

Thermodynamic Analysis of the Molten System KF—K₂MoO₄—B₂O₃

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Received 11 June 1997

The thermodynamically consistent phase diagram of the ternary system KF—K₂MoO₄—B₂O₃ up to 30 mole % B₂O₃ was calculated using the coupled analysis of the thermodynamic and phase diagram data.

In the system KF—K₂MoO₄—B₂O₃ the intermediate compound K₃FMoO₄ melting congruently at 751 °C is formed. This compound divides the binary system KF—K₂MoO₄ into two simple eutectic ones the coordinates of which are: 29.4 mole % K₂MoO₄, 717.7 °C, and 56.9 mole % K₂MoO₄, 747.4 °C. In the binary system KF—B₂O₃ the liquidus curve decreases monotonically with increasing content of B₂O₃. The inflexion point was found in the course of the liquidus curve of K₂MoO₄ in the binary system K₂MoO₄—B₂O₃. The strong positive deviation from ideal behaviour was ascribed to the possible formation of heteropolyanions [BMo₆O₂₄]⁹⁻ in the melt.

In the investigated concentration range of the ternary system one eutectic point has been found the coordinates of which are: 57 mole % KF, 24 mole % K₂MoO₄, 19 mole % B₂O₃, and $\theta_e = 682$ °C. The standard deviation of approximation in the calculated ternary phase diagram is ± 5.2 °C.

The melts of the system KF—K₂MoO₄—B₂O₃ seem to be promising electrolytes for the electrodeposition of molybdenum from fused salts, especially when smooth, adherent molybdenum coating on metallic surfaces has to be prepared [1]. From the theoretical point of view these melts represent very little investigated electrolytes containing both the classical ionic components and the network-forming one. The possible chemical interactions between them are not well understood.

The system KF—K₂MoO₄—B₂O₃ is a considerably complicated subsystem of the quinary reciprocal system K⁺, B³⁺, Mo⁶⁺ // F⁻, O²⁻, in which a number of compounds are formed. The experimental determination of the temperatures of primary crystallization in the ternary system KF—K₂MoO₄—B₂O₃ up to 30 mole % B₂O₃ was published previously [2].

In the present work the coupled analysis of the thermodynamic and phase diagram data of the binary system KF—K₂MoO₄ and of the ternary system KF—K₂MoO₄—B₂O₃ was performed. The optimized phase diagram was constructed.

DATA PROCESSING

The calculation of the phase diagrams of condensed systems using the coupled analysis of the thermodynamic and phase diagram data is based on the solution of a set of equations of the following type

$$\Delta_{\text{fus}}G_i^\circ(T) + RT \ln \frac{a_{l,i}(T)}{a_{s,i}(T)} = 0 \quad (1)$$

where $\Delta_{\text{fus}}G_i^\circ(T)$ is the standard molar Gibbs energy of fusion of the component i at the temperature T , R is the gas constant, and $a_{s,i}(T)$ and $a_{l,i}(T)$ are the activities of component i in the solid and liquid phase, respectively. Assuming immiscibility of components in the solid phase ($a_{s,i}(T) = 1$) and that the enthalpy of fusion of the components does not change with temperature, for the thermodynamic temperature of primary crystallization of the component i , $T_{\text{pc},i}$, we get

$$T_{\text{pc},i} = \frac{\Delta_{\text{fus}}H_i^\circ + RT_{\text{pc},i} \ln \gamma_{l,i}}{\Delta_{\text{fus}}S_i^\circ + R \ln x_{l,i}} \quad (2)$$

where $\Delta_{\text{fus}}H_i^\circ$ and $\Delta_{\text{fus}}S_i^\circ$ is the standard enthalpy and standard entropy of fusion, respectively, $x_{l,i}$ and $\gamma_{l,i}$ is the mole fraction and the activity coefficient of component i , respectively. The activity coefficients can be calculated from the molar excess Gibbs energy of mixing

$$RT_{\text{pc},i} \ln \gamma_{l,i} = \left[\frac{\partial(n\Delta G_{\text{ter}}^E)}{\partial n_i} \right]_{T,p,n_{j \neq i}} \quad (3)$$

where n_i is the amount of component i and n is the total amount of all components.

