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Heat of Fusion of Na_3AlF_6 Eutectic Mixtures with CaF_2 and Al_2O_3

The heat of fusion of eutectic mixtures of sodium cryolite with alumina and calcium fluoride was measured using differential scanning calorimetry. Melting temperatures were found to be in good agreement with literature data. The molar heat of fusion of cryolite salts and eutectic mixtures was found to be directly dependent on melting temperature. The temperature dependence coefficient is the same as that of alkali halides.

Keywords: heat of fusion; melting point; cryolite; heat balance; differential scanning calorimetry.

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Introduction

Molten cryolites are applied as electrolytes in industrial production of aluminum due to high alumina solubility and high electrical conductivity [1]. However, it is difficult to use them due to their relatively high corrosion activity. One means of avoiding this issue is to create protective layer of frozen salts on the walls of electrolytic cell, but this layer, or ledge, is unstable due to high heat flows in the salt bath. In order to control the thickness of a side ledge, the knowledge of thermophysical properties of both liquid and frozen electrolyte is very important, as well as freezing and melting processes themselves. The heat that is absorbed or realized at melting or freezing is determined by the enthalpy of fusion. The main component of an aluminium bath is sodium cryolite, and its enthalpy of fusion was investigated by many researches. The very first results were very different from later data. Malinovsky [2] analyzed all results available in mid-eighties. His own results on heat of fusion were given as 115.4 $kJ \cdot mol^{-1}$ (considering cryolite as Na_3AlF_6) or 28.83 $kJ \cdot mol^{-1}$ (considering cryolite as 75 NaF — 25 AlF_3 in mol %.The data obtained by Malinovsky do not differ essentially from the previous ones [3, 4]. Latest results are also close to these data [5]. Along with sodium cryolite, the other cryolites were studied in works of Holm and Bjorge [3, 6].

The real bath consists not only of cryolite but also of the other components such as alumina and calcium fluoride. The composition of electrolyte is usually close to some eutectic mixture of sodium cryolite with alumina, calcium fluoride and aluminium fluoride plus some small quantities of initial components. Eutectic mixture behaviour at melting (freezing) is similar to that of individual substance, and it is possible to perform a precise measurement of the heat related to melting of such mixture. Heat of fusion measurements can be carried out by differential scanning calorimetry (DSC) and drop calorimetry. In drop calorimetry, the measured parameter is the enthalpy of the sample. The temperature dependence of enthalpy is discontinuous at a melting point. The difference between values for solid and liquid states is the heat of fusion. With the DSC method, the heat of fusion is calculated from the melting area.

The aim of the work was to measure the melting points and heats of fusion of some eutectic mixtures of cryolite with aluminium oxide and calcium fluoride. The measurements were carried out by DSC method, which can provide precise results.

Experimental

The chemicals used for the sample preparation are listed in Table 1. Aluminum fluoride was purified from oxygen containing admixtures by ammonium fluoride in a glassy carbon crucible. Part of NH_4F (10% of AlF_3) was placed on the bottom of the crucible, and the other part was mixed with aluminum fluoride in proportion as follows: 12 g of NH_4F per 100 g of AlF_3. The mixture was heated up to 723–773 K and kept for about 6 hours at that temperature. The reaction between aluminum oxide and ammonium fluoride is given below:

$$6NH_4F+Al_2O_3 = \\ = 2AlF_3+6NH_3+3H_2O \qquad (1)$$

The analysis on oxygen after purification had been made using LECO element analyzer (USA). The mass content of oxygen was less than 0.1%. The purity of other reagents was higher than 99.5% content of main component (Table 1); therefore, their purification was not required.

For preparation of cryolites with calcium fluoride and alumina, the aluminum fluoride was mixed with the other components of eutectic mixture, placed into platinum crucible and heated up to 1323 K. To avoid the oxidation, a small amount of NH_4F was added to the mixture. Ammonium fluoride was decomposed at 513 K and did not influence the composition of the mixture. After melting, the sample was poured into a graphite mould.

The investigations were carried out using a STA 449C Jupiter synchronous thermal analyzer (NETZSCH, Germany). The experimental setup ensures high accuracy of the measuring parameters: temperature (< 1 K); mass (± $1\cdot10^{-6}$ g); base line reproducibility (± 2.5 mW); enthalpy (± 3%). The apparatus was calibrated using pure

Table 1

Materials used in this work

Compound	Mass fraction purity, %	Supplier	Purification
NaF	99.5	Vecton	—
AlF_3	95	Vecton	Treatment by NH_4F
Al_2O_3	99.5	Achinsk alumina plant	—
CaF_2	99.5	Vecton	—

salts supplied by NETZSCH (CsCl, $AgSO_4$, $BaCO_3$, $RbNO_3$, $KClO_4$). Monocrystalline sapphire was used to calibrate the sensitivity. The measurements were performed under following conditions: temperature interval — 308–1300 K; heating rate — 10 K min^{-1}; atmosphere — pure argon; crucibles with lids — Pt–Rh. All measurements were carried out under the same conditions. All calculations were performed with NETZSCH Proteus software.

