Thermodynamic Equilibrium between Melt and Crystalline Phase of a Compound A_qB_r with Dystectic Melting Point II. Application to the Systems KF—K_3FMoO_4 and KF—K_3FWO_4

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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_2MoO_4 and KF—K_2WO_4. The dissociation enthalpy, the heat of fusion at dystectic temperature of fusion, and the degree of dissociation of compounds K_3FMoO_4 and K_3FWO_4, formed in the melt, were calculated without using any fictive quantity.

Due to the similarity of properties of the systems KF—K_2MoO_4 and KF—K_2WO_4 the dissociation degree of K_3FMoO_4 and K_3FWO_4 has been found to be $\alpha(T_{fus}) = 0.827$. Similarly, for the dissociation enthalpy of the reaction AB = A + B the value $\Delta_{dis}H_+ = -2462$ J mol^{-1} was calculated in both systems. For the enthalpy of fusion of K_3FWO_4 the value $\Delta_{fus}H(K_3FWO_4, T_{fus}) = 59\,451$ J mol^{-1} was calculated. For the enthalpy of fusion of the fictive nondissociated compounds K_3FMoO_4 and K_3FWO_4 the values $\Delta_{fus}H(K_3FMoO_4, T_{fus}) = 60\,275.8$ J mol^{-1} and $\Delta_{fus}H(K_3FWO_4, T_{fus}) = 61\,486$ J mol^{-1} were calculated.

In our previous paper [1] the LeChatelier—Shreder equation describing the equilibrium between crystalline phase and melt in the system A—A_qB_r when the substance A_qB_r partially dissociates upon melting was derived 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.

In the present paper the proposed method was applied in the systems KF—K_2MoO_4 and KF—K_2WO_4, in which the additive compounds K_3FMoO_4 and K_3FWO_4, respectively, are formed. In this particular case $q = r = 1$.

The phase diagram of the binary system KF—K_2MoO_4 was studied by *Schmitz-Dumont* and *Weeg* [2], *Mateiko* and *Bukhalova* [3], and *Julsrud* and *Kleppa* [4]. The last authors measured also the enthalpy of mixing in this system. These authors found out that in this system the congruently melting additive compound K_3FMoO_4 with the melting point of 752 °C is formed. From the flat course of the liquidus curve of K_3FMoO_4 in this system it may be assumed that the additive compound undergoes at melting considerable thermal dissociation. The obtained values of the enthalpy of mixing indicate that the system KF—K_2MoO_4 deviates only very little from the ideal behaviour.

The phase diagram of the system KF—K_2MoO_4 was later measured also by *Patarák et al.* [5, 6]. These authors found out that the additive compound K_3FMoO_4 melts at 751 °C. The coordinates of the individual eutectic points are 30 mole % K_2MoO_4 and 721 °C in the subsystem KF—K_3FMoO_4 and 59 mole % K_2MoO_4 and 745 °C in the subsystem K_3FMoO_4—K_2MoO_4. These values are very close to those obtained by *Julsrud* and *Kleppa* [4]. The enthalpy of fusion of the additive compound K_3FMoO_4 was measured by *Kosa et al.* [7]. The degree of thermal dissociation of the additive compound K_3FMoO_4 was calculated from the phase diagram using the classical approach as well as from density data [8]. The degree of dissociation of K_3FMoO_4 obtained from the analysis of the phase diagram $\alpha_o = 0.81$ agrees very well with the value $\alpha_o(827 °C) = 0.86$ determined by the analysis of volume properties.

On the other hand, the literature data on the system KF—K_2WO_4 are scarce. Only the phase diagram and the enthalpy of mixing of the binary system KF—K_2WO_4 were studied by *Julsrud* and *Kleppa* [4]. These authors found out that the values of the enthalpy of mixing in the systems KF—K_2MoO_4 and KF—K_2WO_4 are identical within the experimental error, which implies the similar behaviour of both additive compounds.

The existence of the complex anions FXO_4^{3-} (X = Mo, W) in the molten state may be, however, a subject of discussion. It should be emphasized that even when they cannot be identified by spectroscopic methods, obviously due to weak Mo—F or O—F bonds and probably also a short lifetime, these complex anions can be considered as associates. Their acceptance is well founded at least thermodynamically and serves as a useful example to understand the nature and behaviour of the investigated melts.