In the ternary system A—B—C the molar excess Gibbs energy of mixing in the liquid phase, ΔG_{ter}^E can be described by the following general equation

$$\Delta G_{\text{ter}}^E = \sum_j \left(x_A^{k(j)} x_B^{l(j)} x_C^{m(j)} \right) G_j \quad (4)$$

where x_i are the mole fractions of components, G_j are empirical coefficients in the composition dependence

of the molar excess Gibbs energy of mixing and $k(j)$, $l(j)$, $m(j)$ are adjustable integers. For the boundary binary systems one of the integers equals zero.

Using eqn (2), the following mathematical model for the coupled thermodynamic analysis was used

$$T_{pc,i} = F_{0,i} + \sum_j F_{j,i} G_j \quad (5)$$

where $T_{pc,i}$ was obtained from the phase diagram measurement. The first term on the right side represents the ideal behaviour and the second one the deviation from the ideal behaviour. For the auxiliary functions $F_{0,i}$ and $F_{j,i}$, with respect to the Gibbs—Duhem relation, the following equations hold

$$F_{0,i} = \frac{\Delta_{fus} H_i^{\circ}}{\Delta_{fus} S_i^{\circ} - R \ln x_{1,i}} \quad (6)$$

$$F_{j,i} = \frac{\left[\frac{\partial \left(n x_A^{k(j)} x_B^{l(j)} x_C^{m(j)} \right)}{\partial n_i} \right]_{j \neq i}}{\Delta_{fus} S_i^{\circ} - R \ln x_{1,i}} \quad (7)$$

If an intermediate compound $Z = A_p B_q C_r$ ($p+q+r=1$) is formed in the ternary system, eqns (4), (6), and (7) for this compound must be modified [3, 4]

$$\Delta G_{ter}^E = \sum_j \left(x_A^{k(j)} x_B^{l(j)} x_C^{m(j)} - p^{k(j)} q^{l(j)} r^{m(j)} \right) G_j \quad (8)$$

$$F_{0,Z} = \frac{\Delta_{fus} H_Z^{\circ}}{\Delta_{fus} S_Z^{\circ} - R \ln K x_A^p x_B^q x_C^r} \quad (9)$$

$$F_{j,Z} = \frac{p \left[\frac{\partial G'}{\partial n_A} \right]_{n_B, n_C} + q \left[\frac{\partial G'}{\partial n_B} \right]_{n_A, n_C} + r \left[\frac{\partial G'}{\partial n_C} \right]_{n_A, n_B}}{\Delta_{fus} S_Z^{\circ} - R \ln K x_A^p x_B^q x_C^r} \quad (10)$$

where

$$K = (p^p q^q r^r)^{-1} \quad (11)$$

and

$$G' = n \left(x_A^{k(j)} x_B^{l(j)} x_C^{m(j)} - p^{k(j)} q^{l(j)} r^{m(j)} \right) \quad (12)$$

Two different procedures may be used for the calculation of the molar excess Gibbs energy of mixing in the three-component system. In the first one the molar excess Gibbs energy of mixing is calculated separately for the individual binary boundary systems using the binary phase diagram data. The resulting coefficients for the binary systems are then used for the calculation of the molar excess Gibbs energy of mixing in the ternary system using the ternary phase diagram data only. In the second procedure the calculation of the molar excess Gibbs energy of mixing in the ternary system is performed in one step using eqn (4). In the calculation of phase diagrams of ternary systems the

former approach is frequently used [3, 4]. However, in the application to ternary systems exhibiting great differences in the deviation from ideal behaviour of the binary systems (the so-called unsymmetrical systems), this approach describes well the binaries, but does not yield reliable ternary diagram. For such a case the latter approach is more convenient. Since the investigated KF—K₂MoO₄—B₂O₃ system belongs into the group of unsymmetrical systems, the second procedure was used in the calculation.

