

Volume properties of the melts of the system KF—KCl—K₂TiF₆

V. DANĚK, J. ŠIŠKA, and K. MATIAŠOVSKÝ

*Institute of Inorganic Chemistry, Centre for Chemical Research,
Slovak Academy of Sciences, CS-842 36 Bratislava*

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Using the Archimedean method the density of the KF—KCl—K₂TiF₆ melts was measured. The experimentally determined dependences of the density of the investigated melts on the temperature were described by the linear plots $\rho = a - b \cdot T$. On the basis of the determined density values and of the mean molar mass, the values of the molar volumes and of the excess molar volumes at temperatures of 1000 K, 1100 K, and 1200 K were calculated. In the boundary systems KF—K₂TiF₆ and KCl—K₂TiF₆ the congruently melting compounds K₃TiF₇ and K₃TiF₆Cl, respectively, are formed. The arising compounds do not substantially affect the volume properties of the investigated system, which indicates the expressive thermal dissociation of these compounds and/or the similarity in the volumes of the complex TiF₆²⁻, TiF₇³⁻, and TiF₆Cl³⁻ anions. The experimentally determined values of the density of the boundary binary systems KF—K₂TiF₆ and KCl—K₂TiF₆ were used for the calculation of the dissociation degree of the K₃TiF₇ and K₃TiF₆Cl compounds.

Используя метод Архимеда, измерена плотность расплавов KF—KCl—K₂TiF₆. Экспериментально установленные зависимости плотности изучаемых расплавов от температуры описываются линейным соотношением $\rho = a - b \cdot T$. Исходя из определенных величин плотности и средней молярной массы, были рассчитаны значения молярных объемов и избыточных молярных объемов при температурах 1000 К, 1100 К и 1200 К. В граничных системах KF—K₂TiF₆ и KCl—K₂TiF₆ образовывались конгруэнтно плавящиеся соединения состава K₃TiF₇ и K₃TiF₆Cl, соответственно. Возникающие соединения не оказывали существенного влияния на объемные свойства изучаемой системы, что свидетельствует о значительной термической диссоциации этих соединений и/или о схожести объемов комплексных анионов TiF₆²⁻, TiF₇³⁻ и TiF₆Cl³⁻. Экспериментально определенные величины плотностей граничных бинарных систем KF—K₂TiF₆ и KCl—K₂TiF₆ были использованы для расчета степени диссоциации соединений K₃TiF₇ и K₃TiF₆Cl.

The melts of the KF—KCl—K₂TiF₆ system are promising not only as electrolytes for the deposition of titanium, but along with the KBF₄ component they may be utilized as electrolytes for the electrochemical synthesis of TiB₂,

especially in regard of obtaining the TiB_2 coatings on the metal bases. The study of the volume properties of the $\text{KF—KCl—K}_2\text{TiF}_6$ melts is the first part of the complex investigation of the physicochemical properties of the melts of the quaternary $\text{KF—KCl—K}_2\text{TiF}_6\text{—KBF}_4$ system.

The phase diagram of the $\text{KF—KCl—K}_2\text{TiF}_6$ system has been studied by *Chernov* and *Ermolenko* [1]. According to their results, as well as the results in [2,3] where the phase equilibria of the boundary binary $\text{KF—K}_2\text{TiF}_6$ and $\text{KCl—K}_2\text{TiF}_6$ systems were studied, two congruently melting compounds K_3TiF_7 and $\text{K}_3\text{TiF}_6\text{Cl}$ are formed in the given system. The phase diagram of the $\text{KF—KCl—K}_2\text{TiF}_6$ system according to *Chernov* and *Ermolenko* [1] is shown in Fig. 1. The authors [1] pointed out that according to the results of the chemical analysis of the frozen melts, the system is thermally stable and the titanium loss after long-term melting does not exceed 0.5%. From the phase diagram of the system under investigation it follows that the measurement of the density, as well as of the other physicochemical properties, can be realized at temperatures above 700°C , however the electrochemical measurements, which were carried out at low concentration of the depolarizator, can be realized already above 600°C .

