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Determination of the enthalpy of fusion of K_3TiF_7

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Abstract

The enthalpy of fusion of K_3TiF_7 at the melting temperature (1048 K) has been determined by treatment of the values measured using a high-temperature calorimeter in the DSC mode with a scanning rate of 1 K min^{-1}. The value obtained was $\Delta_{fus}H_m(K_3TiF_7) = 57 \pm 2$ kJ mol^{-1}.

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

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1. Introduction

The melts of the K_2TiF_6–KF–KCl system are possible electrolytes for the electrodeposition of titanium [1]. In this system, the binary compounds K_3TiF_7 and K_3TiF_6Cl, with dystectic melting points, are formed. A knowledge of the enthalpies of fusion of K_3TiF_7 and K_3TiF_6Cl increases the reliability of calculations of their dissociation degree and dissociation enthalpy, and makes it possible to calculate the equilibrium activity of the components of the K_2TiF_6–KF and K_2TiF_6–KCl systems. The values of the enthalpy of fusion of K_3TiF_7 and K_3TiF_6Cl have not yet been determined experimentally. The aim of this work is the calorimetric determination of the heat of fusion of K_3TiF_7.

2. Experimental

The sample of K_3TiF_7 was prepared by melting equimolar amounts of K_2TiF_6 and KF, (analar grade (Merck)) in a platinum crucible. The enthalpy of the solid–liquid phase transition was determined using a high-temperature calorimeter, the Setaram

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HTC 1800 K, working in the DSC mode at a scanning rate of 1 K min^{-1}. A detailed description of the experimental procedure can be found elsewhere [2].

The sample (300.44 mg) of K_3TiF_7 was sealed in a platinum crucible and put in the upper sintered alumina crucible of the calorimetric cell. The platinum crucible containing the reference standard (small pieces of sintered alumina) was placed in the lower sintered alumina crucible of the calorimetric cell. Both the sample temperature and the temperature difference between the upper and lower crucibles, which is proportional to the heat flow, were recorded during the measurements. The accuracy of the absolute temperature measurements was checked with respect to the crystallization temperature of KCl [3]; this was chosen because its crystallization temperature is close to that of K_3TiF_7. The differences between the checked and calibrated temperature values for KCl were 1°C and did not influence the error in the determination of the enthalpy of fusion by the method described in Ref. [2].

3. Results and discussion

The assumptions upon which the experimental data processing are based have been discussed in Ref. [2]. As a result of the evaluation of the measured data, the quantities Q_{fus}/λ_{fus} and $Q_{cryst}/\lambda_{cryst}$, respectively, were obtained. Q_{fus} and Q_{crysy} are the heat effects at melting and at crystallization of the sample, respectively, and λ_{fus} and λ_{cryst} are constants proportional to the heat-transfer coefficient. The arithmetic means $\langle Q_{fus}/\lambda_{fus}\rangle$ and $\langle Q_{cryst}/\lambda_{cryst}\rangle$ at melting and at crystallization of K_3TiF_7 are given in relation to the respective values of the calibration material, KCl, reported in Ref. [3]. Because the temperatures of fusion of K_3TiF_7 and KCl are close to each other (1048 K [1] and 1044 K [4], respectively), the assumption that λ_{fus} and λ_{cryst} are approximately the same for both salts is justified. It follows that the specific enthalpy of fusion or the enthalpy of crystallization of K_3TiF_7 ($\Delta_{trs}h$) can be calculated on the basis of the known value of this quantity for KCl, according to the relationship [2]

$$\frac{\left\langle \frac{Q_{trs}(K_3TiF_7)}{\lambda_{trs}} \right\rangle \frac{1}{m(K_3TiF_7)}}{\left\langle \frac{Q_{trs}(KCl)}{\lambda_{trs}} \right\rangle \frac{1}{m(KCl)}} = \kappa_{trs} = \frac{\Delta_{trs}h(K_3TiF_7)}{\Delta_{trs}h(KCl)} \qquad (1)$$

where trs denotes melting or crystallization, $\langle\ \rangle$ 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_3TiF_7, the values of the arithmetic means of these quantities for K_3TiF_7 and KCl [3] and the values of the errors in their determination are presented in Tables 1 and 2 . The errors in the arithmetic means of these quantities were calculated using the Student distribution at the level of reliability $(1-\alpha)=0.95$.

Introducing the values of $\langle Q_{fus}/\lambda_{fus}\rangle$, and $\langle Q_{cryst}/\lambda_{cryst}\rangle$ for K_3TiF_7 and KCl and the masses of the samples into Eq. (1), we obtain

$$\kappa_{fus}=0.528\pm0.010; \quad \kappa_{cryst}=0.552\pm0.016 \qquad (2)$$

Table 1
Experimental data Q_{fus}/λ_{fus} for K_3TiF_7 and the values of $\langle Q_{fus}/\lambda_{fus}\rangle$ for K_3TiF_7 and KCl

Sample	$(Q_{fus}/\lambda_{fus})/(K\ s)$					$\langle Q_{fus}/\lambda_{fus}\rangle/(K\ s)$
K_3TiF_7	320	323	324	317	324	322 ± 4
KCl						509 ± 7 [3]

