Determination of the Enthalpy of Fusion of K_2NbF_7 and K_3NbF_8

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On the basis of the areas of the fusion and crystallization peaks of K_2NbF_7 and K_3NbF_8 determined using the DSC mode of the high-temperature calorimeter (SETARAM 1800 K), and the temperature dependence of the calorimetric method sensitivity, the values of the enthalpy of fusion of K_2NbF_7 at equilibrium temperature of fusion 1008 K: $\Delta_{fus}H_m(K_2NbF_7) = (38 \pm 1)$ kJ mol^{-1} and the enthalpy of fusion of K_3NbF_8 at equilibrium temperature of fusion 1043 K: $\Delta_{fus}H_m(K_3NbF_8) = (57 \pm 2)$ kJ mol^{-1} have been determined.

The interest in niobium for its good properties grows continuously mainly in nuclear technology, metallurgy, and preparation of superconducting materials. Niobium due to its hardness and corrosion resistance, is an excellent material for surface treatment of steel materials to be used in chemical industry. Preparation of niobium by electrolysis of the molten salts is an alternative process to the classical thermal reduction, enabling to obtain niobium of the required quality.

As the potential source for electrochemical elimination of niobium K_2NbF_7 is considered. One of the most important thermodynamic properties of K_2NbF_7 is its enthalpy of fusion. The value of this quantity, calculated by the cryometric method, was used in determination of thermodynamic consistency of measured phase diagrams of the systems LiF—K_2NbF_7 and LiF—KF—K_2NbF_7 [1]. From the number of systems used as electrolytes for niobium deposition the ternary system LiF—KF—K_2NbF_7 seems to be one of the most promising [2].

In the system KF—K_2NbF_7 the binary compound K_3NbF_8 with dystectic melting point is formed. The knowledge of the enthalpy of fusion of this compound increases the reliability of the calculation of its dissociation degree, based on the thermodynamic analysis of the phase and chemical equilibria in the system KF—K_2NbF_7.

The aim of this work has been the calorimetric determination of the enthalpy of fusion of K_2NbF_7 and K_3NbF_8 on the high-temperature calorimeter, the SETARAM HTC 1800 K, at the equilibrium temperature of fusion 1008 K and 1043 K, respectively.

EXPERIMENTAL

One of the measured substances, K_2NbF_7, was prepared at the Institute of Chemistry and Technology of Rare Elements and Minerals, RAS, Apatite (Russia). As K_2NbF_7 is a very hygroscopic substance, it was weighed in a platinum crucible in a dry box. It was a specially arranged platinum crucible with lid sealed to it by platinum. The small hole for loading the sample into the crucible was closed by platinum wire and soldered using gold. The tightness of the crucible was tested by repeated weighing after it was placed in free air as well as after heating it to temperature higher than the temperature of fusion of K_2NbF_7 (1008 K). The tightness of the crucible is necessary also in order to prevent the corrosion of the calorimeter by destructive products of K_2NbF_7.

K_3NbF_8 used for measurement was prepared by heating equimolar mixture of K_2NbF_7 and KF at temperature about 1173 K for 1 h in the above described platinum crucible. The tightness of the crucible was verified by its repeated heating at temperature about 1173 K for 1 h. Prior to weighing in the crucible K_2NbF_7 and KF were dried in vacuum at temperature about 453 K and kept in a dry box.

The enthalpy of fusion of K_2NbF_7 and K_3NbF_8 was determined using a high-temperature calorimeter, the SETARAM HTC 1800 K, working in the DSC mode. In this mode, the temperature and the temperature difference between two crucibles of the calorimetric cell are recorded at a constant rate of the temperature change. The crucibles are placed one above the other in a homogeneous temperature field within a vertical furnace. The crucibles are made of sintered alumina with a replaceable lining of Pt90Rh10. The investigated samples of K_2NbF_7 and K_3NbF_8, respectively, sealed in a platinum crucible were put into the upper crucible of the calorimetric cell. The platinum crucible containing the reference standard (small pieces of sintered alumina) was placed in the lower crucible of the calorimetric cell. The temperature difference between the middle parts of crucibles, proportional to the heat flow between the crucibles, is measured by