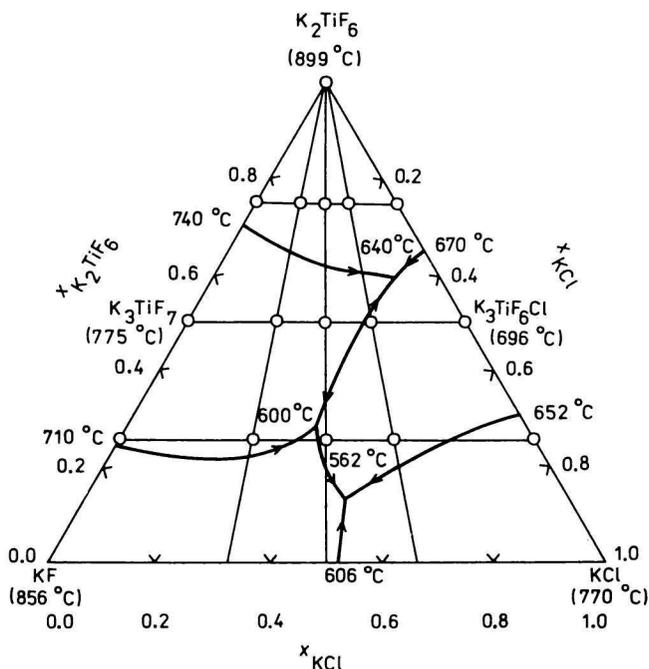


Fig. 1. Phase diagram of the $\text{KF—KCl—K}_2\text{TiF}_6$ system according to *Chernov* and *Ermolenko* [1]. The circles represent figurative points of composition of the melts used by the density measurements.

Experimental

The density measurement of the KF—KCl—K₂TiF₆ melts has been realized using the Archimedean method. As the measuring body the platinum sphere with a diameter of 20 mm was used. The volume of the sphere and its change with temperature was determined by calibration according to the known density values of water and of the NaCl, KCl, and KNO₃ melts. The error of the density measurement was lower than 0.2%. The measurement was realized in the temperature range of *ca.* 100 K starting from the temperature of 20 to 30 K above the temperature of the primary crystallization of the respective melt. In the concentration triangle KF—KCl—K₂TiF₆ the boundary KF—K₂TiF₆ and KCl—K₂TiF₆ systems as well as intersections with the constant ratio of the KF and KCl components $x(\text{KF})/x(\text{KCl}) = 0.5, 1, \text{ and } 2$ were chosen. Within the boundary systems and the given intersections the figurative points with 25, 50, and 75 mole % of K₂TiF₆ were chosen. The figurative points of composition of the investigated melts are represented in Fig. 1. The density values of the KF—KCl melts are taken from the literature [4].

For the preparation of the samples the following reagents were used: KF, KCl, anal. grade (Lachema, Brno), K₂TiF₆, NaCl, KNO₃, anal. grade (Merck).

The experimentally determined dependences of the density of the investigated melts on the temperature were described by the linear equations

$$\rho = a - b \cdot T \quad (1)$$

The values of the constants a and b were calculated by the least-square method and are together with the values of the standard deviations given in Table 1. On the basis of the

Table 1

The values of the regression coefficients in the equation $\rho = a - b \cdot T$ and the standard deviations of the experimental density values for the KF—KCl—K₂TiF₆ melts

