

Enthalpic Analysis of Potassium Heptafluorotantalate

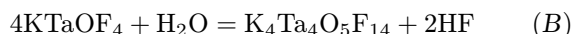
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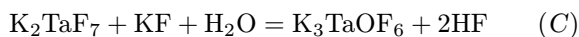
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The relative enthalpies of two crystalline samples K_2TaF_7 A, K_2TaF_7 B and of K_2TaF_7 melt have been measured by the use of the drop calorimetry in the temperature intervals 600–752 °C, 615–750 °C, and 758–880 °C, respectively. The heat capacities have been determined differentiating the temperature dependences of the relative enthalpies: $C_p(K_2TaF_7 \text{ cr, A}) = (314 \pm 6) \text{ J mol}^{-1} \text{ K}^{-1}$, $C_p(K_2TaF_7 \text{ cr, B}) = (356 \pm 7) \text{ J mol}^{-1} \text{ K}^{-1}$, and $C_p(K_2TaF_7 \text{ melt}) = (315 \pm 9) \text{ J mol}^{-1} \text{ K}^{-1}$. Considerable prefreezing was observed in the temperature dependence of the relative enthalpy of the melt. The onset of the prefreezing effect at cooling of the melt was estimated to be at about 820 °C. The depression of the freezing temperature reached down to the temperature of crystallization of 755 °C. The calorimetric experiments have shown the temperature of fusion to be $752^\circ\text{C} < t_{\text{fus}} < 758^\circ\text{C}$. The enthalpies of fusion at the temperature of 755 °C, $\Delta_{\text{fus}}H(K_2TaF_7 \text{ A, } 755^\circ\text{C}) = (37.2 \pm 0.7) \text{ kJ mol}^{-1}$ and $\Delta_{\text{fus}}H(K_2TaF_7 \text{ B, } 755^\circ\text{C}) = (34.6 \pm 1.0) \text{ kJ mol}^{-1}$, inclusive enthalpy of prefreezing, have been determined from experimental data.

The compound K_2TaF_7 is a crucial component of molten salts electrolytes used to prepare and refine tantalum metal by electrolysis [1]. According to [2] the salt is not hygroscopic and crystallizes in the form of thin prismatic needles belonging to the monoclinic system. The literature data about the behaviour of the salt at heating are often contradictory. According to [2], when heated, K_2TaF_7 initially produces clear melt, which later starts to emit fumes and changes to solid sediment. The presence of water vapour in the ambient atmosphere has substantial influence on the thermal stability of K_2TaF_7 . According to Hahn and Püller [3] at heating of K_2TaF_7 in an atmosphere containing water vapour rapid hydrolysis occurs. HF is released and heavily soluble product $K_4Ta_4O_5F_{14}$ is formed. According to Buslaev *et al.* [4] hydrolysis of K_2TaF_7 takes place in the temperature interval 200–400 °C in two steps



In the presence of water vapour oxyfluorotantalate is produced in the melts of the K_2TaF_7 —KF—LiF system according to the reaction scheme [5]



Agulyanskii *et al.* [6] described a reversible polymorphic transformation at the mean temperature of 202 °C. The observed effects on the thermograms were

readily reproduced in repeated heating and cooling in an inert gas, in a moderate vacuum and in air. This was also observed after the specimen had been fused. Konstantinov and Ts'ui Ping-hsin [7] followed the thermal stability and fusion of K_2TaF_7 in both extra pure Ar and air atmospheres using visual method coupled with simultaneous recording of the curves of cooling. The samples were placed in Ni and Pt crucibles. The temperature of fusion was determined to be $(775 \pm 2)^\circ\text{C}$. It was the same in both Ar and air atmospheres. A polymorphic transition was observed at $(741 \pm 2)^\circ\text{C}$. These authors mentioned that K_2TaF_7 melt is relatively stable in air, if not heated for a long time. This was confirmed by optical microscopy and X-ray diffraction. Nevertheless, according to [7], the vapour of K_2TaF_7 easily decomposes under the influence of water vapour from the air, producing oxygen-bearing compound, which condenses from the gas phase in the form of needles or sticks on the top part of the crucible. It is also possible that on the surface of the melt some K_2TaF_7 decomposes under the influence of the water vapour from the air. This may explain the increased fluidity of the substance at heating in air and also the emitting of the fumes containing HF. In the Ar atmosphere Konstantinov and Ts'ui Ping-hsin [7] did not observe these effects.

