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DISSOCIATION OF ALKALI METAL BORATES AND ACID-BASE INTERACTIONS IN OXIDE SYSTEMS

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The stability relative to decomposition to oxides has been estimated for alkali metal borates $M_2O \cdot nB_2O_3$ (M = Li, Na, K, Rb and Cs), where $n = 1, 2, 3$ and 4. The correlation between the degrees of dissociation and the enthalpies of formation is discussed.

Results and discussion

The enthalpies of solution in 2 N nitric acid at 298 K were measured for alkali metal borates of the type $M_2O \cdot nB_2O_3$, where M = Li, Na, K, Rb, Cs; and $n = 1$, 2, 3 and 4. (The compositions will be noted as 1 : 1, 1 : 2, 1 : 3 and 1 : 4.) From the experimental results [1], the enthalpies of formation of borates from crystalline oxides (ΔH^1_{ox}) were calculated according to the reaction:

$$M_2O + nB_2O_3 = M_2O \cdot nB_2O_3 \tag{1}$$

The concentration-dependences of the ΔH^1_{ox} values are given in Fig. 1a.

In any system, the acid-base interaction of its components is characterized by the thermodynamic stability of the compounds which the components form. The degrees of dissociation of the compounds quantitatively define this stability.

Suppose alkali metal borates dissociate as follows:

$$M_2O \cdot nB_2O_3 \rightarrow M_2O + nB_2O_3 \tag{2}$$

Let us establish the correlation between their enthalpies of decomposition and the degree of dissociation. According to [2], the equilibrium constant of dissociation (k) for alkali metal borates may be written with considerable accuracy as

$$k = \exp(-\Delta H/RT) \tag{3}$$

where ΔH° is the standard enthalpy of dissociation of a compound, R is the gas constant, and T is temperature.

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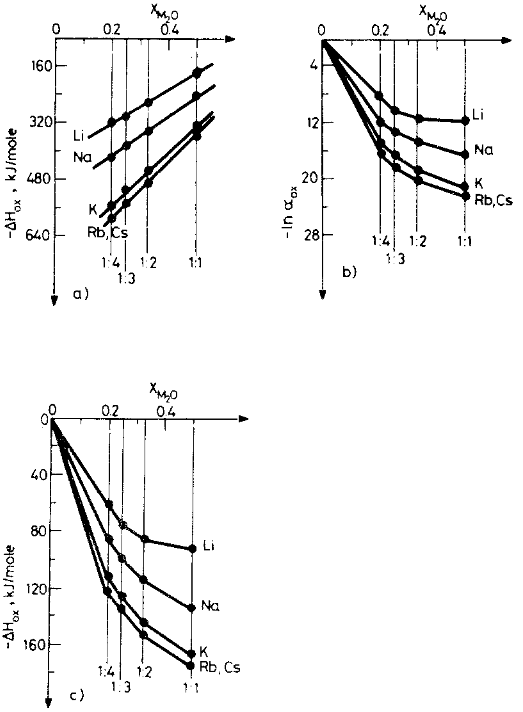

Fig. 1 Concentration dependences of the values ΔH^1_{ox} (a), $\ln \alpha_{ox}$ (b) and ΔH_{ox} (c) for alkali borates

If the law of mass action is applied to (2) the equilibrium constant is

$$k = (X_M \cdot X_B^n)/X_{M.nB} \tag{4}$$

where X_M, X_B and $X_{M.nB}$ are the mole fractions of M_2O, B_2O_3 and $M_2O \cdot nB_2O_3$, respectively. These values may be written using the degree of dissociation of the borates into the oxides (α_{ox}), which leads to:

$$k = [n^n \cdot \alpha_{ox}^{(n+1)}]/[(1-\alpha_{ox}) \cdot (1+n\alpha_{ox})^n] \tag{5}$$

The combination of this with (3) gives

$$\exp(-\Delta H^\circ/RT) = [n^n \cdot \alpha_{ox}^{(n+1)}]/[(1-\alpha_{ox}) \cdot (1+n\alpha_{ox})^n] \tag{6}$$

From the enthalpies of formation of the studied compounds, their degrees of dissociation into oxides (α_{ox}) were calculated at 1000 K using (6). The concentration-dependences of $\ln \alpha_{ox}$ are shown in Fig. 1b.

A comparison of Fig. 1a and Fig. 1b shows that the enthalpies of formation of the alkali metal borates calculated for reaction (1), i.e. per mole of alkali metal oxide

(ΔH^1_{ox}), adequately characterize the stability changes only for a series of similar compounds. In the case of different crystals of the same system, there is no such correlation between ln α and ΔH^1_{ox}. To explain this fact, one should take logarithms of (6), making some transformations, which leads to

$$-\Delta H^0/[RT\cdot(n+1)] = [n/(n+1)]\cdot\ln n+\ln\alpha_{ox} \tag{7}$$

Since $-\Delta H^0 = \Delta H^1_{ox}$ for reaction (2), it follows that

$$\Delta H^1_{ox}/[RT\cdot(n+1)] = [n/(n+1)]\cdot\ln n+\ln\alpha_{ox} \tag{8}$$

This relationship indicates that the above-mentioned disproportionality between ln α_{ox} and ΔH^1_{ox} for different compounds of the same system is due to the presence of the term $1/(n+1)$ on the left-hand side of (8), the term being dependent on the composition of a dissociating compound.

By definition

$$\Delta H^1_{ox}/(n+1) = \Delta H_{ox} \tag{9}$$

where ΔH_{ox} is the enthalpy of formation calculated per total mole of oxides forming a compound according to the following reaction ($x+y = 1$):

$$xM_2O+yB_2O_3 = xM_2O\cdot yB_2O_3 \tag{10}$$

Substitution of (9) into (8) gives

$$\Delta H_{ox}/RT = [n/(n+1)]\cdot\ln n+\ln\alpha_{ox} \tag{11}$$

From the experimental enthalpies of solution of alkali metal borates, their enthalpies of formation were calculated according to reaction (10). The results obtained are presented in Fig. 1c.

As can be seen from Fig. 1b and Fig. 1c, the ΔH_{ox} values do characterize the stability of the crystals studied, both in a series of similar compounds belonging to different systems and within each system when the composition of the borates varies.

Thus, thermal effects of formation of compounds characterize their stability relative to their decomposition into their components only when these effects are related to 1 total mole of components.

References

1 M. M. Shultz, N. M. Vedishcheva and B. A. Shakhmatkin, Fiz. Khim. Stekla, 6 (1986) 651.

2 M. H. Karapetyants, Methods of Comparative Calculations of Physical and Chemical Properties, Nauka, Moskva, 1965, p. 265.

Zusammenfassung — Es wurde die relative Stabilität von Alkalimetallboraten der Formel $M_2O \cdot nB_2O_3$ mit M = Li, K, Rb, Cs und n = 1, 2, 3, 4 gegenüber der der Oxide ermittelt. Der Zusammenhang von Dissoziationsgrad und Bildungsenthalpie wird besprochen.

Резюме — Изучена устойчивость боратов щелочных металлов общей формулы $M_2O \cdot nB_2O_3$, где M = литий, натрий, калий, рубидый и цезий, а n = 1—4, относительно разложения их до окислов. Обсуждена корреляция между степенью их диссоциации и энтальпией образования.