1. Simplifications in the LeChatelier—Shreder Equation

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

$$AB \Leftrightarrow A + B(l) \qquad (A)$$

However, there are not three components in the system, 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 $dp = 0$, $\Delta_{fus}C_p(AB) = const$, and $\Delta_{dis}C_{p,(A),+} = 0$ ($T_{fus} \equiv T_{fus}(\mathbf{AB})$) in the form

$$\ln \frac{a(AB,T)}{a_+(AB,T)} =$$
$$= \left[\Delta_{fus,exp}H(\mathbf{AB},T_{fus}) - (\Delta_{fus}C_p(AB)T_{fus} + \right.$$
$$\left. + \Delta_{dis}H_{(A),+}\alpha_{(A),+}(T_{fus}))\right] \Big/ \left[RTT_{fus}(T - T_{fus})^{-1}\right] +$$
$$+ \frac{\Delta_{fus}C_p(AB)}{R} \int_{T_{fus}}^{T} d\ln T +$$
$$+ \frac{\Delta_{dis}H_{(A),+}}{R} \int_{T_{fus}}^{T} \frac{\alpha_{(A),+}(T)}{T^2} dT \qquad (1)$$

In our previous work [1] it was claimed that the dissociation degree of the reaction (A), $\alpha_{(A),+}$, is given by the equation

$$\alpha_{(A),+}(T) = \sqrt{\frac{K_{(A),x,+}(T)}{1 + K_{(A),x,+}(T)}} \qquad (2)$$

and the equilibrium constant of this reaction, $K_{(A),x,+}(T)$ by the relation

$$K_{(A),x,+}(T) = K_{(A),x,+}(T_{fus}) \cdot$$
$$\cdot \exp\left(\frac{\Delta_{dis}H_{(A),+}(T - T_{fus})}{RTT_{fus}}\right) \qquad (3)$$

In a narrow temperature interval it is possible to substitute the temperature dependence of $\alpha_{(A),+}$ by the linear regression function

$$\alpha_{(A),+}(T) = \alpha_{(A),+}(T_{fus}) + \delta_{(A)}(T - T_{fus}) \qquad (4)$$

The activities of AB in eqn (1) are, however, not known and they can be substituted by calculated true mole fractions multiplied by correction factors:

a) The deviation from ideal behaviour is expressed by the correction coefficient "cor_1". Since $\gamma(AB,T) \neq \gamma_+(AB,T)$ the left side of eqn (1) has the form

$$\ln \frac{a(AB,T)}{a_+(AB,T)} = \ln \left(\frac{x(AB,T)}{x_+(AB,T)} \, cor_1\right) \qquad (5)$$

The values of $x(AB,T)$ and $x_+(AB,T)$ may be estimated under the following simplifying assumptions.

b) The quantities $\alpha_{(A)}(T)$ and $\alpha_{(A),+}(T)$ are bound by the relation

$$K_{(A),x}(T) = K_{(A),\gamma}(T) \cdot \left(x_w\left(\alpha_{(A)}(T) - 1\right) + 1\right) \cdot$$
$$\cdot x_w\alpha_{(A)}(T)\left(x_w\alpha_{(A)}(T) + 1\right) \Big/$$
$$\left[\left(x_w\alpha_{(A)}(T) + 1\right)^2\left(1 - \alpha_{(A)}(T)\right)x_w\right] =$$
$$= K_{(A),\gamma,+}(T)\frac{\left(\alpha_{(A),+}(T)\right)^2}{1 - \left(\alpha_{(A),+}(T)\right)^2} \qquad (6)$$

In the calculation the validity of the following relations is assumed

$$K_{(A),\gamma}(T) = K_{(A),\gamma,+}(T); \; i.e.$$
$$K_{(A),x}(T) = K_{(A),x,+}(T) \qquad (7)$$

In such a case $\alpha_{(A)}(T)$ depends only on x_w and $K_{(A),x,+}(T)$, or on x_w and $\alpha_{(A),+}(T)$. These simplifications are expressed by the correction factor "cor_2".

c) In many cases the value of $\Delta_{dis}H_{(A),+}$ in eqn (3) is not known. In such a case we may start the calculation using the following starting assumptions

$$\Delta_{dis}H_{(A),+} = 0 \qquad (8)$$
$$K_{(A),x,+}(T) = K_{(A),x,+}(T_{fus}) \qquad (9)$$
$$\alpha_{(A),+}(T) = \alpha_{(A),+}(T_{fus}) \qquad (10)$$

These three simplifications can be expressed by the correction factor "cor_3".

2. Quantitative Evaluation of Correction Factors cor_i

2.1. If the dissociation degree $\alpha_{(A),+}(T)$ is sufficiently high (≈ 0.8), then for the dependence of the activity on mole fraction the Henry's law is practically valid

$$\gamma(AB,T) = \frac{a(AB,T)}{x(AB,T)} \cong$$
$$\cong \frac{a_+(AB,T)}{x_+(AB,T)} = \gamma_+(AB,T) = \text{const} \qquad (11)$$

In the vicinity of pure **AB**, when x_w decreases, the amount of the nondissociated constituent AB relatively increases since $\alpha_{(A)}(T)$ decreases (*i.e.* when $x(A)$ increases) and simultaneously decreases the value of $x(AB,T)$ because of the substantial increase of the content of **A**. Thus for $x_w \approx 1$ the change of $x(AB,T)$ is relatively small and eqn (11) is again valid. The resulting limiting relation thus follows from paragraph 2.1.

