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Determination of the enthalpy of fusion of K_3TiF_6Cl

K. Adamkovičová *, L. Kosa, I. Nerád, I. Proks

Institute of Inorganic Chemistry, Slovak Academy of Sciences, 842 36 Bratislava, Slovak Republic

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Abstract

The enthalpy of fusion K_3TiF_6Cl at the melting temperature (964 K) has been determined by treatment of the data for K_3TiF_6Cl and calibration substances measured by a high-temperature calorimeter in the DSC mode with a scanning rate of 1 K min^{-1}. The obtained value was $\Delta_{fus}H_m(K_3TiF_6Cl) = (42 \pm 3)$ kJ mol^{-1}.

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

1. Introduction

K_3TiF_6Cl is one of the two binary compounds with dystectic melting points, which arise in the K_2TiF_6–KF–KCl system. The melts of this system are interesting as potential electrolytes for the electrodeposition of titanium and the electrochemical synthesis of titanium diboride which is considered to be the most promising inert cathode material in aluminum electrolysis [1].

Knowledge of the heat of fusion of K_3TiF_6Cl makes calculation of its dissociation degree and dissociation enthalpy, based on thermodynamic analysis of the phase equilibrium of the K_2TiF_6–KCl system, more reliable. As the enthalpy of fusion of K_3TiF_6Cl has not been determined experimentally thus far, the aim of this work is the calorimetric determination of the heat of fusion of K_3TiF_6Cl at its melting temperature ($T_{fus} = 964$ K[1]) in a high-temperature calorimeter (Setaram 1800 K) working in the DSC mode at a scanning rate of 1 K min^{-1}.

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* Corresponding author.

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2. Theoretical

Treatment of the measured data in this method of determination of the enthalpy of fusion is based on the assumptions previously discussed in detail [2]. The quantity $Q_{\text{trans}}/\lambda_{\text{trans}}$ is determined, corresponding to the area of the fusion or crystallization peak on the curve of the time dependence of the temperature difference between the studied and reference substances. (Q_{trans} is the heat effect at melting or crystallization of the pertinent mass of the sample and λ_{trans} is a constant proportional to the heat transfer coefficient).

In Eq. (1), used for determination of the enthalpy of fusion or crystallization [2], the arithmetic mean $\langle Q_{\text{trans}}/\lambda_{\text{trans}} \rangle$ related to mass (m) unit of the studied substance (X) is in relation to the arithmetic mean of this quantity for the calibration substance (calib), and their ratio is equal to the ratio of their specific enthalpies of fusion or crystallization ($\Delta_{\text{trans}} h$)

$$\frac{\left\langle \dfrac{Q_{\text{trans}}(\mathrm{X})}{\lambda_{\text{trans}}} \right\rangle \dfrac{1}{m(\mathrm{X})}}{\left\langle \dfrac{Q_{\text{trans}}(\text{calib})}{\lambda_{\text{trans}}} \right\rangle \dfrac{1}{m(\text{calib})}} = \frac{\Delta_{\text{trans}} h(\mathrm{X})}{\Delta_{\text{trans}} h(\text{calib})} \tag{1}$$

Eq. (1) can be used to determine the heat of fusion only in the case when the temperatures of fusion of both the studied and the calibration substances are close to each other. The quantity $Q_{\text{trans}}/\lambda_{\text{trans}}$ is also a function of the melting temperatures in the case of substances with the same value of ($\Delta_{\text{trans}} h \times m$), because the sensitivity of the calorimetric method $\varepsilon_{\text{trans}}$, expressed by relation (2), is a function of temperature

$$\varepsilon_{\text{trans, exp}} = \frac{\left\langle \dfrac{Q_{\text{trans}}(\text{calib})}{\lambda_{\text{trans}}} \right\rangle \dfrac{1}{m(\text{calib})}}{\Delta_{\text{trans}} h(\text{calib})} \tag{2}$$

