

Calorimetric Study of Melts in the System KF – K₂TaF₇

Research Article

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Abstract: Enthalpy increment measurements on melts in the system KF–K₂TaF₇ were carried out by drop calorimetry at temperatures between 298 K and 1063, 1103 and 1143 K for selected compositions. Heat capacities of the melted mixtures and enthalpies of mixing have been determined. Careful calorimetric experiments showed small but distinct non-ideality of the melt. The molar heat capacity of melt exhibits small positive divergence from additivity. The molar enthalpy of mixing shows negative deviation from ideality which decreases with increasing temperature. The thermal effect at mixing was assigned predominantly to association reactions producing more complex fluorotantalate anions. The formation of complex anions with lower coordination number of Ta may not be excluded.

Keywords: KF–K₂TaF₇ melts • Enthalpy of mixing • Heat capacity • Drop calorimetry

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1. Introduction

Molten salts containing tantalum are widely used for the production of tantalum by electrolysis. This initiated intensive investigations of processes that take place in molten halides containing dissolved Ta in the form of complex compounds [1]. Sodium reduction processes currently predominantly used in production of Ta as well as the surface counting of metallic bases by tantalum and syntheses of various compounds of tantalum are also based on K₂TaF₇ in molten salt media. The KF–K₂TaF₇ system plays a crucial role in this media.

The phase diagram of the KF–K₂TaF₇ system was reported by several investigators [2–5]. It shows the congruently melting compound K₃TaF₈ along with two eutectic points. The melting temperatures of K₃TaF₈ published by different authors varied from 1049 to 1053 K. Some discrepancies exist in the interpretation of the diagram in the K₂TaF₇ rich side and in the interpretation of melting of K₂TaF₇ itself, due to complicated character of reactions which accompany this process. According to Agulyansky and Bessonova [5] and Agulyansky [1,6] partial decomposition of the

K₂TaF₇ occurs at 1003 K due to the incongruent melting, yielding molten KTaF₆ and solid K₃TaF₈. The rest of the K₂TaF₇ melts, probably by some different mechanism, in a separate step at 1019 K. Finally, K₃TaF₈, produced by the incongruent decomposition at 1003 K, melts at 1051 K. Recently a new interpretation has been published, based on DSC and high temperature neutron diffraction [7]. At 976 K a solid-solid phase transformation was observed. The thermal effect at 1019 K was ascribed to the incongruent decomposition of K₂TaF₇ into two immiscible melts. The third effect at 1044 K was attributed to the mixing of both melts. The incongruent character of the thermal decomposition of K₂TaF₇ was confirmed by Kubiková *et al.* [8]. The modified phase diagram of the KF–K₂TaF₇ system with the immiscibility gap was also published [9].

The mechanisms of the chemical reactions and the properties of the final products at the reduction of metals in molten salt media depend on the ionic composition and structure of the melt. While structure and properties of crystalline complex fluorotantalates are in many cases known, (recently comprehensive review of fluorometalates including fluorotantalates has been

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published [10]), the understanding of the ionic structure of melts is still in development. According to Agulyansky [1,6] three conceptual steps can be discerned in definition of the ionic structure of fluoride melts containing tantalum. The first attempt, based on analyses of melting diagrams and available estimated thermodynamic data assumes that in molten systems containing alkali-metal fluorides, tantalum forms complex ions in which the coordination number of tantalum increases up to 8. Typical representative of these complex ions is TaF_8^{3-} . The second step, based on investigation of the physical-chemical properties and IR spectra of melts with relatively low metal concentrations assumes that there are two types of complex ions, namely octafluorotantalate TaF_8^{3-} and heptafluorotantalate TaF_7^{2-} that determine the properties of melts. The third step, according to Agulyansky, consisted of the direct investigation of IR emission spectra of melts. The investigation showed the tendency of tantalum to reduce its coordination number when moving from crystalline to molten state. Accordingly, the properties of melts depend on the equilibrium between two types of complex ions, TaF_7^{2-} and TaF_6^- .

