

# Phase Diagram of the KF—K<sub>2</sub>MoO<sub>4</sub>—B<sub>2</sub>O<sub>3</sub> System

<sup>a</sup>O. PATARÁK, <sup>b</sup>Z. JANTÁKOVÁ, and <sup>a</sup>V. DANĚK

<sup>a</sup>Institute of Inorganic Chemistry, Slovak Academy of Sciences, SK-842 36 Bratislava

<sup>b</sup>Department of Inorganic Technology, Faculty of Chemical Technology, Slovak Technical University, SK-812 37 Bratislava

Received 18 February 1993

In the binary system KF—K<sub>2</sub>MoO<sub>4</sub> two eutectics with the coordinates 30 mole % K<sub>2</sub>MoO<sub>4</sub>, 720 °C and 59 mole % K<sub>2</sub>MoO<sub>4</sub>, 745 °C were found. The additive compound K<sub>3</sub>FMoO<sub>4</sub> melts congruently at 751 °C. In the binary system KF—B<sub>2</sub>O<sub>3</sub> the liquidus curve decreases monotonically with the increasing content of B<sub>2</sub>O<sub>3</sub>. The inflection point was found in the course of the liquidus curve of K<sub>2</sub>MoO<sub>4</sub> in the binary K<sub>2</sub>MoO<sub>4</sub>—B<sub>2</sub>O<sub>3</sub> system. The strong positive deviation from ideal behaviour was ascribed to the formation of heteropolyanions [BMo<sub>6</sub>O<sub>24</sub>]<sup>9-</sup> in the melt.

The liquidus surfaces of KF, K<sub>3</sub>FMoO<sub>4</sub>, and K<sub>2</sub>MoO<sub>4</sub> are present in the investigated part of the ternary system KF—K<sub>2</sub>MoO<sub>4</sub>—B<sub>2</sub>O<sub>3</sub>. No ternary eutectic point was found. The greatly enlarged liquidus surface of K<sub>2</sub>MoO<sub>4</sub> was ascribed to the substitution of oxygen atoms of the coordination sphere of molybdenum in the heteropolyanions by fluorine ones.

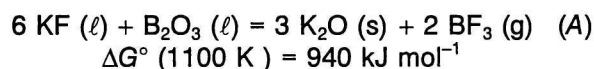
The melts of the system KF—K<sub>2</sub>MoO<sub>4</sub>—B<sub>2</sub>O<sub>3</sub> seem to be promising electrolytes for the electro-deposition of molybdenum from fused salts, especially when smooth, adherent molybdenum layers on metallic surfaces have to be prepared [1]. From the theoretical point of view these melts represent very little investigated electrolytes containing both the classical ionic components as well as the network forming ones. The possible chemical interactions between them are still not well understood.

The system KF—K<sub>2</sub>MoO<sub>4</sub>—B<sub>2</sub>O<sub>3</sub> is a considerably complicated subsystem of the quaternary reciprocal system K<sup>+</sup>, B<sup>3+</sup>, Mo<sup>6+</sup> // F<sup>-</sup>, O<sup>2-</sup>, in which a number of compounds are formed. The phase equilibria in the ternary system KF—K<sub>2</sub>MoO<sub>4</sub>—B<sub>2</sub>O<sub>3</sub> have not been studied till now. The existing phase equilibrium studies are as follows.

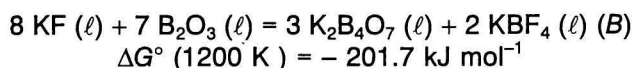
The phase diagram of the binary system KF—K<sub>2</sub>MoO<sub>4</sub> was studied by *Schmitz-Dumont* and *Weeg* [2], *Mateiko* and *Bukhalova* [3], and *Julsrud* and *Kleppa* [4]. The last authors measured also the enthalpies of mixing of this system. These authors found that in this system the congruently melting additive compound K<sub>3</sub>FMoO<sub>4</sub> with the melting point of 752 °C is formed. This compound divides the system into two simple eutectic ones with the coordinates of the eutectic points of 29.2 mole % K<sub>2</sub>MoO<sub>4</sub> and 720.4 °C in the subsystem KF—K<sub>3</sub>FMoO<sub>4</sub> and 58.4 mole % K<sub>2</sub>MoO<sub>4</sub> and 748.6 °C in the subsystem K<sub>3</sub>FMoO<sub>4</sub>—K<sub>2</sub>MoO<sub>4</sub>. The obtained values of the enthalpy of mixing indicate that the system KF—K<sub>2</sub>MoO<sub>4</sub> deviates only very little from the ideal behaviour. This observation was confirmed very recently by the measurements of the volume properties of this system [5] and by the calculation of the thermal dissociation of the additive compound

K<sub>3</sub>FMoO<sub>4</sub>. In [5] it was found that the degree of thermal dissociation of K<sub>3</sub>FMoO<sub>4</sub> at the temperature of fusion attains the value 0.81, which refers to the very low thermal stability of this compound.

