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CALORIMETRIC INVESTIGATIONS OF SOME PHASES IN THE SYSTEM SODIUM FLUORIDE – ALUMINIUM FLUORIDE

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Abstract

Beside the two well-known minerals cryolite, Na_3AlF_6, and chiolite, $Na_5Al_3F_{14}$, the binary system NaF–AlF_3 also contains a third compound, $NaAlF_4$, sodium tetrafluoroaluminate. Solid $NaAlF_4$ has been prepared from its vapour under controlled conditions. The stability of $NaAlF_4$ has been investigated by differential scanning calorimetry. It is shown that the disproportionation of the compound: $5NaAlF_{4(s)}=Na_5Al_3F_{14(s)}+2AlF_{3(s)}$ takes place at considerable rate between 700 and 900 K. The enthalpy of this reaction is calculated and found to be –66.9 kJ. Enthalpies of the two solid state transitions α-$Na_3AlF_6 \rightarrow \beta$-$Na_3AlF_6$ and α-$AlF_3 \rightarrow \beta$-AlF_3 have also been measured and new values are reported.

The enthalpy of formation of chiolite, $Na_5Al_3F_{14}$, at 900 K has been recalculated from enthalpy increment data obtained by drop calorimetry. A value of $\Delta H^{\circ}_{900} = -7513.6 \pm 12.0$ kJ mol^{-1} has been obtained. This value is in disagreement with the recommended value given in JANAF Thermochemical Tables given at 900 K $\Delta H_f^{\circ} = -7559.2$ kJ mol^{-1}.

Keywords: DSC, enthalpies, $NaAlF_4$, $Na_5Al_3F_{14}$

Introduction

It is today generally accepted that cryolite, Na_3AlF_6, during melting at temperatures above the melting point 1283 K dissociates according to the reaction scheme:

$$Na_3AlF_{6(l)}=2NaF_{(l)}+NaAlF_{4(g)} \quad (1)$$

The fluoride emisson from the cryolite bath in alumina reduction cells has therefore been the subject of several investigations. Due to the technical importance of the system, the phase diagram NaF–AlF_3 has been investigated by a number of workers throughout the last 85 years, since Fedofieff and Iljinskii [1] published their work in 1913.

The binary system contains to compounds, one at the composition $3NaF+AlF_3$ corresponding to the mineral cryolite, Na_3AlF_6, and another compound at the composition $5NaF+3AlF_3$ corresponding to the mineral chiolite, $Na_5Al_3F_{14}$.

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About 40 years ago in 1954 Howard [2] demonstrated the existence of a third compound, $NaAlF_4$, by quenching the vapour above a molten mixture of NaF and AlF_3. The existence of $NaAlF_4$ both as a compound in the gas phase as given by Eq. (1), and as a solid phase have earlier been verified by several authors. These investigations have been summarized by Holm [3]. Holm [4] also demonstrated some years earlier in 1963 on the basis of equilibrium phase studies including microscopy, X-ray investigations and DTA studies that $NaAlF_4$ is a metastable compound. It disproportionates to $Na_5Al_3F_{14(s)}$ and $AlF_{3(s)}$ upon heating according to the reaction scheme:

$$5NaAlF_{4(s)}=Na_5Al_3F_{14(s)}+2AlF_{3(s)} \quad (2)$$

in agreement with Howard's [2] own results.

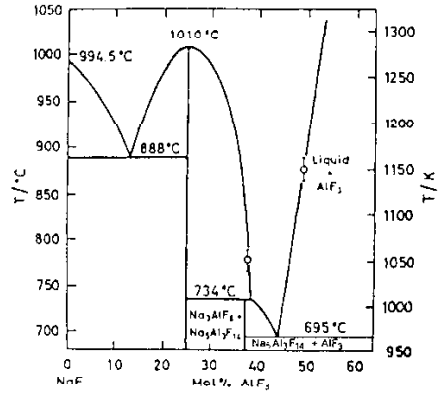

Fig. 1 The phase diagram of the system NaF–AlF_3 according to Holm [3]

On the basis of his heat content studies of some NaF–AlF_3 mixtures by drop calorimetry, Holm [3] presented a revised phase diagram for the system in 1974. This diagram is shown in Fig. 1.

Experimental

Chemicals

AlF_3

Anhydrous from MacKay, USA, was sublimed twice in a vacuum furnace at 910°C. Pure transparent hexagonal crystals were picked out from the product and used for these experiments. Analysis showed that the product contained 99.2 mass% AlF_3 as a mean. One would expect that the clear crystals which were used have an even higher purity than 99.2 mass%.

Na_3AlF_6

Handpicked cryolite from Ivigtut, Greenland, special pure quality (not washed), gift from Kryolitselskabet Øresund, Copenhagen.

$Na_5Al_3F_{14}$

Chiolite, handpicked mineral from Greenland, clear crystals of the highest purity available.