In our investigation relative enthalpies, *i.e.* enthalpy increments of the liquid and crystalline K_2TaF_7 at the temperature T , referred to the enthalpy of the K_2TaF_7 in the crystalline state at 298 K, $H_{\text{rel}} = H(K_2TaF_7, T) - H(K_2TaF_7 \text{ cr, } 298 \text{ K})$, were determined by the drop calorimetry. The experimental

data have been used to perform the thermodynamic analysis, including determination of the isobaric heat capacities, enthalpy and entropy of fusion of the crystalline substance, and enthalpy of prefreezing of the melt. The enthalpy of fusion of K_2TaF_7 was also estimated by the use of suitable phase diagram to assess the thermodynamic consistency of thermochemical and phase equilibria data. The phase composition of the studied substances was followed by the X-ray diffraction, infrared spectroscopic investigations, and crystal-optical analysis at room temperature.

EXPERIMENTAL

The specimens K_2TaF_7 were obtained from the Institute of Chemistry and Technology of Rare Elements and Minerals, Russian Academy of Sciences, Apatity, Russia. They were kept in hermetically closed containers. Before using for calorimetric experiments they were dried for 15 h at 180 °C in a vacuum furnace at the reduced pressure. The X-ray diffraction patterns of the samples were very similar to one of the two patterns given for this substance in the PDF-2 International Centre for Diffraction Data database, and also to the X-ray data for this substance published by *Eberts* and *Pink* [8]. Infrared investigations of both samples showed a weak peak at about 70 cm^{-1} in the spectra of the sample K_2TaF_7 B, which may indicate small amount of an oxyfluorotantalate in this sample. The peak was not identified in sample A.

Calorimetric Measurements

Relative enthalpies have been measured using the high-temperature isoperibol drop calorimeter [9]. The PtRh 10 % crucibles with sealed covers were used in calorimetric experiments. Through a small hole drilled in the cover about 1 g of the fine powdered sample was loaded into the crucible. The operation was carried out in a glove box under dry nitrogen. The holes in crucible covers were then closed by soldering with gold to prevent any contamination of the samples with ambient atmosphere. The tightness of the crucibles was checked by an initial test described below and by weighting after each calorimetric measurement. During the calorimetric experiment the temperature was measured by a thermocouple placed close to the crucible cover. The temperature difference due to the different positions of the sample and the thermocouple was compensated by calibration. During the calibration the temperature difference between the standard measuring thermocouple and the calibrating thermocouple was followed as a function of temperature and position of the crucible in the furnace. The standard measuring thermocouple was placed in its normal position close to the crucible cover and the calibrating thermocouple was placed inside the crucible in the position of the sample. At the calibration measurements

an inert material, usually Al_2O_3 , substituted the sample in the crucible.

The calorimetric experiment starts with temperature equilibration of the crucible with the sample. After having been heated for >1 h at constant temperature in the calorimetric furnace the crucible is dropped into a calorimetric copper block, in which the heat released is measured. The directly measured quantity, hence, is the enthalpy of cooling $\Delta_{cool}H = -H_{rel}$. At the lower temperatures (below 750 °C) the prolonged equilibration (2–3 h) was shown to be necessary to get reproducible results. The cooling of the block with the dropped sample is followed approximately for 1 h. The heat released from the calorimetric block into its surrounding after this period is calculated by extrapolation [10].