Table 2
Experimental data $Q_{cryst}/\lambda_{cryst}$ for K_3TiF_7 and the values of $\langle Q_{cryst}/\lambda_{cryst}\rangle$ for K_3TiF_7 and KCl

Sample	$-(Q_{cryst}/\lambda_{cryst})/(K\ s)$					$-\langle Q_{cryst}/\lambda_{cryst}\rangle/(K\ s)$
K_3TiF_7	342	357	353	356	346	351 ± 8
KCl						531 ± 9 [3]

Their arithmetic mean is

$$\langle\kappa\rangle = 0.540 \pm 0.013 \qquad (3)$$

Then, for the specific enthalpy of fusion of K_3TiF_7, one obtains

$$\Delta_{fus}h(K_3TiF_7) = \langle\kappa\rangle\Delta_{fus}h(KCl) = 191 \pm 5\,kJ\,kg^{-1} \qquad (4)$$

The value of $\Delta_{fus}h(KCl) = 353\,kJ\,kg^{-1}$ was taken from Ref. [4]. The error in κ and in $\Delta_{fus}h(K_3TiF_7)$ was determined using Gauss's law of error propagation.

The molar enthalpy and molar entropy of fusion of K_3TiF_7 at the melting temperature, 1048 K, are respectively

$$\Delta_{fus}H_m(K_3TiF_7) = 57 \pm 2\,kJ\,mol^{-1} \qquad (5)$$

and

$$\Delta_{fus}S_m(K_3TiF_7) = 54 \pm 2\,J\,mol^{-1}\,K^{-1} \qquad (6)$$

The calorimetrically determined value of the enthalpy of fusion of K_3TiF_7 is very close to that of the estimate of this quantity, $\Delta_{fus}\hat{H}_m(K_3TiF_7) = 56\,kJ\,mol^{-1}$ (where ^ indicates an estimate), calculated by Daněk and Matiašovský [1] who calculated the entropy of fusion of K_3TiF_7 as the sum of the entropies of fusion of K_2TiF_6 and KF, neglecting the entropy of mixing in the liquid phase. As the input data, they used the value of the estimate for the enthalpy of fusion of K_2TiF_6, obtained by the cryometric method on the basis of the analysis of the liquidus curve in the K_2TiF_6–LiF system [1].

When calculating $\Delta_{fus}\hat{H}_m(K_3TiF_7)$ according to the procedure given in Ref. [5] by using the calorimetrically determined value of the heat of fusion of K_2TiF_6 ($\Delta_{fus}H_m(K_2TiF_6) = 21\,kJ\,mol^{-1}$ [6]) and considering the entropy of mixing in the liquid phase, we obtain practically the same value as in Ref. [1]. In this calculation, as in Ref. [1], we neglected the differences in the heat capacities of the liquid and solid phases with regard to the small differences between the melting temperatures of KF, K_2TiF_6 and K_3TiF_7. Another simplification was that the entropy of mixing in the liquid phase of K_3TiF_7 composition had been calculated from the relation for the entropy of mixing in the formation of an ideal solution of composition K_3TiF_7 from the melts KF and K_2TiF_6. This assumption is probably correct for AB compounds, the dissociation degree of which in the melt is close to 1, i.e. a high value. In this case the relation for estimation of the heat of fusion of a binary compound [5] will have the form

$$\Delta_{\mathrm{fus}}\hat{H}_{\mathrm{m}}(\mathrm{K_3TiF_7};\,1048\,\mathrm{K}) \approx 1048\,\mathrm{K}\left[\frac{\Delta_{\mathrm{fus}}H_{\mathrm{m}}(\mathrm{KF};\,1127\,\mathrm{K})}{1127\,\mathrm{K}}+\frac{\Delta_{\mathrm{fus}}H_{\mathrm{m}}(\mathrm{K_2TiF_6};\,1172\,\mathrm{K})}{1172\,\mathrm{K}}-2R\ln 0.5\right] \quad (7)$$

Introducing the value of the enthalpy of fusion of KF used in Ref. [1] and the value of the enthalpy of fusion of K_2TiF_6 from Ref. [6] into relation (7), we obtain the following value for the estimate of the heat of fusion of K_3TiF_7

$$\Delta_{\mathrm{fus}}\hat{H}_{\mathrm{m}}(\mathrm{K_3TiF_7};\,1048\,\mathrm{K}) \approx 56.1\,\mathrm{kJ\,mol^{-1}} \quad (8)$$

The differences in the values of the enthalpy of fusion of K_2TiF_6 used in the calculation of $\Delta_{\mathrm{fus}}\hat{H}_{\mathrm{m}}(\mathrm{K_3TiF_7})$ in Ref. [1] and according to the procedure in Ref. [5] were practically compensated for by neglecting the entropy of mixing in the liquid phase in Ref. [1].

The small difference between the measured value of the heat of fusion of K_3TiF_7 and that calculated by using the calorimetrically determined heat of fusion of K_2TiF_6 is another proof for the relatively reliable estimation of the heats of fusion of binary compounds according to the procedures given in Ref. [5]. The estimate of the error in the calculation of the heat of fusion according to Ref. [5] is about ±20%.

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