$NaAlF_4$

Sodium tetrafluoroaluminate. The preparation of solid $NaAlF_4$ from its vapour under controlled conditions, was performed by vaporization at 1073 K of a melt of bulk composition corresponding to $5NaF:3AlF_3$. A sample of the mineral chiolite, $Na_5Al_3F_{14}$, from Ivigtut, Greenland was used as a starting material. During the experiment dry nitrogen gas was flushed through the furnace and the condensation product from the vapour was collected on an alumina filter at room temperature.

Experimental techniques

DSC

DSC-2 instrument from Perkin-Elmer. Platinum crucibles were used as containers. The heating rate was 20°C min^{-1} for all experiments and the calibration of the instrument followed the procedure given by ICTAC [5]. Heating rates during the experiments were 10 and 20°C min^{-1}, and the sample masses were between 40 and 60 mg. In the case of the investigation of $NaAlF_4$, about 40 mg of $NaAlF_4$ fibres were compressed into a tablet and put into a platinum crucible with a well-fitted lid. Purified nitrogen (99.99%) was used as inert gas during all experiments.

X-ray equipment

X-ray investigations were carried out by use of a Phillips PW 1730/10 instrument using CuK_α-radiation (λ=1.5418 Å).

Calorimetry

The calorimeter proper used during the drop calorimetric experiments, the calibration of the calorimeter, and the method of calculating the enthalpy increments $H_T-H_{298.15}$ have been described in detail by Grønvold [6].

Results and discussion

DSC-investigations

The DSC-diagrams for the investigations of AlF_3 and Na_3AlF_6 are given in Figs 2a and b.

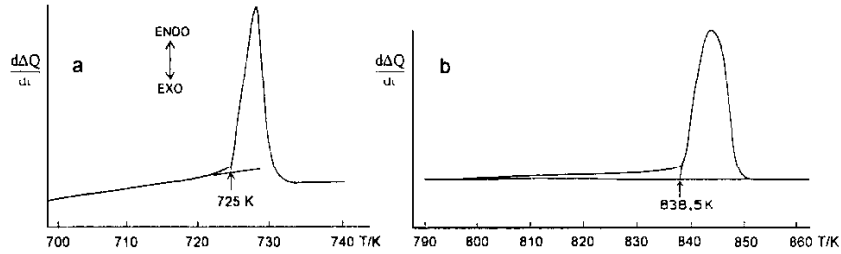

Fig. 2 a) DSC-diagram for AlF_3; b) DSC-diagram for Na_3AlF_6. Showing solid state transformations at 725 K for AlF_3 and at 838.5 K for Na_3AlF_6

AlF_3

AlF_3 undergoes a phase transformation at 725 K. The enthalpy of transition is measured to be 530 J mol^{-1}, in reasonable agreement with literature values as shown in Table 1. During the transition AlF_3 goes from a rhombohedral structure with cell parameters a=4.9278 Å and c=12.446 Å (Z=6) to primitive cubic structure with cell parameter a=3.583 Å (Z=3) at 775 K [7].

Table 1 Enthalpies of transition of AlF_3

T_0/K	ΔH_t/J mol^{-1}	Ref.
725 (onset)	530±10	This work
728	600	[9]
728	563±42	[10]

Na_3AlF_6

Cryolite undergoes a phase transition at 836 K from a monoclinic low-temperature modification, α-cryolite (space group P21/n) with cell parameters a=5.412 Å, b=5.599 Å, c=7.777 Å and β=90.19°, to a cubic structure, β-cryolite, (space group Fm3m) with cell parameter a=7.960 Å at 873 K [4].

The measured enthalpy of the transition

$$\alpha\text{-cryolite} \rightarrow \beta\text{-cryolite} \qquad (3)$$

is 9600±200 J mol^{-1} and the measured onset temperature is 838.5 K. JANAF Thermochemical Tables [8] report values from 5120 to 9960 J mol^{-1} for this enthalpy. The discrepancies are most probably due to the fact that the transition is not a pure first order transition, but starts about 50 degrees below the transition point as can be seen from Fig. 2b.

$NaAlF_4$

The DSC-diagram for $NaAlF_4$ is given in Fig. 3 and shows a pronounced exothermic heat effect appearing from about 780–950 K at scan rate 20°C min^{-1}. Since the reaction takes place over a wide temperature range (~180°), one has to establish a base line (reference line) for an unreacting sample with an equal mass and heat capacity. This was obtained by running a second experiment using the disproportionated sample from the former experiment. The dotted line (base line) in Fig. 3 was established in this way. The calorimetric measurements for the disproportionation reaction, $5NaAlF_{4(s)} \rightarrow Na_5Al_3F_{14(s)}+2AlF_{3(s)}$, give an enthalpy value at the average temperature 900 K of ΔH° (900 K) = –66.9±7 kJ mol^{-1}.