The liquidus curve of KF in the system KF—B<sub>2</sub>O<sub>3</sub> up to 20 mole % B<sub>2</sub>O<sub>3</sub> was determined recently by *Chrenková* and *Daněk* [6]. According to the value of the standard Gibbs energy of the metathetical reaction



the system KF—B<sub>2</sub>O<sub>3</sub> should formally be the stable diagonal of the ternary reciprocal system K<sup>+</sup>, B<sup>3+</sup> // F<sup>-</sup>, O<sup>2-</sup>. However, a number of compounds are formed in this ternary reciprocal system. From the thermodynamic analysis of the liquidus curve of KF it follows that the reaction



creating two complex compounds KBF<sub>4</sub> and K<sub>2</sub>B<sub>4</sub>O<sub>7</sub> takes place in the melts. The presence of both the compounds was confirmed also by means of the X-ray powder diffraction analysis and IR spectroscopy in the quenched molten mixtures. The positive deviation of the real liquidus curve from the theoretical one is most probably due to the further polymerization of the borate species.

The phase diagram of the binary system K<sub>2</sub>MoO<sub>4</sub>—B<sub>2</sub>O<sub>3</sub> was not studied till now.

The aim of the present work was to determine the solidus—liquidus equilibria in the system KF—K<sub>2</sub>MoO<sub>4</sub>—B<sub>2</sub>O<sub>3</sub> in the concentration region interesting from the point of view of the electrochemical

deposition of molybdenum, *i.e.* up to 30 mole % B<sub>2</sub>O<sub>3</sub>.

## EXPERIMENTAL

The temperatures of primary crystallization were determined by means of the thermal analysis method, registering the cooling and heating curves of the investigated mixtures. The samples ( *ca.* 40 g in mass ) were placed in a platinum crucible in the resistance furnace with an adjustable cooling rate. The temperature control and the data processing were performed using a computerized measuring device. The temperature was measured using a Pt—PtRh10 thermocouple calibrated to the melting points of well defined simple salts. The hot junction of the thermocouple was immersed directly in the melt. The measured temperatures of primary crystallization were reproducible in the range of 2 °C.

Reagent grade KF (Lachema) was dehydrated by heating at 120 °C for two weeks in the presence of P<sub>2</sub>O<sub>5</sub>. K<sub>2</sub>MoO<sub>4</sub> (pure, Fluka) was dried at 600 °C for 6 h. Reagent grade B<sub>2</sub>O<sub>3</sub> (Merck) was premelted after drying in vacuum for one week in the presence of P<sub>2</sub>O<sub>5</sub>.

Besides the binary systems the liquidus temperatures in the ternary system KF—K<sub>2</sub>MoO<sub>4</sub>—B<sub>2</sub>O<sub>3</sub> were measured in the cross-sections with constant mole fraction ratio  $x(\text{KF})/x(\text{K}_2\text{MoO}_4) = 4, 2.333, 1.5, 0.667, 0.2$  and up to 30 mole % B<sub>2</sub>O<sub>3</sub>. Most experimental difficulties were brought by samples with increased B<sub>2</sub>O<sub>3</sub> content, which show considerable evaporation and increased tendency to undercooling. Careful adjustment of the cooling rate and registration of the heating curves were used in such cases.

The measured temperatures of primary crystallization of investigated samples are given in Table 1.

## RESULTS AND DISCUSSION

### The System KF—K<sub>2</sub>MoO<sub>4</sub>

The phase diagram of the system KF—K<sub>2</sub>MoO<sub>4</sub> measured in this work is shown in Fig. 1. It was found that the melting point of the additive compound