In determination of the enthalpy of fusion of a substance for which it is not possible to find a calibration substance with similar melting temperature, as in the case of K_3TiF_6Cl under study, it is necessary to determine the temperature dependence of the sensitivity of the calorimetric method $\varepsilon_{\text{trans, calc}}$ (calibration curve). Using relation (2), the Eq. (1) becomes

$$\Delta_{\text{trans}} h(\mathrm{X}) = \left\langle \frac{Q_{\text{trans}}(\mathrm{X})}{\lambda_{\text{trans}}} \right\rangle \frac{1}{m(\mathrm{X})} \frac{1}{\varepsilon_{\text{trans, calc}}(T_{\text{trans}})} \tag{3}$$

which then allows the determination of the enthalpy of fusion of the studied substance on the basis of the measured $\langle Q_{\text{trans}}(\mathrm{X})/\lambda_{\text{trans}} \rangle$ value and the value of $\varepsilon_{\text{trans, calc}}(T_{\text{trans}})$ calculated from the temperature dependence of $\varepsilon_{\text{trans, calc}}$ at the temperature of transformation of the studied substance.

3. Experimental

To determine the temperature dependence of the sensitivity of the calorimetric method, the following calibration substances were used: KNO_3 (the equilibrium melting temperature given in the literature is 607 K), LiCl (883 K), KCl (1044 K), NaCl (1074 K), Na_2SO_4 (1157 K), and K_2SO_4 (1342 K). All chemicals were of analytical grade.

The studied sample, K_3TiF_6Cl was prepared by melting equimolar amounts of analytical grade (Merck) K_2TiF_6 and KCl in a platinum crucible.

The pertinent calibration substance and the sample of K_3TiF_6Cl ($m = 0.30055$ g), respectively, were 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. During the experiment, the temperature and the temperature difference between the upper and lower crucibles, proportional of the heat flow, were recorded.

The reliability of the temperature measurements in the region under consideration (600–1350 K) was checked with regard to the temperatures of the beginning of the crystallization process of the individual calibration substances, which can be monitored with more accuracy than the temperatures of the beginning of the fusion process. The differences found between the temperatures of the beginning of crystallization of the calibration substances and their equilibrium values given in the literature were within the interval of ± 4K and did not influence of the error in the determination of the enthalpy of fusion using the method described in Ref. [2]. Noticeable undercooling of the melts of calibration substances were not observed at the relatively small scanning rate of 1 K min^{-1}.

4. Results and discussion

On the basis of the measured values of $Q_{trans}/\lambda_{trans}$ for all the calibration substances (about 3–5 values for fusion and crystallization, respectively), the values of $\varepsilon_{fus, exp}$ and $\varepsilon_{cryst, exp}$ have been determined according to relation (2). The temperatures of the fusion and crystallization processes determined for each calibration substance as the arithmetic mean from the average temperatures between the beginning and the end of the peaks, were coordinated to the values of the arithmetic means $\langle \varepsilon_{fus, exp} \rangle$ and $\langle \varepsilon_{cryst, exp} \rangle$, respectively. In this manner, determined "mean temperatures" of fusion of calibration substances were 6–12 K higher than the equilibrium values given in the literature, while those of crystallization were 8–16 K lower than the equilibrium values. The statistical treatment of the $\varepsilon_{fus, exp}$ and $\varepsilon_{cryst, exp}$ values by the weighted least-squares method led to a linear dependence of their arithmetic means on temperature

$$\varepsilon_{trans, calc}/(\mathrm{K\ s\ J^{-1}}) = 14.156 - 7.881 \times 10^{-3} T/\mathrm{K} \tag{4}$$

The values of $\langle \varepsilon_{fus, exp} \rangle$ and $\langle \varepsilon_{cryst, exp} \rangle$ for all calibration substances at the "mean temperatures" of fusion and crystallization, respectively, as well as the curve described by Eq. (4) are in Fig. 1. From this dependence it can be seen that the sensitivity of the calorimetric method decreases with increasing temperature.

The experimentally obtained values of Q_{fus}/λ_{fus} and $Q_{cryst}/\lambda_{cryst}$ for K_3TiF_6Cl, the arithmetic means of these quantities, and the errors of their determination are given in

