

# Phase Diagram of the System $\text{KBF}_4\text{—KF—KCl}$

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Received 30 April 1991

Using the thermal analysis method the phase diagram of the  $\text{KBF}_4\text{—KF—KCl}$  system was determined. The system is a simple eutectic one with the coordinates of the eutectic point of 61.4 mole %  $\text{KBF}_4$ , 19.4 mole %  $\text{KF}$ , 19.2 mole %  $\text{KCl}$  and the temperature of the eutectic crystallization of 422 °C. The dependence of the excess Gibbs energy of mixing on the composition was calculated using the theory of regular solutions. From the analysis of this property it follows that a significant ternary interaction of all present anions takes place, most probably due to the exchange substitution of fluorine atoms in the complex fluoroborate anion by chlorine ones.

The study of the phase diagram of the  $\text{KBF}_4\text{—KF—KCl}$  system is a part of the complex investigation of the physicochemical properties of the molten quaternary system  $\text{KF—KCl—KBF}_4\text{—K}_2\text{TiF}_6$ , which is a potential electrolyte for the electrochemical synthesis of titanium diboride, especially for obtaining  $\text{TiB}_2$  layers on metallic substrates [1].

The density and the electric conductivity of the molten system  $\text{KBF}_4\text{—KF—KCl}$  have been published formerly [2, 3]. The phase diagrams of the boundary binary systems may also be found in the literature [4—7]. In all cases they are simple eutectic systems. The coordinates of the eutectic point in the  $\text{KF—KCl}$  system are 47 mole %  $\text{KF}$  and 976 K [4], in the  $\text{KF—KBF}_4$  system 74.5 mole %  $\text{KBF}_4$  and 733 K [5] and in the  $\text{KCl—KBF}_4$  system 75 mole %  $\text{KBF}_4$  and 737 K [6]. The phase diagram of the system  $\text{KBF}_4\text{—KCl}$  was studied also in [7], where a formation of a congruently melting compound 11  $\text{KBF}_4 \cdot \text{KCl}$  was suggested. However, the existence of this compound was not confirmed in the later measurements [6]. From the published data it may be concluded that no additional compounds are formed in the binary systems.

In the present work the phase diagram of the ternary system  $\text{KBF}_4\text{—KF—KCl}$  was studied using the thermal analysis method. On the basis of the thermodynamic analysis the character of interaction of components was discussed.

## EXPERIMENTAL

The temperatures of the primary crystallization were measured using the thermal analysis method recording the cooling curves of the studied samples. A computer-controlled automatic thermal

analysis device with a subsequent statistical processing of the output data was used. The sample was placed in a platinum crucible in a resistance furnace. The temperature of the sample was measured using a Pt—PtRh10 thermocouple. The reproducibility of the temperature of primary crystallization measurement was  $\pm 1$  °C. Detailed description of the experimental device used is given in [8].

The reagent grade  $\text{KCl}$  ( $T_f = 1044$  K,  $\Delta H_f = 27\,301$  J mol<sup>-1</sup>),  $\text{KF}$  ( $T_f = 1131$  K,  $\Delta H_f = 27\,214$  J mol<sup>-1</sup>), and  $\text{KBF}_4$  ( $T_f = 844$  K,  $\Delta H_f = 17\,688$  J mol<sup>-1</sup>) were used for the preparation of samples. The thermodynamic data of the pure components were taken from [9]. The temperature of primary crystallization was determined in the cross-sections of the ternary system with a constant mole ratio  $n(\text{KF}) : n(\text{KCl}) = 0.25, 0.67, 1.5, 4$ . In the cross-sections the mixtures with 20, 40, 60, and 80 mole %  $\text{KBF}_4$  were examined.

## Data Processing

For the dependence of the temperature of primary crystallization  $T_{pc}(i)$  on the composition the simplified Le Chatelier—Shreder equation is valid ( $\Delta H_f = \text{const.}$ )

$$T_{pc}(i) = \frac{\Delta H_f(i) + RT_{pc}(i) \ln \gamma(i)}{\frac{\Delta H_f(i)}{T_f(i)} - R \ln x(i)} \quad (1)$$

where  $T_f(i)$  and  $\Delta H_f(i)$  is the temperature and the enthalpy of fusion of the pure  $i$ -th component, respectively,  $x(i)$  and  $\gamma(i)$  is the mole fraction and the activity coefficient of the  $i$ -th component in the mixture, respectively. For the dependence of the molar excess Gibbs energy on the composi-