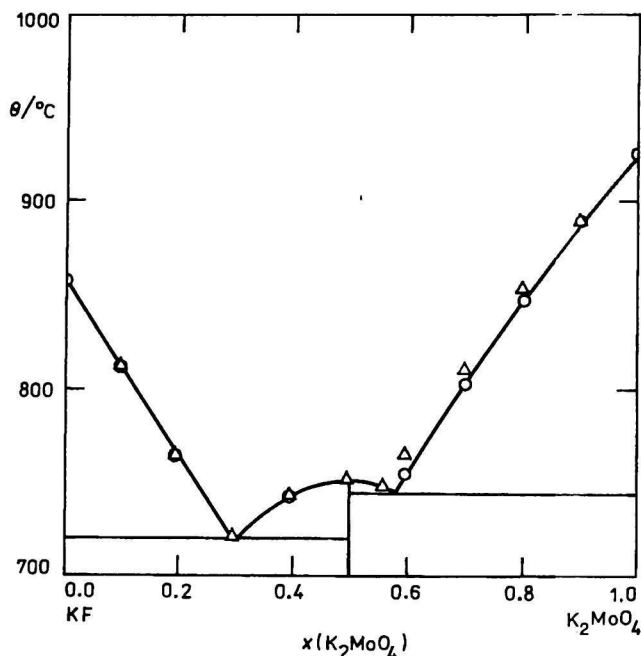


Fig. 1. Phase diagram of the binary system KF—K<sub>2</sub>MoO<sub>4</sub>.  
○ This paper, △ Julsrud and Kleppa [4].

Table 1. Temperatures of Primary Crystallization of the Melts of the System KF—K<sub>2</sub>MoO<sub>4</sub>—B<sub>2</sub>O<sub>3</sub>

$x(\text{KF})$	$x(\text{K}_2\text{MoO}_4)$	$x(\text{B}_2\text{O}_3)$	$\theta/^\circ\text{C}$	$x(\text{KF})$	$x(\text{K}_2\text{MoO}_4)$	$x(\text{B}_2\text{O}_3)$	$\theta/^\circ\text{C}$
1.000	0.000	0.000	858	0.720	0.180	0.100	741
0.900	0.100	0.000	813	0.540	0.360	0.100	733
0.800	0.200	0.000	763	0.450	0.450	0.100	742
0.700	0.300	0.000	720	0.360	0.540	0.100	779
0.600	0.400	0.000	743	0.180	0.720	0.100	848
0.500	0.500	0.000	751	0.640	0.160	0.200	728
0.400	0.600	0.000	755	0.480	0.320	0.200	741
0.300	0.700	0.000	803	0.400	0.400	0.200	784
0.200	0.800	0.000	848	0.320	0.480	0.200	814
0.100	0.900	0.000	891	0.160	0.640	0.200	844
0.000	1.000	0.000	927	0.560	0.140	0.300	715
0.950	0.000	0.050	836	0.420	0.280	0.300	782
0.900	0.000	0.100	819	0.350	0.350	0.300	808
0.850	0.000	0.150	803	0.280	0.420	0.300	835
0.800	0.000	0.200	787	0.140	0.560	0.300	840
0.750	0.000	0.250	775	0.665	0.285	0.050	717
0.700	0.000	0.300	762	0.630	0.270	0.100	728
0.000	0.950	0.050	892	0.595	0.255	0.150	725
0.000	0.900	0.100	876	0.560	0.240	0.200	727
0.000	0.850	0.150	869	0.525	0.225	0.250	723
0.000	0.800	0.200	868	0.490	0.210	0.300	738
0.000	0.750	0.250	863				
0.000	0.700	0.300	857				
0.000	0.600	0.400	827				

$K_3FMoO_4$  has the value of 751 °C. The coordinates of the individual eutectic points are as follows: 30 mole %  $K_2MoO_4$  and 720 °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 only difference is in the course of the liquidus curve of  $K_2MoO_4$ , where the temperatures of primary crystallization of  $K_2MoO_4$  measured in [4] are a little higher. This leads to the slightly different coordinates of the respective eutectic point.

### The System $KF—B_2O_3$

The investigated part of the liquidus curve of  $KF$  in the binary system  $KF—B_2O_3$  is shown in Fig. 2 together with the values measured in [6]. The temperatures of primary crystallization of  $KF$  measured

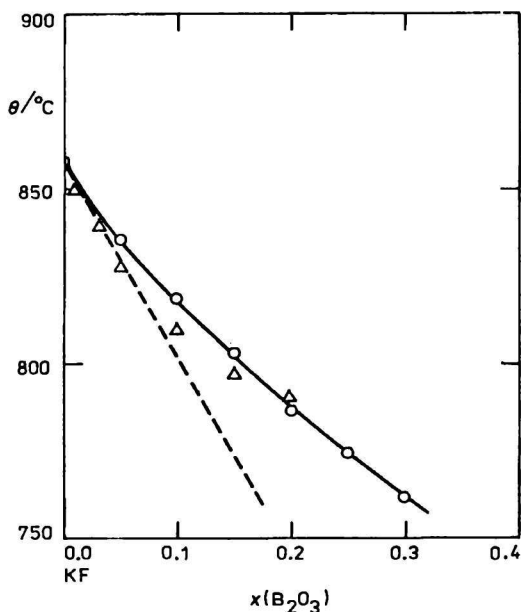


Fig. 2. Liquidus curve of  $KF$  in the system  $KF—B_2O_3$ . ○ This paper, △ *Chrenková and Daněk* [6], - - - limiting course for two new particles.