RESULTS AND DISCUSSION

The coupled thermodynamic analysis, *i.e.* the calculation of the coefficients G_j in eqn (4) has been performed using the multiple linear regression analysis omitting the statistically unimportant terms according to the Student test on the 0.99 confidence level. As the optimizing criterion for the best fit between the experimental and calculated temperatures of primary crystallization the following condition was used for all the p measured points

$$\sum_{i=1}^p (T_{pc,exp,i} - T_{pc,calc,i})^2 = \min \quad (13)$$

The values of the enthalpy of fusion of individual components were taken from the literature and are summarized in Table 1. The experimentally determined temperatures of primary crystallization for the system KF—K₂MoO₄—B₂O₃ were taken from [2]. Beside condition (13) for the calculation of the molar excess Gibbs energy of mixing the minimum necessary G_j coefficients for attaining thermodynamically consistent phase diagram and a reasonable standard deviation of approximation were required. The calculation was performed assuming $\Delta_{fus} H_i \neq f(T)$ and $\Delta G_{ter}^E \neq f(T)$.

The calculated phase diagram of the system KF—K₂MoO₄—B₂O₃ is shown in Fig. 1. Three crystallization fields are present in the phase diagram corresponding to the primary crystallization of KF, K₂MoO₄, and the intermediate compound K₃FMoO₄. The calculated coordinates of the ternary eutectic point are 57 mole % KF, 24 mole % K₂MoO₄, 19 mole % B₂O₃, and $\theta_e = 682^\circ\text{C}$. The standard deviation of approximation in the calculated ternary phase diagram is $\pm 5.2^\circ\text{C}$.

Table 1. Enthalpy and Temperature of Fusion of Pure Compound Used for the Calculation

Component	θ_{fus}	$\Delta_{fus} H^{\circ}$	Ref.
	$^{\circ}\text{C}$	kJ mol^{-1}	
KF	858	28.26	[6]
K ₂ MoO ₄	928.2	34.7	[5]
K ₃ FMoO ₄	751	58.0	[7]

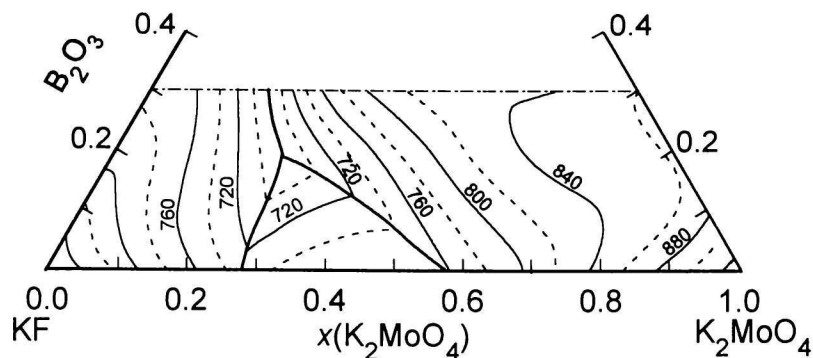


Fig. 1. Optimized phase diagram of the ternary system KF—K₂MoO₄—B₂O₃.

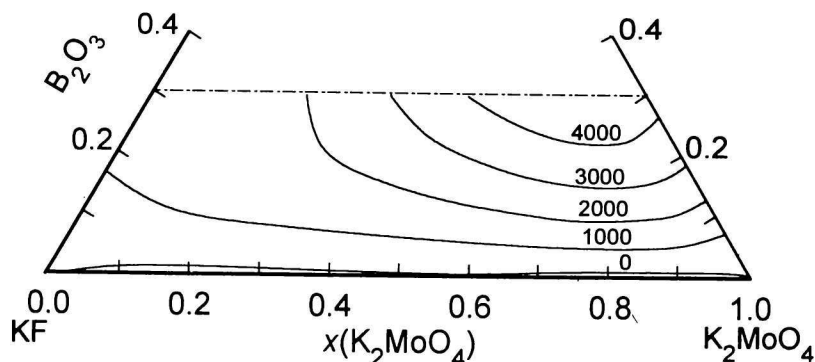


Fig. 2. Molar excess Gibbs energy of mixing in the system KF—K₂MoO₄—B₂O₃.

