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Thermochemical properties of the Fe-analogue of cryolite, Na_3FeF_6

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Abstract: Relative enthalpies for low- and high-temperature modifications of Na_3FeF_6 and for the Na_3FeF_6 melt have been measured by drop calorimetry in the temperature range 723 – 1318 K. Enthalpy of modification transition at 920 K, $\Delta_{trans}H(Na_3FeF_6, 920\ K) = (19 \pm 3)$ kJ mol^{-1} and enthalpy of fusion at the temperature of fusion 1255 K, $\Delta_{fus}H(Na_3FeF_6, 1255\ K) = (89 \pm 3)$ kJ mol^{-1} have been determined from the experimental data. Following heat capacities were obtained for the crystalline phases and for the melt, respectively: $C_p(Na_3FeF_6, cr, \alpha) = (294 \pm 14)$ J (mol K)$^{-1}$, for $723 \leq T/K \leq 920$, $C_p(Na_3FeF_6, cr, \beta) = (300 \pm 11)$ J (mol K)$^{-1}$ for $920 \leq T/K \leq 1233$ and $C_p(Na_3FeF_6, melt) = (275 \pm 22)$ J (mol K)$^{-1}$ for $1258 \leq T/K \leq 1318$. The obtained enthalpies indicate that melting of Na_3FeF_6 proceeds through a continuous series of temperature dependent equilibrium states, likely associated with the production of a solid solution.

Keywords: Na_3FeF_6, enthalpy, heat capacity, calorimetry

1 Introduction

Iron is one of the most common impurities in the industrial production of aluminium by the Hall-Héroult process. The main part of iron is introduced into aluminium cells as an admixture in alumina in form of Iron (III) oxide and as a result of the corrosion of steel parts of the electrolyser. In the electrolyte iron oxide dissolves in cryolite. In the conditions of aluminium electrolysis, the content of iron oxide 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 a decrease of the current efficiency and

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contamination of the aluminium. According to Sterten et al. [2], the lowering in current efficiency is 0.23 % per 0.01 wt% of Fe(III). Contamination as high as 0.086 wt% iron in aluminium has been reported according to Thonstad [3]. In order to explain the role of iron-bearing impurities in the aluminium electrolysis, it is important to know the mechanism of reactions of Fe_2O_3 with molten cryolite and to know the nature of the dissolved species in which iron is present in the electrolyte. Numerous works on solution of iron oxides in cryolite can be found in literature. Most assume the presence of FeF_6^{3-} ions in cryolite – Fe_2O_3 melt. From the slope of the freezing point depression data in the system Na_3AlF_6 – Fe_2O_3, Johansen [4] concluded that the most probable iron species was FeF_6^{3-}, with some $(FeF_4)_n^{n-}$. Diep [5] suggested from the solubility measurements in alumina-saturated melts at 1020 °C that Na_3FeF_6 was the most important species apart from $Na_2AlFeOF_6$, $Na_6AlFeOF_{10}$ and $Na_2AlFeO_2F_4$. Šimko and Daněk [6] studied the mechanism of Fe_2O_3 dissolution in cryolite by the use of cryoscopy and IR spectroscopy. The presence of oxofluoroaluminates and a stable non-volatile fluorine species, involving paramagnetic nuclei, probably FeF_6^{3-}, in the cryolite melts with addition of Fe_2O_3 at 1293 K was also confirmed by high temperature NMR spectroscopy [7, 8]. The results of solubility, cryoscopy, and spectroscopy investigation confirmed that Na_3FeF_6 must be considered as a constituent of the electrolyte in industrial aluminium cells.

Na_3FeF_6 occurs in low-temperature and high-temperature crystalline modifications. The structure of the low-temperature form has been determined by Croft and Kestigian [9] and Matvienko et al. [10]. They found out that it is close to the structure of Na_3AlF_6 in the frame of the monoclinic group $C_{2h}^5 P2_1/n$. Fe^{3+} in the structure of Na_3FeF_6 like Al^{3+} in the structure of Na_3AlF_6 is in octahedral coordination. Na atoms have two types of environments; an octahedral one and a very distorted CN = 12 one.