in this work are little higher in the region of 5–10 mole %  $B_2O_3$ , compared with those obtained in [6]. The conclusions concerning the region of diluted solutions were, however, confirmed also in this work. It should be noted that the uncertainty caused by the tendency of the melts to undercooling did not enable to obtain more accurate data. The decreasing slope of the liquidus curve indicates the formation of the more polymerized borate ions.

### The System $K_2MoO_4—B_2O_3$

The measured liquidus curve of  $K_2MoO_4$  in the binary system  $K_2MoO_4—B_2O_3$  is shown in Fig. 3. From the figure the strong positive deviation from the ideal

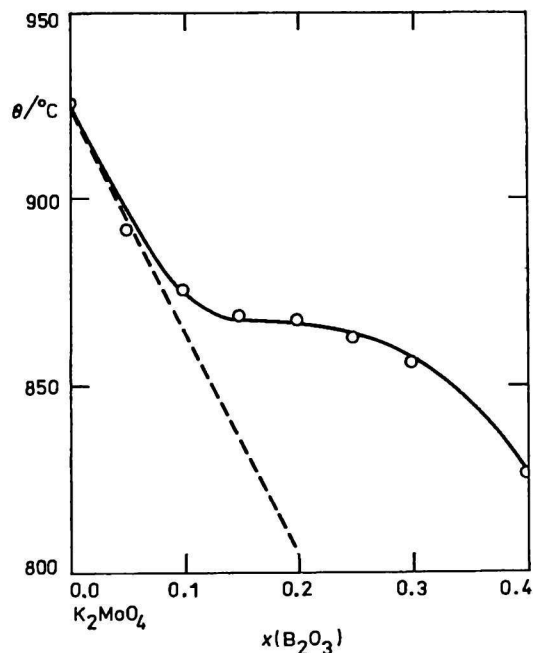


Fig. 3. Liquidus curve of  $K_2MoO_4$  in the system  $K_2MoO_4—B_2O_3$ . ○ Experimental, — liquidus curve, if formation of heteropolyanions  $[BMo_6O_{24}]^{9-}$  is considered, - - - limiting course for two new particles.

behaviour is obvious. Similar course may be observed in systems with a strong tendency to immiscibility, or when more polymerized ions are formed in the liquid phase.

The ability of molybdate to form isopolyanions is well known. Moreover, in the presence of some foreign atoms, like B, Si, P, etc., molybdates form heteropolyanions, the central foreign atoms being coordinated by six, nine or twelve  $MoO_6$  octahedra. Therefore it was assumed that the strong positive deviation of the liquidus curve is caused by the formation of such heteropolyanions in the melt. The formation of the following heteropolycompound was considered



Let us consider a mixture of  $x$  mol  $K_2MoO_4$  and  $(1-x)$  mol  $B_2O_3$ . Taking into account this chemical reaction and the conversion degree being approximately equal to 1, the following relation may be derived for the equilibrium mole fraction of  $K_2MoO_4$  in the mixture

$$x(K_2MoO_4, eq) = \frac{4x(K_2MoO_4) - 3}{2x(K_2MoO_4) - 1} \quad (1)$$

Using formally the theory of regular solutions, for the activity of  $K_2MoO_4$  in the mixture we have [7]

$$a(K_2MoO_4, eq) = x(K_2MoO_4, eq) \times \exp \left[ \frac{\Delta G^0}{RT} (1 - x(K_2MoO_4, eq))^2 \right] \quad (2)$$

