

# Cryoscopy in the System $\text{Na}_3\text{AlF}_6\text{—Fe}_2\text{O}_3$

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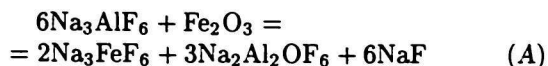
Iron(III) oxide is regarded as impurity introduced into the aluminium reduction cells together with alumina. Reactions taking place in the melt at the dissolution of  $\text{Fe}_2\text{O}_3$  in molten cryolite were studied using the cryoscopic method. Three different reaction schemes were taken into account, leading to the formation of  $\text{Na}_3\text{FeF}_6$  and  $\text{Na}_2\text{Al}_2\text{OF}_6$ , and/or  $\text{Na}_2\text{Al}_2\text{O}_2\text{F}_4$ . The cryoscopic experiments were supplemented by the calculation of equilibrium composition using material balance.

From the results of the cryoscopic measurements it follows that the number of new species is close to 5, which indicates that  $\text{Fe}_2\text{O}_3$  reacts with cryolite under formation of  $\text{Na}_3\text{FeF}_6$  and  $\text{Na}_2\text{Al}_2\text{OF}_6$ . Next addition of  $\text{Fe}_2\text{O}_3$  enables also the formation of  $\text{Na}_2\text{Al}_2\text{O}_2\text{F}_4$ , the presence of which was confirmed by the IR spectroscopic analysis of quenched melts.

The  $\text{Na}_3\text{AlF}_6$  liquidus curve in the phase diagram of the system  $\text{Na}_3\text{AlF}_6\text{—Fe}_2\text{O}_3$  shows an inflex point, which is characteristic of reciprocal systems and indicates that some chemical reaction takes place in the melt. The coordinates of the eutectic point are 1.06 mole %  $\text{Fe}_2\text{O}_3$  and 1002.7°C. The chemical nature of the substance crystallizing on the right side of the phase diagram could not be identified due to its very low concentration in the quenched samples. However, according to the result of the IR spectroscopy, it could be probably  $\text{Na}_2\text{Al}_2\text{O}_2\text{F}_4$ .

Iron(III) oxide is introduced into the aluminium cells in different ways. The main source in the electrolyte is alumina, which introduces approximately 190 g Fe/t of produced aluminium. Next iron, or iron oxide sources are *e.g.*  $\text{AlF}_3$ , prebaked anode blocks, corroded nipples of anode butts, steel rods serving as cathode current supply, *etc.* In the conditions of the aluminium electrolysis the content of iron oxide in the electrolyte may attain up to 0.4 % [1]. Due to its lower decomposition potential compared with that of alumina, the main amount of iron oxide decomposes on the cathode causing decrease of the current efficiency and lowering of the aluminium quality.

The phase diagram of the system  $\text{Na}_3\text{AlF}_6\text{—Fe}_2\text{O}_3$  and the reactions between  $\text{Fe}_2\text{O}_3$  and cryolite, as the main component of the aluminium electrolyte were recently studied by Diep [2]. From the results of his investigation it followed that  $\text{Na}_3\text{AlF}_6\text{—Fe}_2\text{O}_3$  forms a simple eutectic system with the coordinates of the eutectic point 0.85 mole %  $\text{Fe}_2\text{O}_3$  and 997°C. From the course of the liquidus curve of cryolite the author suggested that  $\text{Fe}_2\text{O}_3$  dissolves in cryolite according to the following reaction



