

Thermodynamic Equilibrium between Melt and Crystalline Phase of a Compound A_qB_r with Dystectic Melting Point

III. Application to the Systems $KF-K_3TiF_7$ and $KCl-K_3TiF_6Cl$

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Received 5 September 2000

The special form of the LeChatelier—Shreder equation describing the equilibrium between crystalline phase and melt in the system $A-AB$ when substance AB partially dissociates upon melting was applied in the systems $KF-K_3TiF_7$ and $KCl-K_3TiF_6Cl$. Because all the three characteristic parameters, *i.e.* the dissociation degree of the dystectic melting binary compounds, their enthalpy of fusion, and their phase diagrams, were determined experimentally, the LeChatelier—Shreder equation was used in order to determine the thermodynamic consistency of these quantities and thus also their reliability.

Using two known phase diagrams of the system $KF-K_3TiF_7$ and the measured enthalpy of fusion of K_3TiF_7 the value of the dissociation degree of K_3TiF_7 was calculated. The value 0.720 was calculated on the basis of the phase diagram measured by Chernov *et al.* while the value 0.404 resulted from that measured by Chrenková *et al.* The experimentally determined values are 0.65 or 0.67.

From the same phase diagrams and the measured values of the dissociation degree the enthalpy of fusion of K_3TiF_7 was calculated. The value 62 446 J mol⁻¹ was obtained using the dissociation degree 0.65, while the value 60 623 J mol⁻¹ corresponds to the dissociation degree 0.67. The calorimetrically measured value is (57 000 ± 2000) J mol⁻¹.

Using the lowest measured eutectic temperature in known phase diagrams of the system $KCl-K_3TiF_6Cl$ (925 K) and the calorimetrically determined enthalpy of fusion of K_3TiF_6Cl , the composition of the eutectic point $x_{eut}(K_2TiF_6) = 0.314$ was calculated, while the measured values are 0.250, 0.297, and 0.307.

The LeChatelier—Shreder equation describing the equilibrium between the crystalline phase and melt in the system $A-A_qB_r$ when the substance A_qB_r partially dissociates upon melting, was derived in [1] without assuming any hypothetical equilibrium states and without the occurrence of any hypothetical thermodynamic quantities. To fit both the phase and the chemical equilibrium in the system $A-A_qB_r$, an original method for the calculation of the dissociation enthalpy, the heat of fusion at dystectic temperature of fusion, and the degree of dissociation of the compound A_qB_r in the melt was proposed. The application of this new method to the systems $KF-K_2MoO_4$ and $KF-K_2WO_4$, in which the additive compounds K_3FMO_4 and K_3FWO_4 , respectively, are formed, was presented in [2]. In the present paper the proposed method was applied to the systems $KF-K_3TiF_7$ and $KCl-K_3TiF_6Cl$, which are subsystems of the binary systems $KF-K_2TiF_6$ and $KCl-K_2TiF_6$, in which the additive compounds K_3TiF_7 and K_3TiF_6Cl , respectively, are formed. In this particular case $q = r = 1$.

The thermodynamic analysis of the systems $KF-$

K_3TiF_7 and $KCl-K_3TiF_6Cl$, in which the components K_3TiF_7 and K_3TiF_6Cl exhibit dystectic melting, is based on relations derived in [1]. Similarly as in our previous work, all considerations made in this work are based on the assumption that in any liquid phase of the considered system there is a permanent chemical equilibrium in the reaction



However, in the system there are not three components, but according to the Gibbs phase law only two. The weighted-in substances A and AB are thus components and the present substances at equilibrium, A , B , AB , are called constituents. In order to distinguish between them the components will be in the subsequent text denoted as bold characters, the constituents of the quasi-ternary system as plain ones.

