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 ($\Delta H_{\text{form}}$) of alkali metal borate glasses containing (mol\% M$_2$O) 0-40 Li$_2$O, 0-35 Na$_2$O, 0-36 K$_2$O, 0-35 Rb$_2$O and 0-43 Cs$_2$O, 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 ($\Delta H_{\text{form}}$) values reveals that in all the systems studied the metaborates M$_2$O(MO)$\cdot$B$_2$O$_3$ appear to be the most stable compounds relative to decomposition into the oxides M$_2$O(MO) and B$_2$O$_3$ [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:
M₂O(MO)·nB₂O₃ → M₂O(MO)·B₂O₃ + (n−1) B₂O₃  

(1)

where \( n \) is the number of B₂O₃ moles per mole M₂O(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 (\( \alpha \)), which characterizes their stability relative to decomposition according to reaction (1). The \( \alpha \) values are calculated via the following equation:

\[
K = \frac{[(n - 1) \cdot \alpha^n]}{[(1 - \alpha) \cdot [1 + (n - 1)]^{(n - 1)}]}
\]

(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

\[
K = \exp \left(-\frac{\Delta H^0}{RT}\right)
\]

(3)

where \( \Delta H^0 \) 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 B₂O₃: 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 \( \alpha \) 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