$x(\text{KF})$	$x(\text{KCl})$	$x(\text{K}_2\text{TiF}_6)$	a g cm ⁻³	$b \cdot 10^3$ g cm ⁻³ K ⁻¹	$\sigma \cdot 10^4$ g cm ⁻³
0	0	1	2.7715	0.6102	2.2
0.25	0	0.75	2.7326	0.5874	2.1
0.5	0	0.5	2.7073	0.5882	3.9
0.75	0	0.25	2.6911	0.6100	5.4
0	0.25	0.75	2.6988	0.6117	3.1
0	0.5	0.5	2.5909	0.6062	4.8
0	0.75	0.25	2.4839	0.6247	1.9
0.25	0.5	0.25	2.4709	0.5567	1.9
0.167	0.333	0.5	2.6256	0.6031	1.6
0.083	0.167	0.75	2.7051	0.5976	1.4
0.375	0.375	0.25	2.5610	0.6085	3.0
0.25	0.25	0.5	2.6326	0.5878	2.1
0.125	0.125	0.75	2.6718	0.5584	5.0
0.5	0.25	0.25	2.5808	0.5925	2.6
0.333	0.167	0.5	2.6386	0.5702	5.2
0.167	0.083	0.75	2.7056	0.5799	1.5

determined density values and of the mean molar mass of the investigated melts the values of the molar volumes and the excess molar volumes in the studied system at temperatures of 1000 K, 1100 K, and 1200 K were calculated.

Results and discussion

In Fig. 2 the density of the KF—KCl—K₂TiF₆ melts at the temperature 1100 K is shown. It is obvious that the density of the melts is mostly influenced by the KCl component, which strongly decreases the density of the melt. There is no substantial change in the density of the melts in the boundary KF—K₂TiF₆ system. The dotted lines in Fig. 2 represent the isotherm of the primary crystallization of the melts at the temperature 1100 K.

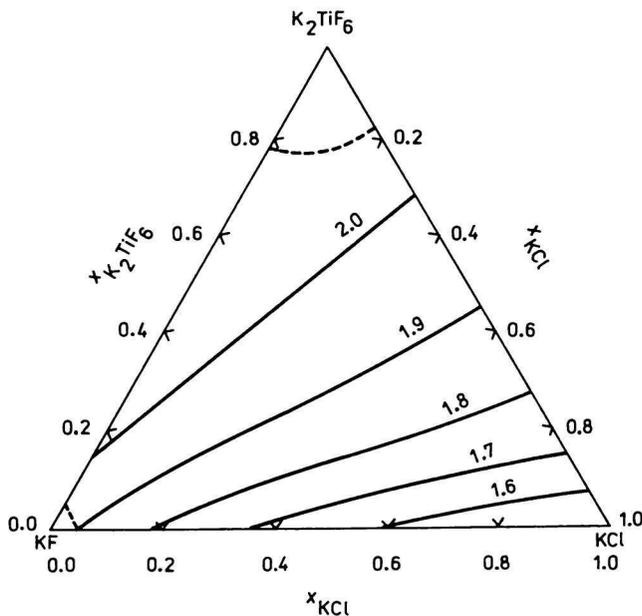


Fig. 2. The density of the KF—KCl—K₂TiF₆ system at the temperature of 1100 K. The dotted lines represent the isotherms of the primary crystallization at temperature of 1100 K.

The molar volumes of the KF—KCl—K₂TiF₆ melts are calculated according to the equation

$$V = \frac{x(\text{KF}) \cdot M(\text{KF}) + x(\text{KCl}) \cdot M(\text{KCl}) + x(\text{K}_2\text{TiF}_6) \cdot M(\text{K}_2\text{TiF}_6)}{\rho} \quad (2)$$

This approach has been chosen because till now there is nothing known concerning the properties of the K₃TiF₇ and K₃TiF₆Cl compounds, especially of the

equilibrium composition of the melt. It was supposed that the formation of both compounds becomes evident at the shape of the molar volume and excess molar volume *vs.* composition plots. For the expression of the deviation from the ideal mixing the values of the excess molar volumes were calculated according to the equation

$$V^E = V - V^{id} = V - [x(\text{KF}) \cdot V^\circ(\text{KF}) + x(\text{KCl}) \cdot V^\circ(\text{KCl}) + x(\text{K}_2\text{TiF}_6) \cdot V^\circ(\text{K}_2\text{TiF}_6)] \quad (3)$$

