Thermochimica Acta, 191 (1991) 57–61
Elsevier Science Publishers B.V., Amsterdam

Determination of the enthalpy of fusion of Na_3FSO_4

K. Adamkovičová [a], P. Fellner [b], L. Kosa [a], P. Lazor [a], I. Nerád [a]
and I. Proks [a]

[a] *Institute of Inorganic Chemistry, Slovak Academy of Sciences, 842 36 Bratislava (Czechoslovakia)*
[b] *Department of Inorganic Technology, Slovak Technical University, 812 37 Bratislava (Czechoslovakia)*

(Received 20 March 1991)

Abstract

The enthalpy of melting of Na_3FSO_4 at a temperature of 1060 K was measured by a high-temperature calorimeter, the SETARAM HTC 1800 K. It was found that $\Delta H_{fus}(Na_3FSO_4) = 69$ kJ mol$^{-1} \pm 4$ kJ mol^{-1}. The given error is calculated at the level of confidence $(1 - \alpha) = 0.95$.

INTRODUCTION

Sodium sulphate is often present in different amounts in cryolite-based electrolytes used for electrowinning of aluminium. The behaviour of sulphates in the electrolyte is not well understood [1]. From the phase diagrams of alkali fluoride–sulphate systems it has been found [2] that all of them except lithium-containing systems show the presence of an equimolar compound $MF \cdot M_2SO_4$ (M being the alkali metal).

The thermodynamic properties of molten mixtures of the type $MF–M_2SO_4$ have been studied by Kleppa and Julsrud [3]. These authors published enthalpies of mixing and partial thermodynamic data based on calorimetric and cryoscopic measurements. They found that partial entropies were significantly larger than those calculated from the Temkin model. They suggested that these excess entropies may be due either to the charge asymmetry or to the large difference in size between the small F^- and the large SO_4^{2-} anions.

Koštenská and Maliňovský [4] analysed the cryoscopic data for the system $Na_3FSO_4–NaCl$. They came to the conclusion that only about 70% of Na_3FSO_4 thermally dissociates under melting. From the cryometric data they estimated the enthalpy of fusion of Na_3FSO_4 to be 62.3 kJ mol^{-1}.

In this paper we will present the results of calorimetric measurement of the enthalpy of fusion of Na_3FSO_4. It is expected that this will contribute to a deeper understanding of the interaction between fluoride and sulphate ions in molten mixtures.

EXPERIMENTS

Samples of Na_3FSO_4 were prepared by melting equimolar amounts of NaF and Na_2SO_4 in a platinum crucible. All chemicals were of “pro analysis” grade (Merck).

The heat of solid–liquid phase transition was measured by a high-temperature calorimeter, the SETARAM HTC 1800 K. This calorimeter can work in two modes, namely as a reverse drop calorimeter (the sample at ambient temperature is placed in the calorimeter heated to the required temperature) or as a DSC instrument. In this study the latter mode was used. The principle of both methods consists in measurement of the temperature difference between two crucibles. The crucibles are placed in a homogeneous temperature field within a vertical furnace. The upper crucible contains the investigated sample and the lower one is empty (or filled with an inert material). The crucibles are made of sintered alumina (height 30 mm, inner diameter 9.4 mm) with a replaceable lining of PtRh 10. The temperature difference between the middle parts of the crucibles is measured by a set of 18 thermocouples connected in series. The heat flux between the crucibles is a function of the temperature difference between them. The control unit assures a constant rate of change of temperature, or else it keeps the temperature constant. In this work a rate of change of temperature of 2°C min^{-1} was used. Analogue signals of the thermoelectric voltage of the thermocouples were digitized and treated by a computer connected on-line with the calorimetric unit.

Samples of Na_3FSO_4 (308.65 mg) and of NaCl (88.61 mg), respectively, were sealed in cylindrical PtRh-10 foil in order to prevent evaporation of the samples. Sodium chloride was used as a reference substance for calibration.

RESULTS AND DISCUSSION

The signal from the thermocouples was treated by the modified procedure proposed by Guttman and Flynn [5]. This method is based on a non-isothermal Hess law, and it can be used for determination of reaction enthalpies at an arbitrary temperature chosen from the investigated temperature range. Determination of the enthalpy of fusion by this method is based on three assumptions, as follows.