Cryoscopy is a useful experimental method frequently applied in the study of chemical reactions tak-

ing place in melts between components. For the lowering of the temperature of fusion of the solvent A,  $\delta_{\text{fus}}T(\text{A})$ , caused by the addition of the solute B the following equation holds

$$\delta_{\text{fus}}T(\text{A}) = \frac{RT_{\text{fus,A}}^2}{\Delta_{\text{fus}}H_{\text{A}}} x_{\text{B}} k_{\text{St}} \quad (1)$$

where  $R$  is the gas constant,  $T_{\text{fus,A}}$  and  $\Delta_{\text{fus}}H_{\text{A}}$  is the temperature and enthalpy of fusion of the solvent A, respectively,  $x_{\text{B}}$  is the mole fraction of the solute B, and  $k_{\text{St}}$  is the semiempirical correction factor introduced by *Stortebeker* [3], representing the number of foreign particles, which introduces the solute B into the solvent A. Differentiating eqn (1) according to  $x_{\text{A}}$  and setting for  $x_{\text{A}} \rightarrow 1$  we get the relation for the tangent to the liquidus curve of the solvent A,  $k_0$ , at the temperature of fusion of the solvent A

$$\lim_{x_{\text{A}} \rightarrow 1} \frac{d(\delta_{\text{fus}}T(\text{A}))}{dx_{\text{A}}} = \frac{RT_{\text{fus,A}}^2}{\Delta_{\text{fus}}H_{\text{A}}} k_{\text{St}} = k_0 \quad (2)$$

Knowing  $T_{\text{fus,A}}$  and  $\Delta_{\text{fus}}H_{\text{A}}$ , from the tangent  $k_0$  we can then calculate  $k_{\text{St}}$ , which enables one to elucidate the possible chemical reactions between components.

In the present work the reactions between cryolite and  $\text{Fe}_2\text{O}_3$  were studied using the cryoscopic method. The experiment was supplemented by the relevant thermodynamic calculation and IR spectroscopic analysis of quenched melts.

## EXPERIMENTAL

For the preparation of samples the following chemicals were used:  $\text{Na}_3\text{AlF}_6$ , handpicked natural Greenland cryolite, and  $\text{Fe}_2\text{O}_3$ , reagent grade, Fluka.

The reactions between  $\text{Fe}_2\text{O}_3$  and cryolite were studied in mixtures containing  $\text{Fe}_2\text{O}_3$  in the range  $0 < x(\text{Fe}_2\text{O}_3) < 0.02$ . 10 g of the homogenized sample was placed in a Pt crucible and melted in a resistance furnace. The temperature of the mixture was measured using a Pt/Pt10Rh thermocouple immersed directly into the melt. The thermocouple was calibrated to the melting point of pure NaCl and NaF. The accuracy in the temperature difference measurement between the temperature of fusion of cryolite and the temperature of primary crystallization of the given mixture was  $\pm 0.2$  K. Cooling curves were recorded using a computerized measuring device. The cooling rate did not exceed  $2 \text{ K min}^{-1}$ .

The experimentally determined values of the temperature of primary and eutectic crystallization of individual samples in the investigated systems are given in Table 1. The value of the Stortenbeker's correction factor was calculated from the tangent of the experimental liquidus curve of cryolite at the melting point of pure cryolite according to eqn (2). For the enthalpy of fusion of cryolite the calorimetrically determined value  $\Delta_{\text{fus}}H_{\text{Na}_3\text{AlF}_6} = 106.75 \text{ kJ mol}^{-1}$  was used [4]. The dependence of  $T_{\text{pc}}$  on  $x_{\text{Na}_3\text{AlF}_6}$  was expressed in the form of the third-order polynomial

$$T_{\text{pc}}(\text{Na}_3\text{AlF}_6) = (-6.9496 \times 10^6 + 2.0949 \times 10^7 x_{\text{Na}_3\text{AlF}_6} - 2.1047 \times 10^7 x_{\text{Na}_3\text{AlF}_6}^2 + 7.0482 \times 10^6 x_{\text{Na}_3\text{AlF}_6}^3) \text{ K} \quad (3)$$

For the constant of thermal depression,  $\frac{RT_{\text{fus},A}^2}{\Delta_{\text{fus}}H_A}$ , the value 126.71 K was obtained. For  $k_0$  and  $k_{\text{St}}$  the values  $k_0 = 680 \text{ K}$  and  $k_{\text{St}} = 5.39$ , respectively, were then calculated. The results of the cryoscopic measurements in the investigated system are shown in Fig. 1.

