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Determination of the enthalpy of fusion of K_2TiF_6

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Abstract

The enthalpy of fusion of K_2TiF_6 at the melting temperature (1172 K) was measured by a high-temperature calorimeter in the DSC mode with a scanning rate of 1 K min^{-1}. The measured value was $\Delta_{\mathrm{fus}}H_{\mathrm{m}}(K_2TiF_6) = (21 \pm 1)\,\mathrm{kJ\,mol^{-1}}$.

Keywords: Enthalpy of fusion; High-temperature calorimeter; Potassium hexafluorotitanate

1. Introduction

Melts of the system K_2TiF_6–KF–KCl are prospective electrolytes for the electrodeposition of titanium. Such melts with the additional component KBF_4 are also used as electrolytes for the synthesis of TiB_2, which is considered to be the most promising inert cathode material for the electrowinning of aluminium [1,2].

The mechanism of both these processes depends on the structure of the melts and thus also on the degree of thermal dissociation of the anions of the binary compounds K_3TiF_7 and K_3TiF_6Cl, which arise in the given system. The enthalpies of fusion of K_2TiF_6, K_3TiF_7 and K_3TiF_6Cl are also the quantities which enter into the calculation of the degree of thermal dissociation of K_3TiF_7 and K_3TiF_6Cl on the basis of the thermodynamic analysis of the phase equilibrium. These quantities have not yet been measured calorimetrically. The aim of this work is the calorimetric determination of the heat of fusion of K_2TiF_6.

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2. Experimental

The enthalpy of fusion of K_2TiF_6 at its melting temperature of 1172 K was determined with a high-temperature calorimeter, the SETARAM HTC 1800 K, working in the DSC mode at a scanning rate of $1\,K\,min^{-1}$. The sample (300.45 mg) of analytical grade K_2TiF_6 (Merck) was sealed in a platinum crucible and placed in the upper alumina crucible of the calorimetric cell. The lower alumina crucible of this cell contained a platinum crucible with small pieces of Al_2O_3 as reference substance. Data of the sample temperature and the temperature difference between the crucibles were recorded. The correctness and accuracy of measurements of temperature in the region under consideration have been checked with regard to the crystallization temperature of the melt of the calibration salt Na_2SO_4 [3], which was chosen because its crystallization temperature was close to that of the compound under study. The differences found between the checked and the calibrated temperature values for Na_2SO_4 were within an interval of $\pm 3°C$ and did not influence the error in the determination of enthalpy of fusion by using the method described in [4].

3. Results and discussion

The data measured with the calorimeter were treated by the modified procedure proposed by Guttman and Flynn [5], which is based on a non-isothermal Hess law. Assumptions upon which this method of data treatment is based have previously been discussed in detail [4]. The quantities Q_{fus}/λ_{fus} and $Q_{cryst}/\lambda_{cryst}$ for the fusion and crystallization of K_2TiF_6, respectively, were obtained from the evaluation of the measured data; Q_{fus} and Q_{cryst} are the heats of fusion and crystallization of the sample, respectively, and λ_{fus} and λ_{cryst} are constants proportional to the heat transfer coefficient. The arithmetic means of the measured values at melting and at crystallization of K_2TiF_6 $(Q_{fus}/\lambda_{fus})_\Phi$ and $(Q_{cryst}/\lambda_{cryst})_\Phi$ are given in relation to the respective values for the calibration substance Na_2SO_4, which were measured in [3]. As the temperatures of fusion of K_2TiF_6 (1172 K [1]) and Na_2SO_4 (1157 K [6]) are close to one another, the assumption that λ_{fus} and λ_{cryst} are approximately the same is justified. The value of the specific enthalpy $\Delta_{trans}h$ of fusion or crystallization of K_2TiF_6 can then be calculated on the basis of the known value of this quantity for Na_2SO_4 according to the relationship [4]

$$\frac{\left[\dfrac{Q_{trans}(K_2TiF_6)}{\lambda_{trans}}\right]_\Phi \dfrac{1}{m(K_2TiF_6)}}{\left[\dfrac{Q_{trans}(Na_2SO_4)}{\lambda_{trans}}\right]_\Phi \dfrac{1}{m(Na_2SO_4)}} = K_{trans} = \frac{\Delta_{trans}h(K_2TiF_6)}{\Delta_{trans}h(Na_2SO_4)} \qquad (1)$$

In this relationship, 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 $Q_{cryst}/\lambda_{cryst}$ for K_2TiF_6, the arithmetic means of these quantities for K_2TiF_6 and Na_2SO_4 [3] and the values of the errors in their determination are given in Tables 1 and 2. The errors in the arithmetic means of these quantities were obtained under consideration of the Student distribution at the level of reliability $(1-\alpha)=0.95$.