For the molar excess Gibbs energy of mixing in the system KF(1)—K₂MoO₄(2)—B₂O₃(3) the following equation was obtained

$$\begin{aligned} \Delta G_{\text{ter}}^E = & x_1 x_2 (G_{12,1} + G_{12,2} x_2 + G_{12,3} x_2^2) + x_1 x_3 G_{13,1} + \\ & + x_2 x_3^2 (G_{23,1} + G_{23,2} x_3 + G_{23,3} x_3^2 + G_{23,4} x_3^3) + \\ & + x_1^2 x_2 x_3 (G_{123,1} x_1 + G_{123,2} x_1 x_3 + G_{123,3} x_2^2) + \\ & + x_1 x_2^2 x_3 (G_{123,4} x_2 + G_{123,5} x_2 x_3 + G_{123,6} x_3^2) + \\ & + x_1 x_2 x_3^3 G_{123,7} \end{aligned} \quad (14)$$

The first term represents the molar excess Gibbs energy of mixing in the binary system KF—K₂MoO₄, the second one in the binary system KF—B₂O₃, and the third one in the binary system K₂MoO₄—B₂O₃. The last three terms represent the interaction in the ternary system. The coefficients G_j are given in Table 2. The molar excess Gibbs energy of mixing in the ternary system KF—K₂MoO₄—B₂O₃ is shown in Fig. 2.

In addition, the calculation of the phase diagram of the binary system KF—K₂MoO₄, based on the experimental data presented in [2] and those of *Julsrud* and *Kleppa* [5], was performed particularly in order to obtain more information on the structure of these melts. The latter authors measured also the enthalpy of mixing of this system. The obtained values of the enthalpy of mixing indicate that the system KF—K₂MoO₄ deviates only very little from the ideal behaviour. This

Table 2. Coefficients G_j of the Molar Excess Gibbs Energy of Mixing in the System KF—K₂MoO₄—B₂O₃

Coefficient	G_j	$t_{\text{Stud.}}$	System	
	kJ mol ⁻¹			
$G_{12,1}$	-4.6 ± 0.58	8.0	KF—K ₂ MoO ₄	
$G_{12,2}$	15 ± 2.0	7.5		
$G_{12,3}$	-16 ± 2.0	8.1		
$G_{13,1}$	6.9 ± 1.2	5.6	KF—B ₂ O ₃	
$G_{23,1}$	220 ± 21	10.5		
$G_{23,2}$	-905 ± 95	9.5	K ₂ MoO ₄ —B ₂ O ₃	
$G_{23,3}$	1620 ± 200	8.0		
$G_{23,4}$	-995 ± 150	6.7		
$G_{123,1}$	1260 ± 21	6.1		KF—K ₂ MoO ₄ —B ₂ O ₃
$G_{123,2}$	-430 ± 100	4.3		
$G_{123,3}$	-310 ± 63	5.0		
$G_{123,4}$	294 ± 25	11.6		
$G_{123,5}$	-990 ± 170	6.1		
$G_{123,6}$	1800 ± 230	8.0		
$G_{123,7}$	-370 ± 100	4.0		

observation was confirmed recently by the measurements of the volume properties of this system [8] and by the calculation of the thermal dissociation of the additive compound K₃FMoO₄. In [9] it was found that the degree of thermal dissociation of K₃FMoO₄ at the temperature of fusion attains the value $\alpha_o = 0.81$, which refers to the very low thermal stability of this compound.