1. Heat transfer into or from the crucible containing the investigated sample is proportional to the temperature difference ΔT_i between the two crucibles. Thus the thermal energy flowing to the crucible during the time interval Δt_i equals $\lambda \Delta T_i \Delta t_i$ (λ is the formal coefficient of heat transfer between the crucibles). In the time interval $t = \sum_i \Delta t_i$ the total transferred heat equals

$$Q = \lambda \sum_i \Delta T_i \Delta t_i \tag{1}$$

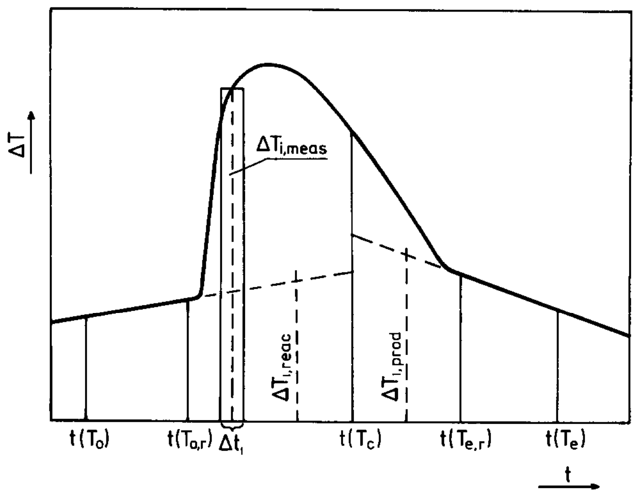

Fig. 1. Schematic plot of the time dependence of the temperature difference between the crucibles in the calorimeter: $t(T_0)$ = beginning of measurement; $t(T_{0,r})$ = time corresponding to the beginning of the temperature of transition; $t(T_{e,r})$ = time corresponding to the end of transition; $t(T_e)$ = end of measurement.

For Δt_i constant, it holds that

$$Q = \lambda \Delta t \sum_i \Delta T_i \tag{2}$$

In this work Δt was 2 s or 4 s and the total time of measurement was about 2000 s.

2. From the non-isothermal Hess law it follows that the thermal energy passing during the measurement into the crucible with the investigated sample consists of three apparent heats (see Fig. 1): (a) apparent heat corresponding to heating of the reactant from an initial temperature T_0 to the chosen temperature T_c, (b) apparent heat of the phase transition (melting or crystallization) occurring at the temperature T_c, (c) apparent heat needed for heating the product of transformation to the final temperature T_e.

As can be seen from Fig. 1, it holds that

$$Q_{\text{trans}}(T_c) = \lambda_{\text{trans}} \Delta t \left(\sum_{T_0}^{T_e} \Delta T_{i,\text{meas}} - \sum_{T_0}^{T_c} \Delta T_{i,\text{reac}} - \sum_{T_c}^{T_e} \Delta T_{i,\text{prod}} \right) \tag{3}$$

In this equation, the following abbreviations are used: trans = transition, meas = measured, reac = reactant, prod = product. The temperature T_c can be chosen arbitrarily in any part of the peak on the ΔT–t curve. However, it is convenient to place this temperature within the beginning or the end of the peak. These temperatures are denoted as $T_{0,r}$ and $T_{e,r}$. The choice of T_0, T_e and T_c is influenced by the time dependence of ΔT_i prior to the beginning and/or after the ending of the phase transition. No correction of the values of $Q_{\mathrm{trans}}/\lambda_{\mathrm{trans}}$ taking into account the difference between T_c and the experimental value of T_{fus} was necessary because the difference between the heat capacities of the solid and liquid phases, which is used in the Kirchhoff equation, gives a lower contribution than the error of the method used. The values of $C_p(\mathrm{NaCl})$ were taken from [6], and the values of $C_p(\mathrm{Na_3FSO_4})$ were estimated using the Neumann–Kopp rule. The values of C_p for NaF and $\mathrm{Na_2SO_4}$ were taken from [6].

3. The heat of fusion of $\mathrm{Na_3FSO_4}$ was calculated from the three experimental values of $Q_{\mathrm{fus}}/\lambda_{\mathrm{fus}}$ and the three values of $Q_{\mathrm{cryst}}/\lambda_{\mathrm{cryst}}$ both for $\mathrm{Na_3FSO_4}$ and for NaCl. The corresponding arithmetic means are denoted by the index ϕ. Assuming that, for the investigated salt and the reference NaCl, the coefficients of heat transition λ_{fus} and λ_{cryst} are the same, the ratio can be written

$$\frac{\left(\dfrac{Q_{\mathrm{trans}}(\mathrm{Na_3FSO_4})}{\lambda_{\mathrm{trans}}}\right)_{\phi}\dfrac{1}{m(\mathrm{Na_3FSO_4})}}{\left(\dfrac{Q_{\mathrm{trans}}(\mathrm{calib})}{\lambda_{\mathrm{trans}}}\right)_{\phi}\dfrac{1}{m(\mathrm{calib})}} = \kappa_{\mathrm{trans}} = \frac{\Delta h_{\mathrm{trans}}(\mathrm{Na_3FSO_4})}{\Delta h_{\mathrm{trans}}(\mathrm{calib})} \tag{4}$$