The equilibrium phase coexistence in the system $A-AB$ is described by the special form of the LeChatelier—Shreder equation, which can be expressed at the conditions $dp = 0$, $\Delta_{fus}C_p(AB) = \text{const.}$, and $\Delta_{dis}C_{p,(A),+} = 0$ and inserting all rear-

rangements and simplifications described in [2] in the form (see eqn (21) in [2])

$$\begin{aligned} \ln \frac{x(\text{AB}, T)}{x_+(\text{AB}, T)} &= \\ &= [\Delta_{\text{fus,exp}} H(\text{AB}, T_{\text{fus}}) - T_{\text{fus}}(\Delta_{\text{fus}} C_p(\text{AB}) + \\ &+ \Delta_{\text{dis}} H_{(A),+} \delta_{(A)})] / [RT \cdot T_{\text{fus}} (T - T_{\text{fus}})^{-1}] + \\ &+ \frac{\Delta_{\text{fus}} C_p(\text{AB}) + \Delta_{\text{dis}} H_{(A),+} \delta_{(A)}}{R} \int_{T_{\text{fus}}(\text{AB})}^T d \ln T + \\ &+ \text{cor}_{\text{tot}} \end{aligned} \quad (1)$$

The function Ψ is then introduced having the form

$$\Psi = \frac{T T_{\text{fus}}(\text{AB})}{T - T_{\text{fus}}(\text{AB})} \ln \frac{x(\text{AB}, T)}{x_+(\text{AB}, T)} \quad (2)$$

For limiting values of Ψ and its derivative the following relations, consistent with eqn (1), are then valid

$$\lim_{\substack{x_w \rightarrow 1 \\ T \rightarrow T_{\text{fus}}}} \Psi = \frac{\Delta_{\text{fus,exp}} H(\text{AB}, T_{\text{fus}})}{R} = \text{const.} \quad (3)$$

$$\lim_{\substack{x_w \rightarrow 1 \\ T \rightarrow T_{\text{fus}}}} \frac{d\Psi}{dx_w} = 0 \quad (4)$$

For the equilibrium mole fractions of individual constituents the following relations, obtained by means of the weighted-in equilibrium mole fraction, x_w , and the dissociation degree of reaction (A), $\alpha_{(A)}$, are valid

$$x(\text{AB}) = \frac{(1 - \alpha_{(A)}(T))x_w}{x_w \alpha_{(A)}(T) + 1} \quad (5)$$

$$x(\text{A}) = \frac{1 - (1 - \alpha_{(A)}(T))x_w}{x_w \alpha_{(A)}(T) + 1} \quad (6)$$

$$x(\text{B}) = \frac{x_w \alpha_{(A)}(T)}{x_w \alpha_{(A)}(T) + 1} \quad (7)$$

For the equilibrium constant of reaction (A) we then get

$$K_{(A),x} = \frac{x(\text{A}) \cdot x(\text{B})}{x(\text{AB})} = \frac{x_+(\text{A}) \cdot x_+(\text{B})}{x_+(\text{AB})} = K_{(A),x,+} \quad (8)$$

where $K_{(A),x}$ and $K_{(A),x,+}$ are the equilibrium constants in the melt of the composition x_w and in the molten pure **AB**, respectively. For ideal solutions eqn (8) holds exactly, its use for real solutions requires corrections totally summarized in cor_{tot} . From eqn (8) it follows that $\alpha_{(A)}$ depends on $\alpha_{(A),+}$. However, with regard to the relatively narrow temperature interval used in the calculation, the temperature dependence of $\Delta_{\text{fus}} H(\text{AB})$ and $\Delta_{\text{dis}} H_{(A)}$ was not taken into account (*i.e.* $\Delta_{\text{fus}} C_p(\text{AB}) = 0$, $\Delta_{\text{dis}} C_p(\text{A}),+ = 0$).

Eqn (1) describes quantitatively the relation between three thermodynamic parameters of **AB**: $\alpha_{(A),+}(T_{\text{fus}}(\text{AB}))$, $\Delta_{\text{fus,exp}} H(\text{AB}, T_{\text{fus}}(\text{AB}))$, and the liquidus curve of **AB**. When two of these characteristic parameters are known it is possible to use eqn (1) to calculate the third one. When all three parameters are measured, eqn (1) can be used to prove their thermodynamic consistency.