An additional tool to examine possible reactions and the nature of equilibrium states in studied systems would be the calculation of their thermodynamic properties. However, even fundamental thermodynamic properties of Na_3FeF_6, like heat capacities, enthalpies and entropies are not available today. Only some partial molar enthalpies evaluated from solubility measurements (De Yong [11], Diep [5]) were previously reported. Therefore, the goal of this study is to calorimetrically measure enthalpies of the low- and high-temperature crystalline forms of this substance, as well as of the Na_3FeF_6 melt. The current study makes it possible to evaluate heat capacities of the studied phases, enthalpy and entropy of the transition between high- and low-temperature modifications, as well as the enthalpy and entropy of fusion of the substance. The behavior of the substance during phase transitions may help to explain mechanism of the associated processes.

2 Experimental methods

The reagent grade Sodium hexafluoroferrate(III) (Aldrich) was used for experiments. The substance was stored in a closed container and manipulated in glove box under dried nitrogen. The X-ray pattern of the sample did not significantly differ from patterns for this substance present in the ICCD PDF - 2 database. Thermal analysis showed two

conspicuous endothermic effects, both with reversible behaviour at cooling. The X-ray pattern of the sample recorded after completion of measurements was very similar to its original state.

The relative enthalpy $H_{rel} = H(T) - H(298\ \mathrm{K})$ has been measured by the use of an isoperibol high temperature drop calorimeter [12]. The sample was loaded in a closed Pt-Rh crucible (90 % Pt, 10 % Rh) and annealed in a calorimetric furnace at constant temperature T for at least one hour. The temperature T is measured by a thermocouple placed close to the crucible cover. A temperature difference due to different positions of the sample and the thermocouple is compensated for by calibration. By calibration, an additional standard thermocouple and a special crucible similar to the measuring crucible is used. The standard thermocouple is placed inside the special crucible in the position of the sample where an inert material is loaded. The measuring thermocouple is in its normal position close to the crucible cover. The temperature difference between both thermocouples is measured as a function of temperature. This difference corrects the temperature of the measuring thermocouple. After one hour or longer of heating in the furnace, the crucible is dropped into a calorimetric copper block. The surrounding jacket of the block is kept at constant temperature, 298 ± 0.003 K, by the use of a thermostat. The temperature increase of the calorimetric block is measured with a Wheatstone bridge made of two temperature-dependent and two temperature-independent resistors, which are placed in a groove at the surface of the block. The diagonal of the bridge is fed with constant current of 230 μA. The output voltage of the bridge is linear with respect to temperature. The temperature sensitivity of the measuring apparatus is 600 $\mu\mathrm{V\ K^{-1}}$. The measured enthalpy, determined by evaluating the temperature difference between the block and the surroundings as a function of time, corresponds to the amount of heat transferred from the block into its surroundings. After dropping the sample, the temperature of the block is recorded for approximately 1 h. The heat released from the block into its surroundings after this period is calculated by extrapolation [13]. The measured heat Q is the enthalpy difference between the two equilibrium states at the temperatures T and 298 K, $Q(T,\ 298\ \mathrm{K}) = H(T) - H(298\ \mathrm{K})$. The typical measured enthalpy is 1 – 4 kJ, the typical relative error of a single measurement is about 0.3 %.

3 Results and discussion

The enthalpy data of Na_3FeF_6 measured in the temperature range 723 – 1318 K are listed in Table 1. In Fig. 1, the measured enthalpy data are plotted versus temperature. Fig. 1 shows two leaps in the temperature dependence of the enthalpy, corresponding to the solid state transformation and the melting of the substance.

It is impossible to determine the phase transition temperature exactly using calorimetric experiments. However, it is usually possible to estimate this temperature by interpolation. The experimental data show that the temperature of the modification transition lies between 918 and 923 K. These values are in the same temperature range as those of previous data obtained for the transformation of the low-temperature monoclinic

Table 1 Experimental enthalpy increments $H(\mathrm{T}) - H(298\ \mathrm{K})$ of Na_3FeF_6.