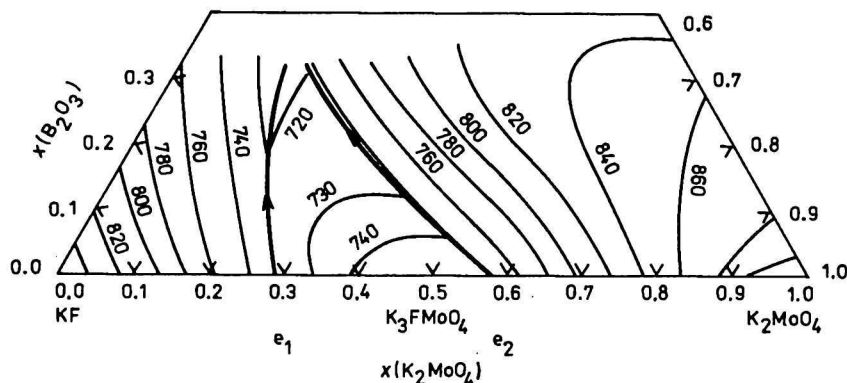


Fig. 4. Phase diagram of the ternary system KF—K<sub>2</sub>MoO<sub>4</sub>—B<sub>2</sub>O<sub>3</sub>.

where  $\Delta G^\circ$  is the standard Gibbs energy of the chemical reaction (C) related to 1 mol K<sub>2</sub>MoO<sub>4</sub> instead of the classical interaction parameter  $\omega$ . The liquidus curve of K<sub>2</sub>MoO<sub>4</sub>, calculated according to eqn (2) for the chosen value  $\Delta G^\circ = -20\,000\text{ J mol}^{-1}$  is shown in Fig. 3. The value of the enthalpy of fusion of K<sub>2</sub>MoO<sub>4</sub> was taken from [4]. The standard Gibbs energy of reaction (C) should then attain the value of  $-120\,000\text{ J mol}^{-1}$ . Unfortunately, the true value of the standard Gibbs energy of reaction (C) might not be calculated because of lack of the thermodynamic data needed. However, the very good agreement of the experimental and calculated liquidus curve does not reject the above chemical reaction. This conclusion is confirmed also by the fulfilment of the limiting relation

$$\lim_{x \rightarrow 1} \frac{da(\text{K}_2\text{MoO}_4)}{dx(\text{K}_2\text{MoO}_4)} = 2 \quad (3)$$

It means that by addition of one molecule of B<sub>2</sub>O<sub>3</sub> into molten K<sub>2</sub>MoO<sub>4</sub> two new particles, the anions [BMo<sub>6</sub>O<sub>24</sub>]<sup>9-</sup> and BO<sub>2</sub><sup>-</sup> are formed.

### The System KF—K<sub>2</sub>MoO<sub>4</sub>—B<sub>2</sub>O<sub>3</sub>

The phase diagram of the investigated part of the ternary system KF—K<sub>2</sub>MoO<sub>4</sub>—B<sub>2</sub>O<sub>3</sub> is shown in Fig. 4. The very extended liquidus surface of K<sub>2</sub>MoO<sub>4</sub> shifts the boundary line of the primary crystallization

of the additive compound K<sub>3</sub>FMoO<sub>4</sub> expressively to the KF corner, evidently due to the formation of the [BMo<sub>6</sub>O<sub>24</sub>]<sup>9-</sup> heteropolyanions also in the ternary melts. No ternary eutectic point was observed in the investigated part of KF—K<sub>2</sub>MoO<sub>4</sub>—B<sub>2</sub>O<sub>3</sub> system. The enlarged shape of the isotherms of the liquidus surface of K<sub>2</sub>MoO<sub>4</sub> may be probably due to the substitution of the oxygen atoms of the coordination sphere of molybdenum in the heteropolyanions [BMo<sub>6</sub>O<sub>24</sub>]<sup>9-</sup> by the fluorine ones. However, the existence of more polymerized heteropolyanions with the  $n(\text{B})/n(\text{Mo})$  ratio of 9 or 12 may not be excluded.

### REFERENCES

1. Koyama, K., Hashimoto, Y., Omori, S., and Terawaki, K., *Trans. Jpn. Inst. Met.* 25, 265 (1984).
2. Schmitz-Dumont, O. and Weeg, A., *Z. Anorg. Allg. Chem.* 265, 139 (1951).
3. Mateiko, Z. A. and Bukhalova, G. A., *Zh. Obshch. Khim.* 25, 1673 (1955).
4. Julsrud, S. and Kleppa, O. J., *Acta Chem. Scand.*, A 35, 669 (1981).
5. Daněk, V. and Chrenková, M., *Chem. Papers* 47, 339 (1993).
6. Chrenková, M. and Daněk, V., *Chem. Papers* 46, 222 (1992).
7. Malinovský, M., Roušar, I., et al., *Teoretické základy pochodů anorganické technologie I.* (Theoretical Fundamentals of Inorganic Technological Processes I.) P. 67. Nakladatelství technické literatury (Publishers of Technical Literature)/Alfa Publishers, Prague, 1987.

Translated by V. Daněk