Results and discussion

Some eutectic compositions of cryolite with calcium fluoride and alumina were investigated; their compositions are given in Table 2.

The phase diagrams of these systems were widely studied and can be found in works [7–11]. The DSC curves are shown in Fig. 1. The weight loss was observed only after melting, and its value varied from 0.6 to 3%. There are some solid-solid transitions on the curves. The α–β cryolite solid transition is present in samples 1 and 4 (Figs. 1, *a, d*). The temperature of this transition is in good agreement with literature [12]. All curves containing calcium fluoride have endothermic peaks in the interval of 1060–1080 K.

Fedotieff and Iljinsky found two temperature halts in the cooling curves in this region for calcium fluoride containing compositions [7]. There are no α/β transitions of cryolite in samples 2 and 3. The transitions occur in mixtures which are quasi-binary such as Na_3AlF_6–Al_2O_3, Na_3AlF_6–AlF_3 and Na_3AlF_6–CaF_2. The sample 1 is such quasi-binary Na_3AlF_6–Al_2O_3 and sample 4 is close to quasi-binary Na_3AlF_6–CaF_2 due to the low concentration of alumina in this sample. The multi-component mixtures manifest other DSC peaks. Craig [9] investigated 8 eutectic mixtures of Na_3AlF_6–AlF_3–CaF_2–Al_2O_3. The lowest DSC peak temperature for these mixtures was found to be equal to 948 K. Melting peaks are very broad, but the same lines were observed by other scientists [8, 10].

Melting points of mixtures under investigation are in the interval of 1200–1220 K. It is in good agreement with the results presented in the article [11]. The values of melting points and heats of fusion are given in Table 3. The literature data on heats of fusion and melting points of cryolite salts are given in Table 4. Na_3AlF_6 is a coordination compound. Coordination compounds are inorganic salts formed by the combination of two or more simple compounds in stoichiometric ratio. In order to compare molar properties of coordination compounds and simple compounds, one must consider a coordination compound (in our case Na_3AlF_6) as a combination of simple

Table 2

The composition of samples under investigation

No	Composition/mass%				Composition/mol%			
	NaF	AlF_3	CaF_2	Al_2O_3	NaF	AlF_3	CaF_2	Al_2O_3
1	56.4	37.6	0.0	11.7	70.5	23.5	0.0	6.0
2	50.1	33.4	14.8	3.1	66.1	18.5	10.2	1.7
3	50.5	33.6	10.0	5.9	67.2	22.4	7.2	3.2
4	46.2	30.8	19.9	3.1	62.8	21.0	14.6	1.7

compounds, i.e. 3 molecules of NaF and 1 AlF_3. In order to to equalize cryolite with simple compounds its molecular weight must be given for 1 molecule (0.75 molecular weight of NaF and 0.25 molecular weight of AlF_3).

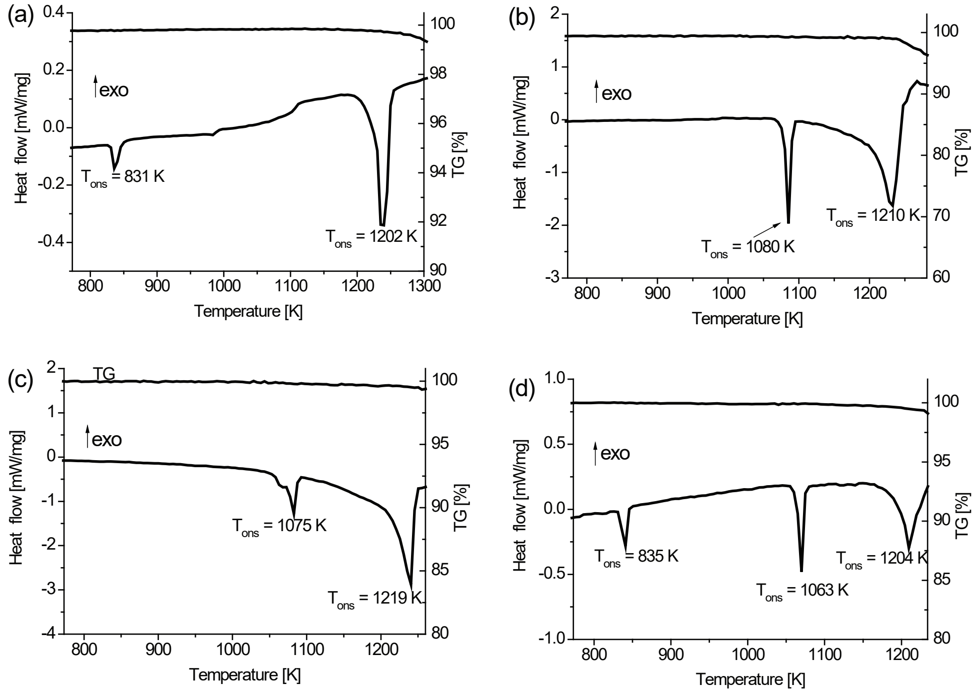

Fig. 1. DSC and thermogravimetric (TG) curves of cryolites with different composition: 1 (*a*), 2 (*b*), 3 (*c*), 4 (*d*) (see Table 2)

