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Determination of enthalpy of fusion of K_3FSO_4

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Abstract

The enthalpy of melting of K_3FSO_4 at 1148 K has been determined using a high-temperature calorimeter, the Setaram HTC 1800 K. $\Delta_{fus}H_m(K_3FSO_4)$ is found to equal 86 ± 3 kJ mol^{-1}. The given error is calculated at the level of reliability $(1 - \alpha) = 0.95$.

INTRODUCTION

Knowledge of thermodynamic properties of charge-unsymmetrical anion mixtures of the type $MF–M_2SO_4$ can increase our understanding of fused salts. In the system $NaF–Na_2SO_4$ and $KF–K_2SO_4$ congruently melting compounds of the type M_3FSO_4 (M = Na, K) are formed [1]. The enthalpy of fusion of Na_3FSO_4 has been published [2]. In this paper we will present the results of the calorimetric determination of the enthalpy of fusion of K_3FSO_4.

EXPERIMENTAL

Samples of K_3FSO_4 were prepared by melting equimolar amounts of KF and K_2SO_4 in a platinum crucible. All chemicals were pro analysis grade (Merck). KF was dried in a vacuum furnace for 24 h in the presence of P_2O_5 and then at gradually increasing temperature up to 120°C for another 10 h.

The enthalpy of fusion of K_3FSO_4 was determined by a high-temperature calorimeter, the Setaram HTC 1800 K working in the DSC

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mode. A detailed description of the experimental procedure can be found elsewhere [2].

In this work a rate of change of temperature of 1 K min^{-1} was used. Sodium sulphate was used as a reference substance for calibration. Samples of K_3FSO_4 (233.54 mg) and of Na_2SO_4 (233.72 mg), respectively, were sealed in platinum crucibles. The crucible containing the investigated or reference substance was placed in the upper crucible of the calorimeter. The lower crucible of the calorimeter was filled with small pieces of sintered alumina (corundum) (183.37 mg). The heat flux between crucibles is proportional to the difference of temperature between them.

RESULTS AND DISCUSSION

The electrical signal from thermocouples corresponding to the temperature difference between the two crucibles was treated by the modified procedure proposed by Guttman and Flynn [3]. This procedure is based on a non-isothermal Hess law. Assumptions upon which this method of treatment of data is based have previously been discussed in detail [2]. Correction of the values of Q_{fus}/λ_{fus} and $Q_{cryst}/\lambda_{cryst}$ with respect to the equilibrium temperatures of fusion was not carried out because the difference between the heat capacities of the solid and liquid phases (both K_3FSO_4 and Na_2SO_4) gives a lower contribution than the error of the method used. The values of molar heat capacities for solid and liquid K_3FSO_4 were estimated using the Neumann–Kopp rule. (In the above discussion Q_{fus} and Q_{cryst} are heat effects at melting and at crystallization of sample and λ_{fus} and λ_{cryst} are the corresponding formal coefficients of heat transfer between the crucibles.)

As the temperatures of phase transition of K_3FSO_4 and Na_2SO_4 are near to each other (1148 K [1] and 1157 K [4], respectively) the assumption that λ_{fus} and λ_{cryst}, respectively, have the same values for both salts is fulfilled. It follows that the enthalpy of phase transition of K_3FSO_4 is related to the enthalpy of phase transition of Na_2SO_4 by the relationship

$$\frac{\left(\frac{Q_{trans}(K_3FSO_4)}{\lambda_{trans}}\right)_{\Phi}\frac{1}{m(K_3FSO_4)}}{\left(\frac{Q_{trans}(Na_2SO_4)}{\lambda_{trans}}\right)_{\Phi}\frac{1}{m(Na_2SO_4)}} = K_{trans} = \frac{\Delta_{trans}h(K_3FSO_4)}{\Delta_{trans}h(Na_2SO_4)} \quad (1)$$

In eqn. (1) the abbreviations and symbols have the following meaning: trans denotes melting or crystallization, Φ is the arithmetic mean, and m is the mass of sample.

Experimentally obtained values of Q_{fus}/λ_{fus} and $Q_{cryst}/\lambda_{cryst}$ as well as the values of their arithmetic means and errors in their determination are presented in Tables 1 and 2.

TABLE 1

Experimental values of Q_{fus}/λ_{fus} and $(Q_{fus}/\lambda_{fus})_{\Phi}$ for K_3FSO_4 and Na_2SO_4

Sample	Q_{fus}/λ_{fus} (K s)	$(Q_{fus}/\lambda_{fus})_{\Phi}$ (K s)
K_3FSO_4	353, 350, 357, 351, 368	356 ± 9
Na_2SO_4	159, 153, 157, 156, 153, 154, 150	155 ± 3

TABLE 2

Experimental values of $Q_{cryst}/\lambda_{cryst}$ and $(Q_{cryst}/\lambda_{cryst})_{\Phi}$ for K_3FSO_4 and Na_2SO_4

Sample	$Q_{cryst}/\lambda_{cryst}$ (K s)	$(Q_{cryst}/\lambda_{cryst})_{\Phi}$ (K s)
K_3FSO_4	392, 380, 384, 386, 389, 387	386 ± 4
Na_2SO_4	170, 176, 176, 166, 169, 165, 167	170 ± 4

Errors in the arithmetic means of these quantities were calculated using the Student distribution at the level of reliability of $(1 - \alpha) = 0.95$.

Introducing the experimental data presented in Tables 1 and 2 and the mass of samples in eqn. (1) we obtain

$$\kappa_{fus} = 2.299 \pm 0.074 \qquad \kappa_{cryst} = 2.272 \pm 0.061 \tag{2}$$

The arithmetic mean of these values equals

$$\kappa_{\Phi} = 2.285 \pm 0.067 \tag{3}$$

Then, for the specific enthalpy of fusion of K_3FSO_4, we obtain

$$\Delta_{fus}h(K_3FSO_4) = \kappa_{\Phi}\Delta_{fus}h(Na_2SO_4) = 370 \pm 11 \text{ kJ kg}^{-1} \tag{4}$$

(The value of $\Delta_{fus}h(Na_2SO_4) = 162$ kJ kg^{-1} was taken from ref. 4.) The error in κ and thus in $\Delta_{fus}h(K_3FSO_4)$ was determined using the Gauss law of propagation of errors.

The molar enthalpy and entropy of fusion of K_3FSO_4 at the temperature of melting $T_{fus} = 1148$ K [1] were found to be

$$\Delta_{fus}H_m(K_3FSO_4) = 86 \pm 3 \text{ kJ mol}^{-1} \tag{5}$$

and

$$\Delta_{fus}S_m(K_3FSO_4) = 75 \pm 3 \text{ J mol}^{-1}\text{ K}^{-1} \tag{6}$$

REFERENCES

1 O.J. Kleppa and S. Julsrud, Acta Chem. Scand. Ser. A, 34 (1980) 655.
2 K. Adamkovičová, P. Fellner, L. Kosa, P. Lazor, I. Nerád and I. Proks, Thermochimica Acta, 191 (1991) 57.
3 C.M. Guttman and J.H. Flynn, Anal. Chem., 45(2) (1973) 408.
4 I. Barin and O. Knacke, Thermochemical Properties of Inorganic Substances, Springer-Verlag, Berlin, 1973, pp. 362, 379, 516, 532.