Two crucibles were used for the measurements. Before starting of the first set of calorimetric measurements the tightness of the first crucible with the sample labelled as K_2TaF_7 A was checked by weighting after 2 h heating at 900 °C in a furnace outside the calorimeter. At this temperature the sample was already melted. Then it was cooled down slowly to allow the salt to crystallize. It was then used in the first series of measurements. The heat treatment of the second sample before calorimetric measurements was different. The tightness of the crucible with the sample K_2TaF_7 B used in the second set of experiments was firstly checked by weighting after 2 h heating at 690 °C. This temperature is in the region of the thermodynamic stability of the low-temperature modification of K_2TaF_7 according to *Konstantinov* and *Ts'ui Ping-hsin* [7]. Then the calorimetric measurements in the temperature region of the solid phase were performed. After finishing of the measurements with the solid phase the tightness of the crucible was checked once again by the same way as it was done with the sample K_2TaF_7 A. Then the measurements were continued with the melt.

The X-ray diffraction patterns of the samples taken after finishing of each set of experiments, represented by several cycles of heating, melting, and subsequent quick cooling in calorimeter, did not show any significant changes with respect to original samples as illustrated in Fig. 1 for the sample A. The X-ray diffraction patterns of the sample K_2TaF_7 B were similar. The measurements were carried out in the order of the run numbers in Table 1.

RESULTS AND DISCUSSION

Relative Enthalpy and Heat Capacity of K_2TaF_7 and K_2TaF_7 Melt

The experimental enthalpy increments $H(T) - H(298\text{ K})$ of crystalline K_2TaF_7 and of K_2TaF_7 melt measured in the temperature range 600–880 °C are listed in Table 1. In Fig. 2 the measured enthalpy

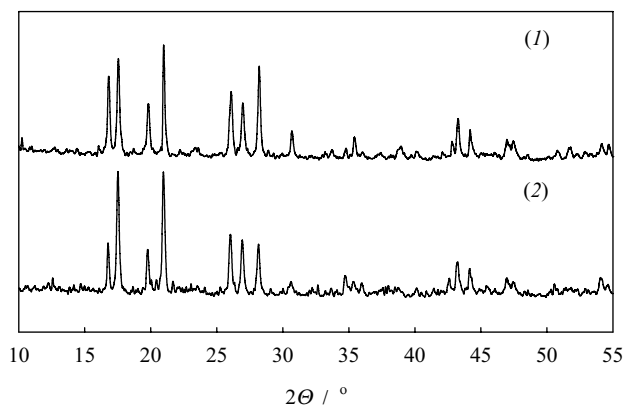


Fig. 1. X-Ray diffraction patterns of the sample K_2TaF_7 A before (1) and after (2) set of calorimetric experiments (runs 1–14).

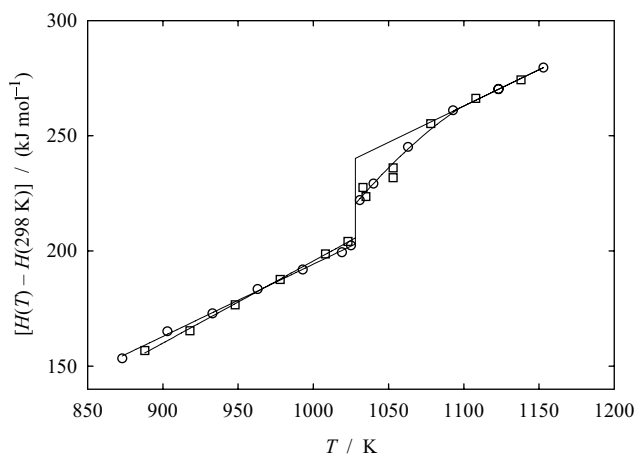


Fig. 2. Relative enthalpies of K_2TaF_7 . Circles and squares represent experimental points for sample A and sample B, respectively.

