

CALORIMETRIC STUDY OF VITREOUS AND CRYSTALLINE ALKALI METAL BORATES

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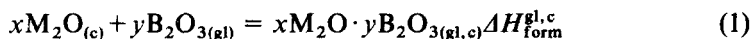
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The enthalpies of solution in 2 N nitric acid at 298 K were measured for alkali metal borate glasses and crystals. From the data obtained, their enthalpies of formation from the oxides and the heats of crystallization of the glasses were calculated.

The negative deviation from ideality observed in alkali metal borate systems is interpreted in terms of the acid–base interaction of their components. The heats of crystallization of the glasses appeared to be mainly determined by the ordering effect of the boron–oxygen network. The contents of different borate groupings in the glasses studied were estimated. The structures of the borate glasses are discussed.

A calorimetric study of vitreous and crystalline alkali metal borates has been carried out. The enthalpies of solution in 2 N nitric acid at 298 K were measured for glasses containing (mol. % 0–39.5 Li₂O, 0–35.1 Na₂O, 0–35.9 K₂O, 0–34.7 Rb₂O or 0–42.5 Cs₂O, and for crystals of the type M₂O · nB₂O₃, where M = Li or Na (n = 1–4); M = K (n = 1–3, 3.8, 5); M = Rb (n = 1–5); or M = Cs (n = 1–5, 9).

From the experimental data on borates and boron oxide and the calculated enthalpies of solution of alkali metal oxides, the enthalpies of formation of the glasses ($\Delta H_{\text{form}}^{\text{gl}}$) and crystals ($\Delta H_{\text{form}}^{\text{c}}$) from crystalline M₂O oxides and vitreous B₂O₃ oxide were calculated according to the following reaction ($x + y = 1$):



The accuracy of this calculation is $\pm(0.8\text{--}1.6) \text{ kJ} \cdot \text{mol}^{-1}$, depending on the compositions of the samples studied. The concentration-dependences of $\Delta H_{\text{form}}^{\text{gl},\text{c}}$ are given in Fig. 1.

The results obtained reveal that the formation of alkali metal borates (glasses and crystals) is highly exothermic, this effect increasing in the sequence Li → Cs for different systems. The observed negative deviation from ideality is due to the acid–base interaction of the components (M₂O and B₂O₃). This interaction results in an

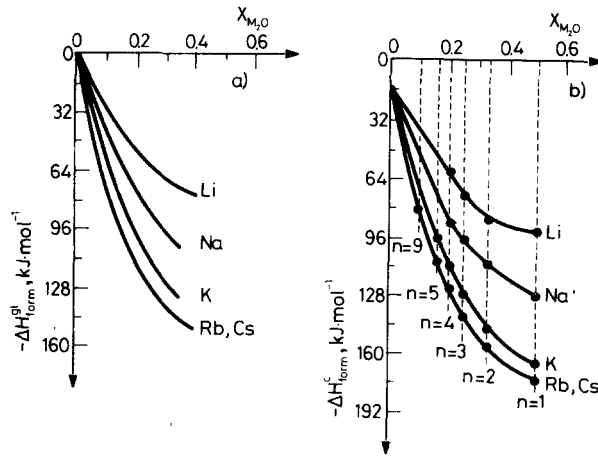


Fig. 1 Enthalpies of formation from oxides of alkali borate glasses (a) and crystals (b).

increase in the ionicity of the chemical bonds in the borates as compared with that in oxides [1].

A comparison of the ΔH_{form} values for the crystals and the glasses indicates the non-equilibrium nature of the glassy state.

The heats of crystallization of the glasses (ΔH_{cryst}) were calculated over the concentration range 0–33.3 mol% M_2O , as the difference between the enthalpies of

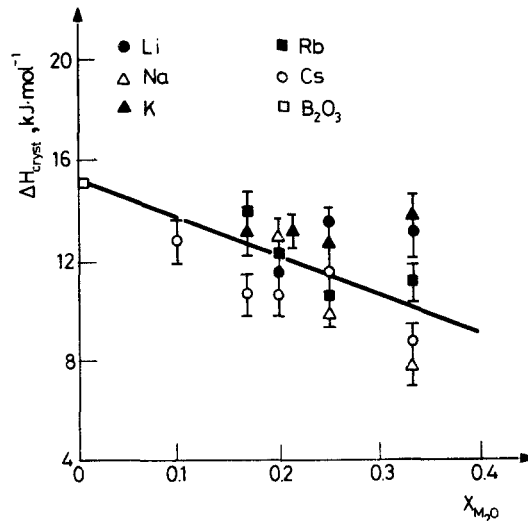


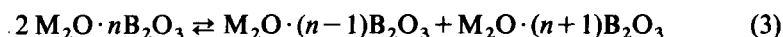
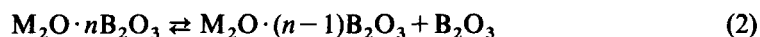
Fig. 2 Heats of crystallization of alkali borate glasses