The IR spectra of pure cryolite,  $\text{Fe}_2\text{O}_3$ , prepared  $\text{Na}_2\text{Al}_2\text{O}_2\text{F}_4$ , containing small amount of  $\text{Al}_2\text{O}_3$ , as well as of the quenched mixture cryolite + 1 mole %  $\text{Fe}_2\text{O}_3$ , were measured using a Perkin—Elmer 983G spectrophotometer in order to determine the possible reaction products. The spectra were recorded at 300 K as KBr pellets and they are shown in Fig. 2.

## RESULTS AND DISCUSSION

In the region of diluted solutions the following limiting relation holds

$$\lim_{x_i \rightarrow 1} \frac{\partial a_i}{\partial x_i} = k_{\text{St}} \quad (4)$$

where  $a_i$  is the activity of the solvent expressed in mole fractions  $x_i$  using a suitable thermodynamic model

Table 1. Temperatures of Primary and Eutectic Crystallization in Melts of the System  $\text{Na}_3\text{AlF}_6$ — $\text{Fe}_2\text{O}_3$

$x(\text{Fe}_2\text{O}_3)$	$t_{\text{pc}}(\text{Na}_3\text{AlF}_6)$	$t_{\text{pc}}(\text{Na}_2\text{Al}_2\text{O}_2\text{F}_4)$	$t_{\text{eut}}$
	$^{\circ}\text{C}$	$^{\circ}\text{C}$	$^{\circ}\text{C}$
0.0000	1008.6	—	—
0.0000	1008.4	—	—
0.0025	1007.0	—	1002.4
0.0025	1006.6	—	1002.7
0.0050	1006.2	—	1002.6
0.0050	1005.9	—	1002.1
0.0065	1005.7	—	1002.7
0.0065	1006.0	—	—
0.0085	1004.5	—	1003.0
0.0085	1004.3	—	1003.1
0.0100	1003.6	—	1002.1
0.0100	1003.4	—	1002.5
0.0120	—	1005.3	1003.4
0.0120	—	1006.1	1002.7
0.0150	—	1011.8	1003.2
0.015	—	1011.5	1002.4
0.02	—	1020.0	1002.5
0.02	—	—	1002.7

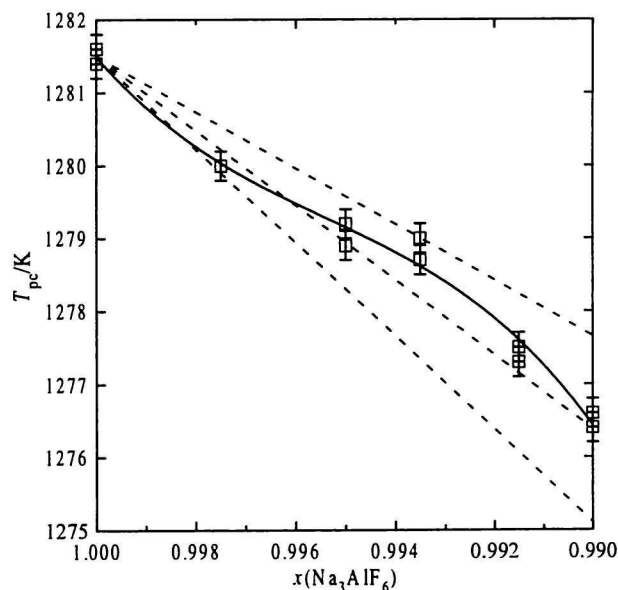


Fig. 1. Results of cryoscopic measurements in the system  $\text{Na}_3\text{AlF}_6$ — $\text{Fe}_2\text{O}_3$ .