$$\lim_{T \to T_{fus}} cor_1 = 1 \qquad (12)$$

2.2. From the Debye—Hückel's theory it follows that the activity coefficient of the admixture depends on its mole fraction, the properties of the solvent (ε_r), and the temperature. For the products of dissociation A and B in the melt of the pure component **AB** ($x_w = 1$) all the above-mentioned quantities are equal and thus the following relation holds

$$\gamma_+(A,T) = \gamma_+(B,T) \qquad (13)$$

The numerator product on the right side of eqn (7) has the form

$$\gamma_+(A,T)\,\gamma_+(B,T) = (\gamma_+(X,T))^2 = \Pi_+ \qquad (14)$$

In the vicinity of the pure component **AB** ($x_w \to 1$) the dependence of activity on mole fraction $a(A) = f[x(A)]$, resp. $a(B) = f[x(B)]$, is practically linear. It can be proved in this case that the following relation is also valid

$$\gamma(A,T)\,\gamma(B,T) \approx \Pi_+ \qquad (15)$$

With regard to eqn (15) and the conclusions resulted from paragraph 2.1., eqn (7) is in the limiting case fulfilled and the following relation holds

$$\lim_{T \to T_{fus}} cor_2 = 1 \qquad (16)$$

2.3. For $x_w \to 1$ also the value of cor_3 approaches 1 for two reasons:

a) The error in the estimation of $x(AB,T)$ and $x_+(AB,T)$ originating from neglecting the temperature dependence of $\alpha_{(A),+}(T)$ occurs in the numerator

as well as in the denominator of the quotient of both pure mole fractions $x(AB,T)/x_+(AB,T)$, thus being in substantial part eliminated.

b) At dystectic melting, for $x_w \to 1$ the difference $(T - T_{fus})$ on the right side of eqn (3) approaches zero, therefore this equation transforms to the form

$$K_{(A),x,+}(T) \approx K_{(A),x,+}(T_{fus}) = \text{const} \qquad (17)$$

From all the above-mentioned paragraphs the following limiting relation holds for the total correction "cor_{tot}"

$$\lim_{T \to T_{fus}} [-\ln(cor_1\,cor_2\,cor_3)] = \lim_{T \to T_{fus}}(cor_{tot}) = 0 \qquad (18)$$

The temperature dependence of the total correction "cor_{tot}" can be substituted by the function

$$cor_{tot} = \lambda_1 (T - T_{fus})^2 + \lambda_2 (T - T_{fus})^3 =$$
$$= (T - T_{fus})^2 [\lambda_1 + \lambda_2 (T - T_{fus})] \qquad (19)$$

Inserting all the mentioned rearrangement into eqn (1) we obtain its final form

$$\ln \frac{x(AB,T)}{x_+(AB,T)} = \Big[\Delta_{fus,exp}H(AB,T_{fus}) -$$
$$- T_{fus}\left(\Delta_{fus}C_p(AB) + \Delta_{dis}H_{(A),+} \delta_{(A)}\right)\Big] \Big/$$
$$\Big/ \left[R\,T\,T_{fus}\,(T - T_{fus})^{-1}\right] +$$
$$+ \frac{\Delta_{fus}C_p(AB) + \Delta_{dis}H_{(A),+} \delta_{(A)}}{R} \cdot$$
$$\cdot \int_{T_{fus}}^{T} d\ln T + (T - T_{fus})^2 [\lambda_1 + \lambda_2 (T - T_{fus})] \qquad (20)$$

In the logarithm of the left side are estimations of the true mole fractions of the constituent AB calculated with respect to all the above-mentioned simplifications.

For $x_w \to 1$, the functions $\ln \frac{a(AB,T)}{a_+(AB,T)}$ and $\ln \frac{x(AB,T)}{x_+(AB,T)}$ approach unlimitedly zero and it would not be possible to calculate the final values of quantities characterizing the system **A—AB**. However, in our previous paper [1] we claimed that it is advantageous to multiply these functions by the term

$$W = \frac{T\,T_{fus}}{T - T_{fus}} \qquad (21)$$

For $x_w \to 1$ W approaches infinity, however, its product with both mentioned functions approaches a finite value. We can thus introduce the functions

$$\Theta = W \ln \frac{a(AB,T)}{a_+(AB,T)} \qquad (22)$$

Table 1. Thermodynamic Data of the System KF—K$_2$XO$_4$ (X = Mo, W) Used in the Calculation