Introducing the values of $(Q_{\mathrm{fus}}/\lambda_{\mathrm{fus}})_{\Phi}$ and $(Q_{\mathrm{cryst}}/\lambda_{\mathrm{cryst}})_{\Phi}$ for K_2TiF_6 and Na_2SO_4 and the masses of the samples in Eq. (1), one obtains

$$\kappa_{\mathrm{fus}}(K_2TiF_6)=(0.542\pm0.032);\quad \kappa_{\mathrm{cryst}}(K_2TiF_6)=(0.558\pm0.026) \tag{2}$$

The arithmetic mean of these values equals

$$\kappa_{\Phi}(K_2TiF_6)=(0.550\pm0.029) \tag{3}$$

On the basis of this value and the value of the specific heat of fusion of Na_2SO_4 $\Delta_{\mathrm{fus}}h(Na_2SO_4)=162\,\mathrm{kJ\,kg^{-1}}$ [6], the specific heat of fusion of K_2TiF_6 was determined

$$\Delta_{\mathrm{fus}}h(K_2TiF_6)=(89\pm5)\,\mathrm{kJ\,kg^{-1}} \tag{4}$$

The error in κ and in $\Delta_{\mathrm{fus}}h(K_2TiF_6)$ was determined using the Gauss's law of propagation of errors.

The molar enthalpy and molar entropy of fusion of K_2TiF_6 at the melting temperature of 1172 K are respectively

$$\Delta_{\mathrm{fus}}H_{\mathrm{m}}(K_2TiF_6)=(21\pm1)\,\mathrm{kJ\,mol^{-1}} \tag{5}$$

$$\Delta_{\mathrm{fus}}S_{\mathrm{m}}(K_2TiF_6)=(18\pm1)\,\mathrm{J\,mol^{-1}\,K^{-1}} \tag{6}$$

In ref. [1] the value of enthalpy of fusion of K_2TiF_6 $\Delta_{\mathrm{fus}}H_m(K_2TiF_6)=34.4\,\mathrm{kJ\,mol^{-1}}$ is given. This value was obtained on the basis of an analysis of the liquidus curve of K_2TiF_6 in the K_2TiF_6–LiF system considering the Temkin model of ideal solutions.

Table 1
Experimental data $Q_{\mathrm{fus}}/\lambda_{\mathrm{fus}}$ for K_2TiF_6 and the values of $(Q_{\mathrm{fus}}/\lambda_{\mathrm{fus}})_{\Phi}$ for K_2TiF_6 and Na_2SO_4

Sample	$(Q_{\mathrm{fus}}/\lambda_{\mathrm{fus}})$/(K s)					$(Q_{\mathrm{fus}}/\lambda_{\mathrm{fus}})_{\Phi}$/(K s)
K_2TiF_6	106	105	113	113	103	108 ± 6
Na_2SO_4						155 ± 3 [3]

Table 2
Experimental data $Q_{\mathrm{cryst}}/\lambda_{\mathrm{cryst}}$ for K_2TiF_6 and the values of $(Q_{\mathrm{cryst}}/\lambda_{\mathrm{cryst}})_{\Phi}$ for K_2TiF_6 and Na_2SO_4

Sample	$-(Q_{\mathrm{cryst}}/\lambda_{\mathrm{cryst}})$/(K s)					$-(Q_{\mathrm{cryst}}/\lambda_{\mathrm{cryst}})_{\Phi}$/(K s)
K_2TiF_6	126	119	122	127	118	122 ± 5
Na_2SO_4						170 ± 4 [3]

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