The dependence of the excess molar volume on the composition was calculated by means of the regression analysis method and the following equation was obtained

$$V^E = a_0 \cdot x(\text{KF}) \cdot x(\text{KCl}) + x(\text{KF}) \cdot x(\text{K}_2\text{TiF}_6)[b_0 + b_1 \cdot x(\text{K}_2\text{TiF}_6)] + x(\text{KCl}) \cdot x(\text{K}_2\text{TiF}_6)[c_0 + c_1 \cdot x(\text{K}_2\text{TiF}_6) + c_2 \cdot x^2(\text{K}_2\text{TiF}_6)] \quad (4)$$

The values of the molar volumes of the pure components, the regression coefficients of the dependences of the excess molar volume on the composition, and the standard deviations of the experimental values from eqn (4) at temperatures 1000 K, 1100 K, and 1200 K are given in Table 2. The standard deviation values are in all cases lower than the experimental error.

In Fig. 3 the excess molar volume of the KF—KCl—K₂TiF₆ melts at the temperature 1100 K is shown. From the values of the excess molar volumes it follows that from the point of view of the volume properties the investigated system shows only small deviations from the ideal behaviour. The maximum deviation is $-1.5 \text{ cm}^3/\text{mol}$, which represents 2.23 % of the molar volume for the respective melt. The formation of the K₃TiF₇ and K₃TiF₆Cl compounds does not affect substantially the volume properties. This indicates that either these compounds dissociate to considerable degree in the melt, or the volumes of the anions TiF₆²⁻, TiF₇³⁻, and TiF₆Cl³⁻, respectively, are fairly similar. However, the formation of both compounds presents differently in the course of the volume properties. This can be best seen on the course of the excess molar volumes in the boundary KF—K₂TiF₆ and KCl—K₂TiF₆ systems (Fig. 4). While the formation of K₃TiF₇ is connected with moderate volume expansion with a maximum at *ca.* 40 mole % K₂TiF₆ the formation of K₃TiF₆Cl is connected with substantially more expressed volume contraction with a maximum at *ca.* 25 mole % K₂TiF₆. This difference is probably coherent with the different stereochemistry of both complex anions and with its relation to the other present anions (F⁻, resp. Cl⁻). From the density values of both compounds ($\rho_{\text{K}_3\text{TiF}_7}^{1100} = 2.060 \text{ g/cm}^3$, $\rho_{\text{K}_3\text{TiF}_6\text{Cl}}^{1100} = 1.924 \text{ g/cm}^3$) it can be concluded that the substitution of fluorine by chlorine in the TiF₇³⁻ complex anion is accompanied with its volume increase,

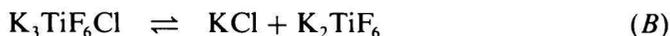
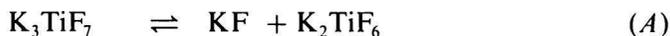
Table 2

The values of the molar volumes of the pure components and the coefficients of the concentration dependence of the excess molar volume of the molten KF—KCl—K₂TiF₆ system. The dimensions of all values are cm³ mol⁻¹

<i>T</i> /K	<i>V</i> ^o (KF)	<i>V</i> ^o (KCl)	<i>V</i> ^o (K ₂ TiF ₆)	<i>a</i> ₀	<i>b</i> ₀	<i>b</i> ₁	<i>c</i> ₀	<i>c</i> ₁	<i>c</i> ₂	<i>σ</i>
1000	28.922	48.048	111.090	0.929	2.477	-2.057	-19.996	62.682	-49.327	0.047
1100	29.956	49.945	114.315	0.763	2.236	-2.956	-21.817	68.506	-54.552	0.047
1200	31.067	51.997	117.731	0.572	1.936	-3.927	-23.847	74.900	-60.264	0.095

which is not compensated by the bigger atomic mass of chlorine with respect to fluorine. The volume change by the substitution of fluorine by chlorine is, however, obviously lower than the difference between the size of the F⁻ and Cl⁻ anions, which leads to the different sign of the excess molar volume.