tion in the boundary binary systems the following relation was considered

$$\Delta G_{\text{bin}}^{\text{ex}} = \sum_{j=1}^5 A_j x_1 x_2^j \quad (2)$$

where  $A_j$  are the binary interaction coefficients. From the Gibbs–Duhem equation it follows for the activity coefficient

$$RT \ln \gamma(i) = \left[ \frac{n \partial \Delta G_{\text{bin}}^{\text{ex}}}{\partial n(i)} \right]_{T, p, n(j) \neq n(i)} \quad (3)$$

where  $n(i)$  is the amount of the  $i$ -th component and  $n$  is the total amount of the system. Considering eqns (1–3) for the temperature of primary crystallization in the binary system it may be written

$$T_{\text{pc, calc}} = F_0 + \sum_{j=1}^5 A_j F_j \quad (4)$$

where

$$F_0 = \frac{\Delta H_f(1) P(1)}{M(1)} + \frac{\Delta H_f(2) P(2)}{M(2)} \quad (5)$$

$$M(i) = \frac{\Delta H_f(i)}{T_f(i)} - R \ln x(i) \quad (6)$$

$P(i)$  is an auxiliary function which attains the value of one for the primarily crystallized component and zero for the second one. With respect to eqns (2) and (3) for  $F_j$  the following relation can be derived

$$F_j = \frac{x_2^j (1 - j x_1) P(1)}{M(1)} + \frac{j x_1 x_2^{j-1} (1 - x_1) P(2)}{M(2)} \quad (7)$$

The coefficients  $A_j$  in eqn (4) were calculated using the multiple linear regression method. The statistical importance of the individual coefficients was checked by means of the Student's criterion at the 0.95 confidence level. The statistically nonimportant coefficients were excluded according to the  $t(\text{crit.})$  value. The results of the regression analysis are summarized in Table 1.

**Table 1.** Coefficients  $A_j$  of Eqn (4) in the Boundary Binary Systems and the Standard Deviations of the Measured and Calculated Temperatures of Primary Crystallization

System	$A_1$	$A_2$	$A_3$	$A_5$	$\sigma/\text{K}$
	$\text{J mol}^{-1}$				
KBF <sub>4</sub> –KF	$-3014 \pm 146$	–	$6760 \pm 325$	$394 \pm 96$	1.7
KCl–KBF <sub>4</sub>	$1437 \pm 145$	–	$1124 \pm 413$	$-721 \pm 64$	2.8
KF–KCl	$1997 \pm 222$	$-7854 \pm 988$	$8722 \pm 938$	–	3.3

The calculation procedure in the ternary system was analogical to that used in the binary ones. For the molar excess Gibbs energy the following relation was used

$$\Delta G_{\text{ter}}^{\text{ex}} = \sum_{i=1}^3 \Delta G_{\text{bin}}^{\text{ex}} + B x_1 x_2 x_3 + \sum_{\substack{i=1 \\ i \neq j < k}}^3 C_i x_i^2 x_j x_k \quad (8)$$

where the first term is the sum of the binary interactions and the last two terms describe the ternary interaction. For the temperature of primary crystallization in the ternary system it may be written

$$T_{\text{pc, calc}} = F'_0 + B F_1 + \sum_{i=1}^3 C_i F_{i+1} \quad (9)$$

where

$$F'_0 = \sum_{i=1}^3 \frac{\left[ \frac{n \partial \Delta G_{\text{bin}}^{\text{ex}}(i)}{\partial n(i)} \right]_{T, p, n(j) \neq n(i)} P(i) + \Delta H_f(i)}{M(i)} \quad (10)$$

$$F_1 = \sum_{i=1}^3 \frac{\left[ \frac{n \partial x_1 x_2 x_3}{\partial n(i)} \right]_{T, p, n(j) \neq n(i)} P(i)}{M(i)} \quad (11)$$

and with respect to eqns (2) and (8) e.g. for  $F_2$  the following relation may be derived

$$F_2 = \sum_{i=1}^3 \frac{\left[ \frac{n \partial x_1^2 x_2 x_3}{\partial n(i)} \right]_{T, p, n(j) \neq n(i)} P(i)}{M(i)} \quad (12)$$

Analogical relations may be derived for  $F_3$  and  $F_4$  where the functions  $M(i)$  and  $P(i)$  have the same meaning as in the binary systems and the binary coefficients  $A_j$  needed for the  $F'_0$  calculation are taken from the binary systems calculation (cf. Table 1). The calculated values of the ternary coefficients  $B$  and  $C_i$  are given in Table 2.