Quantity	Value	Ref.
$T_{\text{fus}}(\text{KF})/\text{K}$	1129.5	[4]
$\Delta_{\text{fus}}H(\text{KF},T_{\text{fus}})/(\text{J mol}^{-1})$	29 500	[4]
$\Delta_{\text{fus}}C_p(\text{KF})/(\text{J mol}^{-1}\text{ K}^{-1})$	$-0.29 + 0.159 \times 10^{-3}\{T\} - 23\,059/\{T\}^2$	[4]
$T_{\text{fus}}(\text{K}_2\text{MoO}_4)/\text{K}$	1201.5	[4]
$\Delta_{\text{fus}}H(\text{K}_2\text{MoO}_4,T_{\text{fus}}(\text{K}_2\text{MoO}_4))/(\text{J mol}^{-1})$	34 700	[4]
$T_{\text{fus}}(\text{K}_3\text{FMoO}_4)/\text{K}$	1024, 1025	[4, 5]
$\Delta_{\text{fus}}H(\text{K}_3\text{FMoO}_4,T_{\text{fus}}(\text{K}_3\text{FMoO}_4))/(\text{J mol}^{-1})$	58 000	[7]
$T_{\text{fus}}(\text{K}_2\text{WO}_4)/\text{K}$	1183.4	[4]
$\Delta_{\text{fus}}H(\text{K}_2\text{WO}_4,T_{\text{fus}}(\text{K}_2\text{WO}_4))/(\text{J mol}^{-1})$	35 100	[4]
$T_{\text{fus}}(\text{K}_3\text{FWO}_4)/\text{K}$	1031.7	[4]
$\Delta_{\text{fus}}C_p(\text{K}_2\text{XO}_4)/(\text{J mol}^{-1}\text{ K}^{-1})$	$300.98 - 25.58 \times 10^{-2}\{T\}$	[4]
$\Delta_{\text{fus}}C_p(\text{K}_3\text{FXO}_4)/(\text{J mol}^{-1}\text{ K}^{-1})$	46.0*	This paper
$\Delta_{\text{mix}}H(\text{KF}\text{—}\text{K}_2\text{XO}_4; x(\text{K}_2\text{XO}_4) = 0.5; 1273\text{ K})/(\text{J mol}^{-1})$	222.5	[4]
$\Delta_{\text{dis}}C_{p,(B)} \approx \Delta_{\text{dis}}C_{p,(C)}$	0	This paper

*Calculated using the Neumann—Kopp's rule according to the relation $\Delta_{\text{fus}}C_p(\text{K}_3\text{FXO}_4,T) = \Delta_{\text{fus}}C_p(\text{KF},T) + \Delta_{\text{fus}}C_p(\text{K}_2\text{XO}_4,T)$.

and

$$\Psi = W \ln \frac{x(\text{AB},T)}{x_+(\text{AB},T)} \qquad (23)$$

It can easily be proved that for limiting values of Ψ and its derivative the following relations are valid

$$\lim_{\substack{x_w \to 1 \\ T \to T_{\text{fus}}}} \Psi = \frac{\Delta_{\text{fus,exp}}H(\text{AB},T)}{T} = \text{const} \qquad (24)$$
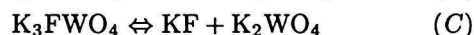
$$\lim_{\substack{x_w \to 1 \\ T \to T_{\text{fus}}}} \frac{\text{d}\Psi}{\text{d}x_w} = 0 \qquad (25)$$

$$\lim_{\substack{x_w \to 1 \\ T \to T_{\text{fus}}}} \frac{\text{d}\Psi}{\text{d}T} = 0 \qquad (26)$$

Thus the calculation procedure of the characteristic quantities of the system A—AB based on the above-mentioned simplifications does not evidently require the choice of any solution model.

3. Results of Calculation in the Systems KF—K$_2$MoO$_4$ and KF—K$_2$WO$_4$

For these systems the general reaction scheme (A) transforms into the forms

$$\text{K}_3\text{FMoO}_4 \Leftrightarrow \text{KF} + \text{K}_2\text{MoO}_4 \qquad (B)$$

$$\text{K}_3\text{FWO}_4 \Leftrightarrow \text{KF} + \text{K}_2\text{WO}_4 \qquad (C)$$

The thermodynamic data used in the calculation are summarized in Table 1.

3.1. Quantities characterizing the system KF—K$_2$MoO$_4$

Based on the optimized phase diagram published by *Patarák et al.* [6] the liquidus curve of K$_3$FMoO$_4$ in the phase diagram KF—K$_2$MoO$_4$ was described by the regression equation

$$T(x_w; \text{KF}\text{—}\text{K}_3\text{FMoO}_4)/\text{K} = 1024 -$$
$$- 68.973(1 - x_w)^{2.15} - 139.025(1 - x_w)^{4.63} \qquad (27)$$

valid for the temperature range $T \in \langle T_{\text{eut}}(\text{KF}\text{—}\text{K}_3\text{FMoO}_4); T_{\text{fus}}(\text{K}_3\text{FMoO}_4)\rangle$.