solution of vitreous and crystalline borates with the same composition. The accuracy of the calculation is $\pm 0.8 \text{ kJ} \cdot \text{mol}^{-1}$. The concentration-dependences of the ΔH_{cryst} values for the glasses with the stoichiometric compositions are shown in Fig. 2. The straight line in the same Figure characterizes the heats of crystallization of the amounts of B_2O_3 contained (according to chemical analysis) in the glasses studied.

The relatively small deviation of the experimental ΔH_{cryst} values from the calculated straight line allows the suggestion that the heats of crystallization of the alkali metal borate glasses are mainly determined by the effects of rearrangement and ordering of the boron-oxygen network. However, it should be taken into consideration that the structure of the latter differs, depending on the composition of the glass. On the addition of alkali metal oxide to boron oxide to 33.3 mol% M_2O , the number of B-O bonds increases, due to the change in the coordination number of boron with respect to oxygen. This factor results in an increase of the linking degree of the boron-oxygen network and thereby reduces its disordering. This tendency is characterized by the observed decrease in ΔH_{cryst} on going from 0 to 33.3 mol% M_2O .

Numerous data from structural investigations of the alkali metal borate glasses permit their structures to be considered, according to [2], as a (to some extent) disordered network of borate groupings similar to those existing in crystalline compounds. However, in any particular case one should determine what groupings form a glass of a given composition.

To solve this problem for the glasses studied, we have estimated the thermodynamic stabilities of alkali metal borates relative to decomposition into compounds which coexist according to the phase diagrams of the systems, i.e. in the following way:



The thermodynamic stabilities of the compounds are characterized by their degrees of dissociation (α), calculated as

$$\alpha = \sqrt{K/(K+1)} \quad (4)$$

and

$$\alpha = 2\sqrt{K_1}/(1+2\sqrt{K_1}) \quad (5)$$

where K and K_1 are the equilibrium constants of reactions (2) and (3), respectively. Equations (4) and (5) were derived on the assumption that the initial substances and the products of dissociation form ideal solutions. The equilibrium constants $K(K_1)$

