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ON THE NATURE OF THERMAL TRANSFORMATIONS IN ALKALI BOROSILICATE GLASSES

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As is known, the structure of porous glasses obtained by treating alkali borosilicate glasses with acid solutions [1−4] depends both on the composition of the initial glass and on its thermal treatment and the conditions of leaching [5,6]. With a view to solving problems of controlling the structure of porous glasses and studying the structure of sodium borosilicate glasses, we undertook an investigation of the kinetics of the processes occurring in sodium borosilicate glass during its thermal treatment.

The investigation was carried out by sorption study of the structure of porous glasses obtained from heat-treated Na-7/23* glass, using spiral quartz balances. Water was used as the sorbate. We have reported [7] that the pore radii of porous glass obtained by leaching samples of Na-7/23 glass subjected to prolonged heat treatment at 530° increase as the heat-treatment time is increased. On the contrary, the values of the radius and volume of the pores of porous glass obtained by leaching samples heat-treated at 650°, already after 1/2 hour of heat treatment, assume constant values, which do not change with a further increase in the time of heat treatment of the glass.

The independence of the value of the radius and the total pore volume of porous glass from the conditions of acid leaching of glass heat-treated at 780° indicates that the finely porous silica network washed free of alkali from the "high-temperature" porous glass is not "secondary silicic acid" coagulated in the pores during the process of leaching the glass in acid [8,9].

In 1956 E. A. Porai-Koshits, D. I. Levin, and N. S. Andreev [10], having shown that the pore sizes of porous glasses obtained by double leaching (in acid and then in alkali) increase with increasing duration of heat treatment of the initial Na-7/23 glass, confirmed this fact, which is of fundamental importance for understanding the processes occurring in sodium borosilicate glasses during their thermal treatment.

The present communication is devoted to setting forth the results we obtained in studying the kinetics and nature of these processes.

Fig. 1. Dependence of the radius and volume of pores of porous glass on the time and temperature of heat treatment of the initial glass A

Figure 1: Fig. 1. Dependence of the radius and volume of pores of porous glass on the time and temperature of heat treatment of the initial glass A

Glass Na-7/23 of the same melt was subjected to thermal treatment in two initial states: A—quenched from 850°, B—having undergone coarse annealing from high temperatures with gradual cooling.

Leaching was carried out at 50° in a 3 N HCl solution, taken in an amount of 15 cm^3 per 1 g of the glass being leached (powder, fraction 100—150μ).

The results of the experiments are given in Figs. 1 and 2 in the form of curves showing the change in pore radius and volume as a function of the duration of heat treatment at different temperatures for the initial glasses A and B, respectively.

* Here and below: 7 mol.% Na_2O, 23 mol.% B_2O_3, 70 mol.% SiO_2.

From glass A, quenched from 850°, the finest-pored glass is obtained (8 Å), with the smallest total pore volume ($V_s = 0.160$ cm^3/g). As the duration of heat treatment of this glass at temperatures up to 580° is increased, the value of the pore radius of the porous glasses obtained from it increases continuously, while the value of the total pore volume increases up to a certain constant value (Fig. 1).

Porous glass obtained from the initial glass B has a somewhat larger pore-radius size (47-48 Å) and total pore-volume value (0.197 cm^3/g), and also a somewhat broader function of the distribution of pore volume over radii than does porous glass obtained from glass A. Glass of type B cooled slowly after high temperatures; its structure reflects the processes of coarsening of regions of chemical inhomogeneity that occurred during cooling.

Fig. 1. Dependence of the radius and volume of pores of porous glass on the time and temperature of heat treatment of the initial glass A

The kinetic curves obtained on samples of type B initially pass through a minimum (Fig. 2). The value of the pore radius of the porous glass, as a function of the heat-treatment time of the initial glass B, first rapidly falls to a certain minimum value and then increases. The value of the total pore volume likewise first falls and then rises and, apparently, tends toward a certain constant value at the given temperature. Thus, during heat treatment of Na-7/23 glass at least two structural processes occur: the first—more rapid, manifested in a decrease in the value of the radius and the total volume of the pores, and the second —slower, causing continuous growth of the pore radius and an increase in the total pore volume up to a certain value. The rate of both processes increases strongly with temperature. Since the process of the first kind is not observed in samples of type A, we believe that the first (rapid) process is associated with

Fig. 2. Dependence of the radius and volume of pores of porous glass on the time and temperature of heat treatment of the initial glass B

Figure 2: Fig. 2. Dependence of the radius and volume of pores of porous glass on the time and temperature of heat treatment of the initial glass B

the destruction of the existing regions of chemical inhomogeneity, restructuring of the spatial network of the glass, and reorientation of chemical bonds. By contrast, the slow process, causing continuous growth of the pore size of the porous glass, appears to be associated with diffusion transfer of substance in the glass.

Fig. 2. Dependence of the radius and volume of pores of porous glass on the time and temperature of heat treatment of the initial glass B

At about 585° we found a critical value (or a narrow critical region) of temperature, above which a sufficiently short heat treatment of the initial glass (at 650° –1/2 hour) is enough for the -

on the radius of the pores of the porous glass obtained from it by acid leaching assumed a constant and, moreover, small value, independent of the duration of heat treatment of the initial glass (Table 1).