3.1.1. Calculation of $\alpha_{(B),+}(T_{\text{fus}}(\text{K}_3\text{FMoO}_4))$ and $K_{(B),x,+}(T_{\text{fus}}(\text{K}_3\text{FMoO}_4))$

The dissociation degree $\alpha_{(B),+}(T_{\text{fus}}(\text{K}_3\text{FMoO}_4))$ was calculated using eqn (24). For different values of x_w and $\alpha_{(B),+}(T_{\text{fus}}(\text{K}_3\text{FMoO}_4))$ the calculated values of T from eqn (27) were used to calculate W. In order to attain a proper confidence level in Ψ a sufficiently large temperature difference $(T - T_{\text{fus}})$ in denominator (eqn (21)) was chosen. The Ψ vs. x_w dependence was for every chosen value of $\alpha_{(B),+}(T_{\text{fus}}(\text{K}_3\text{FMoO}_4))$ described by the empirical regression function

$$\Psi(x_w) = a_i + b_i(1 - x_w)^{[c_i + d_i(1-x_w)+e_i(1-x_w)^{1.1}]} \qquad (28)$$

which fulfils all conditions required by eqns (24) and (25). The final value for $\alpha_{(B),+}(T_{\text{fus}}(\text{K}_3\text{FMoO}_4))$ at 1024 K, obtained by iterative procedure, was

$$\alpha_{(B),+}(T_{\text{fus}}(\text{K}_3\text{FMoO}_4)) = 0.827 \qquad (29)$$

Then from eqns (2) and (29) it follows that

$$K_{(B),x,+}(T_{\text{fus}}(\text{K}_3\text{FMoO}_4)) = 2.160 \qquad (30)$$

All the up-to-now obtained values of $\alpha_{(B),+}(T_{\text{fus}}(\text{K}_3\text{FMoO}_4))$ are summarized in Table 2. From this table it follows that the use of an inappropriate model can considerably affect the calculated $\alpha_{(B),+}(T_{\text{fus}}(\text{K}_3\text{FMoO}_4))$ value.

3.1.2. Calculation of $\Delta_{\text{dis}}H_{(B),+}$, $\delta_{(B)}$, and $\Delta_{\text{fus}}H(\text{K}_3\text{FMoO}_4,T_{\text{fus}}(\text{K}_3\text{FMoO}_4))$

For the mixing of KF and K$_2$MoO$_4$ at the temperature of 1273 K, *Julsrud* and *Kleppa* [4] observed

Table 2. Values of $\alpha_{(B),+}(T_{fus}(K_3FMoO_4))$ Obtained by Different Calculation Procedures

Approach	$\alpha_{(B),+}(T_{fus}(K_3FMoO_4))$	Ref.
Quasi-athermal solutions	0.59	[7]
Real solutions	0.51	[7]
Ideal solutions	0.80	[7]
Hypothetical fusion of **AB**	0.81	[8]
From volume properties	0.84	[8]
This approach	0.827	This paper

Table 3. Values of $\Delta_{dis}H_{(B),+}$ Obtained Using Different Calculation Procedures

Approach	$\dfrac{\Delta_{dis}H_{(B),+}}{\text{J mol}^{-1}}$	Ref.
From $K_{(B),x,+} = f(T)$	18 800	[8]
Ideal solutions	−2900	[7]
Quasi-athermal solutions	−1400	[7]
Real solutions	−1200	[7]
This approach	−2462.1	This paper

an endothermic effect. Assuming that this endothermic effect is caused by the association in the reverse direction of scheme (B), the following relation holds

$$0.5 \left[1 - \alpha_{(B),+}(1273\,\text{K})\right] \left(-\Delta_{dis}H_{(B),+}\right) =$$
$$= \Delta_{mix}H(KF\text{---}K_2MoO_4; x(K_2MoO_4) =$$
$$= 0.5; 1273\,\text{K}) = 222.5\,\text{J mol}^{-1} \quad (31)$$

From eqns (2), (3), (30), and (31) the values of $\alpha_{(B),+}(1273\,\text{K})$ and $\Delta_{dis}H_{(B)}$ were calculated

$$\alpha_{(B),+}(1273\text{K}) = 0.819 \quad (32)$$

$$\Delta_{dis}H_{(B),+} = -2462.1\,\text{J mol}^{-1} \quad (33)$$

The values of $\Delta_{dis}H_{(B),+}$ calculated using different approaches are summarized in Table 3. The evaluation of the obtained values is similar as for those in Table 2. The calculation of the last four values in Table 3 is based on the measured enthalpy of mixing [4].

Using the temperature dependence of $\alpha_{(B),+}(T)$, given by eqns (2), (3), and (33), the slope in eqn (4) $\delta_{(B)}$ was calculated and for the temperature range $\langle T_{eut}(KF\text{---}K_3FMoO_4); T_{fus}(K_3FMoO_4)\rangle$ the following value was obtained

$$\delta_{(B)} = -0.0000377\,\text{K}^{-1} \quad (34)$$

From eqns (29) and (33), the values in Table 1, and from the following relation ($T_{fus} \equiv T_{fus}(K_3FMoO_4)$)

$$\Delta_{fus}H(K_3FMoO_4, T_{fus}) = \Delta_{fus}H(K_3FMoO_4, T_{fus}) +$$
$$+ \alpha_{(B),+}(T_{fus})\,\Delta_{dis}H_{(B),+} \quad (35)$$

the unknown value of the enthalpy of fusion of the nondissociated compound K_3FMoO_4 was calculated