The experimental density values of the boundary KF—K₂TiF₆ and KCl—K₂TiF₆ melts have been used for the calculation of the dissociation degree of the K₃TiF₇ and K₃TiF₆Cl compounds. It was supposed that the volume of the melt equals to the sum of the partial volumes of the individual coexisting components in equilibrium. The equilibrium composition of components in the melt is given by the value of the equilibrium constant of the reactions



Let us consider an arbitrary mixture of (1 - *x*) mol KF and *x* mol K₂TiF₆. In such a mixture K₃TiF₇ is formed, which partially thermally dissociates according to the scheme (A) with a dissociation degree *α*. The following equation for the equilibrium constant of this reaction can be derived from the mass balance (for *x* < 0.5)

$$K = \frac{x(\text{KF}) \cdot x(\text{K}_2\text{TiF}_6)}{x(\text{K}_3\text{TiF}_7)} = \frac{\alpha(1 - 2x + x \cdot \alpha)}{(1 - \alpha)(1 - x + x \cdot \alpha)} \quad (5)$$

where *x* is the mole fraction of K₂TiF₆ in the original mixture. A similar equation can be derived for *x* > 0.5. Choosing the equilibrium constant and solving eqn (5) for a given dissociation degree *α* the values of the equilibrium mole fraction of individual components KF, K₂TiF₆, and K₃TiF₇ in each mixture of the system KF—K₂TiF₆ can be obtained. The detailed calculation procedure is given in [5]. The density of the melt was then calculated according to the equation

$$\rho = \left[\frac{w(\text{KF})}{\rho(\text{KF})} + \frac{w(\text{K}_2\text{TiF}_6)}{\rho(\text{K}_2\text{TiF}_6)} + \frac{w(\text{K}_3\text{TiF}_7)}{\rho(\text{K}_3\text{TiF}_7)} \right]^{-1} \quad (6)$$

where $w(i)$ are the values of the mass fraction of the individual components i and $\varrho(i)$ are the density values of the pure components, whereby $\varrho(\text{K}_3\text{TiF}_7)$ is the hypothetical density of the molten undissociated compound K_3TiF_7 at the considered temperature. For each value of the equilibrium constant and the

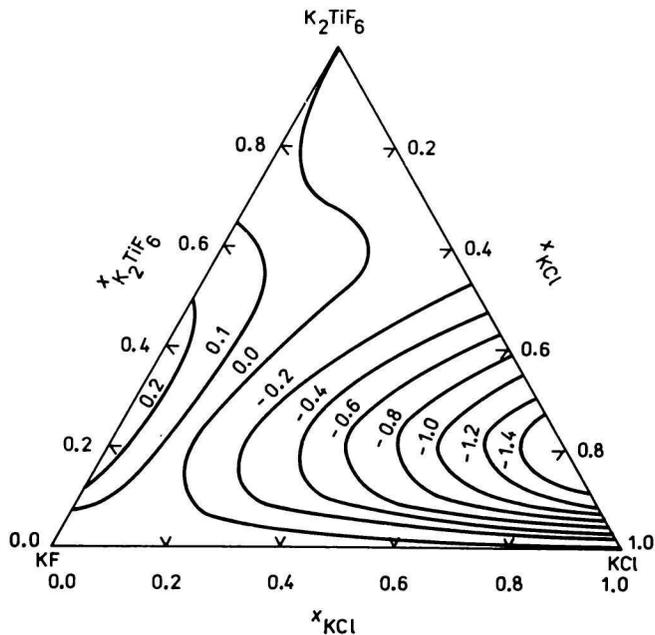


Fig. 3. The excess molar volume of the KF—KCl—K₂TiF₆ melts at the temperature of 1100 K.

