

Cryoscopy of M_2TiO_3 ($M = Li, Na, K$) in Molten Alkali Fluorides

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The mechanism of the dissolution of Li_2TiO_3 , Na_2TiO_3 , and K_2TiO_3 in molten alkali fluorides, NaF and KF, and the ionic structure of created molten mixtures were determined using the cryoscopic method. The composition region of alkali titanates varied from 0 to 3 mole %. It was found that in the given composition region alkali metal titanates electrolytically dissociate according to the scheme $M_2TiO_3 \leftrightarrow 2 M^+ + TiO_3^{2-}$. The created molten mixture contains alkali metal cations and both fluoride and TiO_3^{2-} anions.

The molten mixtures of alkali metal fluorides containing alkali metal titanates and boron oxide appear to be the perspective electrolytes for electrochemical synthesis of titanium diboride. An identification of the ionic structure of the electrolyte is a precondition of the successful determination of the mechanism of the electrode processes taking place at the electrodes during electrolysis.

Cryoscopy is considered as an indirect method for investigation of the ionic structure of molten salts [1, 2]. From an analysis of the liquidus curves in a simple binary system (A—B) it follows that the melting point depression of the component A affected by an addition of the component B can be expressed by the equation

$$\Delta T(A) = K^{tdp} x(B) k^{St} \quad (1)$$

where

$$K^{tdp} = R \{T(\text{fus}, A)\}^2 / \Delta H(\text{fus}, A) \quad (2)$$

where $\Delta T(A)$ is the melting point depression of substance A, K^{tdp} is the thermic depression constant, $x(B)$ is the mole fraction of substance B, k^{St} is the Stortenbeker factor for component B [3], R is the gas constant and $\Delta H(\text{fus}, A)$ is the enthalpy of melting of substance A at melting temperature.

In this type of solutions [4, 5], the Stortenbeker factor is numerically equal to the number of new particles which are introduced to the substance A by one molecule of substance B. Eqn (1) is a limiting relation which is valid exactly only for $x(B) \rightarrow 0$. The limit of the differentiation of eqn (1) according to $x(B)$ for $x(B) \rightarrow 0$ is given by a tangent (k°) of the liquidus curve for an infinitely diluted solution

$$\lim_{x \rightarrow 0} \frac{d\Delta T}{dx} = K^{tdp} k^{St} = k^\circ \quad (3)$$

On the basis of the known value k^{St} the mechanism of dissolution of alkali metal titanates in molten alkali metal fluorides and the ionic structure of the originated solutions can be determined.

The literature review shows that the following phase diagrams of the reciprocal systems $Na^+, K^+ \parallel F^-, TiO_3^{2-}$ [6], $Li^+, K^+ \parallel F^-, TiO_3^{2-}$ [7], and $Li^+, Na^+ \parallel F^-, TiO_3^{2-}$ [8] were studied. It follows from the published results that the cryoscopic measurements can be realized in the systems based on NaF and KF. In the systems based on LiF the minimum addition of Na_2TiO_3 and K_2TiO_3 causes the precipitation of Li_2TiO_3 which is insoluble in molten lithium fluoride.

In the presented work cryoscopy and thermodynamic analysis were used to determine the mechanism of dissolution of alkali metal titanates in molten alkali metal fluorides and ionic structure of created melts.

EXPERIMENTAL

For the sample preparation (total amount 20 g) the following chemicals were used: LiF, NaF, and KF (anal. grade, Lachema, Brno). Alkali metal titanates were prepared at the laboratory [9] using Li_2CO_3 , Na_2CO_3 , and K_2CO_3 (anal. grade, Lachema, Brno) and TiO_2 (anal. grade, Fluka).

A homogenized sample was melted in a platinum crucible placed in a resistance furnace. The temperature was measured using a Pt/Pt10Rh thermocouple. The cooling curves were recorded by means of data acquisition computer system. The applied scheme made it possible to measure the temperature differences with the relative accuracy ± 0.3 K. The cooling rate of the sample did not exceed 1 K min^{-1} .

RESULTS

In Figs. 1–6 the experimentally determined dependences of temperatures of primary crystalli-

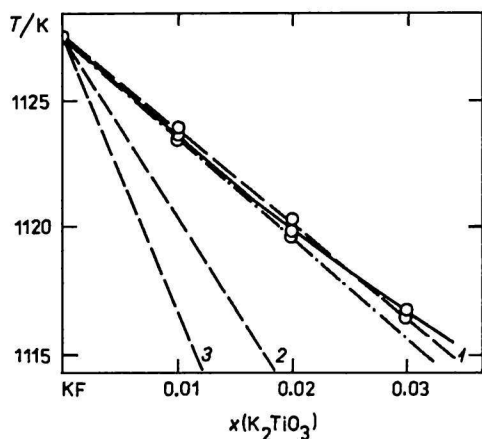


Fig. 1. Melting point and temperature of primary crystallization in the system KF–K₂TiO₃. — Experimental liquidus curve; - · - · - tangent of the experimental liquidus curve in $x(\text{K}_2\text{TiO}_3) = 0$; --- theoretical liquidus curves calculated according to eqn (1) using different values of k^{St} (1, 2, and 3).