$$\Delta_{fus}H(K_3FMoO_4, T_{fus}) = 60\,275.8\,\text{J mol}^{-1} \quad (36)$$

3.1.3. Coefficients λ_1 and λ_2 in the total correction cor_{tot} (eqn (19))

The calculation of λ_1 and λ_2 was performed using the quantities given in Table 1 and eqn (20) for two figurative points on the liquidus curve, at $T_{eut} = 990.85$ K; $x_w = 0.416$, and $T = 1002.9$ K; $x_w = 0.5$. The following final values were obtained

$$\lambda_1 = 4.598 \times 10^{-6}\,\text{K}^{-2} \quad (37)$$

$$\lambda_2 = -2.132 \times 10^{-8}\,\text{K}^{-3} \quad (38)$$

3.1.4. Calculation of $\Delta_{mix}S(KF + K_2MoO_4 = K_3FMoO_4, s, 298\,K)$

This quantity may be regarded also as the entropy of formation. Using the quantities given in Table 1 and assuming the validity of the Neumann—Kopp's rule for the temperature dependence of $C_p(K_3FMoO_4, s)$ the following entropy balance was performed

$$\Delta_{fus}S(K_3FMoO_4, T_{fus} = 1024\,\text{K}) =$$

$$= \int_{298\,\text{K}}^{1129.9\,\text{K}} \frac{C_p(KF,s,T)}{T}\,dT + \frac{29\,500\,\text{J mol}^{-1}}{1129.9\,\text{K}} +$$

$$+ \int_{1129.9\,\text{K}}^{1024\,\text{K}} \frac{C_p(KF,l,T)}{T}\,dT +$$

$$+ \int_{298\,\text{K}}^{1201.5\,\text{K}} \frac{C_p(K_2XO_4,s,T)}{T}\,dT + \frac{34\,700\,\text{J mol}^{-1}}{1201.5\,\text{K}} +$$

$$+ \int_{1201.5\,\text{K}}^{1024\,\text{K}} \frac{C_p(K_2XO_4,l,T)}{T}\,dT -$$

$$- \left[\int_{298\,\text{K}}^{1024\,\text{K}} \frac{C_p(KF,s,T)}{T}\,dT + \right.$$

$$\left. + \int_{298\,\text{K}}^{1024\,\text{K}} \frac{C_p(K_2XO_4,s,T)}{T}\,dT \right] + \Delta_{mix}S_{tot} \quad (39)$$

where

$$\Delta_{mix}S_{tot} = \Delta_{mix}S(sol(KF + K_2MoO_4), l, 1024\,\text{K}) -$$
$$- \Delta_{mix}S(KF + K_2MoO_4, s, 298\,\text{K}) \quad (40)$$

Inserting all known quantities and temperature dependences from Table 1 we get for the entropy of mixing

$$\Delta_{mix}S_{tot} = 4.223\,\text{J mol}^{-1}\,\text{K}^{-1} \quad (41)$$

Assuming that the melt of the equimolar mixture **KF** and **K₂MoO₄** forms at $T_{\mathrm{fus}}(\mathbf{K_3FMoO_4})$ ideal solution, we can express the amounts of individual constituents $n_{\mathrm{r,i}}$ in 1 mol of molten $\mathbf{K_3FMoO_4}$ in the form

$$n_{\mathrm{r}}(\mathbf{KF}) = \frac{n(\mathbf{KF})}{n(\mathbf{K_3FMoO_4})} = \alpha_{(B),+} \qquad (42)$$

$$n_{\mathrm{r}}(\mathbf{K_2MoO_4}) = \frac{n(\mathbf{K_2MoO_4})}{n(\mathbf{K_3FMoO_4})} = \alpha_{(B),+} \qquad (43)$$

$$n_{\mathrm{r}}(\mathbf{K_3FMoO_4}) = \frac{n(\mathbf{K_3FMoO_4})}{n(\mathbf{K_3FMoO_4})} = 1 - \alpha_{(B),+} \qquad (44)$$

With regard to the low value of $\Delta_{\mathrm{dis}}H$ and neglecting the term $(1-\alpha)\Delta_{\mathrm{as}}S$ of the reaction $\mathbf{K_3FMoO_4}(\mathrm{l}) \leftrightarrow \mathbf{KF}(\mathrm{l}) + \mathbf{K_2MoO_4}(\mathrm{l})$ we can calculate the first term on the right side of eqn (40)

$$\Delta_{\mathrm{mix}}S\,(\mathrm{sol}\,(\mathbf{KF} + \mathbf{K_2MoO_4}), \mathrm{l}, 1024\,\mathrm{K}) =$$

$$= -R\left[n_{\mathrm{r}}(\mathbf{KF}) \ln \frac{n_{\mathrm{r}}(\mathbf{KF})}{\sum_i n_{\mathrm{r,i}}} + \right.$$

$$+ n_{\mathrm{r}}(\mathbf{K_2MoO_4}) \ln \frac{n_{\mathrm{r}}(\mathbf{K_2MoO_4})}{\sum_i n_{\mathrm{r,i}}} +$$