Frequently, the ionic compositions of melts are estimated by analysis of melting diagrams and physical-chemical properties like density, surface tension, viscosity and electrical conductivity. From this point of view, the analysis of thermodynamic properties of mixing and of the magnitude of their deviation from ideality is of most interest. So far no measurements of mixing enthalpic properties in this system have been reported in literature. Deviations from the ideal system properties can be used to estimate mainly the type of interaction between the initial components.

In the present study the enthalpic properties of liquids in $\text{KF-K}_2\text{TaF}_7$ system are determined as a function of composition and temperature. The obtained results are compared with studies of physical-chemical properties and spectroscopic investigations with the aim to improve the consistency between these properties, phase equilibria and ionic composition of the melt in this system.

2. Experimental

2.1. Samples preparation

The samples of mixtures were prepared from 99.5 wt% pure K_2TaF_7 obtained from the Institute of Chemistry and Technology of Rare Elements and Minerals, Russian Academy of Sciences, Apatity, Russia and analytical grade KF. The X-ray powder diffraction pattern of the

available K_2TaF_7 is in good agreement with that in PDF-2 database. No foreign diffractions were observed. The IR absorption band near 900 cm^{-1} , typical for Ta–O bond, was also not identified. This indicated absence of oxofluorotantalates in the sample. K_2TaF_7 was dried in the presence of P_2O_5 under reduced pressure at 393 K for 24 h. The analytical grade $\text{KF}\cdot 2\text{H}_2\text{O}$ (Fluka) was vacuum-dried for 100 h at 473 K in the presence of P_2O_5 . The dried substances were kept under dry nitrogen in a glove box, where all further manipulations were carried out.

2.2. Enthalpy measurements

The calorimetric experiments were performed with samples in sealed Pt 90% Rh 10% containers (10 mm diameter, 15 mm high, 0.2 mm thick sheet). The substances were loaded into the containers in a glove box through a small hole drilled in the welded lid. The hole was then closed by soldering with gold. The final weight of the mixture was about 1 g and both components were weighed to 0.001 g accuracy. The weight of the containers with the sample was about 3.8 g. In order to confirm the airtightness of the containers and to premelt the samples the containers were heated for 3 h at 1173 K and the weight change was measured. Since no weight losses were observed due to evaporation of the samples, it was confirmed that the containers were airtight. The tightness of the crucibles was checked again by weighing after each calorimetric experiment.

The molar enthalpy increments $H_{\text{rel}} = H(T) - H(298\text{ K})$ have been measured with an isoperibolic high temperature drop calorimeter. The apparatus and the measuring procedure were described in detail earlier [11,12]. The typical measured enthalpy with this equipment is 1–4 kJ, the typical relative error of a single measurement is about 0.3%.

3. Results

The enthalpy increments of melts in the system $\text{KF-K}_2\text{TaF}_7$ with mole fractions of K_2TaF_7 0.2, 0.4, 0.5, 0.6, and 0.8 were measured at temperatures between 298 K and 1063 K, 1103 K and 1143 K. The chosen temperature range was limited by primary crystallization of solid phases at low temperatures and increasing experimental difficulties in handling of the extremely corrosive and volatile melt at higher temperatures. The arithmetic means of 3 or 4 repeated measurements are summarized in Table 1. The data for KF are from [13], the enthalpy of K_2TaF_7 melt was taken from [14]. The results

published in [14] were based on measurements with the same equipment and at the same conditions as the data in the present work. The standard errors of the arithmetic means estimated considering Student's coefficient are 1.0-2.2 kJ mol⁻¹.