Table 1. Experimental Data $(Q_{\mathrm{fus}}(\mathrm{X})/\lambda_{\mathrm{fus}})$ and the Values of their Arithmetic Mean for K_2NbF_7 and K_3NbF_8

Sample	$(Q_{\mathrm{fus}}(\mathrm{X})/\lambda_{\mathrm{fus}})$/(K s)						$(Q_{\mathrm{fus}}(\mathrm{X})/\lambda_{\mathrm{fus}})_\Phi$/(K s)
K_2NbF_7	190	190	194	189	194		191 ± 3
K_3NbF_8	233	221	229	225	247	221	229 ± 10

Table 2. Experimental Data $(Q_{\mathrm{cryst}}(\mathrm{X})/\lambda_{\mathrm{cryst}})$ and the Values of their Arithmetic Mean for K_2NbF_7 and K_3NbF_8

Sample	$(Q_{\mathrm{cryst}}(\mathrm{X})/\lambda_{\mathrm{cryst}})$/(K s)						$(Q_{\mathrm{cryst}}(\mathrm{X})/\lambda_{\mathrm{cryst}})_\Phi$/(K s)
K_2NbF_7	198	192	199	192	196		195 ± 4
K_3NbF_8	240	246	235	242	238	247	241 ± 5

a set of thermocouples connected in series. The rate of the temperature change used at the measurements was 1 K min^{-1}. The treatment of the measured data of enthalpy of fusion by the modified procedure proposed by *Guttman* and *Flynn* [3] is described in [4].

RESULTS AND DISCUSSION

From the measured data of the temperature difference between the crucibles with the studied (X) and reference substances, the areas of the fusion and crystallization peaks on the curves of the time dependence of the temperature difference are evaluated ($(Q_{\mathrm{fus}}(\mathrm{X})/\lambda_{\mathrm{fus}})$ and $(Q_{\mathrm{cryst}}(\mathrm{X})/\lambda_{\mathrm{cryst}})$, respectively). Q is the heat effect at melting or crystallization of the pertinent mass of the sample, λ is a constant proportional to the heat transfer coefficient, and X is K_2NbF_7 or K_3NbF_8. The experimentally obtained values of $(Q_{\mathrm{fus}}(\mathrm{X})/\lambda_{\mathrm{fus}})$ and $(Q_{\mathrm{cryst}}(\mathrm{X})/\lambda_{\mathrm{cryst}})$ for K_2NbF_7 and K_3NbF_8, the arithmetic means of these quantities (Φ is symbol for arithmetic mean), and the errors of their determination are presented in Tables 1 and 2, respectively.

The errors of arithmetic means of these quantities were calculated using the Student distribution on the level of reliability $(1-\alpha) = 0.95$.

The area of the fusion or crystallization peak ("trans" is a common symbol for fusion and crystallization), related to mass unit of the studied substance, is proportional to the specific enthalpy of fusion or crystallization of the substance $\Delta_{\mathrm{trans}}h(\mathrm{X})$

$$\left(\frac{Q_{\mathrm{trans}}(\mathrm{X})}{\lambda_{\mathrm{trans}}}\right)_\Phi \frac{1}{m(\mathrm{X})} = \varepsilon_{\mathrm{trans}}\ \Delta_{\mathrm{trans}}h(\mathrm{X}) \qquad (1)$$

The coefficient of the proportionality $\varepsilon_{\mathrm{trans}}$ between the peak area (expressed in K s) and heat (expressed in J) is a function of the temperature. The areas of the fusion and crystallization peaks of the substances are different even at the same value of the products $\Delta_{\mathrm{trans}}h(\mathrm{X}) \times m(\mathrm{X})$ for substances with different temperatures of fusion.

