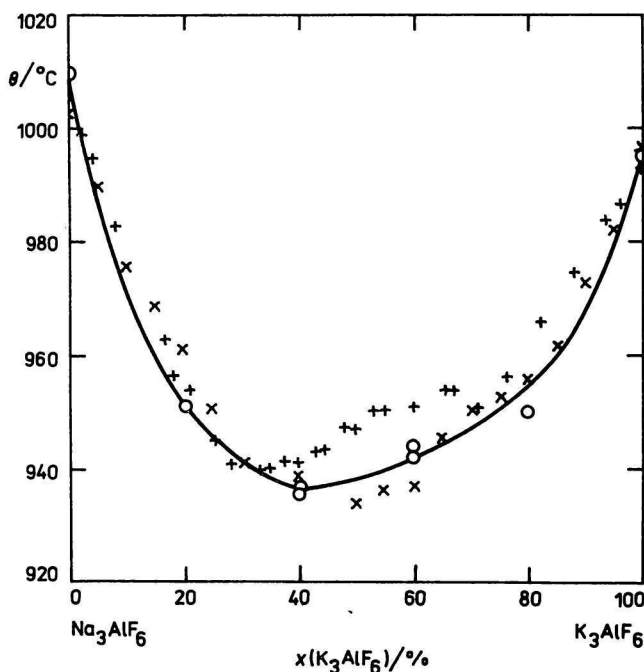


Fig. 2. Liquidus curve of the system  $\text{Na}_3\text{AlF}_6\text{--K}_3\text{AlF}_6$ .  
 ○ This paper, + according to [2], × according to [3].

The system  $\text{Na}_3\text{AlF}_6\text{—K}_3\text{AlF}_6\text{—Al}_2\text{O}_3$ 

Experimental data on the solid—liquid equilibria in the ternary system  $\text{Na}_3\text{AlF}_6\text{—K}_3\text{AlF}_6\text{—Al}_2\text{O}_3$  determined in the present study are presented in Fig. 3. They are in a fair agreement with the results published by *Belyaev* and *Studentsov* [3] and *Mashovets* [6]. Although there are many uncertainties about species present in the melt and about composition of solid phase in this system, an attempt to calculate the temperatures of primary crystallization in this ternary system was made. The following assumptions were adopted:

i) The activities of substances in the melt can be described by the universal model.

ii) The activities of components in the solid phase in the ternary system can be estimated from the activities of the respective component in the binary system  $\text{Na}_3\text{AlF}_6\text{—K}_3\text{AlF}_6$  at the same temperature.

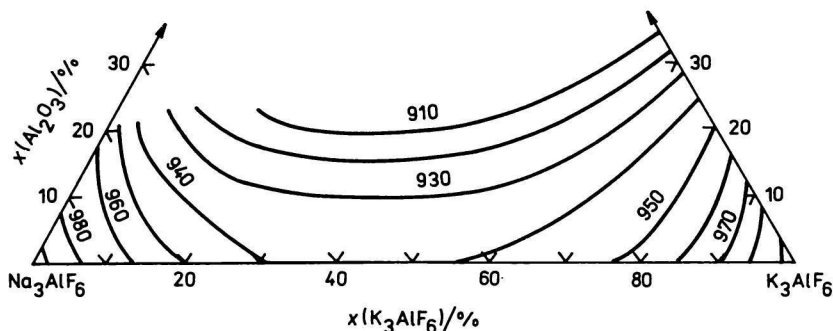


Fig. 3. Experimental curves of liquidus of the system  $\text{Na}_3\text{AlF}_6\text{—K}_3\text{AlF}_6\text{—Al}_2\text{O}_3$ .

