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THERMAL STABILITY OF ALKALI METAL BORATES AND ALKALINE EARTH METAL BORATES

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The correlation between the enthalpies of formation of alkali metal and alkaline earth metal borates and the composition of the vapor in equilibrium with their melts is considered. The thermal stabilities of the studied borates have been estimated. A method is suggested for determination of the relative composition of the vapor over borate melts on the basis of their enthalpies of formation.

In the production of glasses and enamels containing alkali metal or alkaline earth metal borates, the evaporation of these components changes the composition of the melt considerably. For this reason it is important to know how this process occurs. Information on thermodynamic potentials, for example, concerning the enthalpies of formation of borate systems permits estimation of the changes in composition of the melts due to the volatilization of their components.

In [1], solution calorimetry was used to determine the enthalpies of formation (ΔH_{form}) of alkali metal borate glasses containing (mol% M_2O) 0-40 Li_2O, 0-35 Na_2O, 0-36 K_2O, 0-35 Rb_2O and 0-43 Cs_2O, and of alkaline earth metal borate glasses containing (mol% MO) 43-45 MgO, 29-39 CaO, 26-30 SrO, and 18-40 BaO.

Analysis of the (ΔH_{form}) values reveals that in all the systems studied the metaborates $M_2O(MO)\cdot B_2O_3$ appear to be the most stable compounds relative to decomposition into the oxides $M_2O(MO)$ and B_2O_3 [2]. Therefore, the presence of these borates in the vapor over the melt seems most probable. This suggestion is confirmed by the mass-spectrometric data available for alkali metal borate melts [3]. It is easy to show that the relative stabilities of compounds in the melt and in the vapor obey the same rule. Due to this, the vapor composition can be determined by considering the dissociation of borates in the melt according to the following reaction:

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$$M_2O(MO)\cdot nB_2O_3 \rightarrow M_2O(MO)\cdot B_2O_3 + (n-1)\,B_2O_3 \qquad (1)$$

where n is the number of B_2O_3 moles per mole $M_2O(MO)$ in a borate.

To estimate the relative content of products of dissociation in the vapor over a melt, one should determine the degree of dissociation of borates (α), which characterizes their stability relative to decomposition according to reaction (1). The α values are calculated via the following equation:

$$K = \left[(n-1)\cdot\alpha^{n}\right] / \left\{(1-\alpha)\cdot[1+(n-1)]^{(n-1)}\right\} \qquad (2)$$

where K is the equilibrium constant of reaction (1). It should be noted that Eq. (2) is derived on the assumption that the initial substances and the products form ideal solutions. As mentioned in [2], the equilibrium constant of reaction (1) for borates may be estimated with considerable accuracy as

$$K = \exp\left(-\Delta H^{o}/RT\right) \qquad (3)$$

where ΔH^{o} is the standard enthalpy of the process discussed.

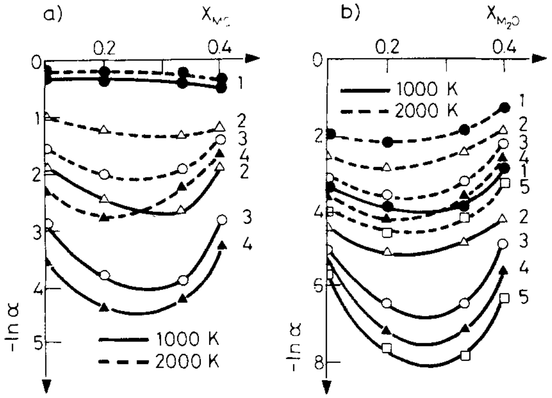

Fig. 1 Stabilities of alkaline earth metal borates (a) and alkali metal borates (b) relative to decomposition into the metaborates and B_2O_3; a: 1 - Mg, 2 - Ca, 3 - Sr, 4 - Ba; b: 1 - Li, 2 - Na, 3 - K, 4 - Br, 5 - Cs

Vie Eqs. (2) and (3), the α values were calculated on the basis of the experimental enthalpies of formation of the alkali (alkaline earth) metal borates. The degrees of dissociation were determined at 1000 K and 2000 K, n being equal to 9, 4, 2 and 1.5, which correspond to the compositions with

10.0, 20.0, 33.3 and 40.0 mol% $M_2O(MO)$, respectively. The concentration dependences of the ln α values are given in Fig. 1 (a, b). This shows that the systems containing more basic oxides are more stable relative to decomposition into B_2O_3 and the corresponding metaborates. This means that the volatilities of the alkaline earth metal metaborates decrease in the sequence $MgO \cdot B_2O_3 > CaO \cdot B_2O_3 > SrO \cdot B_2O_3 > BaO \cdot B_2O_3$, and those of the alkali metal metaborates in the sequence $Li_2O \cdot B_2O_3 > Na_2O \cdot B_2O_3 > K_2O \cdot B_2O_3 > Rb_2O \cdot B_2O_3 > Cs_2O \cdot B_2O_3$. The latter sequence correlates with the mass-spectrometric data for alkali metal borate systems reported in [3]. In addition, Fig. 1 reveals that borates in the concentration range 20-30 mol% $M_2O(MO)$ are most stable relative to the decomposition discussed. On increase of the temperature from 1000 K to 2000 K, the stabilities of all the borates decrease.