and  $k_{\text{St}}$  is the semiempirical Stortenbeker's factor, which equals the amount of substance of new (foreign) species which are introduced by 1 mol of the solute into the infinite amount of solvent. Eqn (4) thus defines the physical meaning of the Stortenbeker's correction factor  $k_{\text{St}}$ . If  $k_{\text{St}} = 1$ , the solutions obey the Raoult's law and belong to the ISt type of solutions [5]. If  $k_{\text{St}} \neq 1$ , the solutions belong to the IInd type of solutions and do not obey the Raoult's law. The knowledge of  $k_{\text{St}}$  thus enables to consider the proba-

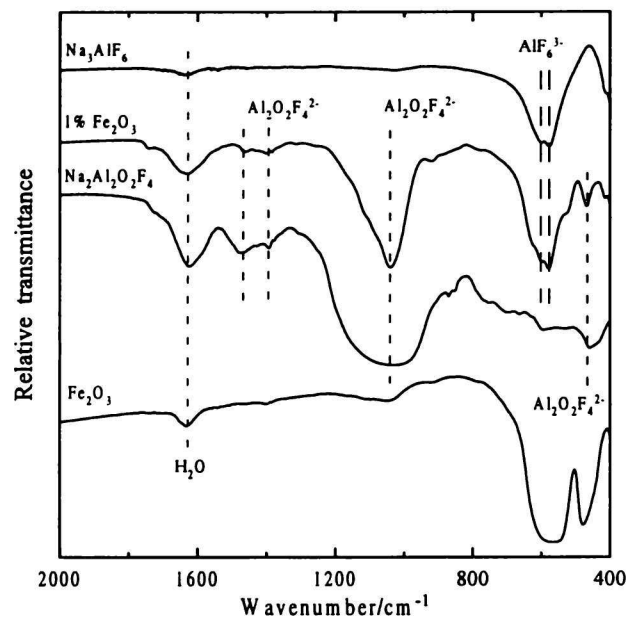


Fig. 2. IR spectra of investigated samples of the system Na<sub>3</sub>AlF<sub>6</sub>—Fe<sub>2</sub>O<sub>3</sub>.

ble chemical reaction between solvent and the solute.

Let us consider 1 mol of mixture with the composition  $x_1$  mol Na<sub>3</sub>AlF<sub>6</sub> +  $x_2$  mol Fe<sub>2</sub>O<sub>3</sub>, where  $x_2 \ll x_1$  where the dissolution of Fe<sub>2</sub>O<sub>3</sub> in cryolite is accompanied with reaction (A). In equilibrium, when all Fe<sub>2</sub>O<sub>3</sub> is dissolved, we get the following equilibrium amounts of the present substances

$$n(\text{Na}_3\text{AlF}_6) = (x_1 - 6x_2) \text{ mol}$$

$$n(\text{NaF}) = 6x_2 \text{ mol}$$

$$n(\text{Na}_3\text{FeF}_6) = 2x_2 \text{ mol}$$

$$n(\text{Na}_2\text{Al}_2\text{O}_2\text{F}_6) = 3x_2 \text{ mol}$$

The total amount of all substances is  $\sum n_i = (x_1 + 5x_2)$  mol. Since we are in the region of diluted solutions, the mole fractions can be set equal to the activities. For the equilibrium activity of cryolite we then get

$$\lim_{x_1 \rightarrow 1} a(\text{Na}_3\text{AlF}_6) = \frac{n(\text{Na}_3\text{AlF}_6) + n(\text{NaF})}{\sum n_i} = \frac{x_1}{x_1 + 5x_2} \quad (5)$$

since due to the thermal dissociation of cryolite according to the scheme



sodium fluoride is not for cryolite a foreign species and must be inserted into its activity, too. Differentiating eqn (5) according to  $x_1$  and inserting the limiting con-

ditions ( $x_1 = 1, x_2 = 0$ ) we get

$$\lim_{x_1 \rightarrow 1} \left( \frac{\partial a(\text{Na}_3\text{AlF}_6)}{\partial x_1} \right) = \frac{x_1 + 5x_2 - x_1(1 - 5)}{(x_1 + 5x_2)^2} = 5 \quad (6)$$

This means that 1 molecule of Fe<sub>2</sub>O<sub>3</sub> introduces into cryolite 5 new species, which is in accordance with the assumed reaction (A). The new species are two molecules of Na<sub>3</sub>FeF<sub>6</sub> and three molecules of Na<sub>2</sub>Al<sub>2</sub>O<sub>2</sub>F<sub>6</sub>, since NaF is in cryolite already present due to its thermal dissociation.

