Structure of the Melts of the System KF—K$_2$MoO$_4$

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The densities of the melts in the system KF—K$_2$MoO$_4$ were measured using the Archimedean method. From the volume properties point of view the investigated system exhibits almost ideal behaviour, which indicates that the congruently melting compound K$_3$FMoO$_4$ which is formed in the system KF—K$_2$MoO$_4$ exhibits a low thermal stability and at melting it undergoes a considerable thermal dissociation. The degree of the thermal dissociation was calculated on the basis of both the thermodynamic analysis of the phase diagram and the volume properties of the investigated system. It was found that the degree of thermal dissociation of K$_3$FMoO$_4$ at the melting point attains the value $\alpha_0 = 0.81$. The dissociation enthalpy, calculated on the basis of the density values, is ΔH(dis, K$_3$FMoO$_4$) = 18.8 kJ mol^{-1}.

In the binary systems of alkali metal fluorides and other salts of alkali metals, such as sulfates, chromates, molybdates, and tungstates, additive compounds like Na$_3$FSO$_4$, K$_3$FCrO$_4$, K$_3$FWO$_4$, etc., are formed. These compounds exhibit probably lowered symmetry of the crystal structure due to the repulsive forces between the complex and the fluoride anions. Owing to this effect and obviously a relatively high energetic state such compounds undergo often at melting a more or less extended thermal dissociation, in some cases they melt even incongruently. Evidences of such behaviour may be found e.g. in [1, 2]. Into this group belongs also the K$_3$FMoO$_4$ compound, which is formed in the system KF—K$_2$MoO$_4$. This system is a part of a more complex system KF—K$_2$MoO$_4$—B$_2$O$_3$, which may be potentially used as the electrolyte for deposition of molybdenum from the fused salts [3].

The phase diagram of the system KF—K$_2$MoO$_4$ was studied by Julsrud and Kleppa [4]. These authors found out that in this system the congruently melting additive compound K$_3$FMoO$_4$ with the melting point of 752 °C is formed. This compound divides the system into two simple eutectic ones with the following coordinates of the eutectic points: 29.2 mole % K$_2$MoO$_4$ and 720.6 °C in the subsystem KF—K$_3$FMoO$_4$ and 56 mole % K$_2$MoO$_4$ and 748.6 °C in the subsystem K$_3$FMoO$_4$—K$_2$MoO$_4$. From the very flat dystecticum of this system it may be assumed that the additive compound undergoes at melting considerable thermal dissociation.

In the present work the densities of the melts of the system KF—K$_2$MoO$_4$ were measured. The density values were employed in the determination of the degree of thermal dissociation of the additive compound K$_3$FMoO$_4$ which was compared with that obtained from the thermodynamic analysis of the phase diagram of the investigated system.

THEORETICAL

With regard to the thermal dissociation of the additive compound K$_3$FMoO$_4$, the calculation of the equilibrium composition of molten mixtures KF—K$_2$MoO$_4$ can be based on the following procedure.

Let us consider an arbitrary mixture of $(1 - x)$ mol of the substance KF and x mol of the substance K$_2$MoO$_4$, in which the additive compound K$_3$FMoO$_4$ is formed. For $x \leq 0.5$ a maximum amount of x mol of K$_3$FMoO$_4$ can be formed in the mixture. In the case of the thermal dissociation of the substance K$_3$FMoO$_4$ according to the scheme

$$K_3FMoO_4 \rightarrow KF + K_2MoO_4 \qquad (A)$$

with the dissociation degree α, the resulting equilibrium amounts of substances in the mixture can be expressed as follows

$$
\begin{aligned}
n(\text{KF}) &= (1 - 2x + \alpha x) \text{ mol} \\
n(\text{K}_2\text{MoO}_4) &= \alpha x \text{ mol} \\
n(\text{K}_3\text{FMoO}_4) &= x(1 - \alpha) \text{ mol}
\end{aligned}
$$

The total amount of substance of all components then will be $(1 - x + \alpha x)$ mol. Consequently, the mole fractions of components are expressed by the equations

$$x(\text{KF}) = \frac{1 - 2x + \alpha x}{1 - x + \alpha x}; \qquad x(\text{K}_2\text{MoO}_4) = \frac{\alpha x}{1 - x + \alpha x};$$

$$x(\text{K}_3\text{FMoO}_4) = \frac{x(1 - \alpha)}{1 - x + \alpha x} \qquad (1)$$

