Reactions of potassium tetrafluoroborate
in molten alkali chlorides

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Dedicated to Professor M. Malinovský, DrSc, on his 50th birthday

The reactions of KBF_4 in molten alkali chlorides, LiCl, NaCl, and KCl, were investigated using the cryoscopic method. It was found that in molten lithium chloride KBF_4 decomposes with the formation of gaseous BCl_3. In molten NaCl, the exchange reaction between KBF_4 and the Cl^- anions with the formation of $KBCl_4$ proceeds at very small concentrations of KBF_4 only, while no reaction occurs in molten KCl. The experimental results have been confirmed by thermodynamic calculations.

On the basis of the experimentally determined depression of the temperature of primary crystallization in the system $NaCl—KBF_4$ the value of equilibrium constant of the reaction $4NaCl + KBF_4 \rightleftarrows 4NaF + KBCl_4$ and the value of Gibbs free energy of liquid $KBCl_4$ at 1073 K were calculated.

С помощью криоскопического метода изучались реакции KBF_4 в расплавах щелочных хлоридов LiCl, NaCl, KCl. Было найдено, что в расплаве LiCl происходит разложение KBF_4 и из системы выделяется газообразный BCl_3. В расплаве NaCl происходит реакция обмена между KBF_4 и хлоридными ионами с образованием $KBCl_4$ только в области очень низких концентраций KBF_4, в отличие от расплава KCl, где реакция не протекает. Экспериментальные результаты были подтверждены термодинамическим расчетом.

На основе полученных данных понижения температуры первичной кристаллизации в системе $NaCl—KBF_4$ вычислилось значение константы равновесия реакции $4NaCl + KBF_4 \rightleftarrows 4NaF + KBCl_4$ и значение энергии Гиббса жидкого $KBCl_4$ при температуре 1073 K.

The study of reactions of KBF_4 in molten alkali chlorides appears to be interesting both from a theoretical aspect and with regard to the possibility of a technical application of these melts, *e.g.* in the electrolytic boride coating of various metals. In this respect, the knowledge of ionic composition of the electrolyte appears to be of a prime importance. Under certain conditions, the ionic composition of a melt can be determined by the cryoscopic method.

Theoretical analysis and determination of the limits of applicability of this method has been carried out by several authors [1—3]. The depression of the

temperature of primary crystallization of the substance A effected by an addition of the substance B can be expressed by the relation

$$\Delta T_A = K_A^{cr} m_B r, \qquad (1)$$

where ΔT_A denotes the depression of the temperature of primary crystallization of the substance A, K^{cr} is the cryoscopic constant of the substance A, m_B denotes the molal concentration of the substance B in the system A—B and r is the correction factor for the substance B in the system A—B and is numerically equal to the number of new particles introduced into the substance A by one molecule of the substance B. Hence, by cryoscopic method the number of new particles formed upon addition of KBF_4 into molten alkali chlorides can be determined and thus the ionic composition of the melt may be found.

In molten alkali chlorides an exchange reaction may occur under certain conditions; in some cases the originating tetrachloroborate anion may further decompose under the formation of gaseous BCl_3 which escapes from the melt, this being important with respect to the application of these melts as electrolytes in the boridizing. The degree of conversion of the exchange reaction

$$4MCl + KBF_4 \rightleftarrows 4MF + KBCl_4 \qquad (2)$$

(M = Li, Na or K) is determined by the value of equilibrium constant of the reaction

$$K = \frac{[MF]^4 [KBCl_4]}{[MCl]^4 [KBF_4]} = \frac{x_{F^-}^4 \, x_{BCl_4^-}}{x_{Cl^-}^4 \, x_{BF_4^-}} \qquad (3)$$

The reaction (2) may be assumed to proceed stepwise, e.g. by a successive exchange of fluorine in the BF_4^- complex anion for chlorine through the reaction steps BF_3Cl^-, $BF_2Cl_2^-$, and $BFCl_3^-$, such a reaction mechanism, however, cannot be determined by means of the cryoscopic method.

In this work on the basis of the published values of cryoscopic constants of LiCl, NaCl, and KCl [4] and of the experimentally determined depressions of the temperature of primary crystallization, ΔT_A, the number of new particles resulting from the reaction of KBF_4 with the above solvents was determined and a tentative picture of the ionic composition was suggested. Experimental results have been confirmed by thermodynamic calculations. Besides, from the experimentally determined dependence ΔT_A vs. composition in the system NaCl—KBF_4 the values of the equilibrium constant of the exchange reaction (2) and of the Gibbs free energy of molten $KBCl_4$ at 1073 K were calculated.

Experimental

For the preparation of samples the following chemicals were used: KBF_4, reagent grade (Lachema, Brno), LiCl, NaCl, and KCl "for single crystals" (Crytur, Turnov).