$$\left. + n_{\mathrm{r}}(\mathbf{K_3FMoO_4}) \ln \frac{n_{\mathrm{r}}(\mathbf{K_3FMoO_4})}{\sum_i n_{\mathrm{r,i}}} \right] =$$

$$= -R\left[2\,\alpha_{(B),+} \ln \left(\frac{\alpha_{(B),+}}{1 + \alpha_{(B),+}} \right) + \right.$$

$$\left. + \left(1 - \alpha_{(B),+}\right) \ln \left(\frac{1 - \alpha_{(B),+}}{1 + \alpha_{(B),+}} \right) \right] =$$

$$= 14.292\,\mathrm{J\,mol^{-1}\,K^{-1}} \qquad (45)$$

Inserting eqns (41) and (45) into eqn (40) we then get

$$\Delta_{\mathrm{mix}}S\,(\mathbf{KF} + \mathbf{K_2MoO_4}, \mathrm{s}, 298\,\mathrm{K}) =$$

$$= 10.069\,\mathrm{J\,mol^{-1}\,K^{-1}} \qquad (46)$$

When assuming the formation of ideal solid solution, this value would be equal to $11.526\,\mathrm{J\,mol^{-1}\,K^{-1}}$. Thus, with regard to the limited validity of assumptions on ideal behaviour of both solid and liquid solutions, the solid $\mathbf{K_3FMoO_4}$ phase may be regarded also as the solid solution of both components.

3.2. Quantities characterizing the systems KF—K₂WO₄

3.2.1. Entropy and enthalpy of fusion of K₃FWO₄

The entropy of fusion of $\mathbf{K_3FWO_4}$ was calculated by comparing the entropy increase in the formation of the equimolar liquid solution at the temperature $T_{\mathrm{fus}}(\mathbf{K_3FWO_4})$ at

a) heating the individual crystalline compounds to their melting points, their melting and subsequent mixing of their melts, and

b) forming the $\mathbf{K_3FWO_4}$ compound by solid state reaction, its heating to the melting point, its melting, and eventual heating to the final temperature.

In [4] it was found that in the limit of the experimental errors of investigation both systems, **KF—K₂MoO₄** and **KF—K₂WO₄**, exhibit in the whole concentration region and at the same temperature the same value of the enthalpy of mixing and also the same temperature dependence of $\Delta_{\mathrm{fus}}C_p(\mathbf{K_2XO_4}, T)$. With regard to the similar properties of both the **KF—K₂MoO₄** and **KF—K₂WO₄** systems the following relation can be assumed for $\Delta_{\mathrm{mix}}S_{\mathrm{tot}}$ (eqn (40))

$$\Delta_{\mathrm{mix}}S_{\mathrm{tot}}\,(\mathbf{KF—K_2MoO_4}, T_i) =$$

$$= \Delta_{\mathrm{mix}}S_{\mathrm{tot}}\,(\mathbf{KF—K_2WO_4}, T_i) \qquad (47)$$

Using the values given in Table 1, eqn (47) and assuming the validity of Neumann—Kopp's rule the following value of entropy of fusion was obtained

$$\Delta_{\mathrm{fus}}S\,(\mathbf{K_3FWO_4}, T_{\mathrm{fus}} = 1031.7\,\mathrm{K}) =$$

$$= 57.624\,\mathrm{J\,mol^{-1}\,K^{-1}} \qquad (48)$$

After multiplying by the temperature of fusion the enthalpy of fusion is

$$\Delta_{\mathrm{fus}}H\,(\mathbf{K_3FWO_4}, T_{\mathrm{fus}} = 1031.7\,\mathrm{K}) =$$

$$= 59\,451\,\mathrm{J\,mol^{-1}} \qquad (49)$$

On the other hand, using the "model of entropic similarity", *i.e.* the equality of entropies of fusion of both binary $\mathbf{K_3FXO_4}$ compounds at the individual temperatures of fusion, we get

$$\Delta_{\mathrm{fus}}H\,(\mathbf{K_3FWO_4}, T_{\mathrm{fus}} = 1031.7\,\mathrm{K}) =$$

$$= 58\,379\,\mathrm{J\,mol^{-1}} \qquad (50)$$

3.2.2. Calculation of $\Delta_{\mathrm{dis}}H_{(C),+}$, $\alpha_{(C),+}(T_{\mathrm{fus}}(\mathbf{K_3FWO_4}))$, $K_{(C),x,+}(T_{\mathrm{fus}}(\mathbf{K_3FWO_4}))$, $\delta_{(C)}$, and $\Delta_{\mathrm{fus}}H(\mathbf{K_3FWO_4}, T_{\mathrm{fus}}(\mathbf{K_3FWO_4}))$