In the work [5] the temperature dependence of $\varepsilon_{\mathrm{trans}}$, *i.e.* the sensitivity of the calorimetric method, was determined on the basis of the areas of the fusion and crystallization peaks $(Q_{\mathrm{trans}}(\mathrm{calib})/\lambda_{\mathrm{trans}})_\Phi$ for six calibration substances (calib) (KNO_3, LiCl, KCl, NaCl, Na_2SO_4, and K_2SO_4) with known $\Delta_{\mathrm{trans}}h(\mathrm{calib})$ values. This dependence has also with the calculated values of the standard deviation of its coefficients the following form

$$\varepsilon_{\mathrm{trans}}/(\mathrm{K\ s\ J}^{-1}) = (14.156 \pm 0.190) - (7.881 \times 10^{-3} \pm 1.79 \times 10^{-4})T/\mathrm{K} \qquad (2)$$

The covariance of coefficients of eqn (*2*) is (-3.35×10^{-5}). From this dependence it can be seen that the sensitivity of the calorimetric method decreases with increasing temperature. It is evidently caused by higher proportion of the heat transfer by radiation against the heat transferred between the crucibles by conduction with the thermocouples at higher temperatures. In calculation of the dependence (*2*), the "mean temperatures" of fusion and crystallization of each calibration substance, determined as the arithmetic mean from the average temperatures between the beginning and the end of the peaks of fusion and crystallization, respectively, were considered.

For the "mean temperatures" of the fusion and crystallization peaks of K_2NbF_7 (1019 K and 999 K, respectively) and K_3NbF_8 (1045 K and 1026 K, respectively) related to the areas $(Q_{\mathrm{fus}}(\mathrm{X})/\lambda_{\mathrm{fus}})$ and $(Q_{\mathrm{cryst}}(\mathrm{X})/\lambda_{\mathrm{cryst}})$, respectively (Tables 1 and 2), the values $\varepsilon_{\mathrm{fus}}$ and $\varepsilon_{\mathrm{cryst}}$ were calculated from eqn (*2*)

$$\{\varepsilon_{\mathrm{fus}}(1019\ \mathrm{K})\} = 6.125 \pm 0.033 \qquad (3)$$

$$\{\varepsilon_{\mathrm{cryst}}(999\ \mathrm{K})\} = 6.283 \pm 0.034 \qquad (4)$$

and

$$\{\varepsilon_{\mathrm{fus}}(1045\ \mathrm{K})\} = 5.920 \pm 0.033 \qquad (5)$$

$$\{\varepsilon_{\mathrm{cryst}}(1026\ \mathrm{K})\} = 6.070 \pm 0.033 \qquad (6)$$

The values of the standard deviation $\sigma(\varepsilon)$ were determined according to the relation

$$\sigma(\varepsilon) = (\mathrm{var}(b)T^2 + 2T\mathrm{cov}(a,b) + \mathrm{var}(a))^{1/2} \quad (7)$$

where a and b are the coefficients of the dependence $\varepsilon = a + bT$ (according to eqn (*2*)).

By introducing the values $\varepsilon_{\mathrm{fus}}$ and $\varepsilon_{\mathrm{cryst}}$ from eqns (*3*), (*5*) and (*4*), (*6*), respectively, the values $(Q_{\mathrm{fus}}(\mathrm{X})/\lambda_{\mathrm{fus}})_\Phi$ and $(Q_{\mathrm{cryst}}(\mathrm{X})/\lambda_{\mathrm{cryst}})_\Phi$ from Tables 1 and 2, respectively, and the masses $m(K_2NbF_7) = 0.25154$ g and $m(K_3NbF_8) = 0.24989$ g into the relation (*1*), the values of the specific enthalpy of the fusion process and the specific enthalpy of the crystallization process of K_2NbF_7 and K_3NbF_8 were obtained

$$\Delta_{\mathrm{fus}}h(K_2NbF_7) = (124 \pm 2)\ \mathrm{J\ g^{-1}} \quad (8)$$

$$-\Delta_{\mathrm{cryst}}h(K_2NbF_7) = (123 \pm 3)\ \mathrm{J\ g^{-1}} \quad (9)$$

and

$$\Delta_{\mathrm{fus}}h(K_3NbF_8) = (155 \pm 7)\ \mathrm{J\ g^{-1}} \quad (10)$$

$$-\Delta_{\mathrm{cryst}}h(K_3NbF_8) = (157 \pm 6)\ \mathrm{J\ g^{-1}} \quad (11)$$