Table 3

Heats of fusion and melting points of eutectics under investigation

Comp. No	Transition point/K	ΔH_{tr}/ J g^{-1}	ΔH_{tr}/ kJ mol^{-1}	Melting point/K	ΔH_m/ J g^{-1}	ΔH_m/ kJ mol^{-1}
1	831	43.3	2.4	1202	476.6	26.4
2	1080	95.5	5.1	1210	501.8	26.6
3	1075	71.7	4.0	1219	477.2	26.7
4	835	44.2	2.5	1204	455	26.0
	1063	84.3	4.8	—	—	—

Table 4

Heats of fusion and melting points of cryolites

Compound	T_{mp}/K	H_{fus}/kJ mol^{-1}	Compound	T_{mp}/K	H_{fus}/kJ mol^{-1}
Li_3AlF_6	1058 [4]	21.0 [4]	Na_3AlF_6	1284 [2]	28.3 [2]
Li_3AlF_6	1058 [2]	22.0 [2]	Na_3AlF_6	1284 [1]	28.9 [1]
Na_3AlF_6	1284 [3]	28.8 [3]	K_3AlF_6	1273 [2]	30.8 [2]

Thus, the literature data were recalculated using the molecular mass of mixture as a sum of 75% of molecular mass of alkali halide and 25% of molecular mass of aluminium fluoride. It allows comparing results with data on individual salts. All the results are presented in Fig. 2 in coordinates as follows: heat of fusion — melting point.

There is a clear correlation between the enthalpy of melting and the melting point. The nature of this correlation is in thermodynamics, because

$$T_m = \Delta H_m / \Delta S_m, \quad (2)$$

where T_m is the melting temperature, ΔH_m is the enthalpy of fusion, and ΔS_m is the entropy of fusion.

The correlation between the enthalpy of melting and the melting point for alkali halide salts was found in our previous article [13]. The same correlation was shown for nitrates, carbonates and sulphates [14]. This trend is the part of more broad relationship known as Trouton's rule, which connect enthalpy of phase transition with its temperature. It is valid both for vaporization of pure elements [15] and for melting [16, 17].

According to LSM (least-squares method) estimations, the coefficients in the equation $H = A + B \cdot T$ are as follows: B_{SQ} = 0.034 kJ mol^{-1} K^{-1}; A_{SQ} = −14.25 kJ mol^{-1}; T — temperature, K. The standard deviation σ_{SQ} is equal to 0.815 kJ mol^{-1}, and the determination coefficient R^2=0.94.

Thus, the equation is:

$$\Delta H_m/\text{kJ mol}^{-1} = B_{SQ} \cdot T_m - A_{SQ} = 0.034\ T_m - 14.25 \quad (3)$$

Table 5
The values of coefficients in equations for heat of fusion dependence on the melting point

Compounds	Parameter A_{SQ}/kJ mol^{-1}	Parameter B_{SQ}/kJ mol^{-1} K^{-1}
Cryolites	−14.25	0.034
Alkali halides [7]	−12.12	0.036

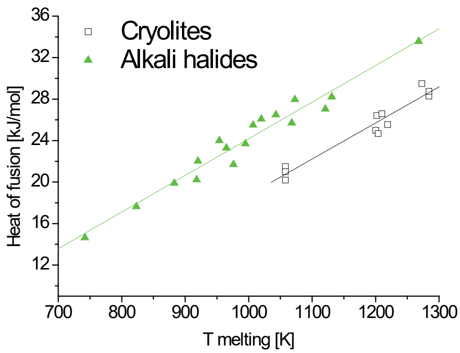

Fig. 2. Heat of fusion dependence on the melting point for cryolites and alkali halides

The heat of fusion temperature coefficient of cryolites is close to that of alkali halides. Thus, the temperature dependence of heat of fusion is the same for halide compounds and equal to the value for alkali halide salts. The values of temperature coefficients are close to 4R. It is the same number as heat capacity of halide salts per atom [18].

Thus, the heat of fusion is directly proportional to the melting point for simple halide salts, salts compounds and eutectic mixtures. The fusion properties of all these substances are possibly connected due to the fact that the main components of these compounds are halide salts.

Conclusions

1. Heats of fusion were measured for some eutectic mixtures of sodium cryolite with alumina and calcium cryolite.

2. The heat of fusion was found to be directly proportional to the melting point.

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