Table 1. Molar relative enthalpy of melts.

x(K ₂ TaF ₇)	H _{rel} / (kJ mol ⁻¹)		
	1063 K	1103 K	1143 K
0	69.2*	72.0*	74.9*
0.2	104.6	109.3	114.5
0.4	138.6	146.1	152.8
0.5	155.5	163.9	172.5
0.6	172.1	181.6	191.0
0.8	208.7	220.7	231.6
1.0	251.2**	264.2**	276.5**

* [13]

** [14], Eq. 3

The molar enthalpy increments were fitted to polynomial expressions as follows:

$$H_{rel}(1063 \text{ K}) / (\text{kJ mol}^{-1}) = (70.4 \pm 1.6) + (159.7 \pm 7.1)x + (19.7 \pm 6.7)x^2$$

$$1.0 \leq \sigma(H_{rel}) \leq 1.6 \text{ kJ mol}^{-1} \quad (1)$$

$$H_{rel}(1103 \text{ K}) / (\text{kJ mol}^{-1}) = (73.0 \pm 1.4) + (172.5 \pm 5.9)x + (17.6 \pm 5.6)x^2$$

$$0.8 \leq \sigma(H_{rel}) \leq 1.4 \text{ kJ mol}^{-1} \quad (2)$$

$$H_{rel}(1143 \text{ K}) / (\text{kJ mol}^{-1}) = (75.8 \pm 1.2) + (184.8 \pm 5.4)x + (14.8 \pm 5.1)x^2$$

$$0.7 \leq \sigma(H_{rel}) \leq 1.3 \text{ kJ mol}^{-1}, \quad (3)$$

where x is mole fraction of K₂TaF₇. The regression coefficients in these equations are given in parentheses along with their standard deviations. The standard deviations of H_{rel} , $\sigma(H_{rel})$, were calculated using variances and covariances of coefficients by the error propagation law. They depend on the composition of the melt and may thus be calculated for arbitrary composition of the melt, including pure components KF and K₂TaF₇. This was employed later by evaluation of uncertainties of the enthalpy of mixing. The variation of the enthalpy with composition is presented in Fig. 1.

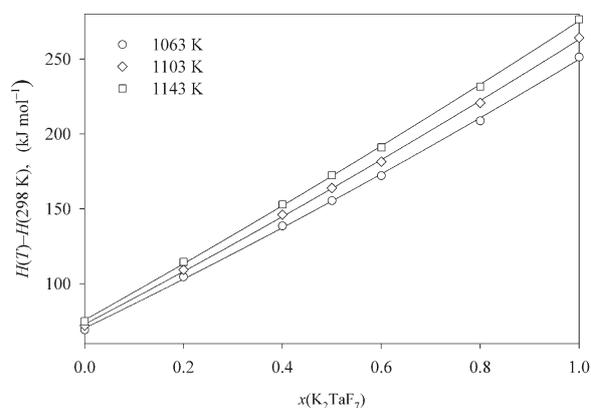


Figure 1. Composition dependences of the relative enthalpy of melt in the system KF–K₂TaF₇. Curves represent Eqs. 1, 2 and 3.

The variation of the enthalpy with composition is presented in Fig. 1. The straight line fits of the measured enthalpy data *versus* temperature are shown in Fig. 2. The molar heat capacities of melts, obtained from the first derivatives of the straight line fits of the measured enthalpy data with respect to temperature are presented in Fig. 3. The evaluated C_p data, show asymmetric positive deviation from additivity, represented by the dashed line in Fig. 3.

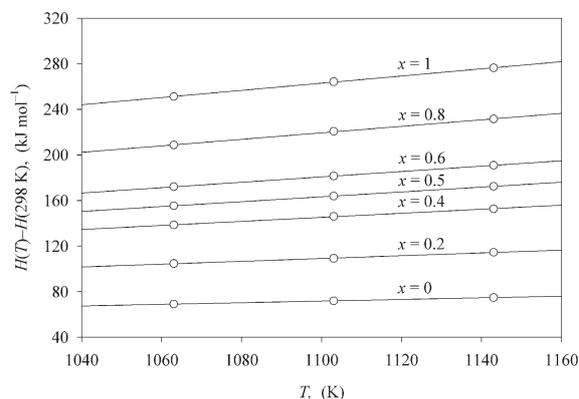


Figure 2. Temperature dependences of the relative enthalpy of melts in the system KF–K₂TaF₇. x are mole fractions of K₂TaF₇.