A homogenized sample (30 g) in a Pt crucible was melted in a resistance furnace. The temperature was measured using a Pt/Pt10Rh thermocouple. The cooling curves were recorded using a curve-drawing recorder EZ-2. The applied scheme made it possible to measure the temperature differences with a relative accuracy of ± 0.2 K. The cooling rate of a sample did not surpass 2 K/min.

Results and discussion

In Figs. 1—3 the experimentally determined dependences ΔT_A vs. composition in the proximity of melting points of the investigated solvents are compared with the theoretical course of liquidus curves for different arbitrary chosen values of the correction factor r calculated by means of eqn (1) using the values of cryoscopic constants presented in [4].

From cryoscopic measurements in the system LiCl—KBF$_4$ (Fig. 1) it follows that in molten LiCl the BF$_4^-$ anions undergo an exchange reaction with the formation of BCl$_4^-$ ions. At concentrations surpassing 0.05 m-BCl$_4^-$ the tetrachloroborate anions decompose owing to the polarizing ability of the Li$^+$ cations according to the equation

$$BCl_4^- = BCl_3 + Cl^- \tag{4}$$

and gaseous BCl$_3$ escapes from the melt. Consequently, the number of new particles in the melt is reduced ($r < 6$) and the composition of the melt changes in such a way that it corresponds to the ternary system LiF—LiCl—KCl which probably effects an increase of the temperature of primary crystallization of LiCl. In order to verify this presumption the weight loss of a sample containing 0.2 m-KBF$_4$ kept at 950 K for 2 hrs has been determined. The determined value corresponds to the escape of $ca.$ 65% of BCl$_3$ formed. Most of the escaping gaseous BCl$_3$ condensed on the water-cooled lid of the furnace.

From the results obtained in cryoscopic studies of the system NaCl—KBF$_4$ it follows that in the concentration range 0.02—0.25 m-KBF$_4$ the number of new particles is reduced from 6 to 2, this indicating a change in the direction of the exchange reaction (2) in the above concentration range. At concentrations below 0.02 m-KBF$_4$, and to some extent also in the concentration range 0.02—0.25 m-KBF$_4$, the reaction (2) proceeds with the formation of the BCl$_4^-$ ions, however, owing to the low concentrations of these anions and to the lower polarizing ability of the Na$^+$ cations as compared to that of the Li$^+$ ions there are no conditions favouring the decomposition of the BCl$_4^-$ complex anion. This presumption was confirmed by the fact that no weight losses which would result from the escape of BCl$_3$ were determined in this case. At concentrations higher than 0.25 m-KBF$_4$ there are practically only tetrafluoroborate anions present in the melt and the exchange reaction (2) does not proceed.

In the system KCl—KBF$_4$ the correction factor r achieves the value 1, this corresponding to the introduction of one new particle with the addition of KBF$_4$
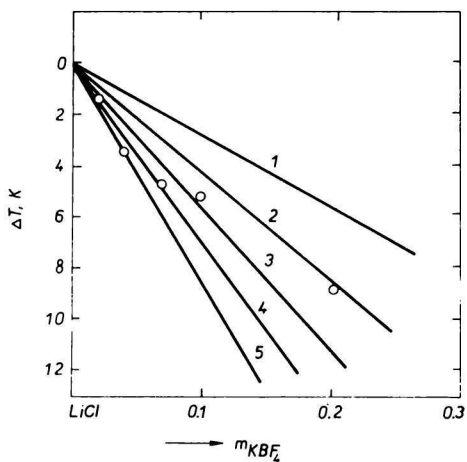
Fig. 1. Depression of the temperature of primary crystallization of LiCl in the system LiCl—KBF₄.
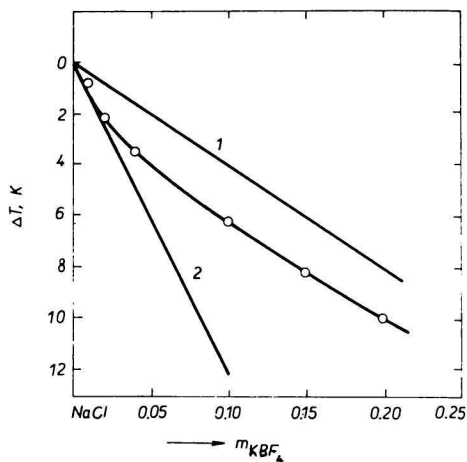1. $r = 2$; 2. $r = 3$; 3. $r = 4$; 4. $r = 5$; 5. $r = 6$.