Since the molar enthalpy of mixing in the system KF—K₂MoO₄ is known [5], the molar excess Gibbs energy of mixing can be expressed as follows

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} + T\Delta S_{\text{mix}} \quad (15)$$

The enthalpy of mixing was measured in [5] at one temperature only. Thus it can be expressed as function of composition in the form

$$\Delta H_{\text{mix}} = \sum_i x_{\text{AX}}^{\alpha_i} x_{\text{BX}}^{\beta_i} H_i \quad (16)$$

where H_i are empirical coefficients determined *e.g.* using the least-squares method from experimental data, and α_i and β_i are integers. Similar equation can be written for the entropy of mixing

$$\Delta S_{\text{mix}} = \sum_i x_{\text{AX}}^{\alpha_i} x_{\text{BX}}^{\beta_i} S_i \quad (17)$$

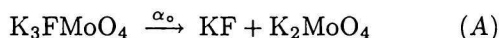
In Table 3 the calculated values of the coefficients H_i and S_i are given. The optimized phase diagram of the system KF—K₂MoO₄ is shown in Fig. 3. The coordinates of the eutectic points are as follows

$$E_1: x(\text{K}_2\text{MoO}_4) = 0.294, \quad \theta_{e1} = 717.7^\circ\text{C}$$

$$E_2: x(\text{K}_2\text{MoO}_4) = 0.569, \quad \theta_{e2} = 747.4^\circ\text{C}$$

The course of the mixing quantities for the system KF—K₂MoO₄ is shown in Fig. 4.

For the calculation of the entropy of mixing the approach based on the idea of the thermal dissociation of the intermediate compound K₃FMoO₄ in the melt according to the scheme



was used as well. After thermal dissociation the ideal mixing of constituents is assumed. The configuration entropy of mixing can be then expressed by the equation

$$\Delta S_{\text{mix}} = -R(x_{\text{KF}} \ln x_{\text{KF}} + x_{\text{K}_2\text{MoO}_4} \ln x_{\text{K}_2\text{MoO}_4} + x_{\text{K}_3\text{FMoO}_4} \ln x_{\text{K}_3\text{FMoO}_4}) \quad (18)$$

Table 3. Coefficients of the Composition Dependence of the Molar Enthalpy and Entropy of Mixing (Eqn (16)) in the System KF—K₂MoO₄

	α_i	β_i	H_i^*	S_i
			J mol ⁻¹	J mol ⁻¹ K ⁻¹
1	1	1	810 ± 43	7.0 ± 0.4
2	1	2	—	-6.0 ± 1.2
3	1	3	420 ± 140	5.8 ± 1.3

* Calculated according to the experimental data published in [5].

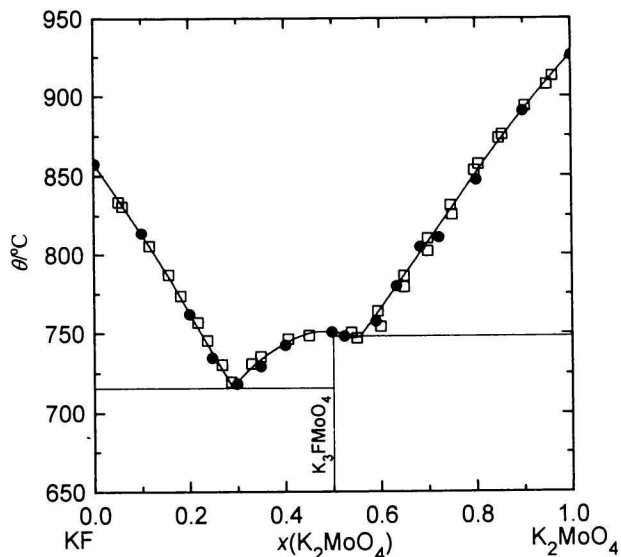


Fig. 3. Optimized phase diagram of the binary system KF—K₂MoO₄. ● Patarák *et al.* [2], □ Julsrud and Kleppa [5], — calculated.