Integrated temperature and composition dependence of the relative enthalpy were obtained by multiple least squares regression analysis of the measured enthalpy data:

$$H_{rel} / (\text{kJ mol}^{-1}) = (6.625 \times 10^{-2} \pm 6.5 \times 10^{-4}) T / \text{K} - (109 \pm 17)x + (0.255 \pm 1.6 \times 10^{-2}) x T / \text{K} + (1.57 \times 10^{-2} \pm 2.7 \times 10^{-3}) x^2 T / \text{K} \quad (4)$$

where x is mole fraction of K₂TaF₇.

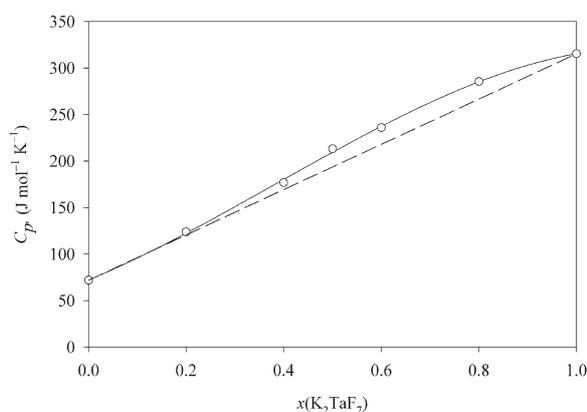


Figure 3. Molar heat capacity of the melt in the system KF–K₂TaF₇. The dashed line represents additivity.

For calculation of the molar enthalpy of mixing, the measured enthalpies of melted mixtures, enthalpies of liquid KF from [13] and enthalpies of the K₂TaF₇ melt from [14] have been used. In [14] the function for enthalpy of K₂TaF₇ melt was obtained evaluating the data from the temperature region above 1051 K, where homogeneous liquid is present, regardless of the mechanism of melting of this substance. The enthalpies of undercooled melt of KF at 1063 K and 1103 K were obtained by extrapolation. The uncertainties of the enthalpies of mixing were evaluated using standard deviations of enthalpies of melted mixtures and pure component melts. These quantities were determined using standard deviations of the molar relative enthalpy calculated by the use of equations (1-3), as mentioned above. The analysis shows that $\sigma(\Delta_{\text{mix}}H)$ of individual $\Delta_{\text{mix}}H$ data points changes from 1.4 to 1.6 kJ mol⁻¹ at all temperatures. The evaluated enthalpies of mixing are plotted in Fig. 4, with standard deviations, $\sigma(\Delta_{\text{mix}}H)$, as error bars. Due to rather small values of the enthalpy of mixing its relative errors are quite large (26% at 1063 K, 22% at 1103 K and 25% at 1143 K). Nevertheless, the negative deviation from ideality, as shown in Fig. 4, is significant and the investigated melts show distinctly nonideal behavior.

For analytical expression of the composition dependence of the enthalpy of mixing the equation

$$\Delta_{\text{mix}}H / (\text{kJ mol}^{-1}) = ax(1-x)^2 + bx^2(1-x) \quad (5)$$

was chosen. The regression coefficients with standard deviations, obtained by the least squares fits of the enthalpy of mixing values by the use of Eq. 5 are summarized in Table 2. Eq. 5 is represented by curves in Fig. 4.

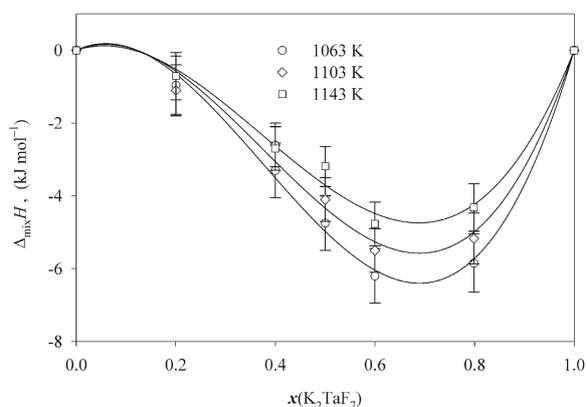


Figure 4. Enthalpy of mixing of melt in the system KF–K₂TaF₇. Error bars are $\sigma(\Delta_{\text{mix}}H)$ values.