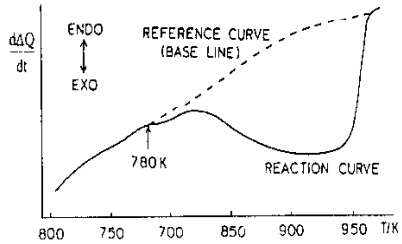

Fig. 3 DSC-recording of the disproportionation of solid $NaAlF_4$ between 700 and 950 K. The area between the solid and dotted line gives together with a calibration factor the size of the enthalpy of disproportionation

To control the results from the DSC experiments, a sample of $NaAlF_4$ was heated at 873 K for 2 h in controlled atmosphere and thereafter examined by XRD analysis. The results from the X-ray investigation of the heated sample is given in Fig. 4. As

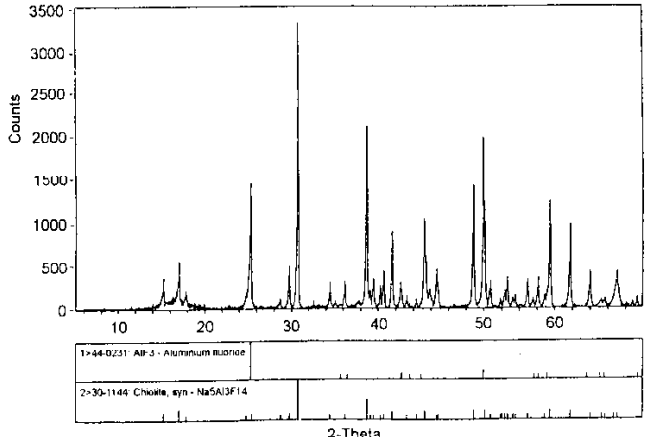

Fig. 4 XRD data of $NaAlF_4$ heated 3 h at 923 K in controlled atmosphere. $NaAlF_4$ has disproportionated to $Na_5Al_3F_{14}+AlF_3$

can be seen solid $NaAlF_4$ has disproportionated completely to $Na_5Al_3F_{14}$ and AlF_3 during the heating experiment.

Calorimetry

$Na_5Al_3F_{14}$

The enthalpy of formation of chiolite $Na_5Al_3F_{14}$ has been calculated from the enthalpy increment data obtained by drop calorimetry and reported earlier by Holm [3]. The data are recalculated from calories to joules and given in Table 2.

Table 2 Enthalpy increments $H_T-H_{298.15}=a+bT$ as a function of temperature and standard deviations

Compound (mixture)	$H_T-H_{298.15}$/J mol^{-1}	δ/J mol^{-1}
$Na_5Al_3F_{14(s)}$	−184.975+574.588 T	1138
$0.425Na_3AlF_{6(s)}+0.575AlF_{3(s)}$	−66.927+182.297 T	364
$0.333Na_3AlF_{6(s)}+0.667AlF_{3(s)}$	−53.614+159.12 T	556

From reaction (4)

$$0.425Na_3AlF_{6(s)}+0.575AlF_{3(s)}=0.255Na_5Al_3F_{14(s)}+0.235AlF_{3(s)} \quad (4)$$

and from reaction (5)

$$0.333Na_3AlF_{6(s)}+0.667AlF_{3(s)}=0.2Na_5Al_3F_{14(s)}+0.4AlF_{3(s)} \quad (5)$$

one obtains from the drop calorimetry data given in Table 2, a mean value of $\Delta H^\circ(900\ K) = -34.9\pm1.5$ kJ mol^{-1} for the raction:

$$5/3Na_3AlF_{6(s)}+4/3AlF_{3(s)}=Na_5Al_3F_{14(s)} \quad (6)$$

From this value combined with available data for Na_3AlF_6 [9], NaF [9] and AlF_3 [10] it is possible to calculate the enthalpy of formation of chiolite from the component fluorides:

$$5NaF_{(s)}+3AlF_{3(s)}=Na_5Al_3F_{14(s)} \quad (7)$$

We obtain ΔH_f° (900 K) = −129.5 kJ mol^{-1} while the value calculated from JANAF [8] is −181.4 kJ mol^{-1}.

We also report a new value for the formation of chiolite from the elements at 900 K.

$$\Delta H_f^\circ\ (900\ K) = -7513.6\pm12.0\ kJ\ mol^{-1}.$$

This enthalpy value should be compared with the recommended enthalpy of formation given in the JANAF Thermochemical Tables [8]; ΔH_f° (900 K) = −7559.2 kJ mol^{-1}.

In Table 3 the new value is compared with other enthalpies of formation of chiolite at 900 K found in the literature.

Table 3 Standard enthalpy of formation of solid $Na_5Al_3F_{14}$ at 900 K

Source	ΔH_f°/kJ mol^{-1}
Dewing*	−7539.8
Grjotheim *et al.***	−7472.9
Cantor *et al.*#	−7488.5
Sterten *et al.*##	−7462.5
This work	−7513.6±12.0

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Summary

A solid compound corresponding to the molar 1:1 composition in the system NaF–AlF_3, $NaAlF_4$ (sodium tetrafluoroaluminate), can be obtained by quenching the vapour form above AlF_3-rich melts. This compound is however metastable at all temperatures. It disproportionates to $Na_5Al_3F_{14}$ and AlF_3 by heating, and therefore $NaAlF_4$ should not be presented as an equilibrium phase in the NaF–AlF_3 phase diagram as has been done recently [11]. The enthalpy of formation of chiolite obtained in this work from drop calorimetric experiments is in disagreement with the recommended value given in the JANAF Thermochemical Tables.

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