RESULTS AND DISCUSSION

1. System **KF—K₃TiF₇**

All three of the above thermodynamic characteristics are known for this system. On the basis of the measured dependence of density of melts of this system on composition the following values of the dissociation degree of **K₃TiF₇** were calculated: $\alpha_{+,1000 \text{ K}}(\text{K}_3\text{TiF}_7) = 0.60$, $\alpha_{+,1100 \text{ K}}(\text{K}_3\text{TiF}_7) = 0.70$, $\alpha_{+,1200 \text{ K}}(\text{K}_3\text{TiF}_7) = 0.79$ [3]. Using the high-temperature calorimetry, the enthalpy of fusion of **K₃TiF₇**, $\Delta_{\text{fus,exp}} H(\text{K}_3\text{TiF}_7, T_{\text{fus}}) = (57 \pm 2) \text{ kJ mol}^{-1}$, was measured in [4].

The phase equilibrium in the system **KF—K₃TiF₇** was examined in [5–7]. The theoretical course of the liquidus curves using the hypothetical temperature of fusion of the nondissociated **K₃TiF₇**, 1382 K, was calculated in [6]. In [7] the experimentally determined phase diagram of this system was corrected using the regression dependence of $\Delta_{\text{mix}} G^{\text{Ex}}$ on composition of the ternary system **KF—KBF₄—K₂TiF₆**.

1.1. Comparison of the Measured and Calculated Liquidus Curve of **K₃TiF₇**

In the calculation according to eqn (1) the ideal behaviour of the melts was assumed (*i.e.* $\text{cor}_{\text{tot}} = 0$). $\Delta_{\text{dis}} H_{(A),+}$ was calculated in two ways.

a) Using the regression function

$$\ln K_{(A),+}(T_i) = -\frac{\Delta_{\text{dis}} H_{(A),+}}{R} \cdot \frac{1}{T_i} + q \quad (9)$$

and the dissociation degree $\alpha_{(A),+}$ taken from [3] the value of the dissociation enthalpy $\Delta_{\text{dis}} H_{(A),+} = 53\,826 \text{ J mol}^{-1}$ was obtained.

In a narrow temperature interval and using eqns (9) and (10) the following empirical linear equation was derived for $\alpha_{(A),+}$

$$\alpha_{(A),+,a}(T_i) = \alpha_{(A),+,a}(T_{\text{fus}}(\text{K}_3\text{TiF}_7)) + \delta_{(A),a}(T_i - T_{\text{fus}}(\text{K}_3\text{TiF}_7)) \quad (10)$$

where $\alpha_{(A),+}(T_{\text{fus}}(\text{K}_3\text{TiF}_7)) = 0.65$ and $\delta_{(A),a} = 0.00118 \text{ K}^{-1}$.

b) Inserting the molar enthalpy of mixing of molten **KF** and **K₂TiF₆** in the equimolar ratio at 1200 K