Assuming the ideal behaviour of the solutions (a(X) = x(X)) the equilibrium constant of eqn (A) can be written as

$$K = \frac{\alpha_0^2}{1 - \alpha_0^2} = \frac{\alpha(1 - 2x + \alpha x)}{(1 - \alpha)(1 - x + \alpha x)} \qquad (2)$$

where α_0 is the dissociation degree of pure K_3FMoO_4. Similar expression for the equilibrium constant can be derived for $x \geq 0.5$

$$K = \frac{\alpha[x - (1 - \alpha)(1 - x)]}{(1 - \alpha)[x + \alpha(1 - x)]} \quad (3)$$

By means of eqns (2) and (3) it is possible to calculate the degree of thermal dissociation α of K_3FMoO_4 for any arbitrary selected value of α_0 and, after inserting the calculated value α into eqns (1), to obtain the values of the equilibrium mole fractions of the individual components. In the calculation it was assumed that in the given temperature range of the liquidus the equilibrium constant does not change with the temperature. Introducing the values of the equilibrium mole fractions of the individual components $x(i)$ into the Le Chatelier—Shreder's equation, the values of the temperature of primary crystallization of components, $T_{pc}(i)$, may be calculated, which makes it possible to draw the hypothetical liquidus curves of the investigated system corresponding to the appropriate value of the dissociation degree α_0. The melting temperature of the hypothetical undissociated compound K_3FMoO_4 for the given equilibrium composition was calculated from the experimentally determined melting temperature of this compound.

The criterion for the selection of the correct value of the dissociation degree, α_0, is the best fit between the experimental and calculated liquidus temperatures according to the condition

$$\sum_{i=1}^{n}[T_{pc}(i, \exp) - T_{pc}(i, \text{calc})]^2 = \min \quad (4)$$

The experimentally determined phase diagram by *Julsrud* and *Kleppa* [4] was taken for the calculation. The data for the temperatures and enthalpies of melting of KF and K_2MoO_4 were taken from [4] as well, the enthalpy of fusion for K_3FMoO_4 has been taken from [5]. The values $\Delta H(f,KF) = 29.5$ kJ mol^{-1}, $\Delta H(f,K_2MoO_4) = 34.7$ kJ mol^{-1}, and $\Delta H(f,K_3FMoO_4) = 62.0$ kJ mol^{-1} were adopted for the calculation.

In the determination of the degree of thermal dissociation of the additive compound K_3FMoO_4, based on the volume properties, the theoretical density of the melts has been calculated according to the equation

$$\rho(\text{calc}) = \left[\frac{w(KF)}{\rho(KF)} + \frac{w(K_2MoO_4)}{\rho(K_2MoO_4)} + \frac{w(K_3FMoO_4)}{\rho(K_3FMoO_4)}\right]^{-1} \quad (5)$$

where $w(X)$ and $\rho(X)$ are the equilibrium mass fraction and the densities of the components X, respec-

tively, $\rho(K_3FMoO_4)$ being the hypothetical density of the undissociated molten compound K_3FMoO_4 at the given temperature. For each selected value of the equilibrium constant (eqns (2) and (3)) and the selected hypothetical density of undissociated molten K_3FMoO_4, a set of hypothetical density values has been obtained for each initial composition of the melt. Here again, the condition

$$\sum_{i=1}^{n}[\rho(i, \exp) - \rho(i, \text{calc})]^2 = \min \quad (6)$$

was the criterion of the correctness of the selection.

EXPERIMENTAL

The density of the melts of the system KF—K_2MoO_4 was measured by means of the Archimedean method. The platinum sphere with a diameter of 20 mm suspended on a platinum wire ($d = 0.3$ mm) has been used as the measuring body. The dependence of the volume of the sphere on the temperature was determined by calibration using molten NaCl and KCl. The experimental error of the density measurement did not surpass 0.3 %. The detailed description of the measuring device used is given in [6].

The measurements were performed on cooling within a temperature range of about 100 K, the lower limit of this interval being 10—20 °C above the temperature of primary crystallization of the respective melts.

For the description of the temperature dependences of the density the linear equation in the form

$$\rho = a - b \cdot \theta \quad (7)$$

was used, where ρ is the density in g cm^{-3} and θ is the temperature in °C. The values of the constants a and b are given together with the standard deviations of approximation in Table 1.