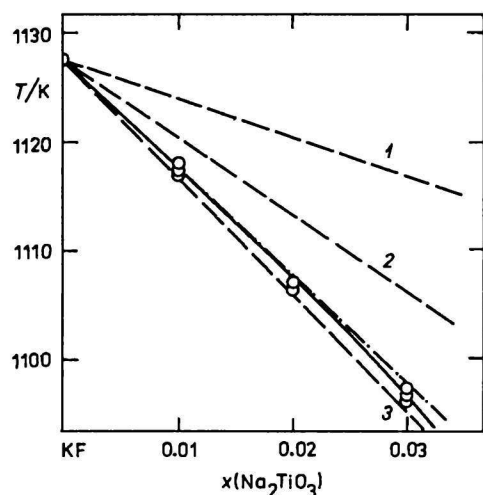


Fig. 2. Melting point and temperature of primary crystallization in the system KF–Na₂TiO₃. — Experimental liquidus curve; - · - · - tangent of the experimental liquidus curve in $x(\text{Na}_2\text{TiO}_3) = 0$; --- theoretical liquidus curves calculated according to eqn (1) using different values of k^{St} (1, 2, and 3).

zation of alkali metal fluorides on mole fraction of alkali metal titanates in the proximity of the melting point of the solvent are compared with the liquidus curves calculated according to eqn (1) on the basis of published thermodynamic data [10, 11] for different values of k^{St} . Also, tangents of the experimental liquidus curves in the melting point of the pure solvent are drawn in the figures. The values of the Stortenbeker factor calculated from the tangents are

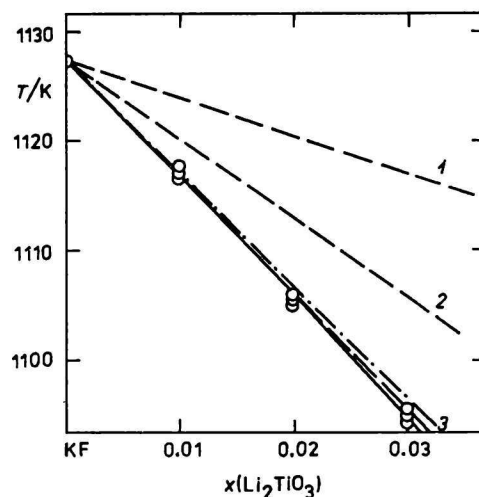


Fig. 3. Melting point and temperature of primary crystallization in the system KF–Li₂TiO₃. — Experimental liquidus curve; - · - · - tangent of the experimental liquidus curve in $x(\text{Li}_2\text{TiO}_3) = 0$; --- theoretical liquidus curves calculated according to eqn (1) using different values of k^{St} (1, 2, and 3).

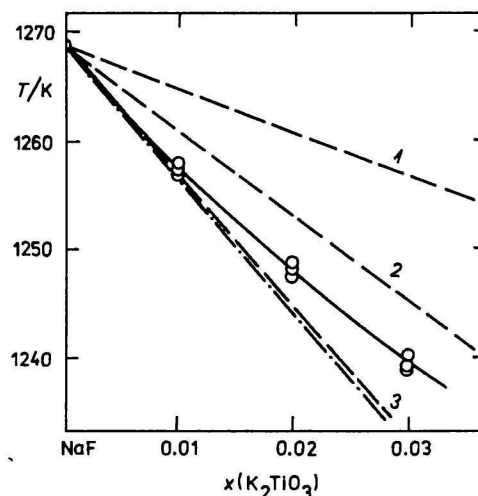


Fig. 4. Melting point and temperature of primary crystallization in the system NaF–K₂TiO₃. — Experimental liquidus curve; - · - · - tangent of the experimental liquidus curve in $x(\text{K}_2\text{TiO}_3) = 0$; --- theoretical liquidus curves calculated according to eqn (1) using different values of k^{St} (1, 2, and 3).

in Table 1. It can be seen from the figures and Table 1 that the values of k^{St} approach 3 for systems with different cations and 1 for systems with common cation, respectively.