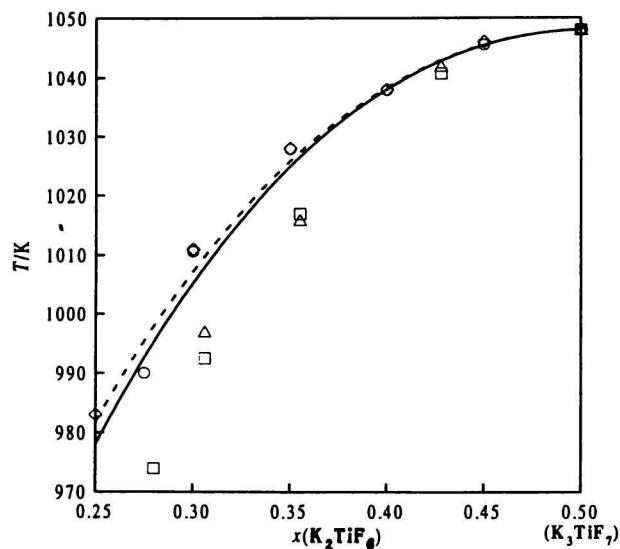


Fig. 1. Experimentally determined and calculated liquidus curve of K_3TiF_7 in the system $\text{KF}-\text{K}_3\text{TiF}_7$. — Calculated according to the procedure given in 1.1.a), - - - calculated according to the procedure given in 1.1.b), O calculated in [6], □ calculated in [7], ◇ measured in [6], Δ measured in [7].

($\Delta_{\text{mix}}H(x=0.5) = -4900 \text{ J mol}^{-1}$ [4]) and the dissociation degree $\alpha_{(A),+}$ [3] into the relation

$$0.5(1 - \alpha_{(A),+})\Delta_{\text{dis}}H_{(A),+} = 4900 \text{ J mol}^{-1} \quad (11)$$

we get for the dissociation enthalpy of K_3TiF_7 the value $\Delta_{\text{dis}}H_{(A),+,b} = 46\,015 \text{ J mol}^{-1}$.

Similarly as in paragraph a), for the temperature dependence of $\alpha_{(A),+}$ the empirical linear equation was derived using eqn (9)

$$\alpha_{(A),+,b}(T_i) = \alpha_{(A),+,b}(T_{\text{fus}}(\text{K}_3\text{TiF}_7)) + \delta_{(A),b}(T_i - T_{\text{fus}}(\text{K}_3\text{TiF}_7)) \quad (12)$$

where $\alpha_{(A),+,b}(T_{\text{fus}}(\text{K}_3\text{TiF}_7)) = 0.67$ and $\delta_{(A),b} = 0.000996 \text{ K}^{-1}$. The comparison of experimental and calculated results is shown in Fig. 1.

1.2. Calculation of $\alpha_{(A),+}$ Using the Phase Diagram of the System $\text{KF}-\text{K}_3\text{TiF}_7$ and the Measured Enthalpy of Fusion of K_3TiF_7

The dissociation degree $\alpha_{(A),+}$ was calculated using eqn (1). The function ψ (eqn (2)) was determined for three equilibrium values of T_i taken from [5–7] for sufficiently large temperature difference ($T_i - T_{\text{fus}}$). With regard to the limiting relations (3) and (4) the temperature dependence of $\alpha_{(A),+}$ was neglected.

The composition dependence of Ψ for $T \rightarrow T_{\text{fus}}(\text{K}_3\text{TiF}_7)$ was extrapolated using the regression function which fulfils the conditions (2) and (3)

$$\Psi = A + B(1 - x_w)^C \quad (13)$$

where

$$A = \frac{\Delta_{\text{fus,exp}}H(\text{K}_3\text{TiF}_7)}{R} \quad (14)$$

For the chosen values of $\alpha_{(A),+,j}$ (0.4; 0.5; 0.6) the values of $\Delta_{\text{fus,exp}}H_j(\text{K}_3\text{TiF}_7)$, fulfilling eqn (3), consistent with eqn (1), were calculated and from the empirical dependence

$$f(\Delta_{\text{fus,exp}}H_j(\text{K}_3\text{TiF}_7), \alpha_{(A),+,j}) = 0 \quad (15)$$

the dissociation degree of K_3TiF_7 at the temperature of fusion was calculated. The results of calculation are summarized in Table 1.

