Reactions of potassium tetrafluoroborate in molten alkali chlorides

V DANĚK, I. VOTAVA, and K. MATIAŠOVSKÝ

Institute of Inorganic Chemistry, Slovak Academy of Sciences, 809 34 Bratislava

Received 13 June 1975

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\textsuperscript{−} anions with the formation of KBCl 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$_4$ $\rightleftharpoons$ 4NaF + KBCl$_4$ and the value of Gibbs free energy of liquid KBCl$_4$ at 1073 K were calculated.

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

$$\Delta T_A = K_A^{cr} m_B r,$$

where $\Delta T_A$ denotes the depression of the temperature of primary crystallization of the substance A, $K_A^{cr}$ 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

$$4\text{MCl} + \text{KBF}_4 \rightleftharpoons 4\text{MF} + \text{KBCl}_4$$

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

$$K = \frac{[\text{MF}]^4[\text{KBCl}_4]}{[\text{MCl}]^4[\text{KBF}_4]} = \frac{x_{\text{F}}^4 - x_{\text{BCl}_4}^4}{x_{\text{Cl}}^4 - x_{\text{BF}_4}^4}$$

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$_3$Cl$^-$, BF$_2$Cl$_2$, 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, $\Delta T_A$, 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 $\Delta T_A$ 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).
REACTIONS OF POTASSIUM TETRAFLUOROBORATE

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 $\Delta T_A$ 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

$$\text{BCl}_4^- = \text{BCl}_3 + \text{Cl}^-$$

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 KBF₄ into K⁺ and BF₄⁻ ions is not accompanied by an exchange reaction of the BF₄⁻ anion with the chloride anions which are present in the melt.

The probability of the occurrence 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 approximate, 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 KBF₄ into molten MCI only the BF₄⁻ and BCl⁻ 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⁻ 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 KBF₄ to one mole of MCI (n ≪ 1) then, according to Temkin, x₀⁻ = 1 and for the equation of equilibrium constant of the reaction (2) the simplified equation can be derived

\[ K = 256 \, n^4 \, \frac{\alpha^5}{1 - \alpha} \]  

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
REACTIONS OF POTASSIUM TETRAFLUOROBorate

in [4]. Thus far, the Gibbs free energy of liquid KBCl₄ is not known, therefore it had to be estimated. The change of enthalpy in the reaction

$$\text{KCl}(s) + \text{BCl}_3(g) = \text{KBCl}_4(s) \quad (6)$$

at 298 K was found to be $\Delta H = -96$ kJ [5]. Gibbs energy of KBCl₄(l) was estimated approximately as a sum of the heat of reaction (6) and of the Gibbs free energies of MCl(l) and BCl₃(g) at respective melting temperatures. Thus, for KBCl₄(l) the values $\Delta G_{883K}^o = -800$ kJ mol⁻¹, $\Delta G_{1044K}^o = -783$ kJ mol⁻¹, and $\Delta G_{1073K}^o = -779$ kJ mol⁻¹ were obtained and applied in the calculation. The error was estimated to ca. ± 10 kJ mol⁻¹.

For the exchange reaction (2) in the system LiCl—KBF₄ the value of Gibbs free energy, $\Delta G_{883K}^o \approx 35.2$ kJ, was calculated to which corresponds the value of equilibrium constant of the reaction $K \approx 8 \times 10^{-3}$. Hence, according to eqn (5) for $n < 10^{-2}$ the degree of conversion of the reaction (2), $\alpha \approx 1$. Consequently, the equilibrium of the exchange reaction is shifted practically completely towards the right side and the BF₄⁻ anions are converted quantitatively into the BCl₄⁻ 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—KBF₄, $\Delta G_{1073K}^o \approx 189.4$ kJ, corresponds to the value of the equilibrium constant $K \approx 2 \times 10^{-9}$. 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—KBF₄.

1. $r = 1$; 2. $r = 2$.

Fig. 4. Dependence of the degree of conversion $\alpha'$ of the reaction (7) on the concentration of KBF₄.

Chem. zvesti 30 (3) 377—383 (1976)
for \(n < 10^{-3}\) the value \(\alpha = 1\) and for \(n = 1.5 \times 10^{-2}\) (i.e. \(m = 0.25\)) the value \(\alpha = 0.5\) 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 BC\(_1\)\(_4^-\) 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: \(\Delta G_{\text{KBF}_4}^\text{f, liquid} = 302\) kJ and \(K = 10^{-15}\) Consequently, for \(n > 10^{-3}\), the degree of conversion \(\alpha = 0\). 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 BC\(_1\)\(_4^-\) 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 BC\(_1\)\(_4^-\) 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

\[
4\text{NaCl} + \text{KBF}_4 \rightleftharpoons 4\text{NaF} + \text{KBCl}_4
\] (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 \(\Delta T = \Delta T_1 = K^{e\alpha} m_0 r_1 = K^{e\alpha} m_0 2\)
and for \(\alpha = 1\) \(\Delta T = \Delta T_2 = K^{e\alpha} m_0 r_2 = K^{e\alpha} m_0 6\). \hspace{1cm} (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\(_3\)Cl, etc.) may be omitted and only the BF\(_4^-\) and BC\(_1\)\(_4^-\) 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

\[
r = 1 + [1 - \alpha'] + \alpha' + 4\alpha' = 2 + 4\alpha',
\] (9)

where \(\alpha'\) 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

\[
\Delta T = K^{e\alpha} m_0 [2 + 4\alpha'].
\] (10)
After rearranging and substituting we get

\[ \alpha' = \frac{\Delta T - K^{cr} m_B}{K^{cr} m_B} = \frac{\Delta T - K^{cr} m_B}{K^{cr} m_B} \]

On the basis of thus calculated \( \alpha' \) 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 \( \Delta G_{1073K} = 188 \pm 10 \) 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, \( \Delta G^0_{1073K} = -769 \pm 10 \) 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


Translated by K. Matiašovský