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High-Pressure Effects on Oxide Glasses: II, Subsequent Heat Treatment

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The annealing or volume variation with time of both silica and boron oxide glasses densified in the rigid state was studied. Appreciable annealing of silica glass was observed at temperatures as low as 200°C and of boron oxide glass at even room temperature. This anomalous volume flow depended on temperature, time, and specific volume and was characterized by small apparent relaxation times and activation energies. The differences between this type of volume relaxation and other properties such as delayed elasticity, cold flow, and stabilization are discussed. Devitrification to α-cristobalite observed at temperatures as low as 500°C is attributed to the presence of shear stresses.

I. Introduction

In Part I of this series,[1] it was shown that at constant temperature and pressure, simple oxide glasses such as SiO_2, B_2O_3, and GeO_2 can be densified in the rigid state to a varying degree, depending on the externally applied shear. A simple model involving molecular entanglement of adjacent parts of the random M–O network was postulated to account for such densification in the rigid state. Such entanglement will occur more readily when the network is sufficiently compressed and thus densification will be possible at high pressures even when the applied pressure is hydrostatic. It was suggested that the increase of densification with increasing temperature was primarily related to the vibrational motions of the atoms comprising the network and only to a minor extent were the usual flow mechanisms such as in diffusion or viscous transport involved. Because of experimental difficulties, an accurate study of the kinetics of densification was not possible. The reverse phenomenon, that of volume increase at atmospheric pressure, and some constant temperature, or annealing, is more amenable to accurate experimental measurements and should furnish important information on the densification process. In this communication the writer describes such heat treatment at atmospheric pressure of silica glass densified in the *rigid state* under varying conditions of shear. A limited number of experiments were also carried out on densified B_2O_3 glass. The annealing of oxide glasses densified in the nonrigid state is described in Part III of this series.[2]

II. Experimental

Silica glass disks approximately $^1/_2$ mm thick and 2 mm in diameter densified in the rigid state by the technique described in Part I were wrapped tightly in thin platinum foil and placed inside an electric furnace in contact with a Pt10Rh thermocouple. After atmospheric annealing at intervals ranging from 15 minutes to several days, the specimens were withdrawn, air-quenched, and placed in density columns. Periodic microscopic and X-ray examinations were carried out to ensure the absence of devitrification during the annealing. After each density determination, the specimens were washed in benzene and acetone before replacement in the annealing furnace. Since the time for the small specimens to reach the annealing temperature was less than 1 minute, and the shortest test period was 15 minutes (but the test periods generally were much longer), the heating time less the time for quenching was considered to be negligible. Annealing was studied at 100° intervals from 200° to 1000°C for specimens having $\Delta\rho/\rho$ values of from 2 to 18%, where $\Delta\rho$ is the density increase over the density ρ of uncompressed vitreous silica (2.207). The infrared absorption of partly annealed densified silica glasses was compared with that of the unannealed materials using the KBr disk technique and a Beckman IR–7 spectrophotometer.

The annealing of boron trioxide glasses was examined only at 25°C. The densified specimens having $\Delta\rho/\rho$ values of 5

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[1] J. D. Mackenzie, "High-Pressure Effects on Oxide Glasses: I, Densification in Rigid State"; pp. 461–70, this issue.

[2] J. D. Mackenzie, "High-Pressure Effects on Oxide Glasses: III, Densification in Nonrigid State"; to be published in the *Journal of the American Ceramic Society.*

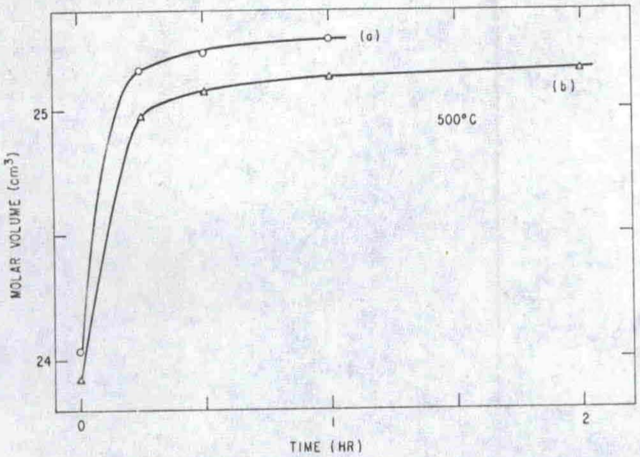

Fig. 1. Annealing behavior of silica glass densified in different cells. (*a*) Densification in Al_2O_3 cell at 70 kb and 500°C for 2 minutes and (*b*) densification in AgCl cell at 80 kb and 400°C for 2 minutes.

