Thermochimica Acta, 110 (1987) 443–447
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

ACID–BASE CONCEPT IN OXIDE GLASSES

M.M. SHULTZ, N.M. VEDISHCHEVA and B.A. SHAKHMATKIN

Institute of Silicate Chemistry, Academy of Sciences of the U.S.S.R., Leningrad (U.S.S.R.)

ABSTRACT

The relationship between the acid–base properties of oxide glasses and the atomic characteristics of their components was studied. It has been found that the increase in the basicity of oxides in the order $Li_2O < Na_2O < K_2O < Rb_2O < Cs_2O$ is due to an increase in the ionic character of metal–oxygen bonds during the formation of alkali metal borate glasses from oxides.

INTRODUCTION

Oxide glasses are widely used in different branches of industry and considerable information concerning the properties of oxide systems has been accumulated. However, the absence of a general approach prevents the interrelationship between these properties from being elucidated. The acid–base concept, widely used for solutions, when applied to oxide systems enables the chemistry of the processes involved to be related to their thermodynamics. In this way one can determine the character of the interaction of the components, the type of phase diagram, the probability of the formation of compounds and their stability. The acid–base concept also enables one to compare the thermodynamic, optical and spectral properties of oxide systems and to establish their correlations and find their dependence on the nature and concentration of the components.

RESULTS AND DISCUSSION

The enthalpies of reactions between oxides are an integral measure of the acid–base interactions of the components in oxide systems. However, the use of enthalpies is sometimes impossible; they are mainly determined experimentally and are frequently unavailable. Therefore, in practice, one often uses different atomic parameters characterizing the acid–base proper-

---

Thermal Analysis Highlights, 8th ICTA, Bratislava, Czechoslovakia.

0040-6031/87/$03.50

ties of elements, such as electronegativities, ionization potentials, relative polarizing potentials and atomic, ionic and orbital radii. These parameters are available for most elements and are adequate for describing acid–base interactions in systems consisting of two types of atoms, but those involving several kinds of atoms are much more complicated. However, even in multi-component systems one may find some correlations between the atomic and integral characteristics of acid–base interactions.

We have attempted to establish such a relationship for M_2O–B_2O_3 alkali metal borate systems (M = Li, Na, K, Rb, Cs), which are important components of many industrial glasses and enamels. The enthalpies of formation from the elements (δH_{form}) for glasses and crystals of the same compositions (with 20–50 mol% of M_2O) were calculated from their experimental enthalpies of solution in 2 N nitric acid at 298 K [1–4]. The ΔH_{form} values were plotted against the different atomic parameters mentioned above and it was found that only the dependence $\Delta H_{\text{form}} = f(1/r_M)$ is linear, where r_M is the atomic or ionic radius of the alkali metal (these values are proportional). These dependences for alkali metal borates (glasses and crystals) together with those for alkali metal oxides are shown in Fig. 1, the ΔH_{form} values for both oxides and borates being re-calculated per mole of M_2O. This enables the compositions of the borates studied to be represented as $M_2O \cdot nB_2O_3$, where $n = 1$–4. Owing to the scale used in Fig. 1, the enthalpies of formation for vitreous and crystalline borates are indistinguishable, although their diffence is beyond the limits of the experimental error [1–4]. It should be noted that the observed character of the dependence $\Delta H_{\text{form}} = f(1/r_M)$ for alkali metal oxides is contrary to that expected from Pauling's equation: $\Delta H_{\text{form}} = 23.06(\chi_O - \chi_M)$, where χ_O and χ_M are the electronegativities of oxygen and alkali metal, respectively. To explain this fact, one must consider the character of the interactions between atoms and the way it is related to atomic parameters.