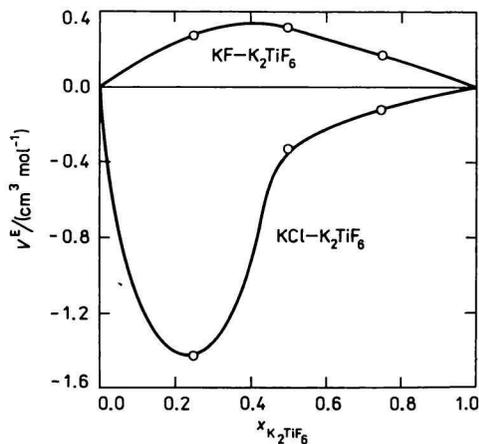


Fig. 4. The excess molar volume of the KF—K₂TiF₆ and KCl—K₂TiF₆ systems at the temperature of 1100 K.

hypothetical density of the molten undissociated compound a set of theoretical density values for chosen original compositions was obtained. The choice of the right value of the equilibrium constant must obey the condition

$$\sum_{i=1}^n (\varrho_{\text{exp}}^{(i)} - \varrho_{\text{calc}}^{(i)})^2 = \min \quad (7)$$

Table 3

The values of the equilibrium dissociation constants, the dissociation degrees, and the density of undissociated compounds K_3TiF_7 and $\text{K}_3\text{TiF}_6\text{Cl}$

Compound	T/K	K_{dis}	α	$\frac{\varrho}{\text{g cm}^{-3}}$
K_3TiF_7	1000	0.57	0.60	2.105
	1100	0.90	0.70	2.045
	1200	1.63	0.79	1.985
$\text{K}_3\text{TiF}_6\text{Cl}$	1000	1.10	0.71	2.050
	1100	1.90	0.81	2.025
	1200	2.80	0.88	2.000

Similar approach was taken in the case of the $\text{KCl}-\text{K}_2\text{TiF}_6$ system. In Table 3 the calculated values of the equilibrium constant, the dissociation degree, and the density of the molten undissociated compounds K_3TiF_7 and $\text{K}_3\text{TiF}_6\text{Cl}$ at temperatures 1000 K, 1100 K, and 1200 K are given. As follows from the values of the dissociation degree both compounds undergo at melting relatively marked thermal dissociation, whereby the thermal stability of the $\text{K}_3\text{TiF}_6\text{Cl}$ compound is lower than that of the K_3TiF_7 . This is obviously the consequence of the lower energy of the Ti—Cl bond in the coordination polyhedron of $\text{TiF}_6\text{Cl}^{3-}$ anion compared with the Ti—F ones. From the plot of the equilibrium dissociation constant *vs.* temperature the values of the dissociation enthalpy of both compounds $\Delta H_{\text{dis}}^\circ(\text{K}_3\text{TiF}_7) = 52.4 \text{ kJ/mol}$ and $\Delta H_{\text{dis}}^\circ(\text{K}_3\text{TiF}_6\text{Cl}) = 46.6 \text{ kJ/mol}$ were calculated. From the calculated values it follows that the part of the dissociation enthalpy in the whole enthalpy of fusion will be appreciable there and that the dissociation degree depends mainly on the temperature. With decreasing temperature the stability of the K_3TiF_7 and $\text{K}_3\text{TiF}_6\text{Cl}$ compounds in the melt increases as well as their concentration in the melt at the same original content of K_2TiF_6 . This fact is important for the application of those melts of the $\text{KX}-\text{K}_2\text{TiF}_6$ ($\text{X} = \text{F}, \text{Cl}$) type for the electrochemical deposition of titanium. It may also affect the interpretation of the electrochemical reactions in the above-mentioned melts.

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