In eqn. (4), m denotes the mass of the samples. The assumption (3) is fulfilled with good approximation when the transformation temperature of the reference substance is near to the temperature of transition of the investigated substance. Sodium chloride fulfils well this requirement because $T_{\mathrm{fus}}(\mathrm{NaCl}) - T_{\mathrm{fus}}(\mathrm{Na_3FSO_4}) \approx 13$ K; $\Delta h_{\mathrm{fus}}(\mathrm{NaCl}) = 482$ J g^{-1} [6].

The experimentally determined values of $Q_{\mathrm{fus}}/\lambda_{\mathrm{fus}}$ and $Q_{\mathrm{cryst}}/\lambda_{\mathrm{cryst}}$ and the arithmetic mean of these quantities are presented in Table 1. Errors in the arithmetic means were calculated using the Student distribution at the level of reliability of $(1-\alpha) = 0.95$. It follows that

$$\kappa_{\mathrm{fus}} = 0.757 \pm 0.057;\ \kappa_{\mathrm{cryst}} = 0.796 \pm 0.041 \tag{5}$$

The arithmetic mean of these values equals

$$\kappa_{\phi} = 0.777 \pm 0.049 \tag{6}$$

TABLE 1

Experimental data $Q_{\mathrm{fus}}/\lambda_{\mathrm{fus}}$, $Q_{\mathrm{cryst}}/\lambda_{\mathrm{cryst}}$ and the values of $(Q_{\mathrm{fus}}/\lambda_{\mathrm{fus}})_{\phi}$, $(Q_{\mathrm{cryst}}/\lambda_{\mathrm{cryst}})_{\phi}$ for $\mathrm{Na_3FSO_4}$ and NaCl

Sample	$Q_{\mathrm{fus}}/\lambda_{\mathrm{fus}}$ (K s)			$(Q_{\mathrm{fus}}/\lambda_{\mathrm{fus}})_{\phi}$ (K s)	$Q_{\mathrm{cryst}}/\lambda_{\mathrm{cryst}}$ (K s)			$(Q_{\mathrm{cryst}}/\lambda_{\mathrm{cryst}})_{\phi}$ (K s)
$\mathrm{Na_3FSO_4}$	586	607	609	601 ± 32	665	679	660	668 ± 24
NaCl	228	223	232	228 ± 12	242	243	237	241 ± 9

Then, for the specific enthalpy of fusion of Na_3FSO_4, we obtain

$$\Delta h_{fus}(Na_3FSO_4) = \kappa_\phi \Delta h_{fus}(NaCl) = 375\ J\ g^{-1} \pm 24\ J\ g^{-1} \tag{7}$$

The error in κ and thus in $\Delta h_{fus}(Na_3FSO_4)$ was determined using the Gauss law of propogation of errors. The molar enthalpy and entropy of fusion of Na_3FSO_4 at the temperature of melting $T_{fus} = 1060$ K were found to be

$$\Delta H_{fus}(Na_3FSO_4) = 69 \pm 4\ kJ\ mol^{-1} \tag{8}$$

$$\Delta S_{fus}(Na_3FSO_4) = 65 \pm 4\ J\ mol^{-1}\ K^{-1} \tag{9}$$

It can be seen that the heat of fusion determined by calorimetry is higher by 6.7 kJ mol^{-1} than the cryometric value.

REFERENCES

1 K. Grjotheim, C. Krohn, M. Malinovksý, K. Matiašovský and J. Thonstad, Aluminium Electrolysis, Aluminium-Verlag, Düsseldorf, 2nd edn., 1982, pp. 378–379.
2 O. Schmitz-Dumont and I. Heckmann, Z. Anorg. Chem., 260 (1949) 49.
3 O.J. Kleppa and S. Julsrud, Acta Chem. Scand., Ser. A, 34 (1980) 655.
4 I. Koštenská and M. Malinovský, Chem. Zvesti, 36 (1982) 151.
5 C.M. Guttman and J.H. Flynn, Anal. Chem., 45 (2) (1973) 408.
6 I. Barin and O. Knacke, Thermochemical Properties of Inorganic Substances, Springer-Verlag, Berlin, Verlag Stahleisen GmbH, Düsseldorf, 1973, pp. 516, 519, 532.