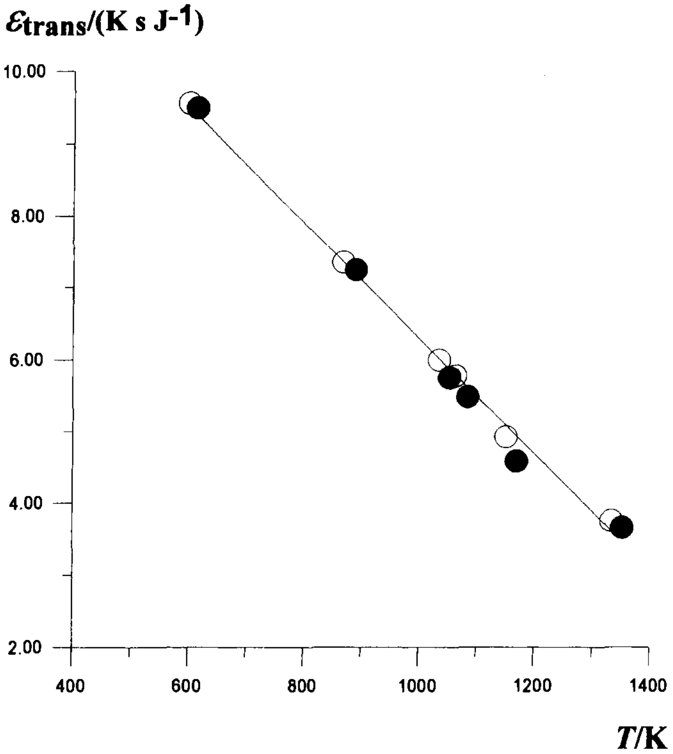

Fig. 1. Temperature dependence of the sensitivity of the calorimetric method $\varepsilon_{trans,\,calc} = f(T)$. The arithmetic means of $\langle \varepsilon_{fus,\,exp} \rangle$ and $\langle \varepsilon_{cryst,\,exp} \rangle$ for calibration substances at their "mean temperatures" of fusion and crystallization are denoted by ● and ○, respectively.

Tables 1 and 2. The errors were obtained by considering the Student distribution at the reliability level $(1 - \alpha) = 0.95$. Tables 1 and 2 also present the values of $\varepsilon_{fus,\,calc}$ and $\varepsilon_{cryst,\,calc}$ calculated for the "mean temperature" of fusion of K_3TiF_6Cl (970 K) and for the "mean temperature" of crystallization of K_3TiF_6Cl (954 K) from Eq. (4), respectively.

By introducing the data from Tables 1 and 2 and the mass of K_3TiF_6Cl into relation (3), the values of the specific enthalpy of the fusion process and the specific enthalpy of the crystallization process of K_3TiF_6Cl were obtained

$$\Delta_{fus}h(K_3TiF_6Cl) = (125 \pm 12)\ J\ g^{-1} \tag{5}$$

$$|\Delta_{cryst}h(K_3TiF_6Cl)| = (140 \pm 10)\ J\ g^{-1} \tag{6}$$

We assume that for the studied substance K_3TiF_6Cl, as for the calibration substances, the change in the transformation enthalpy resulting from Krichhoff's law is lower than the error of the used method. The values from Eqs. (5) and (6) were, therefore, coordinated to the equilibrium temperature of transformation of K_3TiF_6Cl (964 K). The errors of the determination of these quantities were calculated using Gauss's law of

Table 1
Experimental data $Q_{\mathrm{fus}}/\lambda_{\mathrm{fus}}$, and the values of $\langle Q_{\mathrm{fus}}/\lambda_{\mathrm{fus}}\rangle$ for K_3TiF_6Cl and of $\varepsilon_{\mathrm{fus,\,calc}}(970\ \mathrm{K})$

$(Q_{\mathrm{fus}}/\lambda_{\mathrm{fus}})/(\mathrm{K\ s})$				$\langle Q_{\mathrm{fus}}/\lambda_{\mathrm{fus}}\rangle/(\mathrm{K\ s})$	$\varepsilon_{\mathrm{fus,\,calc}}(970\ \mathrm{K})/(\mathrm{K\ s\ J^{-1}})$
223	243	255	253	244 ± 23	6.51 ± 0.03

Table 2
Experimental data $Q_{\mathrm{cryst}}/\lambda_{\mathrm{cryst}}$, and the values of $\langle Q_{\mathrm{cryst}}/\lambda_{\mathrm{cryst}}\rangle$ for K_3TiF_6Cl and of $\varepsilon_{\mathrm{cryst,\,calc}}(954\ \mathrm{K})$