Table 1

Effect of the duration of heat treatment of glass Na-7/23 (specimen A), quenched from 850°, on the magnitude of the volume (V_s) and radius (r) of the pores of the porous glass obtained from it by leaching at 50° in 3 N HCl

	580°	580°	580°	580°	580°	580°	590°	590°	600°	600°	620°
Time, h	0	1	5	48	120	480	48	240	120	264	48
V_s, cm^3/g	0.160	0.171	0.180	0.213	0.244	0.291	0.180	0.177	0.174	0.162	0.176
r, Å	~ 8	15	34	39	170	200	19	20	24	18	15

According to our ideas, at this temperature a continuous silica framework, not destroyed by acid, begins to be built up in the borosodium regions (ˆ7).

The value of the pore radius of porous glass decreases with increasing temperature of heat treatment of the initial glass in the region above 585°.

Fig. 3. Dependence of the magnitude of the unit volume $\frac{1}{N}$ on the time of heat treatment $t\left(\frac{1}{N}=\frac{1}{N_0}+kt\right)$.
a –initial 530°, b –quenched 530°, v –quenched 510°, g –quenched 485°.

Opalescence of the glass at temperatures below 730° increases continuously as the duration of heat treatment increases, and no visible jump in the rate of its increase in the region of 585° is observed.

The growth of the pore radius with relative constancy of their total volume means that the total number of pores in the porous glass and, consequently, the regions of chemical inhomogeneity in the initial glass, decreases during its heat treatment. A decrease in the total number of particles while their average size increases is a sign of the processes of isothermal distillation and recondensation. Assuming that the processes occurring in the glass under study are a consequence of the system' s tendency toward separation, we consider the above analogy appropriate. As O. M. Todes (^12) showed, the kinetics of recondensation processes is described by equation (1), formally analogous to Smoluchowski' s equation for the coagulation of colloidal particles, but differing from it in the value of the rate constant.

$$\frac{1}{N} = \frac{1}{N_0} + k \cdot t. \tag{1}$$

Here N is the number of particles per unit volume of the system at time t, N_0 is the number of particles per unit volume at the initial time, and k is the rate constant of the process.

Formula (1) is statistical in character and is rigorous only after a certain interval of time has elapsed, during which the system reaches a stationary form of distribution. This period is the shorter, the higher the temperature.

Assuming the pore shape to be close to spherical, the number of pores (and consequently also the number of leached regions of chemical inhomogeneity) in 1 cm^3

we calculated for porous glass by the formula:

$$N = \frac{v_s}{\frac{4}{3}\pi r^3} \cdot \frac{1}{\frac{1}{\Delta} + v_s}, \tag{2}$$

where v_s is the total volume, r is the pore radius of the porous glass under study, and $\Delta = 2.18$ cm^3/g is the specific gravity of the "sintered" porous glass (quartz glass).

The results of the calculations are presented in Fig. 3 in the coordinates $\frac{1}{N} - t$, where N is the value per unit volume.

As can be seen from Fig. 3, the kinetics of the coarsening process of the acid-leachable regions of chemical heterogeneity is described quite satisfactorily by equation (1) of O. M. Todes.

Table 2 gives the values of the rate constant of recondensation at different temperatures, determined from the tangent of the angle of inclination of the straight lines $\frac{1}{N}(t)$.

Table 2

Glass	t, °C	k, $\mathrm{cm}^3/\mathrm{h} \cdot 10^{22}$
A	485	0.0965
A	510	0.27
A	530	2.04
B	485	0.0667
B	530	1.99

The mean value of the apparent activation energy of the recondensation process in glass Na-7/23 proves to be equal to 90 kcal/mol, which apparently indicates a connection with processes of viscous flow in the glass ([13]).

Elucidation of the nature and kinetics of the processes occurring in sodium borosilicate glass during its heat treatment makes it possible to obtain porous glasses with a desired structure in a controlled manner, including bidisperse and wide-pore glasses (with radii on the order of hundreds to thousands of Å).

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REFERENCES CITED

1. I. V. Grebenshchikov, T. A. Favorskaya, Tr. GOI, **7**, No. 72 (1931).
2. I. V. Grebenshchikov, Mat. soveshch. po stekloobraznomu sostoyaniyu, L., 1939.
3. I. V. Grebenshchikov, O. S. Molchanova, ZhOKh, **12**, 588 (1942).
4. O. S. Molchanova, Dissertation, L., 1943.
5. L. A. Kachur, Dissertation, L., 1946.
6. S. P. Zhdanov, Dissertation, L., 1949.
7. D. P. Dobychin, *The Structure of Glass*, Tr. soveshch. po stroeniyu stekla, 1953, Izd. AN SSSR, 1955, p. 176.
8. S. P. Zhdanov, *The Structure of Glass*, Tr. soveshch. po stroeniyu stekla, 1953, Izd. AN SSSR, 1955, p. 162.

9. E. A. Porai-Koshits, S. P. Zhdanov, D. I. Levin, Izv. AN SSSR, OKhN, 1955, No. 3, 395.

10. E. A. Porai-Koshits, D. I. Levin, N. S. Andreev, Izv. AN SSSR, OKhN, 1956, No. 3, 287.

11. D. I. Levin, S. P. Zhdanov, E. A. Porai-Koshits, Izv. AN SSSR, OKhN, 1955, No. 1, 31.

12. O. M. Todes, Dissertation, M., 1944; *Problems of Kinetics and Catalysis*, **7**, 137 (1949); Kolloid. zhurn., **15**, 391 (1953).

13. V. A. Florinskaya, Tr. GOI, **19**, No. 131 (1950).

Note: Figure translations are in progress. See original paper for figures.