The linearity of the dependence $\Delta H_{\text{form}} = f(1/r_M)$ for borates and oxides indicates a considerable contribution from Coulomb interactions. One should not neglect covalent binding forces, however. There are methods of calculating the enthalpies of formation of crystals with mixed ionic–covalent types of chemical bonds. Neglecting Van der Waals interactions, the enthalpies of formation of crystals from elements are given by the following equation (ref. 5, p. 219):

$$\Delta H_{\text{form}} = \epsilon^2 \left[-\frac{A}{r_M + r_O}\left(1 - \frac{\rho}{r_M + r_O}\right) + \frac{\sum \Delta H_{\text{at}}}{2} \right] \tag{1}$$

where A is Madelung's constant, ρ is the repulsion constant, ϵ is the degree of ionicity (ionic character) of a chemical bond, ΔH_{at} is the enthalpy of atomization for elements in their standard states and r_M and r_O are the atomic (ionic) radii of metals and oxygen, respectively. As shown (ref. 5, p. 72), eqn. (1) is also valid for the amorphous state.

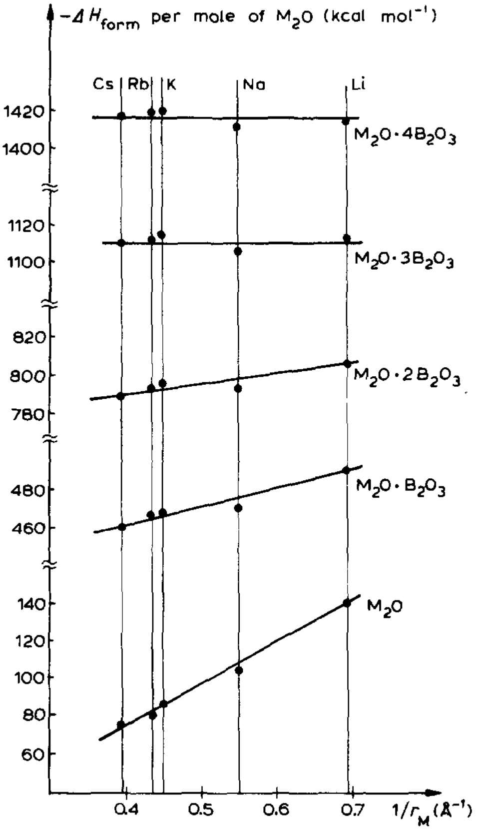

Fig. 1. $\Delta H_{form} = f(1/r_M)$ dependences for alkali metal borates ($M_2O \cdot nB_2O_3$) and alkali metal oxides (M_2O).

For alkali metal oxides the degree of ionicity of the M–O bonds (ϵ_{M-O}) has not been determined experimentally. We have estimated this parameter for M_2O using the following approximate equation (ref. 5, p. 152):

$$\epsilon_{M-O} \approx \frac{\chi_O - \chi_M}{\chi_O + \chi_M} \qquad (2)$$

The calculation using Pauling's electronegativities gives the following values for ϵ_{M-O}: Li_2O 0.56, Na_2O 0.59, K_2O 0.63, Rb_2O 0.65 and Cs_2O 0.67. It will be noted that for monovalent atoms the degree of ionicity of a chemical bond coincides with the effective charge: by definition $\epsilon = \delta/z$, where δ is the effective charge and z is the formal charge of an atom. Hence one may consider the ϵ_{M-O} values calculated from eqn. (2) as the effective charges of alkali metals in oxides.

The substitution of the above-mentioned ϵ_{M-O} values in eqn. (1) leads to significant deviations of the calculated enthalpies of alkali metal oxide

TABLE 1

Degree of ionicity of metal–oxygen bonds in alkali metal oxides (M_2O) and borates ($M_2O \cdot nB_2O_3$)

M	M_2O	$M_2O \cdot B_2O_3$	$M_2O \cdot 2B_2O_3$	$M_2O \cdot 3B_2O_3$	$M_2O \cdot 4B_2O_3$
Li	0.46	0.53	0.53	0.53	0.53
Na	0.42	0.56	0.57	0.58	0.58
K	0.42	0.61	0.63	0.64	0.64
Rb	0.42	0.63	0.65	0.66	0.66
Cs	0.43	0.66	0.68	0.69	0.70