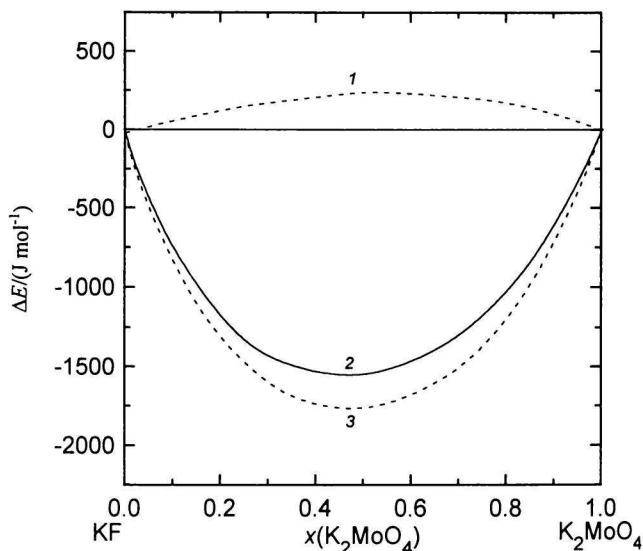


Fig. 4. Molar excess quantities in the system KF—K₂MoO₄ at the temperature 1000°C. 1. ΔH_{mix} ; 2. ΔG^E ; 3. $T\Delta S^E$

The equilibrium mole fractions of constituents are given by the equilibrium constant of the reaction (A)

$$K_A = \frac{x_{\text{KF}} x_{\text{K}_2\text{MoO}_4}}{x_{\text{K}_3\text{FMoO}_4}} = \frac{\alpha_o^2}{1 - \alpha_o} \quad (19)$$

and they can be calculated for every composition from the material balance (see *e.g.* in [10] for details). The best fit of the configuration entropy with the course of the entropy of mixing calculated according to the coupled thermodynamic analysis was obtained for the dissociation degree $\alpha_o = 0.89$, which is in good agreement with the value calculated on the basis of the

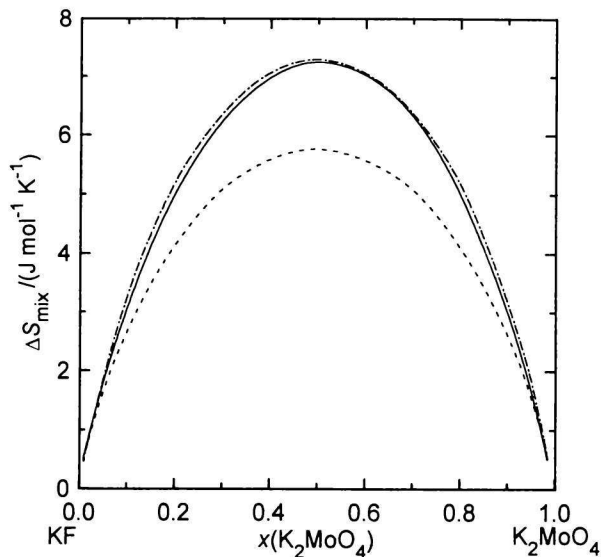


Fig. 5. Molar entropy of mixing in the system KF—K₂MoO₄. Solid line - calculated using the coupled thermodynamic analysis, dashed line - calculated using the dissociation model with $\alpha_{0, K_3FMoO_4} = 0.89$, dotted line - ideal course assuming the total dissociation of components.

density measurements. In Fig. 5 the comparison of the entropy of mixing calculated according to different approaches is shown.

Acknowledgements. The present work was financially supported by the Scientific Grant Agency of the Ministry of Educa-

tion of the Slovak Republic and the Slovak Academy of Sciences under the No. 2/4032/97.

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Translated by V. Daněk