The values $\Delta_{\mathrm{fus}}h(K_2NbF_7)$ and $-\Delta_{\mathrm{cryst}}h(K_2NbF_7)$ from eqns (*8*) and (*9*) are coordinated to the equilibrium temperature of transformation of K_2NbF_7 (1008 K) and $\Delta_{\mathrm{fus}}h(K_3NbF_8)$ and $-\Delta_{\mathrm{cryst}}h(K_3NbF_8)$ from eqns (*10*), (*11*) to that of K_3NbF_8 (1043 K). We assume that the temperature change of the enthalpy of fusion and crystallization of K_2NbF_7 and K_3NbF_8 occurs in a relatively narrow temperature interval, lower than the error of the method used. The Kirchhoff's law could not be used for calculation of the change of enthalpy of fusion with temperature because the temperature dependences of the heat capacity of K_2NbF_7 for either crystalline phase or melt are unknown. The errors of the determination of $\Delta_{\mathrm{fus}}h(K_2NbF_7)$, $-\Delta_{\mathrm{cryst}}h(K_2NbF_7)$ and $\Delta_{\mathrm{fus}}h(K_3NbF_8)$, $-\Delta_{\mathrm{cryst}}h(K_3NbF_8)$ were calculated according to eqn (*1*) from the errors of determination of $(Q_{\mathrm{trans}}(K_2NbF_7)/\lambda_{\mathrm{trans}})_\Phi$, $(Q_{\mathrm{trans}}(K_3NbF_8)/\lambda_{\mathrm{trans}})_\Phi$, and $\sigma(\varepsilon)$, using Gauss' law of propagation of errors. From the relations (*8*), (*9*) and (*10*), (*11*) we receive the mean values of the enthalpy of transformation of K_2NbF_7 and K_3NbF_8, respectively

$$\Delta_{\mathrm{trans}}h(K_2NbF_7) = (124 \pm 2)\ \mathrm{J\ g^{-1}} \quad (12)$$

$$\Delta_{\mathrm{trans}}h(K_3NbF_8) = (156 \pm 7)\ \mathrm{J\ g^{-1}} \quad (13)$$

The molar enthalpy and entropy of fusion of K_2NbF_7 at the temperature of fusion 1008 K were found to be

$$\Delta_{\mathrm{fus}}H_{\mathrm{m}}(K_2NbF_7) = (38 \pm 1)\ \mathrm{kJ\ mol^{-1}} \quad (14)$$

$$\Delta_{\mathrm{fus}}S_{\mathrm{m}}(K_2NbF_7) = (38 \pm 1)\ \mathrm{J\ mol^{-1}\ K^{-1}} \quad (15)$$

The values of these quantities for K_3NbF_8 at the temperature of fusion 1043 K are

$$\Delta_{\mathrm{fus}}H_{\mathrm{m}}(K_3NbF_8) = (57 \pm 2)\ \mathrm{kJ\ mol^{-1}} \quad (16)$$

$$\Delta_{\mathrm{fus}}S_{\mathrm{m}}(K_3NbF_8) = (55 \pm 2)\ \mathrm{J\ mol^{-1}\ K^{-1}} \quad (17)$$

The measured values of enthalpy of fusion of K_2NbF_7 and K_3NbF_8 (38 kJ mol^{-1} and 57 kJ mol^{-1}, respectively) differ considerably from the calculated values of this quantity (70.9 kJ mol^{-1} and 98.6 kJ mol^{-1}, respectively) presented in work [1]. On the other hand, the enthalpy of fusion of K_3NbF_8 determined by the DSC method is relatively close to the value of this quantity determined by the method of drop calorimetry ($\Delta_{\mathrm{fus}}H_{\mathrm{m}}(K_3NbF_8) = (60.5 \pm 3.1)$ kJ mol^{-1}) [6] which can be considered as a good agreement in the frame of the errors of measurement by both calorimetric methods. The reliability of the measured values of the enthalpy of fusion of K_2NbF_7 and K_3NbF_8 is, however, reduced due to the presence of water impurities in the sample of K_2NbF_7 which was used also to prepare K_3NbF_8. Vibrational spectroscopy of the K_2NbF_7 sample proved the presence of very small amount of water and the Nb—O binding, indicating the contamination of K_2NbF_7 by oxyfluoroniobates. It is, however, impossible to get rid off them.

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