Let us now consider that the dissolution of Fe<sub>2</sub>O<sub>3</sub> in cryolite is accompanied with the reaction



After dissolution of Fe<sub>2</sub>O<sub>3</sub> according to reaction (C) we get the following equilibrium amount of substances

$$n(\text{Na}_3\text{AlF}_6) = (x_1 - 3x_2) \text{ mol}$$

$$n(\text{Na}_3\text{FeF}_6) = 2x_2 \text{ mol}$$

$$n(\text{Na}_2\text{Al}_2\text{O}_2\text{F}_4) = 1.5x_2 \text{ mol}$$

The total amount of all substances is  $\sum n_i = (x_1 + 0.5x_2)$  mol. The mole fraction of cryolite we can again set equal to its activity, for which we get now the expression

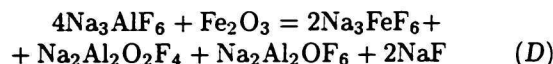
$$a(\text{Na}_3\text{AlF}_6) = \frac{n(\text{Na}_3\text{AlF}_6)}{\sum n_i} = \frac{x_1 - 3x_2}{x_1 + 0.5x_2} \quad (7)$$

Differentiating eqn (7) according to  $x_1$  and inserting the limiting conditions ( $x_1 = 1, x_2 = 0$ ) we get

$$\lim_{x_1 \rightarrow 1} \left( \frac{\partial a(\text{Na}_3\text{AlF}_6)}{\partial x_1} \right) = \frac{4(x_1 + 0.5x_2) - 0.5(x_1 - 3x_2)}{(x_1 + 0.5x_2)^2} = 3.5 \quad (8)$$

It means that in this case 1 molecule of Fe<sub>2</sub>O<sub>3</sub> introduces into cryolite 3.5 new species, which are two molecules of Na<sub>3</sub>FeF<sub>6</sub> and 1.5 molecule of Na<sub>2</sub>Al<sub>2</sub>O<sub>2</sub>F<sub>4</sub>.

Let us finally assume that at the dissolution of Fe<sub>2</sub>O<sub>3</sub> in cryolite the reaction



takes place. After dissolution of Fe<sub>2</sub>O<sub>3</sub> according to eqn (D) we get the following equilibrium amounts of substances

$$n(\text{Na}_3\text{AlF}_6) = (x_1 - 4x_2) \text{ mol}$$

$$n(\text{Na}_3\text{FeF}_6) = 2x_2 \text{ mol}$$

$$n(\text{Na}_2\text{Al}_2\text{O}_2\text{F}_4) = x_2 \text{ mol}$$

$$n(\text{Na}_2\text{Al}_2\text{OF}_6) = x_2 \text{ mol}$$

$$n(\text{NaF}) = 2x_2 \text{ mol}$$

The total amount of all substances is  $\sum n_i = (1 + x_2)$  mol. For the activity of cryolite we now get the expression

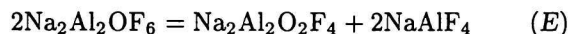
$$\begin{aligned} \lim_{x_1 \rightarrow 1} a(\text{Na}_3\text{AlF}_6) &= \\ &= \frac{n(\text{Na}_3\text{AlF}_6) + n(\text{NaF})}{\sum n_i} = \frac{x_1 - 2x_2}{1 + x_2} \quad (9) \end{aligned}$$

Differentiating eqn (9) according to  $x_1$  and inserting the limiting conditions we get

$$\lim_{x_1 \rightarrow 1} \left( \frac{\partial a(\text{Na}_3\text{AlF}_6)}{\partial x_1} \right) = \frac{3(1 + x_2) + (x_1 - 2x_2)}{(1 + x_2)^2} = 4 \quad (10)$$

In this case 1 molecule of  $\text{Fe}_2\text{O}_3$  introduces into cryolite 4 new species, two molecules of  $\text{Na}_3\text{FeF}_6$ , one molecule of  $\text{Na}_2\text{Al}_2\text{O}_2\text{F}_4$ , and one molecule of  $\text{Na}_2\text{Al}_2\text{OF}_6$ .