Fig. 2. Depression of the temperature of primary crystallization of NaCl in the system NaCl—KBF₄.
1. $r = 2$; 2. $r = 6$.

into molten KCl. This indicates that the simple dissociation of KBF_4 into K^+ and BF_4^- ions is not accompanied by an exchange reaction of the BF_4^- anion with the chloride anions which are present in the melt.

The probability of the occurence of the exchange reaction (2) in the respective alkali chlorides may be estimated also on the basis of the thermodynamic calculation of the degree of conversion. In these calculations some simplifying assumptions were made, hence, the results can be looked upon as only approximative, which, however, proved satisfactory with respect to the study of the exchange reaction.

For the sake of simplicity let us assume that after introduction of a small amount of KBF_4 into molten MCl only the BF_4^- and BCl_4^- complex anions and not the suggested intermediate products of the exchange reaction will be present in the melt. The proportion of the number of the BCl_4^- anions formed to the total number of the borate anions corresponds to the degree of conversion of the reaction, α. If we add n moles of KBF_4 to one mole of MCl ($n \ll 1$) then, according to Temkin, $x_{Cl^-} \doteq 1$ and for the equation of equilibrium constant of the reaction (2) the simplified equation can be derived

$$K = 256 \, n^4 \, \frac{\alpha^5}{1 - \alpha} \tag{5}$$

The values of equilibrium constants of the reaction (2) in molten LiCl, NaCl, and KCl at the respective melting temperatures 883, 1073, and 1044 K were calculated on the basis of the values of Gibbs free energy of the reacting substances presented

380

in [4]. Thus far, the Gibbs free energy of liquid $KBCl_4$ is not known, therefore it had to be estimated. The change of enthalpy in the reaction

$$KCl(s) + BCl_3(g) = KBCl_4(s) \qquad (6)$$
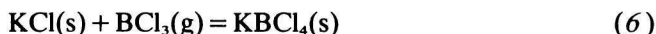
at 298 K was found to be $\Delta H = -96$ kJ [5]. Gibbs energy of $KBCl_4(l)$ was estimated approximately as a sum of the heat of reaction (6) and of the Gibbs free energies of $MCl(l)$ and $BCl_3(g)$ at respective melting temperatures. Thus, for $KBCl_4(l)$ the values $\Delta G^0_{883\,K} = -800$ kJ mol^{-1}, $\Delta G^0_{1044\,K} = -783$ kJ mol^{-1}, and $\Delta G^0_{1073\,K} \doteq -779$ kJ mol^{-1} were obtained and applied in the calculation. The error was estimated to $ca. \pm 10$ kJ mol^{-1}

For the exchange reaction (2) in the system LiCl—KBF_4 the value of Gibbs free energy, $\Delta G^0_{883\,K} \doteq 35.2$ kJ, was calculated to which corresponds the value of equilibrium constant of the reaction $K \doteq 8 \times 10^{-3}$. Hence, according to eqn (5) for $n < 10^{-2}$ the degree of conversion of the reaction (2), $\alpha \doteq 1$. Consequently, the equilibrium of the exchange reaction is shifted practically completely towards the right side and the BF_4^- anions are converted quantitatively into the BCl_4^- ions which is in agreement with the experimental findings.

The value of Gibbs free energy calculated for the exchange reaction (2) in the system NaCl—KBF_4, $\Delta G_{1073\,K} \doteq 189.4$ kJ, corresponds to the value of the equilibrium constant $K \doteq 2 \times 10^{-9}$. For the degree of conversion of reaction (2) we obtain
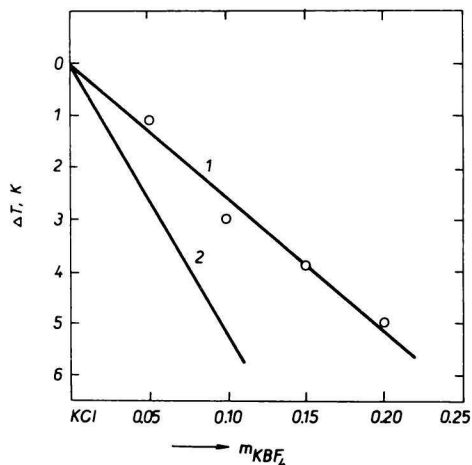

Fig. 3. Depression of the temperature of primary crystallization of KCl in the system KCl—KBF_4.
1. $r = 1$; 2. $r = 2$.