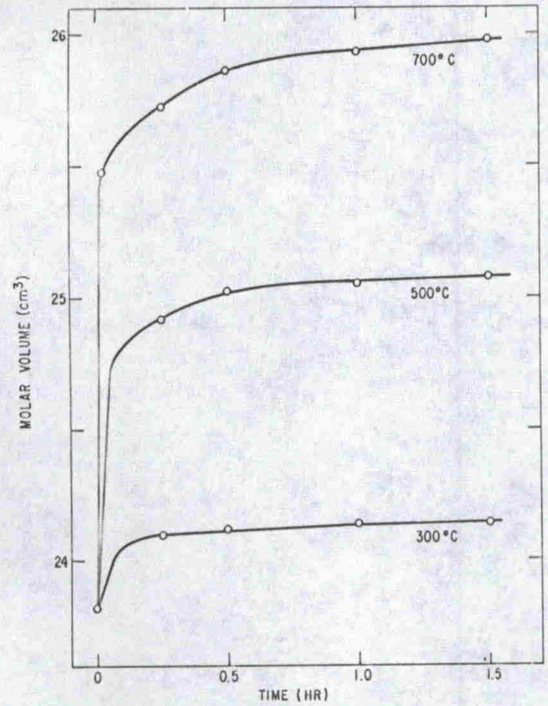

Fig. 2. Annealing of densified silica glass of $V_0 = 23.83$ cm³ at 300°, 500°, and 700°C.

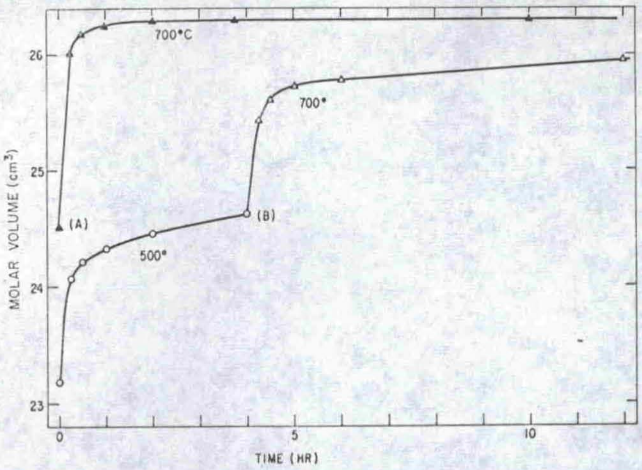

Fig. 3. Annealing of two specimens of densified silica glass. Effect of thermal history on initial annealing behavior is shown by (*A*) and (*B*)

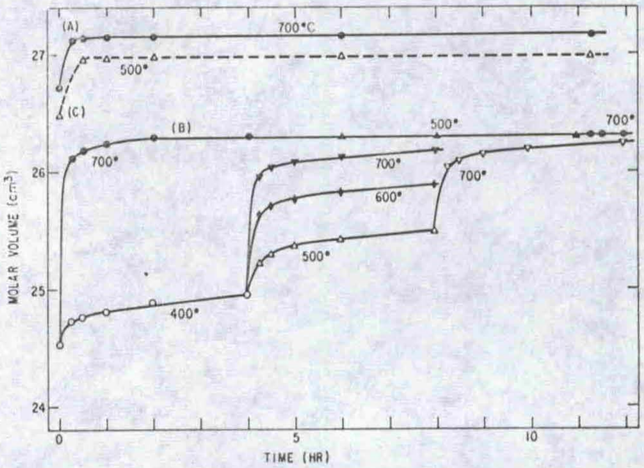

Fig. 4. Annealing of densified silica glasses of different V_0 and thermal history at 400° to 700°C.

to 6% and stored in liquid nitrogen were dropped into the CCl_4-$CHBr_3$ density column kept at 25°C in a water bath. The decrease of density with time was easily followed by observing the variation of the vertical position of the specimen with a cathetometer.