Table 1. Values of Stortenbeker Factor k^{St} Calculated from Eqn (3)

Solvent	k^{St}		
	Li ₂ TiO ₃	Na ₂ TiO ₃	K ₂ TiO ₃
NaF	3.04	0.96	3.01
KF	2.91	2.83	1.09

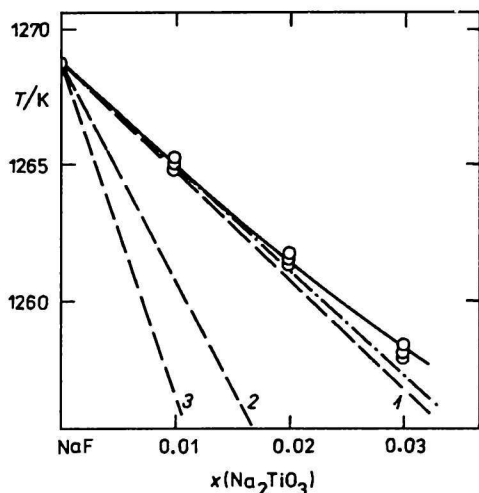


Fig. 5. Melting point and temperature of primary crystallization in the system NaF– Na_2TiO_3 . — Experimental liquidus curve; - - - tangent of the experimental liquidus curve in $x(Na_2TiO_3) = 0$; --- theoretical liquidus curves calculated according to eqn (1) using different values of k^{St} (1, 2, and 3).

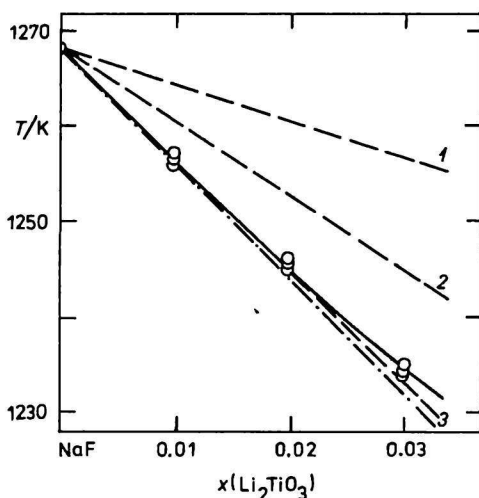
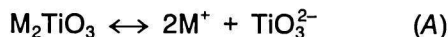


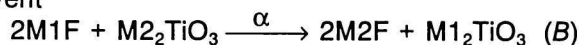
Fig. 6. Melting point and temperature of primary crystallization in the system NaF– Li_2TiO_3 . — Experimental liquidus curve; - - - tangent of the experimental liquidus curve in $x(Li_2TiO_3) = 0$; --- theoretical liquidus curves calculated according to eqn (1) using different values of k^{St} (1, 2, and 3).

DISCUSSION

On the basis of the experimental results the following mechanism of dissolution has been proposed. Alkali metal titanates electrochemically dissociate according to the scheme



Moreover, in reciprocal systems alkali metal titanates can undertake exchange chemical reaction with the solvent



where α is a degree of conversion.

It follows from an analysis of the above reaction schemes for individual systems that the number of new particles created in the melt by introducing one molecule of alkali metal titanate is 1 for systems with common cation and 3 for reciprocal systems. This is in good agreement with the experimental results (Table 1). The proposed mechanism of dissolution also explains both the dissolution of Li_2TiO_3 in NaF and KF and the precipitation of Li_2TiO_3 from the systems containing LiF as a solvent. The explanation is based on the comparison of theoretical (α_{theor}) and experimental (α_{exp}) values of the degree of conversion. The calculations were performed for the temperature 1300 K.

The equilibrium constants of the reaction (B) for individual systems were calculated using the equation

$$-\Delta_r G^\circ = RT \ln K \quad (4)$$

The values of $\Delta_r G^\circ$ were calculated on the basis of published thermodynamic data [10, 11].

The calculation of α_{theor} was based on some simplifying assumptions. In all cases the mole fraction of alkali metal titanates in melts is much smaller than 1, so their activities can be considered to be identical with the concentrations and the activities of alkali metal fluorides can be considered to be 1. With regard to the above conditions the relation for the calculation of equilibrium constant K of the exchange reaction (B) can be expressed as

$$K = \frac{X_{M2F} X_{M1_2TiO_3}}{X_{M_2TiO_3}} \quad (5)$$

The composition of the original mixture of alkali metal titanate and alkali metal fluoride can be expressed as a sum of their mole fractions, $y(M_2TiO_3) + (1 - y)(M1F)$. If the mole fractions in eqn (5) are expressed by the degree of conversion α and by the mole fraction of alkali metal titanate in the original mixture, one obtains the relation for calculation of the equilibrium constant of the exchange reaction (B) in the form

$$K = \frac{4\alpha^3 y^2}{1 - \alpha} \quad (6)$$

The calculation of α_{theor} was carried out by the iterative way. The different values of α were gradually introduced into eqn (6) for the given system and for the given content of alkali metal titanate and the calculated value of the equilibrium constant K was compared with the value obtained from eqn (4).