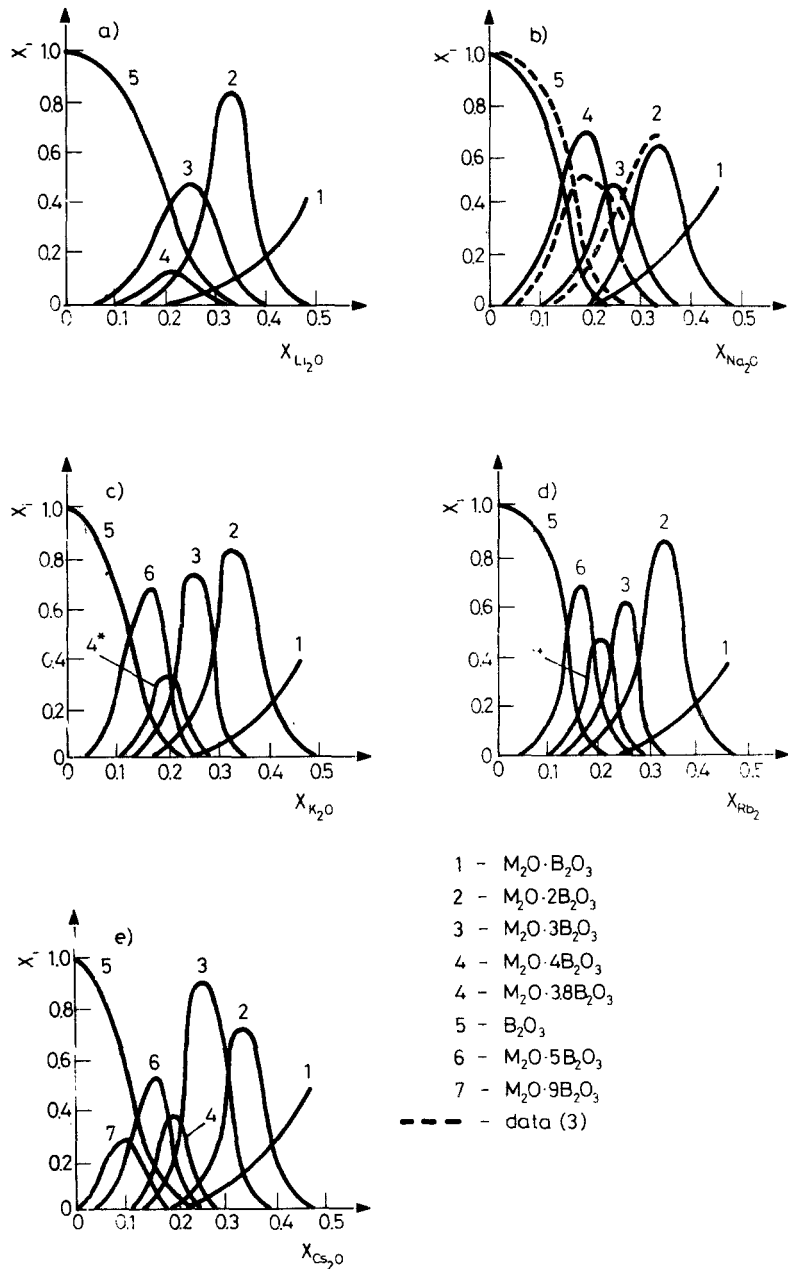


Fig. 3 Relative content of borate groupings in alkali borate glasses. 1. $M_2O \cdot B_2O_3$, 2. $M_2O \cdot 2B_2O_3$, 3. $M_2O \cdot 3B_2O_3$, 4. $M_2O \cdot 4B_2O_3$, 4*. $M_2O \cdot 3.8B_2O_3$, 5. B_2O_3 , 6. $M_2O \cdot 5B_2O_3$, 7. $M_2O \cdot 9B_2O_3$. - - - data [3]

were evaluated by using the following equation:

$$K(K_1) = \exp(-\Delta H^\circ/RT) \quad (6)$$

where ΔH° is the standard enthalpy of reaction (2) or (3).

The α values were determined at $T = 1000$ K, which corresponds approximately to the temperature of freezing of the structural rearrangement in the alkali metal borate glasses. The α values were used to estimate the relative contents of different borate groupings in the glasses studied. The mole fractions of the groupings (x_i) were calculated for reaction (2) as

$$X_{M_2O \cdot nB_2O_3} = \frac{1-\alpha}{1+\alpha}; X_{M_2O \cdot (n-1)B_2O_3} = X_{B_2O_3} = \frac{\alpha}{1+\alpha} \quad (7)$$

and for reaction (3) as

$$X_{M_2O \cdot nB_2O_3} = (1-\alpha); X_{M_2O \cdot (n-1)B_2O_3} = X_{M_2O \cdot (n+1)B_2O_3} = \frac{\alpha}{2} \quad (8)$$

The results obtained are shown in Fig. 3. They indicate that the most stable compounds in the alkali metal borate systems are the characteristic structural units of the glasses, except for the low-alkali metal region, where B_2O_3 is the basic unit. Analogous literature data obtained by means of NMR [3] are given in Fig. 3b for comparison.

References

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Zusammenfassung — Für Alkaliborat-Gläser und Kristalle wurden die Lösungsenthalpien in 2N Salpetersäure bei 298 K gemessen. Daraus wurden die Enthalpien der Bildung aus den Oxiden sowie die Kristallisationswärmen der Gläser berechnet. Die negativen Abweichungen der Bildungsenthalpien vom idealen Verhalten werden als Resultat der Säure-Base-Umsetzung der Oxide gedeutet. Die Kristallisationswärmen der Gläser scheinen im wesentlichen von ordnungsvorgängen des Bor-Sauerstoff-Netzwerks bestimmt zu sein. Der Gehalt der Gläser an den verschiedenen Boratgruppen wird abgeschätzt und die Struktur der Boratgläser diskutiert.

Резюме — При 298 К измерены энтальпии растворения стеклообразных и кристаллических боратов щелочных металлов в 2 н азотной кислоте. На основе полученных данных вычислены энтальпии образования щелочных боратов из окисей и теплоты кристаллизации этих стекол. Отклонение от идеальности в сторону отрицательных значений, интерпретировано на основе кислотно-основного взаимодействия компонент. Теплоты кристаллизации стекол определяются главным образом эффектом упорядочения борокислородного остова. Определено содержание в стеклах различных богатных группировок и обсуждена богатных стекол.