T/ K	$[H(T) - H(298\ \mathrm{K})]$ / kJ mol $^{-1}$	T/ K	$[H(T) - H(298\ \mathrm{K})]$ / kJ mol $^{-1}$
723	96.0	1173	245.7
778	111.1	1213	261.3
823	120.0	1233	270.6
873	138.3	1243	301.7
913	152.6	1245	311.4
918	151.8	1253	340.4
923	176.9	1258	361.5
923	175.0	1263	362.3
973	187.2	1273	360.3
1023	198.3	1283	370.8
1023	199.8	1293	372.0
1073	213.8	1313	376.6
1123	229.1	1318	377.8

form into a cubic one [14]. Processes connected with melting of the substance begin after the temperature of 1233 K is exceeded and the melting is completely finished at 1258 K, however not before 1253 K. The temperature interval of melting is at least 20 K wide, indicating that it is not a simple first order transformation. By analogy with Na_3AlF_6 we may assume that also in the case of Na_3FeF_6 the reason is continuous partial melting of the substance under formation of the solid solution of Na_3FeF_6 enriched with FeF_3, with changeable composition, and NaF melt. Similar creation of the solid solution of Na_3AlF_6 with FeF_2 was also reported [15]. Enthalpy data at 1243, 1245 and 1253 K confirm that different equilibrium systems are produced after annealing of the sample in the melting region at different temperatures. These equilibrium systems with different enthalpies likely contain a solid solution with a different composition. Another explanation of the wide region of melting of Na_3FeF_6 also seems to be plausible. There are three solid phases known for cryolite, unlike the two reported here for Na_3FeF_6. The transition of Solid-ß to γ in cryolite has a small enthalpy value of about 0.4 kJ [16] and occurs relatively close to the melting point. This suggests that the situation with Na_3FeF_6 is similar – and that the extended fusion observed may be a combination of a solid-state transition closely followed by melting. The authors, however, are more inclined to the solid solution explanation due to the fact that drop calorimetry measurements are performed in rigorously equilibrious conditions and all possible kinetic effects, customary by dynamic methods like DSC, are excluded.

The least squares fitting of the measured relative enthalpy data for low-temperature modification α, high-temperature modification β and for the melt, respectively are as follows:

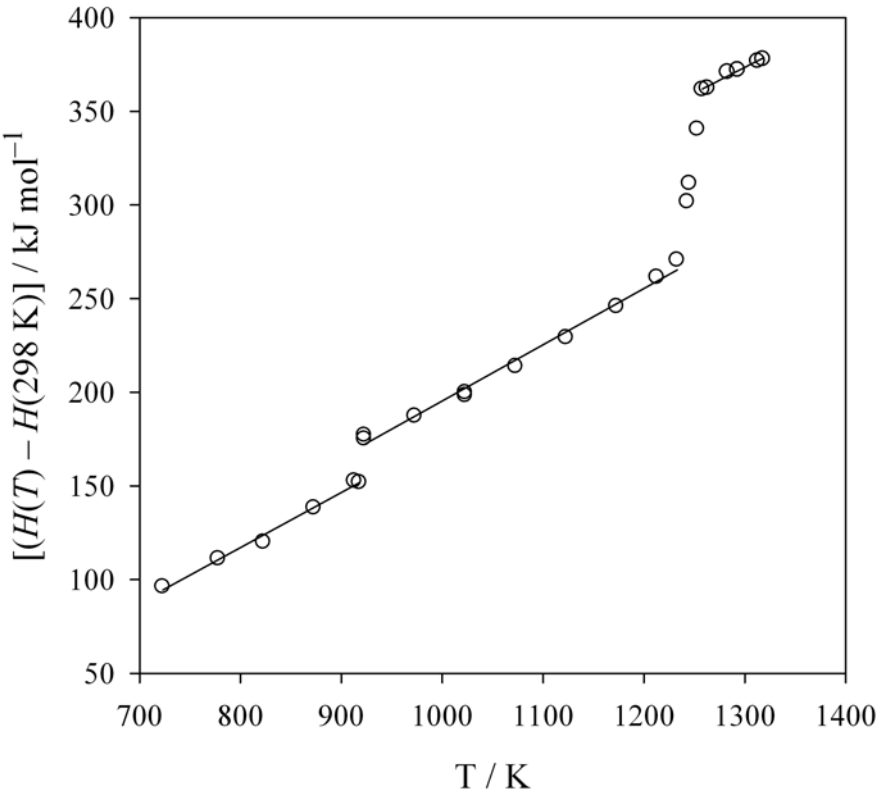

Fig. 1 The enthalpy of Na_3FeF_6.