When mixing the melts **KF** and **K₂MoO₄**, resp. **KF** and **K₂WO₄** at the temperature of 1273 K, *Julsrud* and *Kleppa* [4] found at the same compositions the same values of enthalpies of mixing in the whole concentration range. Assuming that for $x(\mathbf{K_2XO_4})$ a similar relation as eqn (31) is valid in the composition range $x(\mathbf{K_2XO_4}) \in \langle 0; 0.5 \rangle$, *i.e.*

$$x(\mathbf{K_2XO_4}) \left[1 - \alpha_{(A)}(x(\mathbf{K_2XO_4})) \right] \left(-\Delta_{\mathrm{dis}}H_{(A)} \right) =$$

$$= \Delta_{\mathrm{mix}}H(x(\mathbf{K_2XO_4})) \qquad (51)$$

then for every pair of $x_i(K_2XO_4)$ the following relation must hold (under presumption of the same dependence of $\Delta_{dis}H_{(A)}$ on composition)

$$\frac{1 - \alpha_{(B)}(x_1(K_2MoO_4))}{1 - \alpha_{(B)}(x_2(K_2MoO_4))} = \frac{1 - \alpha_{(C)}(x_1(K_2WO_4))}{1 - \alpha_{(C)}(x_2(K_2WO_4))} \quad (52)$$

With regard to the complicated character of the $x_i(K_2XO_4)$ vs. $\alpha_{(A)}(x_i(K_2XO_4))$ and vs. $\alpha_{(A),+}(x_i(K_2XO_4) = 0.5)$ plots, eqn (52) is probably in the frame of the experimental errors fulfilled only when the following equalities are valid

$$\alpha_{(B)}(x_i(K_2MoO_4), T) = \alpha_{(C)}(x_i(K_2WO_4), T) \quad (53)$$

i.e.
$$\alpha_{(B),+}(x_i(K_2MoO_4) = 0.5, T) =$$
$$= \alpha_{(C),+}(x_i(K_2WO_4) = 0.5, T) \quad (54)$$

In this case from eqn (51) follows also the equation

$$\Delta_{dis}H_{(B),+} = \Delta_{dis}H_{(C),+} = -2462.1 \text{ J mol}^{-1} \quad (55)$$

From eqns (2), (3), (31), (54), and (55) and from the relation $T_{fus}(K_3FWO_4) \approx T_{fus}(K_3FMoO_4)$ the following quantities were then calculated

$$\alpha_{(C),+}(T_{fus}(K_3FWO_4)) = 0.827 \quad (56)$$

$$K_{(C),x,+}(T_{fus}(K_3FWO_4)) = 2.160 \quad (57)$$

$$\delta_{(C)} = \delta_{(B)} = -0.0000377 \text{ K}^{-1} \quad (58)$$

From eqn (35), in which the system KF—K_2MoO_4 was substituted by the KF—K_2WO_4 one, it finally follows that for the enthalpy of fusion of the fictive nondissociated compound K_3FWO_4 at the temperature of fusion of K_3FWO_4 the following value was calculated

$$\Delta_{fus}H(K_3FWO_4, T_{fus}(K_3FWO_4)) = 61\,486 \text{ J mol}^{-1} \quad (59)$$

SYMBOLS

A, B, AB	components of the binary systems
A, B, AB	constituents, *i.e.* the "components" of the quasi-ternary system
x_w	weighted-in mole fraction of **AB** in the system **A—AB**
$x(AB,T)$	equilibrium mole fraction of AB in the mixture at temperature T
$x(B)$	mole fraction of B in the system **A—B**

$a(X,T)$	activity of X in the mixture at temperature T
$\gamma(X,T)$	activity coefficient of X in the mixture at temperature T
$n_r(X)$	amount of constituent X related to 1 mol of molten **AB**
$n(X), n(AB)$	amount of substance X and **AB**, resp.
$T_{fus}(AB)$	temperature of fusion of **AB**
$\Delta_{fus,exp}H(AB,T_{fus})$	experimentally determined enthalpy of fusion of **AB** at its temperature of fusion
$\Delta_{mix}H(A\text{—}B; x; T)$	enthalpy of mixing in the system **A—B** at $x(B)$ and temperature T
$\Delta_{dis}H_{(A)}$	dissociation enthalpy of reaction (A)
$\Delta_{mix}S(T)$	entropy of mixing at temperature T
$\Delta_{fus}S(AB,T)$	entropy of fusion of **AB** at temperature T
$\Delta_{as}S$	entropy of association
$\Delta_{fus}C_p(AB,T)$	change in the molar heat capacity of fusion of AB at temperature T
$\Delta_{dis}C_{p,(A)}$	change in the molar heat capacity at reaction (A)
$\alpha_{(A)}(T)$	dissociation degree of **AB** in reaction (A) at temperature T
$K_{(A)}(T)$	equilibrium constant of reaction (A) at temperature T
$K_{(A),x}(T)$	equilibrium constant of reaction (A) related to mole fractions in the mixture at temperature T
$K_{(A),\gamma}(T)$	equilibrium constant increment of reaction (A) related to activity coefficients in the mixture at temperature T
cor_i	correction factors in the LeChatelier—Shreder equation
λ_i	coefficients in temperature dependence of the total correction factor cor_{tot}
$\delta_{(i)}$	coefficient in the linear temperature dependence of dissociation degree in reaction i
l	liquid
s	solid
+	related to pure **AB**

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