data are plotted *vs.* temperature. The least-squares fits of the measured relative enthalpy data, presented in the diagram by straight lines are expressed by the regression equations for the solid samples K_2TaF_7 A, K_2TaF_7 B, and the melt, respectively, as follows

$$H_{\text{rel}}(\text{K}_2\text{TaF}_7 \text{ cr, A})/(\text{kJ mol}^{-1}) = (-119.6608 \pm 6.1045) + (0.3139 \pm 0.0064) T/\text{K} \quad (1)$$

$$\sigma(H_{\text{rel}}) < 0.4 \text{ kJ mol}^{-1}$$

$$H_{\text{rel}}(\text{K}_2\text{TaF}_7 \text{ cr, B})/(\text{kJ mol}^{-1}) = (-160.7754 \pm 6.5601) + (0.3564 \pm 0.0068) T/\text{K} \quad (2)$$

$$\sigma(H_{\text{rel}}) < 0.8 \text{ kJ mol}^{-1}$$

$$H_{\text{rel}}(\text{K}_2\text{TaF}_7 \text{ melt})/(\text{kJ mol}^{-1}) = (-84.0391 \pm 9.8163) + (0.3154 \pm 0.0088) T/\text{K} \quad (3)$$

$$\sigma(H_{\text{rel}}) < 0.7 \text{ kJ mol}^{-1}$$

The regression coefficients in particular equations are given in parentheses along with their standard devia-

Table 1. Experimental Relative Enthalpy of K_2TaF_7

Run	$t/^\circ\text{C}$	$H/(\text{J g}^{-1})$
K_2TaF_7 A		
1	600	390.94
2	630	420.84
3	660	440.70
4	690	467.74
5	720	489.40
6	758	566.21
7	746	508.54
8	767	584.37
9	752	515.91
10	790	624.94
11	820	665.32
12	850	689.36
13	850	689.04
14	880	712.86
K_2TaF_7 B		
15	615	399.70
16	645	421.71
17	675	450.30
18	705	478.45
19	735	506.61
20	750	520.50
21	762	570.23
22	780	590.99
23	805	651.03
24	835	678.94
25	865	699.44
26	780	601.85
27	760	580.22

tions. The standard deviation $\sigma(H_{\text{rel}})$ at each regression equation is the maximum value of this quantity for interpolated relative enthalpy, as well as for up to T_{fus} extrapolated relative enthalpy according to particular equation. This quantity has been calculated applying the law of combination of errors, to variances and the covariance of both regression coefficients. Eqns (1) and (2) are evaluated from data measured in the temperature intervals 600–752 °C and 615–750 °C, respectively. Anomalous decrease of the relative enthalpy of the melt may be observed at progressive cooling, when temperature of crystallization is approached (Fig. 2). This course of the temperature dependence of the relative enthalpy of the melt we suggest to explain with prefreezing effect. The onset of the prefreezing was observed at about 820 °C. The effect stretches down to the temperature of crystallization of 755 °C. The regression equation (3) for the melt has been calculated using the data measured for both samples in the temperature interval 805–880 °C. The experimental points, which lay in the prefreezing region, have not been included. We have not observed any enthalpic effects that could be connected with the modification transition at 741 °C, reported by *Konstantinov* and *Ts'ui Ping-hsin* [7]. It is probably too small to be detected by drop calorimetry. The

other explanation is that the modification transition is irreversible and the high-temperature modification, which probably crystallizes from the melt, persists in the metastable state at low temperatures.

Following values of the heat capacities along with their standard deviations may be evaluated by the differentiating of the temperature dependences of the relative enthalpies of corresponding phases: $C_p(\text{K}_2\text{TaF}_7 \text{ cr, A}) = (314 \pm 6) \text{ J mol}^{-1} \text{ K}^{-1}$, $C_p(\text{K}_2\text{TaF}_7 \text{ cr, B}) = (356 \pm 7) \text{ J mol}^{-1} \text{ K}^{-1}$, and $C_p(\text{K}_2\text{TaF}_7 \text{ melt}) = (315 \pm 9) \text{ J mol}^{-1} \text{ K}^{-1}$. These values are valid in temperature intervals of the data used to evaluate the relative enthalpy equations. The reliability of the calculated C_p values, particularly that of the melt, may be reduced due to the use of the enthalpy data for rather narrow temperature intervals.