From the first assumption it follows that the activity of molten  $\text{Na}_3\text{AlF}_6$  in the ternary system  $\text{Na}_3\text{AlF}_6\text{—K}_3\text{AlF}_6\text{—Al}_2\text{O}_3$  equals

$$a(\text{Na}_3\text{AlF}_6, l) = x^k(\text{Na}_3\text{AlF}_6) \quad k = 3$$

For the activity of molten  $\text{K}_3\text{AlF}_6$  in this system it holds [12]

$$a(\text{K}_3\text{AlF}_6, l) = x^k(\text{K}_3\text{AlF}_6) \quad k = \frac{x(\text{Na}_3\text{AlF}_6) + 2x(\text{Al}_2\text{O}_3)}{x(\text{Na}_3\text{AlF}_6) + x(\text{Al}_2\text{O}_3)}$$

The second assumption is based on the presupposition that only solid solutions of  $\text{Na}_3\text{AlF}_6$  in  $\text{K}_3\text{AlF}_6$  and  $\text{K}_3\text{AlF}_6$  in  $\text{Na}_3\text{AlF}_6$  can exist. In this formal approach, also the deviations from the universal model for the liquid phase are partly considered. The activities of components in the liquid phase were calculated according to the universal model. Based on the experimental data on solid—liquid

Table 1

The experimental and calculated temperatures of primary crystallization of  $\text{Na}_3\text{AlF}_6$  and  $\text{K}_3\text{AlF}_6$  in the system  $\text{Na}_3\text{AlF}_6\text{—K}_3\text{AlF}_6\text{—Al}_2\text{O}_3$

$x/\text{mole } \%$			$\theta_{\text{pc exp}}$	$a_s$ cf. eqn (1)	$\theta_{\text{pc calc}}$
$\text{Na}_3\text{AlF}_6$	$\text{K}_3\text{AlF}_6$	$\text{Al}_2\text{O}_3$	$^{\circ}\text{C}$		$^{\circ}\text{C}$
93	2	5	980	1.00	980
86.5	8.5	5	960	0.97	960
86.0	4	10	960		958
84	1	15	960		950
81.5	13.5	5	950	0.90	950
82	8	10	950		948
80.5	4.5	15	950		944
76	14	10	940	0.80	938
76	9	15	940		938
75.5	4.5	20	940		936
70	15	15	930	0.69	927
71	9	20	930		931
2	94	4	980	1.0	980.5
5	90	5	970	0.96	973
9	86	5	960	0.94	960
4	86	10	960		965
15	80	5	950	0.90	943
10	80	10	950		948
5	80	15	950		954
21	69	10	940	0.65	937
23	62	15	930	0.57	925

equilibria, the activities of components in the solid phase were calculated using the Le Chatelier—Shreder equation (1). These activities were used for calculation of  $\theta_{\text{pc}}$  in the ternary system. The calculated and experimental temperatures of primary crystallization of  $\text{Na}_3\text{AlF}_6$  and  $\text{K}_3\text{AlF}_6$  in the system  $\text{Na}_3\text{AlF}_6\text{—K}_3\text{AlF}_6\text{—Al}_2\text{O}_3$  are compared in Table 1. It can be seen that in the corner of  $\text{K}_3\text{AlF}_6$  there is a good agreement between the calculated and experimental data up to 23 mole %  $\text{Na}_3\text{AlF}_6$  and 15 mole %  $\text{Al}_2\text{O}_3$ . On the side of  $\text{Na}_3\text{AlF}_6$  there is a reasonable agreement between the two sets of data up to 15 mole %  $\text{K}_3\text{AlF}_6$  and 20 mole %  $\text{Al}_2\text{O}_3$ . A better agreement of calculated  $\theta_{\text{pc}}$  values with experiment for  $\text{K}_3\text{AlF}_6$  can be explained by the fact that the universal model describes better the liquidus curve in the system  $\text{K}_3\text{AlF}_6\text{—Al}_2\text{O}_3$  than in the system

$\text{Na}_3\text{AlF}_6\text{—Al}_2\text{O}_3$ . Further improvement of the fit with experiment might be achieved by introducing interaction parameters describing deviations from ideality defined by the universal model.

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