III. Results

(1) *Annealing of Silica Glass*

Annealing, i.e., change of density with time, was observed to take place at all temperatures from 200° to 1000°C, for all specimens having $\Delta\rho/\rho$ values ranging from 2 to 18%. The annealing rates depended on temperature and starting density and only to a relatively minor extent on the preparation history of the specimens. Some typical volume/time curves are shown in Figs. 1 through 4. The results are expressed as molar volumes calculated from the ratio $60.09/\rho$, where ρ is the density of the densified glass. The molar volume of uncompressed vitreous silica (V_∞) was 27.227 cm³. Heating at various temperatures up to 900°C for 4 hours and then quenching in air was found to result in no change in this value. Some results for the relatively slower annealing at 200° and 300°C are shown in Table I.

Table I. Annealing of Densified Silica Glass*

	Temp. (°C)	Time (hr)	Molar volume (cm³)
(*a*)	200	0	24.718
		0.25	24.728
		91	24.769
(*b*)	300	0	23.112
		0.25	23.282
		1.0	23.291
		27	23.327
		309	23.509
(*c*)	700	0	24.627
		0.25	25.890
		0.50	25.968
		1.0	26.036
		2.0	26.126
		4.0	26.183
(*d*)	700	0	24.627
		0.25	25.890
		0.50	25.979
		1.0	26.036
		2.0	26.137
		4.0	26.160

* Results of (*a*), (*b*), and (*c*) were obtained on one specimen at each of the temperatures shown whereas results of (*d*) were obtained on five separate specimens.

The identical behavior of specimens prepared in alumina and in silver chloride cells (preparation described in Part I) is shown in Fig. 1. Specimen (*a*) was prepared by compression in an alumina cell at 70 kb and 500°C for 2 minutes, whereas specimen (*b*) was densified in a silver chloride cell at 80 kb and 400°C for 2 minutes. In another check on the effect of preparation history, a specimen which had been compressed first at 60 kb and 400°C for 10 minutes and then at 20 kb and 500°C for 30 minutes was compared with another specimen densified at 80 kb and 300°C for 2 minutes. The initial molar volumes (V_0) of both specimens were 25.636 cm^3.. After a 15-minute annealing at 700°C, the respective volume increases were 0.844 and 1.071 cm^3.

Because of the limited availability of densified specimens, annealing at any temperature was carried out on one specimen only; i.e., the specimen had to undergo a number of cycling treatments of alternate heating and quenching at various intervals. It was found that this did not have an appreciable effect on the annealing rate. In Table I (*c*) the results for a single "cycled" specimen at 700°C are compared with those for five separate specimens, (*d*), heated for different intervals. The data are seen to be identical.

All the molar volumes reported here were measured at room temperature. A knowledge of the coefficient of expansion of the partly annealed glasses was thus necessary. Specimens of densified glass were annealed at 700°C until the change in rate with time had become negligibly small. The specimens were then quenched from different temperatures from 300° to 700°C. Identical densities were observed over this wide temperature range of quenching. It thus appeared that the coefficient of thermal expansion of the densified glasses was similar to that of uncompressed vitreous silica and can be neglected for the present purpose.

Some linear plots of molar volume versus time are shown in Figs. 1 through 4. The annealing behavior was highly complex and cannot be described by any of the presently known empirical relations. Some significant features revealed in these figures are as follows: (*a*) There was a very rapid initial annealing within the first few minutes, the magnitude of which increased with increasing temperature (Fig. 2). The annealing rate then decreased with time and the molar volume of the glass appeared to approach the molar volume of uncompressed vitreous silica ($V_\infty = 27.227$ cm^3) asymptotically. (*b*) At the same temperature, the *initial* annealing behavior of an unannealed specimen and that of a partly annealed one were dissimilar although their molar volumes may have been equal. This is evident from (*A*) and (*B*) in Fig. 3. (*c*) The *initial* annealing rate of a fresh specimen, for instance (*A*) in Fig. 4, was much greater than the subsequent rate (after, e.g., 1 hour) of another specimen (Fig. 4(*B*)) of *smaller* molar volume. Further, specimen (*C*) in Fig. 4, having a molar volume of 26.48 cm^3, showed a rapid initial volume relaxation at only 500°C whereas specimen (*B*), when the molar volume reached 26.30 cm^3, gave a much slower rate at 700°C. This of course was true only for a comparison of the initial short-time behavior of (*C*) with that of the later-stage behavior of (*B*). (*d*) For the same annealing temperature, the magnitude of the volume change in the first few minutes was larger when V_0 was smaller. This is exemplified by a comparison of (*A*) and (*B*) in Fig. 4 for 700°C and Figs. 3(*B*) and 4(*C*) for 500°C.