$$H_{rel}(Na_3FeF_6, cr, \alpha)/(\text{kJ mol}^{-1}) = (-118.3 \pm 11.7) + (0.2943 \pm 0.0139)\ T/K \qquad (1)$$
$$\sigma(H_{rel}) \leq 1.5 \text{ kJ mol}^{-1}$$

$$H_{rel}(Na_3FeF_6, cr, \beta)/(\text{kJ mol}^{-1}) = (-105.0 \pm 11.5) + (0.3004 \pm 0.0107)\ T/K \qquad (2)$$
$$\sigma(H_{rel}) \leq 2.4 \text{ kJ mol}^{-1}$$

$$H_{rel}(Na_3FeF_6, melt)/(\text{kJ mol}^{-1}) = (16.2 \pm 28.6) + (0.2748 \pm 0.0222)\ \text{T/K} \qquad (3)$$
$$\sigma(H_{rel}) \leq 1.3 \text{ kJ mol}^{-1}$$

Linear equations for solid phases have been selected due to relatively narrow temperature ranges and the small number of experimental data points available. The regression coefficients are given in parentheses along with their standard deviations. The standard deviation of the relative enthalpy, $\sigma(H_{rel})$, given with each regression equation, is the maximum value of this quantity for any interpolated and to T_{trans} or T_{fus} extrapolated relative enthalpies in the considered temperature interval. This quantity has been calculated by means of combination of errors considering variances and covariance of the

regression coefficients. Equations (1), (2) and (3) are evaluated from data measured in the temperature intervals 723 – 918 K, 923 – 1233 K and 1258 – 1318 K, respectively.

The following values of the heat capacities, along with their standard deviations, result from the equations (1), (2) and (3): $C_p(Na_3FeF_6, cr, \alpha) = (294 \pm 14)$ J (mol K)$^{-1}$, $C_p(Na_3FeF_6, cr, \beta) = (300 \pm 11)$ J (mol K)$^{-1}$ for the crystalline phases and $C_p(Na_3FeF_6, melt) = (275 \pm 22)$ J (mol K)$^{-1}$ for the melt. These values are valid in temperature intervals of the data used to evaluate the relative enthalpy equations.

As mentioned above, the calorimetric experiments have shown two leaps in the relative enthalpy. The leap in the crystalline phase corresponds to the low-temperature to high-temperature modification transition at the temperature inside the interval from 918 to 923 K. The enthalpy of this transition was determined as the difference between the extrapolated values of the enthalpy of high-temperature modification and that of the low-temperature one to the temperature of transition. Similarly, the enthalpy of fusion was determined as a difference between extrapolated values of the enthalpy of melt and the enthalpy of the high-temperature crystalline phase at the temperature of fusion. The particular enthalpy values along with their standard deviations have been extrapolated by the use of the equations (1) and (2) for the modification transformation and using equations (2) and (3) for the enthalpy of fusion. Following enthalpies and entropies have been determined:

$$\begin{aligned}
\Delta_{trans}H(Na_3FeF_6, 920\ \text{K}) &= (19 \pm 3)\ \text{kJ mol}^{-1} \\
\Delta_{trans}S(Na_3FeF_6, 920\ \text{K}) &= (21 \pm 3)\ \text{J (mol K)}^{-1} \\
\Delta_{fus}H(Na_3FeF_6, 1255\ \text{K}) &= (89 \pm 3)\ \text{kJ mol}^{-1} \\
\Delta_{fus}S(Na_3FeF_6, 1255\ \text{K}) &= (71 \pm 2)\ \text{J (mol K)}^{-1}
\end{aligned}$$

4 Conclusions

The calorimetric experiments in this work allowed for the evaluation of temperature dependences of the enthalpy of both crystalline modifications of Na_3FeF_6 and of the Na_3FeF_6 melt. These data allowed for the determination of the heat capacity of the studied phases, enthalpy, and entropy of modification transition and enthalpy and entropy of fusion of this substance.

The modification transition proceeds in the narrow temperature interval and has signs of the first order transition. Conversely, the temperature interval of melting is at least 20 K wide, indicating that it is not a simple first order conversion. By analogy with Na_3AlF_6 we may assume that the reason is a continuous partial melting of the substance under formation of the solid solution of Na_3FeF_6 with FeF_3, and NaF melt. The obtained data show that conversion proceeds through continuous series of temperature dependent equilibrium states, associated probably with changing of the composition of solid solution.

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