The experimental values of the degree of conversion α_{exp} of individual systems were determined on the basis of the difference between the melting point

of alkali metal fluoride and the temperature of primary crystallization of the tested melts. The relation for the calculation of α_{exp} can be obtained from eqn (1) under the following boundary conditions

$$\text{for } \alpha = 0 \quad k^{\text{St}} = 1 \\ \Delta T = K^{\text{tdp}} \times 1 = \Delta T_1 \quad (7)$$

$$\text{for } \alpha = 1 \quad k^{\text{St}} = 3 \\ \Delta T = K^{\text{tdp}} \times 3 = \Delta T_3 \quad (8)$$

$$\text{for } \alpha \in <0, 1> \quad k^{\text{St}} = 1 + 2\alpha_{\text{exp}} \\ \Delta T = K^{\text{tdp}} \times (1 + 2\alpha_{\text{exp}}) \quad (9)$$

The experimental value of the degree of conversion is obtained by the combination of eqns (7–9)

$$\alpha_{\text{exp}} = \frac{\Delta T - \Delta T_1}{\Delta T_3 - \Delta T_1} \quad (10)$$

where ΔT is the difference between the melting point of alkali metal fluoride and the temperature of primary crystallization of the tested melt.

The results of calculation of α_{exp} are presented in Table 2. The results show that during the dissolution of lithium titanate in both NaF and KF the ex-

Table 2. Theoretical and Experimental Values of the Degree of Conversion of the Exchange Chemical Reaction (B) in Reciprocal Systems Containing Lithium

System	T/K	$\frac{\Delta_r G^\circ}{\text{kJ mol}^{-1}}$	K	γ	α_{theor}	α_{exp}
KF				0.01	0.999	0.958
+ Li ₂ TiO ₃	1300	-116.5	126.4×10^3	0.02	0.999	0.953
NaF				0.01	0.999	0.995
+ Li ₂ TiO ₃	1300	-2.9	1.3	0.02	0.999	0.939
LiF				0.01	0.244	—
+ K ₂ TiO ₃	1300	116.5	7.9×10^{-6}	0.02	0.157	—
LiF				0.01	0.999	—
+ Na ₂ TiO ₃	1300	2.9	0.764	0.02	0.999	—
Na ₂ TiO ₃				0.03	0.999	—

change chemical reaction (B) takes place followed by the dissociation reaction (A). In both cases the reaction (B) runs quantitatively, which is confirmed by the thermodynamic analysis ($\alpha_{\text{theor}} = 1$, Table 2) and by the fact that in the tested composition region Li₂TiO₃ completely dissolves.

The precipitation of lithium titanate in melts based on LiF is caused by the opposite order of the reactions (A) and (B). After the dissociation of Na₂TiO₃

and/or K₂TiO₃ the created TiO₃²⁻ anion reacts with lithium cation present in the melt under the creation of insoluble lithium titanate. In the system LiF—Na₂TiO₃ the reaction (B) runs quantitatively ($\alpha_{\text{exp}} = 1$, Table 2). On the other hand, in the system containing K₂TiO₃ the equilibrium of the exchange reaction (B) is created. In this case the melt contains, except lithium fluoride, dissociated potassium titanate the amount of which is determined by the degree of conversion ($\alpha_{\text{exp}} = 0.12$ – 0.25 , Table 2). In both LiF—Na₂TiO₃ and LiF—K₂TiO₃ molten mixtures the precipitate of Li₂TiO₃ was proved by X-ray analysis and by the visual observation as well.

CONCLUSION

It can be concluded on the basis of the presented experimental and thermodynamic analysis results that the mechanism of dissolution of alkali metal titanates in alkali metal fluorides is an electrolytic dissociation according to eqn (A). In reciprocal systems the exchange chemical reaction (B) is responsible for dissolution of lithium titanate in sodium and potassium fluoride and for the precipitation of lithium titanate from molten mixtures based on LiF as well. The important result of this work is the fact that titanate anion, TiO₃²⁻, does not react with basic fluoride melt under the formation of oxide-fluoride complexes of titanium.

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