Over a relatively short interval of annealing treatment from 15 minutes to approximately 4 hours, the molar volume at any time *t* apparently was given by the relation

$$V_t = a + b \log t \qquad (1)$$

where *a* and *b* are constants dependent on both V_0 and temperature (Fig. 5). For any V_0, *a* was markedly dependent on temperature, whereas the variation of *b* was negligible. For a given annealing temperature, *b* appeared to decrease with increasing V_0. In Figs. 6 and 7, it is seen that equation (1) was no longer valid for experiments of duration up to 500 hours. Up to 100 hours, however, the results of most of the present study were still describable by equation (1). A strictly empirical analysis of the presently available data showed that for times from 15 minutes to 100 hours, V_t was described approximately by the relation

$$V_t = V_1 + 10^{-2}e^{0.003T}(V_\infty - V_1) \log t \qquad (2)$$

where *t* is the duration of annealing in hours, *T* is the absolute

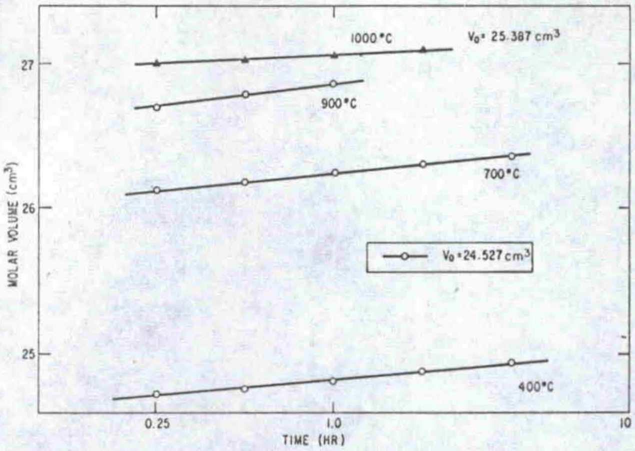

Fig. 5. Apparent linear relation between molar volume and log time in the short-time annealing of densified silica glasses.

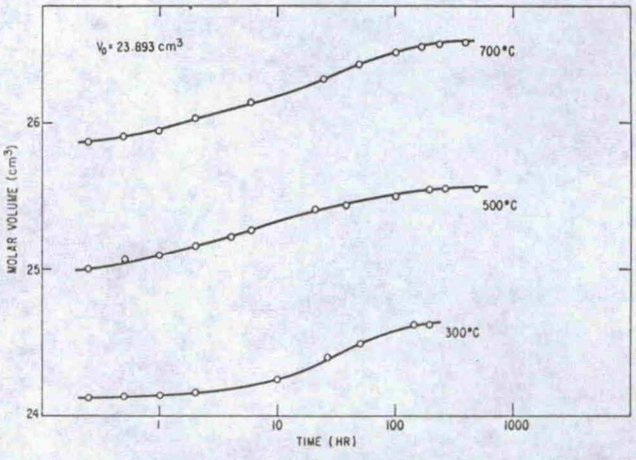

Fig. 6. Long-time annealing of densified silica glass of $V_0 = 23.893$ cm^3, illustrating the nonlinearity of volume/log time relation.