Enthalpy and Entropy of Fusion, Enthalpy of Prefreezing

Konstantinov and *Ts'ui Ping-hsin* [7] list published data of the temperature of fusion ranging from 630 °C to 820 °C [6, 7, 11–13]. They explain this broad span with the use of more or less impure samples. The accepted assessed value is $(775 \pm 5) \text{ °C}$ [6, 7]. However, the calorimetric experiments in this work have shown the jump in the relative enthalpy at the temperature inside the interval 752–758 °C. We also followed visually the melting of K_2TaF_7 at heating in Pt crucible under dried nitrogen atmosphere. These experiments have shown the sample to be completely melted at 755 °C. This was in good agreement with the melting temperature evaluated on the basis of the calorimetric experiments. For this reason we evaluated enthalpy and entropy of fusion for the temperature of fusion 755 °C.

The enthalpy of fusion was determined as a difference between extrapolated values of the enthalpy of melt and the enthalpy of crystalline phase at the temperature of fusion. The particular enthalpy values along with their standard deviations have been extrapolated by the use of eqns (1–3). Due to the prefreezing effect at the enthalpy of the melt, eqn (3) had to be extrapolated quite far. Using eqns (1) and (3) the enthalpy of fusion $\Delta_{\text{fus}}H(\text{K}_2\text{TaF}_7 \text{ A, } 755 \text{ °C}) = (37.2 \pm 0.7) \text{ kJ mol}^{-1}$ and using eqns (2) and (3) the enthalpy of fusion $\Delta_{\text{fus}}H(\text{K}_2\text{TaF}_7 \text{ B, } 755 \text{ °C}) = (34.6 \pm 1.0) \text{ kJ mol}^{-1}$ have been evaluated, respectively. In these values the enthalpy of prefreezing is included. The corresponding entropies of fusion are $\Delta_{\text{fus}}S(\text{K}_2\text{TaF}_7 \text{ A, } 755 \text{ °C}) = (36.2 \pm 0.7) \text{ J mol}^{-1} \text{ K}^{-1}$ and $\Delta_{\text{fus}}S(\text{K}_2\text{TaF}_7 \text{ B, } 755 \text{ °C}) = (33.6 \pm 1.0) \text{ J mol}^{-1} \text{ K}^{-1}$.

The enthalpy of prefreezing at the temperature of fusion is 19.8 kJ mol^{-1} , representing 53 % and 57 % of the enthalpy of crystallization for sample A and sample B, respectively. It was calculated as a difference between the extrapolated value of the enthalpy

according to eqn (3) and the extrapolated value of the enthalpy of melt according to the curve following the experimental points in the prefreezing region, shown in Fig. 2.

Small difference in the slope of the temperature dependence of the relative enthalpy between both crystalline samples is evident in Fig. 2. It may suggest a difference in the phase composition of both samples, indicated by infrared spectroscopy, however, not confirmed by the X-ray diffraction analysis.

Cryoscopic Estimation of the Enthalpy of Fusion

The enthalpy of fusion of K_2TaF_7 may also be calculated from the course of the K_2TaF_7 liquidus curve in independent simple eutectic phase diagrams without formation of solid solutions. For systems of this type and for diluted solutions of K_2TaF_7 the following limiting law holds

$$\lim_{x \rightarrow 1} \frac{dT}{dx} = \frac{RT_{\text{fus}}^2}{\Delta_{\text{fus}}H} \lim_{x \rightarrow 1} \frac{da}{dx} = k_o \quad (4)$$

where a is the activity of K_2TaF_7 and k_o is the slope of the tangent straight line to the K_2TaF_7 liquidus curve for $x(\text{K}_2\text{TaF}_7) = 0$. For ionic systems

$$\lim_{x \rightarrow 1} \frac{da}{dx} = k_{\text{St},j/i} \quad (5)$$

where $k_{\text{St},j/i}$ is the semiempirical Stortenbeker factor [14], which is equal to the number of new “foreign” species introduced into the pure solvent by the solute (the second component). For the enthalpy of fusion of the solvent it then holds

$$\Delta_{\text{fus}}H = \frac{RT_{\text{fus}}^2}{k_o} k_{\text{St},j/i} \quad (6)$$

Some difficulties may arise when the value of the coefficient $k_{\text{St},j/i}$ is estimated. An obstacle in evaluating entropies of fusion from freezing point depression arises for salts, for which the structure of the melt may not correspond with the stoichiometric formula assuming complete dissociation into positive and negative ions [15]. Such situation, however, is not supposed to take place in the systems in question.