Table 2. Regression coefficients and their standard deviations for Eq. 5.

T / K	a	$\sigma(a)$	b	$\sigma(b)$
1063	6.4	1.5	-46.2	1.5
1103	5.6	2.5	-40.3	2.5
1143	4.5	2.0	-34.1	1.9

The combined temperature and composition dependence of the mixing enthalpy was obtained by multiple least squares regression analysis of the evaluated mixing enthalpy data applying the equation as follows:

$$\Delta_{\text{mix}}H / (\text{kJ mol}^{-1}) = \left(a_1 + a_2 \frac{T}{K}\right)x(1-x)^2 + \left(b_1 + b_2 \frac{T}{K}\right)x^2(1-x) \quad (6)$$

The adjusted parameters a_1 , a_2 , b_1 and b_2 are summarized in Table 3.

Table 3. Regression coefficients and their standard deviations for Eq. 6.

Coefficient	a_1	a_2	b_1	b_2
Value	33	-2.5×10^{-2}	-208	1.52×10^{-1}
Standard deviation	37	3.3×10^{-2}	37	3.3×10^{-2}

Considering two parameter Margules type model for excess Gibbs energy of mixing and assuming regular behavior of the melt, activity coefficients have been calculated using relations

$$\begin{aligned} \ln \gamma_1 &= \frac{1}{RT} x_2^2 [a + 2x_1(b-a)] \\ \ln \gamma_2 &= \frac{1}{RT} x_1^2 [b + 2x_1(a-b)] \end{aligned} \quad (7)$$

where x_1 and x_2 are mole fractions of K₂TaF₇ and KF, respectively. The resulting activities of components are shown in Fig. 5.

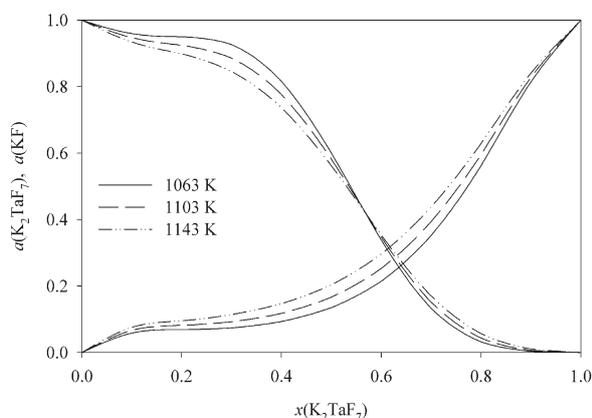


Figure 5. Activities of components in the melt of the system KF–K₂TaF₇.

4. Discussion

Analysis of published phase diagrams with congruently melting compound K₃TaF₈ leads to the conclusion that in fluoride melts tantalum should be present, at least partially, in the form of complex anions TaF₈³⁻ which are, in analogy with Na₃TaF₈, expected to be present in the structure of the solid phase. The conclusions from physical-chemical properties and spectroscopic investigations are less unambiguous. Several property-composition relations for various properties have been reported. Agulyansky *et al.* [15] reported density measurements in the KF–K₂TaF₇ system. The derived composition dependence of the molar volume at 1073 K was linear, with no specific points in the whole composition range which lead these authors to the conclusion that the formation of the TaF₈³⁻ complex by additive interaction between TaF₇²⁻ and F⁻ seemed to be unlikely. The analysis of the data of the parent system KF–TaF₅ by these authors showed that the dissociation scheme



was most probable. This model of the melt structure did not contradict the conductivity data obtained by the same authors [16].

The results of IR reflection spectroscopy [17,18] on the FLINAK melts with up to 0.1 mole fraction of TaF₅ showed the presence of TaF₇²⁻ complexes. Similar results were obtained by IR emission spectroscopy [19]. IR spectra of molten K₂TaF₇ without addition of KF or KF–K₂TaF₇ melts containing up to 0.9 mole fraction of KF showed bands assigned to TaF₇²⁻ and TaF₆⁻ complex ions [20]. No bands were assigned to TaF₈³⁻ anions in the melts. IR and Raman spectra of the crystalline Na₃TaF₈ were reported in [21].