The α values allow estimation of the relative content of B_2O_3 and metaborates in the vapor over the melt. The mole fractions (X_i) of these components in the melt can be calculated by using the following equations, resulting from application of the ideal associated solution theory to borate melts:

$$\begin{array}{ll} \text{for metaborates:} & \left\{ \begin{array}{c} X_{M \cdot B} = \alpha / [1 + (n-1)\alpha] \\ X_B = [(n-1)\alpha] / [1 + (n-1)\alpha] \end{array} \right\} \\ \text{forB}_2\text{O}_3\text{:} & \end{array} \tag{4}$$

The vapor pressure of each component is proportional to its mole fraction in the melt, i.e. to the value of $X_{M \cdot B}$ or X_B.

The results of calculations with Eq. (4) for the magnesium, calcium and barium borates systems are given in Fig. 2 (a, b, c). They indicate that an increase in basicity of the metal oxides in the borates considerably influences the values of $X_{M \cdot B}$ and X_B (i.e. the contents of products of dissociation in the vapor), resulting in their systematic decrease in the series from magnesium borates to barium borates. This tendency is also observed for the alkali metal borates studied.

The composition of the vapor over the melt is determined by the following relationships:

$$\begin{array}{ll} \text{for metaborates:} & \left\{ \begin{array}{c} P_{M \cdot B} = \left[X_{M \cdot B} \cdot P^0_{M \cdot B}\right] / \left[X_{M \cdot B} \cdot P^0_{M \cdot B} + X_B \cdot P^0_B\right] \\ P_B = \left[X_B \cdot P_B\right] / \left[X_{M \cdot B} \cdot P^0_{M \cdot B} + X_B \cdot P^0_B\right] \end{array} \right\} \\ \text{for B}_2\text{O}_3\text{:} & \end{array} \tag{5}$$

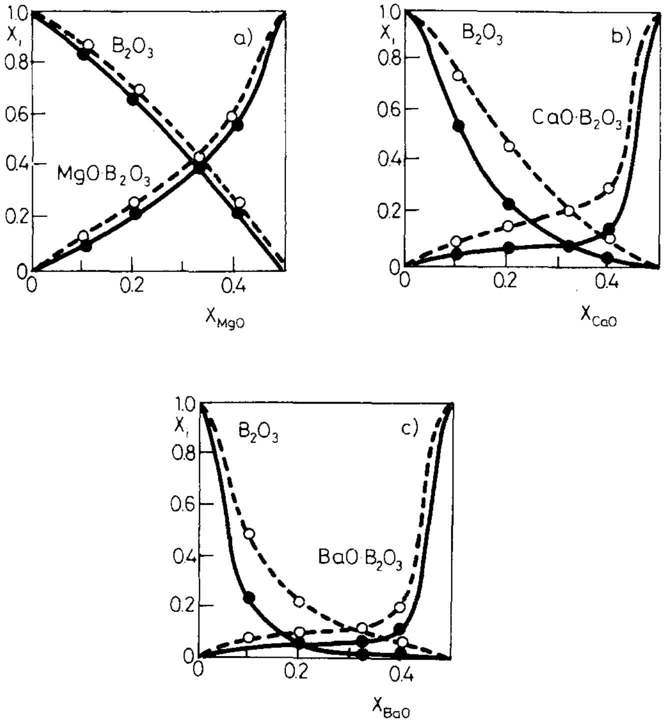

Fig. 2 Relative contents of metaborates and B_2O_3 in magnesium (a), calcium (b), and barium (c) borate melts; — 1000 K, - - - 2000 K

where $P_{M\cdot B}$ and P_B are the partial vapor pressures of the metaborates and B_2O_3, respectively (or their mole fractions in the vapor over the melt), $X_{M\cdot B}$ and X_B are the mole fractions of the same components in the melt, and $P^0_{M\cdot B}$ and P^0_B are the vapor pressures over the pure metaborates and B_2O_3.

The composition of the vapor over the Na_2O–B_2O_3 melt has been calculated from Eqs (2)-(5), the experimental enthalpies of formation of sodium borates being used. The results obtained are in satisfactory agreement with the mass-spectrometric data available for this system [4].

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Zusammenfassung — Es wurde die Beziehung zwischen den Bildungsenthalpien von Alkali- (Erdalkali-)metallboraten und der Zusammensetzung der sich mit der Schmelze im Gleichgewicht befindlichen Gasphase betrachtet. Die thermische Stabilität der untersuchten Borate wurde geschätzt. Es wurde ein Verfahren entwickelt, die relative Zusammensetzung der Gasphase über Boratschmelzen auf Grund ihrer Bildungsenthalpien zu bestimmen.