**Table 2.** Coefficients  $B$  and  $C_i$  of Eqn (9) in the Ternary System and the Standard Deviations of the Measured and Calculated Temperatures of Primary Crystallization

$B$	$C_1$	$C_2$	$\sigma/K$
	$\text{J mol}^{-1}$		
—	—	—	11.4
$-10601 \pm 732$	—	—	6.9
—	$-13243 \pm 2574$	$-24531 \pm 1441$	5.1
—	—	$-25838 \pm 1504$	5.7

## RESULTS AND DISCUSSION

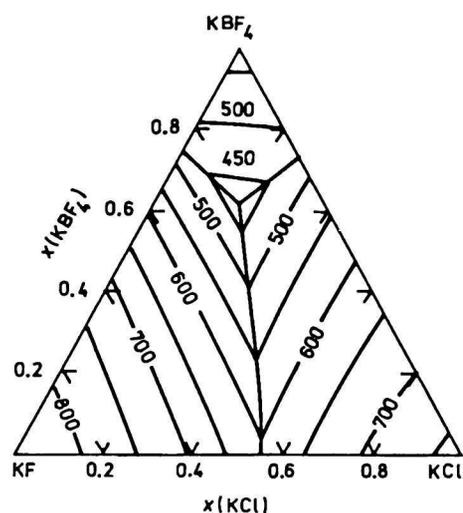
It was found that the system under investigation is a simple eutectic system with the coordinates of the eutectic point of 61.4 mole %  $\text{KBF}_4$ , 19.4 mole %  $\text{KF}$ , 19.2 mole %  $\text{KCl}$  and the temperature of the eutectic crystallization of 422 °C.

From the data given in Table 1 it follows that at the 0.95 confidence level the  $A_4$  coefficient was statistically nonimportant for all binary systems. In the ternary system the first-order  $B$   $x(\text{KBF}_4) x(\text{KF}) x(\text{KCl})$  as well as the second-order  $C_1 x^2(\text{KBF}_4) x(\text{KF}) x(\text{KCl})$ ,  $C_2 x(\text{KBF}_4) x^2(\text{KF}) x(\text{KCl})$ , and  $C_3 x(\text{KBF}_4) x(\text{KF}) x^2(\text{KCl})$  interactions were considered. As follows from Table 2, the  $B$  and  $C_3$  coefficients have been shown as nonimportant. Including the ternary interaction coefficients into the calculations the standard deviation of the experimental and calculated values of the temperature of primary crystallization decreases from the value of 11.4 °C to the value of 5.7 °C (*cf.* Table 3). The significant ternary interaction indi-

**Table 3.** Experimental and Calculated Values of the Temperatures of Primary Crystallization of the Investigated Mixtures

$x(\text{KBF}_4)$	$x(\text{KF})$	$x(\text{KCl})$	$T(\text{exp.})$	$T(\text{calc.})$	$\Delta T$	$T'(\text{calc.})^a$	$\Delta T$
K							
0.20	0.16	0.64	922	928.9	6.9	926.4	4.4
0.20	0.32	0.48	855	859.4	4.4	857.4	2.4
0.20	0.48	0.32	902	899.8	-2.2	896.6	-5.4
0.20	0.64	0.16	997	999.4	2.4	996.5	-0.5
0.40	0.12	0.48	864	861.0	-3.0	857.5	-6.5
0.40	0.24	0.36	792	797.2	5.2	796.1	4.1
0.40	0.36	0.24	818	813.8	-4.2	811.3	-6.7
0.40	0.48	0.12	911	910.4	-0.6	906.1	-4.9
0.60	0.08	0.32	782	775.4	-6.6	775.9	-6.1
0.60	0.16	0.24	720	719.1	-0.9	724.7	4.7
0.60	0.24	0.16	707	712.8	5.8	717.7	10.7
0.60	0.32	0.08	782	791.3	9.3	791.1	9.1
0.80	0.04	0.16	776	773.3	-2.7	772.1	-3.9
0.80	0.08	0.12	776	773.9	-2.1	772.2	-3.8
0.80	0.10	0.10	772	773.9	1.9	772.1	0.1
0.80	0.12	0.08	768	773.4	5.4	771.7	3.7
0.80	0.16	0.04	764	771.2	7.2	770.1	6.1

a) Values calculated using the coefficient  $C_2$  only.