From the results of the cryoscopic measurements (Fig. 1) it follows that in the infinitely diluted solution of  $\text{Fe}_2\text{O}_3$  in cryolite the number of new species is 5.37, which is close to 5. This result suggests that the first molecules of  $\text{Fe}_2\text{O}_3$  react with cryolite according to eqn (A), forming  $\text{Na}_3\text{FeF}_6$  and  $\text{Na}_2\text{Al}_2\text{OF}_6$ . At next additions of  $\text{Fe}_2\text{O}_3$  also reactions (C) and (D) may probably take place, since at 0.4 mole %  $\text{Fe}_2\text{O}_3$  the liquidus curve crosses the tangent corresponding to 4 new species and approaches to that corresponding to 3.5 ones. The presence of  $\text{Na}_2\text{Al}_2\text{O}_2\text{F}_4$  in the quenched melt with the composition 99 mole %  $\text{Na}_3\text{AlF}_6$  + 1 mole %  $\text{Fe}_2\text{O}_3$  was confirmed by the IR spectroscopic analysis comparing the IR spectrum of  $\text{Na}_2\text{Al}_2\text{O}_2\text{F}_4$  with that of the 1 mole %  $\text{Fe}_2\text{O}_3$  quenched mixture. However, this compound can be present in the melt also due to the reaction equilibrium



taking place in oxygen-containing cryolite melts [6].

The phase diagram of the investigated part of the system  $\text{Na}_3\text{AlF}_6$ — $\text{Fe}_2\text{O}_3$  is shown in Fig. 3. The inflex point on the  $\text{Na}_3\text{AlF}_6$  liquidus curve is characteristic of reciprocal systems and indicates that some chemical reaction takes place in the melt. The coordinates of the eutectic point are 1.06 mole %  $\text{Fe}_2\text{O}_3$  and 1002.7°C,

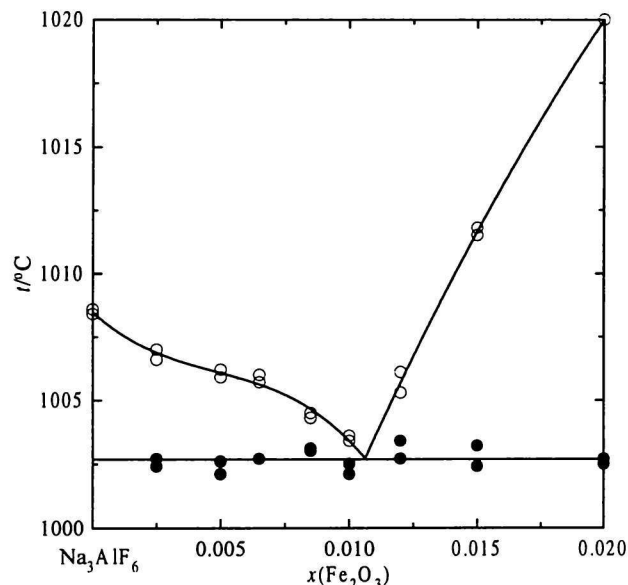


Fig. 3. Phase diagram of the system  $\text{Na}_3\text{AlF}_6$ — $\text{Fe}_2\text{O}_3$ .

which is rather close to the result obtained by Diep [2]. The chemical nature of the substance crystallizing on the right side of the phase diagram could not be identified due to its very low concentration in the quenched samples. However, according to the result of the IR spectroscopy, it could be probably  $\text{Na}_2\text{Al}_2\text{O}_2\text{F}_4$ .

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