$(Q_{\mathrm{cryst}}/\lambda_{\mathrm{cryst}})/(\mathrm{K\ s})$				$\langle Q_{\mathrm{cryst}}/\lambda_{\mathrm{cryst}}\rangle/(\mathrm{K\ s})$	$\varepsilon_{\mathrm{cryst,\,calc}}(954\ \mathrm{K})/(\mathrm{K\ s\ J^{-1}})$
289	262	278	291	280 ± 21	6.64 ± 0.03

propagation of errors. The arithmetic mean of these values is

$$\Delta_{\mathrm{trans}}h(K_3TiF_6Cl) = (133 \pm 11)\ \mathrm{J\ g^{-1}} \tag{7}$$

The molar enthalpy of fusion of K_3TiF_6Cl at 964 K and the molar entropy of fusion of K_3TiF_6Cl at this temperature are respectively

$$\Delta_{\mathrm{fus}}H_{\mathrm{m}}(K_3TiF_6Cl) = (42 \pm 3)\ \mathrm{kJ\ mol^{-1}} \tag{8}$$

$$\Delta_{\mathrm{fus}}S_{\mathrm{m}}(K_3TiF_6Cl) = (44 \pm 3)\ \mathrm{J\ mol^{-1}\ K^{-1}} \tag{9}$$

The value of the estimate of the enthalpy of fusion of K_3TiF_6Cl, calculated on the basis of a thermodynamic analogy in Ref. [1] was $\Delta_{\mathrm{fus}}\hat{H}_{\mathrm{m}}(K_3TiF_6Cl) = 52.9\ \mathrm{kJ\ mol^{-1}}$ (Λ is the symbol for the estimate). The authors of this work calculated the entropy of fusion of K_3TiF_6Cl as the sum of the entropies of fusion of KCl and K_2TiF_6. As the input data, they used the value of the enthalpy of fusion of KCl taken from the literature and the value of the estimate of the enthalpy of fusion of K_2TiF_6 obtained by the clorymetric method on the basis of analysis of the liquidus curve in the K_2TiF_6–LiF system [1]. The value of the estimate of the heat of fusion of K_2TiF_6 ($\Delta_{\mathrm{fus}}\hat{H}_{\mathrm{m}}(K_2TiF_6) = 34.4$ kJ $\mathrm{mol^{-1}}$), higher than the calorimetrically determined value of this quantity ($\Delta_{\mathrm{fus}}H_{\mathrm{m}}(K_2TiF_6) = 21\ \mathrm{kJ\ mol^{-1}}$ [3]), is the evident cause of the difference between the estimate of the enthalpy of fusion of K_3TiF_6Cl and its calorimetrically determined value.

When calculating $\Delta_{\mathrm{fus}}\hat{H}_{\mathrm{m}}(K_3TiF_6Cl)$ after the simplified form of the procedure given in Ref. [4], which is based on the entropic balance, the value obtained is about 26% higher than the measured one (52.9 kJ $\mathrm{mol^{-1}}$ against 42 kJ $\mathrm{mol^{-1}}$). In this calculation, similarly as in Ref. [1], the differences in the heat capacities of the liquid and solid phases were neglected. Another simplification was that the entropy of mixing in the liquid phase of K_3TiF_6Cl composition had been calculated after the relation for the entropy of mixing in formation of an ideal solution of K_3TiF_6Cl composition from the melts of KCl and K_2TiF_6. The difference between the measured value of the enthalpy of fusion of K_3TiF_6Cl and the estimate of this quantity, calculated on the basis of entropic balance, can probably be explained by the following:

(i) The assumption of the formation of an ideal solution of the KCl and K_2TiF_6 components in liquid phase is evidently not fulfilled.

(ii) With regard to the relatively low symmetry of the $[TiF_6Cl]^{3-}$ complex ion a crystalline phase of K_3TiF_6Cl cannot be considered as a mechanical mixture of the two crystalline components. Thus, in calculation of the estimate of the enthalpy of fusion of K_3TiF_6Cl, the mixing entropy of formation of the crystalline phase cannot be neglected.

Applying the procedure for estimation of the heat of fusion of a binary compound [4] to K_3TiF_6Cl has shown that although in some cases this method gives relatively good results, e.g. for K_3TiF_7 [5], the experimental determination of the heat of fusion is, in the case of non-ideal systems, the most correct way to obtain a reliable value.

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