1.3. Calculation of $\Delta_{\text{fus}}H(\text{K}_3\text{TiF}_7, T_{\text{fus}})$ from the Phase Diagram of the System $\text{KF}-\text{K}_3\text{TiF}_7$ and the Measured Value of the Dissociation Degree $\alpha_{(A),+}$

The enthalpy of fusion of K_3TiF_7 was calculated from eqn (15) for the known value of $\alpha_{(A),+}$. The dissociation degree was determined in two ways. Using eqn (10) the value $\alpha_{(A),+,a}(T_{\text{fus}}(\text{K}_3\text{TiF}_7)) = 0.65$ was obtained, while using eqn (12) its value is $\alpha_{(A),+,b}(T_{\text{fus}}(\text{K}_3\text{TiF}_7)) = 0.67$. The results of the enthalpy of fusion calculation are summarized in Table 2.

2. System $\text{KCl}-\text{K}_3\text{TiF}_6\text{Cl}$

In [3] the dissociation degree of $\text{K}_3\text{TiF}_6\text{Cl}$ was calculated from the dependence of density on composition of melts of this system ($\alpha_{+,1000 \text{ K}}(\text{K}_3\text{TiF}_6\text{Cl}) = 0.71$, $\alpha_{+,1100 \text{ K}}(\text{K}_3\text{TiF}_6\text{Cl}) = 0.81$, $\alpha_{+,1200 \text{ K}}(\text{K}_3\text{TiF}_6\text{Cl}) = 0.88$) and in [9] the enthalpy of fusion of $\text{K}_3\text{TiF}_6\text{Cl}$ was measured using the high-temperature

Table 1. Dissociation Degree of K_3TiF_7 at the Temperature of Fusion Calculated according to Different Phase Diagrams

$\alpha_{(A),+}(\Delta_{\text{fus,exp}}H(\text{K}_3\text{TiF}_7))$ [8]	Phase diagram from [7]	Phase diagram from [6]
$\alpha_{(A),+}$ (55 kJ mol ⁻¹)	0.42 ₀	0.74 ₈
$\alpha_{(A),+}$ (57 kJ mol ⁻¹)	0.40 ₄	0.72 ₀
$\alpha_{(A),+}$ (59 kJ mol ⁻¹)	0.39 ₀	0.69 ₄

Table 2. Enthalpy of Fusion of K_3TiF_7 Obtained by Different Procedures

Procedure	$\Delta_{\text{fus}}H(\text{K}_3\text{TiF}_7, T_{\text{fus}})$
	J mol ⁻¹
Calorimetry [4]	57 000 ± 2000
From eqn (10)	62 446
From eqn (12)	60 623

Table 3. Composition of the Eutectic Point in the System $\text{KCl—K}_3\text{TiF}_6\text{Cl}$ Calculated Using Different Values of the Enthalpy of Fusion of $\text{K}_3\text{TiF}_6\text{Cl}$

$\Delta_{\text{fus}}H(\text{K}_3\text{TiF}_6\text{Cl}, T_{\text{fus}})$	Ref.	$x_{\text{eut}}(\text{K}_2\text{TiF}_6)$
J mol ⁻¹		
39 000	[9]	0.320
42 000	[9]	0.314
45 000	[9]	0.307

Table 4. In the Literature Published Coordinates of the Eutectic Point in the System $\text{KCl—K}_3\text{TiF}_6\text{Cl}$

Ref.	Method	$x_{\text{eut}}(\text{K}_2\text{TiF}_6)$	T_{eut}/K
[12]	Experiment	0.307	925
[10]	Calculation	0.297	927
[6]	Exp. + calc.	0.250, 0.283	925, 925

calorimetry ($\Delta_{\text{fus,exp}}H(\text{K}_3\text{TiF}_6\text{Cl}, T_{\text{fus}}) = (42 \pm 3) \text{ kJ mol}^{-1}$).

The phase equilibrium in this system was studied in [5, 6, 10–12]. In [6] the theoretical course of the liquidus curve of $\text{K}_3\text{TiF}_6\text{Cl}$ in this system was calculated using the hypothetical temperature of melting of the nondissociated compound, 1453 K. In [10] the phase diagram of the system $\text{KCl—K}_2\text{TiF}_6$ was further corrected using the regression dependence of $\Delta_{\text{mix}}G^{\text{Ex}}$ on composition of the ternary system $\text{KCl—KBF}_4\text{—K}_2\text{TiF}_6$.