formation from those available in the literature. Therefore, we calculated the ϵ_{M-O} parameters using eqn. (1) from the literature ΔH_{form} values for oxides. The results are given in Table 1. The degree of ionicity of the M–O bonds was found to be constant for all alkali metal oxides, within the accepted accuracy limits (ca. 5%). This can be explained as follows. In an M_2O molecule each oxygen atom is attached to two metal atoms. According to this stoichiometry and the effective charges of alkali metal atoms calculated using eqn. (2), two lithium atoms can donate 1.12 electrons and two caesium atoms can donate 1.34 electrons. However, it is known (ref. 5, pp. 187, 188) that in different compounds the effective charge on oxygen usually does not exceed -1, i.e., when forming a chemical bond an oxygen atom accepts into its vacant orbitals not more than one electron. Thus in oxides the electron-donating capacities of alkali metal atoms are not realized entirely and are restricted by the electron-accepting capacity of oxygen, the latter being practically independent of the nature of the alkali metal atom.

The invariability of ϵ_{M-O} for all alkali metal oxides explains the above-mentioned anomalous (with respect to Pauling's equation) character of their $\Delta H_{\text{form}} = f(1/r_M)$ dependence.

Let us consider the correlation between the degree of ionicity in alkali metal borates (glasses and crystals) and their enthalpies of formation. The former was also calculated from eqn. (1) and the results are given in Table 1. This calculation suggests that the efffective degree of ionicity of chemical bonds formed by three types of atoms (alkali metal, boron and oxygen) is mainly characterized by the contribution of the M–O bonds, which allows the values calculated for borates to be denoted by the same symbol, ϵ_{M-O}.

Table 1 shows that interaction of alkali metal oxides with boric anhydride results in an appreciable increase in the ionicity of M–O bonds. This is due to additional oxygen atoms being contributed to borates by boron oxide, these atoms having lower effective charges than those in alkali metal oxides (δ_0 is ca. -0.6 in B_2O_3 and ca. -1 in M_2O). Hence in borates there are oxygen atoms capable of accepting an extra part of the electron cloud belonging to the alkali metal atoms.

The data in Table 1 indicate that the ϵ_{M-O} values for borates are much closer to those calculated from eqn. (2) than the ϵ_{M-O} values for oxides, where the electron-donating capacities of metal atoms are not completely realized. Thus one may suggest that eqn. (2) enables one to calculate the maximum possible value of ϵ for any pair of atoms.

The increase in the ionicity of the M–O bonds is the greatest for caesium borate and the smallest for lithium borate. This is related to the fact that when forming an oxide lithium realizes its electron-donating capacity much more completely than the other metals, while the latter preserve this capacity to a greater extent even after forming oxides. This tendency characterizes the basicity of alkali metal oxides, being most pronounced for caesium. The difference in the ϵ_{M-O} values for borates and the corresponding oxides may be considered as a quantitative characteristic of the basicity of oxides.

For all of the systems studied there is an increase in ϵ_{M-O} with increasing boron oxide content, i.e., when the ratio of donating atoms to accepting atoms decreases.

CONCLUSIONS

The acid–base properties of alkali metal borate glasses and crystals are almost identical, i.e., the chemical processes of their formation are similar. The basicity of alkali metal oxides is characterized by an increase in the ionicity of the M–O bonds during the formation of borates (glasses and crystals) from oxides.

REFERENCES

1 M.M. Shultz, N.V. Borisova, N.M. Vedishcheva and M.M. Pivovarov, Fiz. Khim. Stekla, 5 (1979) 36.
2 M.M. Shultz, N.V. Borisova, N.M. Vedishcheva and M.M. Pivovarov, Fiz. Khim. Stekla, 7 (1981) 107.
3 M.M. Shultz, N.M. Vedishcheva, B.A. Shakhmatkin and A.M. Starodubtsev, Fiz. Khim. Stekla, 11 (1985) 472.
4 M.M. Shultz, N.M. Vedishcheva and B.A. Shakhmatkin, Proc. 8th ICTA '85, Bratislava, Thermochim. Acta, 92 (1985) 345.
5 V.S. Urusov, Energeticheskaya kirstallokhimiya, Nauka, Moscow, 1975.