The system $\text{K}_2\text{TaF}_7\text{—LiF}$ [11] was used for the calculation of the enthalpy of fusion of K_2TaF_7 . In this system LiF introduces only Li^+ cations as new species, since F^- anions may be present in pure K_2TaF_7 due to the partial dissociation of $[\text{TaF}_7]^{2-}$ to $[\text{TaF}_6]^-$ and F^- . Therefore $k_{\text{St},j/i} = 1$. The dependence of the temperature of primary crystallization of K_2TaF_7 on composition was expressed in the form of a second-order polynomial. Differentiating the polynomial with respect to $x(\text{K}_2\text{TaF}_7)$ and inserting it into eqn (6)

Table 2. Comparison of the Enthalpies of Fusion of K_2TaF_7

Method	System	$t_{fus}/^{\circ}C$	$\Delta_{fus}H/(kJ\ mol^{-1})$
Drop calorimetry	K_2TaF_7 A	755	37.2 ± 0.7
	K_2TaF_7 B	755	34.6 ± 1.0
Cryoscopy	K_2TaF_7 —LiF	775	32.6

the value of the enthalpy of fusion of K_2TaF_7 was calculated. The result of calculation is presented in Table 2 along with the results of calorimetric experiments. The comparison of the calorimetrically measured and cryoscopically estimated values of the enthalpy of fusion showed a bit smaller value evaluated on the basis of the phase equilibria data, which may be caused by the lower precision of the measured phase diagram.

CONCLUSION

The calorimetric experiments in this work have shown the bend of the relative enthalpy curve at the temperature $752^{\circ}C < t < 758^{\circ}C$. Visual observations of the melting of K_2TaF_7 under dried nitrogen have shown that the sample was completely melted at $755^{\circ}C$. The temperature of fusion, determined in this work is thus substantially lower than the values according to *Konstantinov* and *Ts'ui Ping-hsin* [7] and *Eberts* and *Pink* [8].

The enthalpy of fusion was determined as a difference between the enthalpy of melt and the enthalpy of crystalline phase at the temperature of fusion. The values (37.2 ± 0.7) $kJ\ mol^{-1}$ and (34.6 ± 1.0) $kJ\ mol^{-1}$ have been evaluated for the samples K_2TaF_7 A and K_2TaF_7 B, respectively. In these values the enthalpy of prefreezing is included. The corresponding entropies of fusion are (36.2 ± 0.7) $J\ mol^{-1}\ K^{-1}$ and (33.6 ± 1.0) $J\ mol^{-1}\ K^{-1}$, respectively.

Anomalous decrease of the relative enthalpy, connected with the dramatic change of C_p may be observed at the decreasing temperature of the melt, when temperature of crystallization is approached. The constant slope of the relative enthalpy curve does not set on before $820^{\circ}C$, which is substantially higher than the temperature of fusion. This course of the temperature dependence of the relative enthalpy of the melt may be explained by the prefreezing effect.

The enthalpy of prefreezing at the temperature of fusion is $19.8\ kJ\ mol^{-1}$. Possible arising of glass at cooling of the melt in the drop calorimeter was checked by optical microscopy. No significant amount of the isotropic material was observed in investigated samples. Drop calorimetry experiments have shown different heat capacities and enthalpies of fusion of both samples, which may be due to impurities in these samples. The cryometrically estimated value is rather close to the calorimetric values indicating quite good consistency of calorimetric and phase equilibria data.

We have not observed any enthalpic effect at the temperature of phase transition $741^{\circ}C$, reported by *Konstantinov* and *Ts'ui Ping-hsin* [7]. It is probably too small to be detected by drop calorimetry.

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