The measured liquidus curve of $\text{K}_3\text{TiF}_6\text{Cl}$ in the phase diagram of this system shows relatively great differences. For instance, the eutectic point is referred to be in the range $x(\text{K}_2\text{TiF}_6) = (0.25 [6], 0.31 [12])$. The main goal of this work is to determine the most probable course of the liquidus curve of $\text{K}_3\text{TiF}_6\text{Cl}$ and the most probable coordinates of the eutectic point.

In the calculation according to eqn (1) the ideal behaviour of the melts (*i.e.* $cor_{\text{tot}} = 0$) was assumed. Similarly as in paragraph 1.1.a), the values $\Delta_{\text{dis}}H_{(A)} = 60\,602 \text{ J mol}^{-1}$ and $\delta_{(A)} = 0.0015 \text{ K}^{-1}$ were obtained on the basis of data taken from [3].

Inserting the lowest eutectic temperature (925 K [6, 10, 12]) and the different calorimetrically determined enthalpy of fusion of $\text{K}_3\text{TiF}_6\text{Cl}$ into eqn (1) the composition of the eutectic point was calculated. The results are summarized in Table 3. In the literature published coordinates of the eutectic point are summarized in Table 4.

According to the above thermodynamic analysis it can be stated that thermodynamically consistent are the measured enthalpy of fusion of $\text{K}_3\text{TiF}_6\text{Cl}$ and the coordinates of the eutectic point measured in [12].

Inserting the value $\Delta_{\text{fus,exp}}H(\text{K}_3\text{TiF}_6\text{Cl}) = 45\,000 \text{ J mol}^{-1}$ and different mole fractions of K_2TiF_6 near the eutectic point into eqn (1) the temperatures of primary crystallization of $\text{K}_3\text{TiF}_6\text{Cl}$ were calculated. The results are summarized in Table 5.

Acknowledgements. The present work was financially supported by the Scientific Grant Agency of the Ministry of Education of the Slovak Republic and the Slovak Academy of Sciences VEGA under the No. 2/7205/2000.

SYMBOLS

A, B, AB	components of the binary systems
A, B, AB	constituents, <i>i.e.</i> the “components” of the quasi-ternary system
x_w	weighted-in mole fraction of AB in the system A—AB
$x(\text{AB}, T)$	equilibrium mole fraction of AB in the mixture at temperature T
$T_{\text{fus}}(\text{AB})$	temperature of fusion of AB

Table 5. Temperatures of Primary Crystallization of $\text{K}_3\text{TiF}_6\text{Cl}$ Calculated for Different Mole Fractions of K_2TiF_6 near the Eutectic Point

$x_{\text{eut}}(\text{K}_2\text{TiF}_6)$	T_i (eqn (1))/K	T_i (exp. [10])/K	T_i (calc. [10])/K
0.482	968.7	970	968.8
0.420	962.2	960	962.2
0.318	930.5	955	935.1

$\Delta_{\text{fus,exp}}H(\text{AB}, T_{\text{fus}})$	experimentally determined enthalpy of fusion of AB at its temperature of fusion
$\Delta_{\text{dis}}H_{(A),+}$	dissociation enthalpy of reaction (A) in pure AB
$\Delta_{\text{fus}}C_p(\text{AB}, T)$	change in the molar heat capacity of fusion of AB at temperature T
$\Delta_{\text{dis}}C_{p,(A),+}$	change in the molar heat capacity at reaction (A) in pure AB
$\alpha_{(A),+}(T)$	dissociation degree of AB in reaction (A) at temperature T
$K_{(A),x}(T)$	equilibrium constant of reaction (A) related to mole fractions in the mixture at temperature T
cor_{tot}	total correction factor in the LeChatelier—Shreder equation
δ	coefficient in the linear temperature dependence of dissociation degree

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