**Fig. 1.** Experimentally determined phase diagram of the system  $\text{KBF}_4\text{—KF—KCl}$ . The isotherm values are in °C.

cated already by the volume [2] and conductivity [3] measurements was so confirmed also by the phase equilibria study. The final phase diagram of the ternary system  $\text{KBF}_4\text{—KF—KCl}$  shown in Fig. 1 was calculated including the  $C_2 x(\text{KBF}_4) x^2(\text{KF}) x(\text{KCl})$  interaction only.

As mentioned above a significant ternary interaction was found in the ternary  $\text{KBF}_4\text{—KF—KCl}$  system. With regard to the fact that the system has a common cation, the observed ternary interaction must be a consequence of the anionic interaction. In the binary  $\text{KBF}_4\text{—KF}$  system the mixing of small anions  $\text{F}^-$  with relatively large  $\text{BF}_4^-$  ones takes place. In such systems the deviation from ideal behaviour is proportional to the fractional difference in the ionic radii of the different anions [10]. In the binary  $\text{KBF}_4\text{—KCl}$  system there is the mixing of two relatively large and polarizable anions  $\text{BF}_4^-$  and  $\text{Cl}^-$ . In such systems only small deviations from the ideal behaviour are generally observed [4]. Small deviations from ideality are shown also by the system  $\text{KF—KCl}$  [4].

The most probable interaction of all three anions, however, seems to be the exchange of the fluoride atoms, in the  $\text{BF}_4^-$  tetrahedron for chloride ones according to the general scheme



As follows from the course of the excess molar Gibbs energy of mixing in the investigated system (Fig. 2) the maximum interaction effect is localized near the  $\text{KBF}_4\text{—KF}$  boundary, which indicates that the reaction (A) is probably shifted to the right. However, the kinds of the mixed fluoro-chloro-

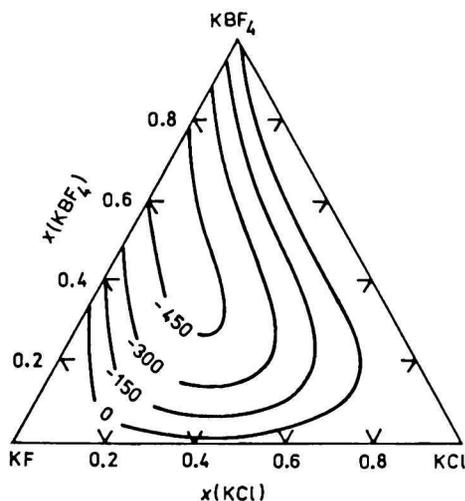


Fig. 2. Excess molar Gibbs energy of mixing in the system  $\text{KBF}_4\text{--KF--KCl}$ . The isoenergy values are in  $\text{J mol}^{-1}$ .

borate anions as well as the extent of the reaction (A) may be determined only by means of other methods.

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Translated by V. Daněk

## Generalizing View on Reduction of Some Cu(II) Complexes

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Received 11 September 1990

Dedicated to Professor V. Gutmann, in honour of his 70th birthday

A general expression describing certain redox processes, in which Cu(II) complexes with the ligands having a reducing and stabilizing influence on the central atom take part, has been derived. The obtained results qualitatively describe the redox processes and enable to obtain by means of some known data also their quantitative evaluation.

It is known that the copper(II) complexes in the presence of some ligands undergo the redox processes in which the central atom is reduced to Cu(I). However, in the presence of the other ligands, central atom is not reduced. This phenomenon was mainly observed at the preparation of Cu(I), Cu(II), and Cu(I)—Cu(II) complexes [1], when the Cu(II) complexes with certain types of ligands could be prepared only under some conditions [2].

On the basis of the experimental results, the ligands in the redox processes of the Cu(II) complexes can be approximately divided [3] into two groups: The ligands which cause the reduction of the central atom (Lr) and the ligands which do not exert this influence on Cu(II) and it can be stated that they stabilize the oxidation state of copper(II) (Ls). As an example of the Lr ligands the following ones can be given:  $\text{Cl}^-$  [4–7],  $\text{Br}^-$  [8, 9],  $\text{I}^-$  [10, 11],  $\text{NC}^-$  [12, 13],  $\text{NCS}^-$  [14, 15],