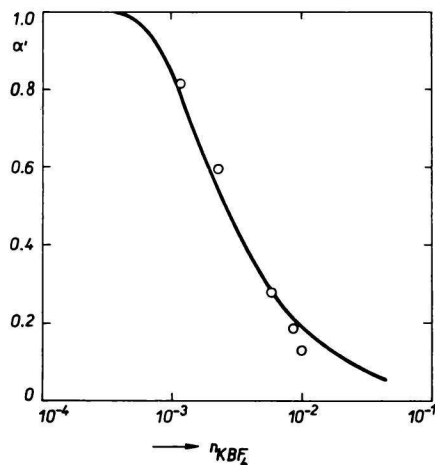Fig. 4. Dependence of the degree of conversion α' of the reaction (7) on the concentration of KBF_4.

for $n < 10^{-3}$ the value $\alpha \doteq 1$ and for $n \doteq 1.5 \times 10^{-2}$ (*i.e.* $m = 0.25$) the value $\alpha \doteq 0.5$ which indicates that with increasing concentration of KBF_4 the equilibrium of the exchange reaction is shifting from the right towards the left side and, beside BF_4^-, also the BCl_4^- anions are present in the melt.

In the system $KCl—KBF_4$ the following values of Gibbs free energy and of the equilibrium constant of the reaction (*2*) were determined: $\Delta G_{1043\,K} \doteq 302$ kJ and $K \doteq 10^{-15}$ Consequently, for $n > 10^{-3}$, the degree of conversion $\alpha \doteq 0$. Hence, the calculations confirm the experimental findings that the exchange reaction does not occur in this system.

From the results of both cryoscopic studies and the thermodynamic calculations it follows that the stability of the BF_4^- anions in the medium of molten alkali chlorides increases in the series $LiCl < NaCl < KCl$; in molten LiCl the BCl_4^- anions formed by the exchange reaction (*2*) decompose owing to the strong polarizing effect of the Li^+ cations and the relatively high concentration anions under the formation of volatile BCl_3. On the other hand, no decomposition of the BCl_4^- anions was observed in the system $NaCl—KBF_4$, most probably owing to a minor concentration of these anions and to a smaller polarizing ability of the Na^+ cations.

Hence, it may be concluded that the LiCl-containing mixtures with KBF_4 as active component cannot be applied as electrolytes for electrolytic boridizing.

From the experimentally determined dependence of depression of the temperature of primary crystallization on the composition in the system $NaCl—KBF_4$ the equilibrium constant of the exchange reaction

$$4NaCl + KBF_4 \rightleftarrows 4NaF + KBCl_4 \tag{7}$$

can be calculated and on this basis the so far unknown value of Gibbs free energy of liquid $KBCl_4$ at 1073 K can be determined.

The equation for the degree of conversion for the reaction (*7*) can be derived from the boundary conditions:

let for $\alpha = 0$ be $\Delta T = \Delta T_1 = K^{cr} m_B r_1 = K^{cr} m_B 2$
and for $\alpha = 1$ $\Delta T = \Delta T_2 = K^{cr} m_B r_2 = K^{cr} m_B 6.$ (*8*)

For the sake of simplicity let us assume that upon addition of a small amount of KBF_4 into molten NaCl the intermediate products (BF_3Cl, *etc.*) may be omitted and only the BF_4^- and BCl_4^- complex anions will be present in the melt. The number r of new particles which are formed by the reaction (*7*) may be expressed as

$$r = 1 + [1 - \alpha'] + \alpha' + 4\alpha' = 2 + 4\alpha', \tag{9}$$

where α' denotes the degree of conversion related to 1 mole of KBF_4. Then the dependence of the depression of the temperature of primary crystallization on the degree of conversion of the reaction may be described by the equation

$$\Delta T = K^{cr} m_B [2 + 4\alpha']. \tag{10}$$

After rearranging and substituting we get

$$\alpha' = \frac{\Delta T - K^{cr} m_B 2}{K^{cr} m_B 4} = \frac{\Delta T - K^{cr} m_B 2 \cdot}{K^{cr} m_B 6 - K^{cr} m_B 2} = \frac{\Delta T - \Delta T_1}{\Delta T_2 - \Delta T_1} \tag{11}$$

On the basis of thus calculated α' values and by means of eqn (5) the value of the equilibrium constant for any arbitrary concentration of KBF_4 can be calculated. The results of this calculation are shown in Fig. 4. The arithmetical mean of the values of equilibrium constants of the reaction (7) at 1073 K calculated in this way is $K = 7 \times 10^{-7}$ to which corresponds the value of Gibbs free energy of the reaction $\Delta G_{1073 K} = 188 \pm 10$ kJ. The value of Gibbs free energy of liquid $KBCl_4$ calculated on the basis of this value and of the known values of Gibbs free energies of the other reacting substances, $\Delta G^0_{1073 K} = -769 \pm 10$ kJ, is in a very good agreement with the estimated value -779 kJ.

The results of the present study allow us to draw the conclusion that in some cases the cryoscopic method may be applied to the determination of thermodynamic quantities. The accuracy and correctness of the value determined in this way evidently depend upon the accuracy of the cryoscopic measurements.

References

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