Recently the density measurements of the KF–K₂TaF₇ system melts were reported by Boča *et al.* [22]. The results showed small but distinct negative deviation in excess molar volume of up to 4% from the additive value at 1223 K. This volume contraction was attributed to the formation of TaF₈³⁻ complexes by interaction of the components in the melt. With increasing temperature the minimum of the molar volume of mixing curve shifts to the K₂TaF₇ richer side of the system. Cibulková *et al.* [23] published the density data for FLINAK(eut)–K₂TaF₇ system at 937 K measured by hydrostatic weighing in the composition interval up to 0.15 mole fraction of K₂TaF₇ which also showed positive deviation from additivity, thus volume contraction at mixing.

The negative deviation of the enthalpy of mixing from ideality observed in the present study indicates a tendency for compound formation in the solution. It may be attributed to the additive interaction of TaF₇²⁻ with F⁻ anions. The formation of the TaF₈³⁻ complexes according to the reaction



seems to be probable. Although we were not able to prove the presence of K₃TaF₈ by X-ray diffraction in the solidified melts, because the diffraction data were not available in the PDF-2 database, we observed the presence of new diffraction peaks, which we could not identify and we supposed that they belonged to K₃TaF₈. The contribution of this process to the enthalpy of mixing is, however, limited by the dissociation of the TaF₈³⁻ anion. The dissociation degree of K₃TaF₈ calculated along the liquidus curves of K₃TaF₈ using thermodynamic data in the KF–K₂TaF₇ system reaches up to 0.69 [24]. With increasing temperature the dissociation degree increases and the influence of the Reaction 9 on thermal effect of mixing decreases. This is in agreement with observed decrease of the mixing enthalpy with increasing temperature. Another factor which may influence the enthalpy of mixing substantially is the enthalpy of formation of the reaction products and its temperature dependence. As expected, due to the fact that only weak bounded additive species with strong tendency to dissociation are produced, the corresponding thermal effect is small. As a result, the energetic effect of the mixing is low.

The curves of enthalpy of mixing are not symmetrical. Minima are shifted to the K₂TaF₇ side. As a result, the energetic effect of the mixing is low. The curves of enthalpy of mixing are not symmetrical. Minima are shifted to the K₂TaF₇ rich side of the system and located near composition of about $x(\text{K}_2\text{TaF}_7) = 0.7$. This indicates that ionic composition of the melt is more

complicated than that represented by the Reaction 9. Complexes with higher molar ratio of tantalum to fluorine with respect to TaF_8^{3-} and TaF_7^{2-} may also be created in the melt. In accord with some spectroscopic investigations [1,25] the formation of TaF_6^- depending on the amount of the KF in the system and the temperature may be expected.

5. Conclusions

The calorimetric study on melts in $\text{KF-K}_2\text{TaF}_7$ system at constant temperatures 1063, 1103 and 1143 K has shown that the variation of the molar relative enthalpy with composition is slightly nonlinear. In the considered temperature interval the enthalpy of mixing shows negative deviation from ideality and decreases with increasing temperature. Maximum mixing effect is located at the mole fraction of K_2TaF_7 close to 0.7. The negative deviation in the studied system may be explained with a tendency to clustering or compound formation at mixing. The formation of TaF_8^{3-} anions

may be responsible for this nonideality. The assumption on the additive interaction of TaF_7^{2-} with F^- anions is supported by the observed positive deviation of the heat capacity of the melt from the additivity. Similarly as by the mixing enthalpy the asymmetry of the composition dependence is obvious. This is in agreement with conclusions of density, measurements as reported in [22,23] and phase equilibria analyses, but not supported by spectroscopic investigations. The shifting of the strong interaction to the K_2TaF_7 richer side of the system shows that except association processes resulting in formation of the TaF_8^{3-} anions in this system also other processes take place. In accord with some spectroscopic studies [1,25] formation of TaF_6^- anions may be assumed.

Acknowledgements

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