RESULTS AND DISCUSSION

The values of the equilibrium dissociation constants, degree of dissociation and densities of the

Table 1. Coefficients a and b in the Equation $\rho = a - b \cdot \theta$ and the Standard Deviation of Approximation for the Investigated KF—K_2MoO_4 Melts

$x(KF)$	$x(K_2MoO_4)$	a g cm^{-3}	$b \cdot 10^4$ g cm^{-3} °C^{-1}	$s \cdot 10^4$ g cm^{-3}
–	1.000	3.3046	10.661	4.2
0.250	0.750	3.1791	9.673	3.5
0.500	0.500	3.0526	9.084	3.1
0.750	0.250	2.8505	9.208	2.9
1.000	–	2.6464	6.515	7.2

Table 2. Values of the Equilibrium Constants, the Degree of Dissociation and the Hypothetical Densities of Undissociated Compound K$_3$FMoO$_4$

$\dfrac{T}{\text{K}}$	K	α_0	$\dfrac{\rho}{\text{g cm}^{-3}}$
1100	2.840	0.860	2.250
1150	4.263	0.900	2.200
1200	15.921	0.970	2.150

molten undissociated compound K$_3$FMoO$_4$ at 1100 K, 1150 K, and 1200 K are summarized in Table 2. As evidenced by the determined values of the dissociation degree, the additive compound K$_3$FMoO$_4$ undergoes a pronounced thermal dissociation on melting. Based on the dependence of the equilibrium dissociation constant on temperature, the enthalpy of dissociation $\Delta H(\text{dis},\text{K}_3\text{FMoO}_4) = 18.8$ kJ mol^{-1} has been calculated. This value represents a substantial part of the enthalpy of fusion.

Fig. 1 shows the phase diagram of the system KF—K$_2$MoO$_4$ according to [4] and the liquidus curves calculated for the value of the equilibrium dissociation constant $K(\text{dis},\text{K}_3\text{FMoO}_4) = 0.656$, the corresponding values of the dissociation degree and the hypothetical melting temperature of the undissociated compound K$_3$FMoO$_4$ being $\alpha_0 = 0.81$ and $T(\text{f,nd},\text{K}_3\text{FMoO}_4) = 1212$ K. The standard deviation of the approximation is 6.8 K. The fulfillment of the limiting laws for $x(\text{X}) \rightarrow 1$ demonstrates the plausibility of the calculated equilibrium composition as well as the thermodynamic consistency of the experimental phase diagram. The determined value of the degree of dissociation of K$_3$FMoO$_4$ agrees very well with the value $\alpha_0(1100 \text{ K}) = 0.86$ determined by the analysis of the volume properties.
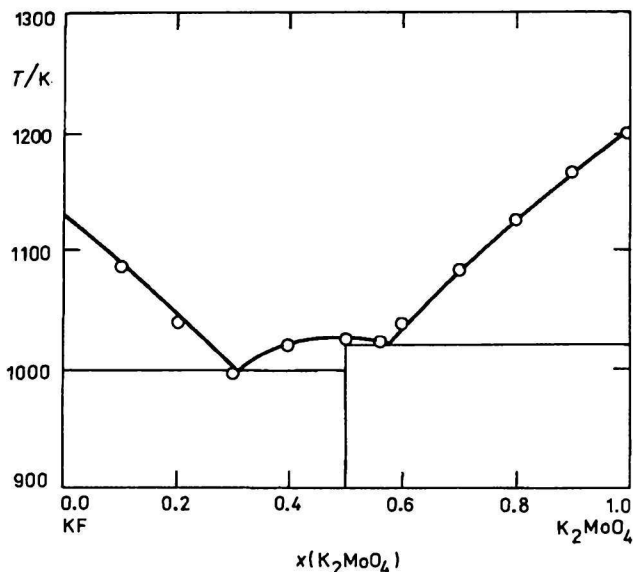
Fig. 1. Phase diagram of the system KF—K$_2$MoO$_4$. o Experiments [4], —— calculated.

REFERENCES

1. Mateiko, Z. A. and Bukhalova, G. A., *Zh. Neorg. Khim. 4*, 1649 (1959).
2. Koštenská, I. and Malinovský, M., *Chem. Zvesti 36*, 159 (1982).
3. Koyama, I. K., Hashimoto, Y., Omori, S., and Teranaki, K., *Trans. J. Inst. Met. 25*, 804 (1984).
4. Julsrud, S. and Kleppa, O. J., *Acta Chem. Scand., A 35*, 669 (1981).
5. Adamkovičová, K., Kosa, L., Proks, I., and Nerád, I., to be published.
6. Silný, A., *Sdělovací Technika 38*, 101 (1990).

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