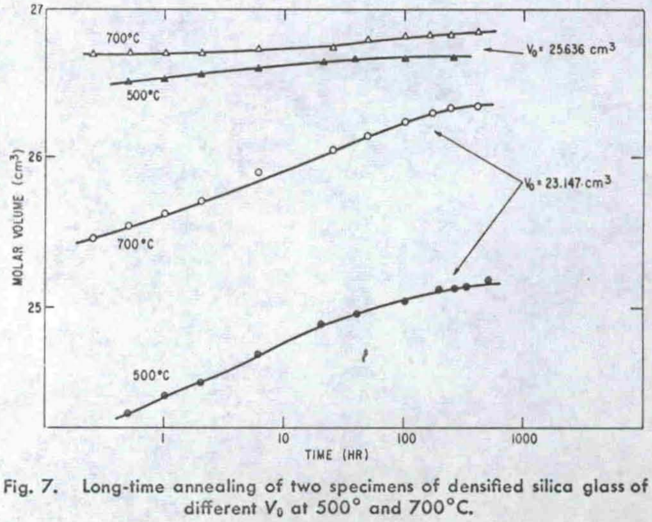

Fig. 7. Long-time annealing of two specimens of densified silica glass of different V_0 at 500° and 700°C.

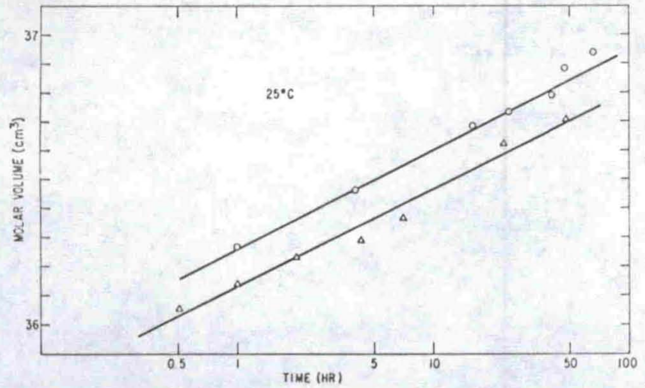

Fig. 8. Annealing of densified boron oxide glass at room temperature

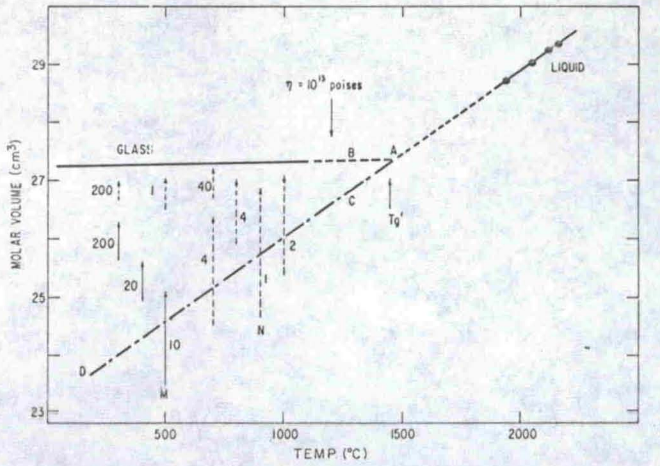

Fig. 9. Volume-temperature relation for silica together with presently observed volume changes during annealing (*arrows*). (Data for liquid obtained from J. F. Bacon, A. A. Hasapis, and J. W. Wholley, Jr., "Viscosity and Density of Molten Silica and High Silica Content Glasses," *Phys.* Chem. *Glasses*, **1** [3] 90–98 (1960); *Ceram. Abstr.*, **1961**, May, p. 115*c*.) Detailed explanation of this figure is in text.

temperature, and V_1, the molar volume after an annealing of 1 hour at temperature T, is given approximately by

$$V_1 = V_\infty - \left[\frac{1.0053}{1 + 5.3 \times 10^{-3}e^{0.006T}}(V_\infty - V_0)\right] \qquad (3)$$

(2) Devitrification of Partly Annealed Silica Glass at Low Temperatures

After prolonged annealing at relatively low temperatures, some of the specimens assumed a cloudy appearance. The presence of α-cristobalite principally on the surface was detected by X-ray analysis. Thus, at 500°C, for instance, after an annealing of about 400 hours, α-cristobalite was detected when the molar volume of the specimen had increased from 23.839 to 25.559 cm³. Another specimen, after a similar annealing period at 700°C, showed the presence of α-cristobalite when the molar volume had increased from 26.719 to 27.153 cm³. In one experiment at 500°C, for a specimen with V_0 = 26.495 cm³, α-cristobalite was found after only 10 hours. The molar volume of α-cristobalite is 25.845 cm³. In the foregoing examples, devitrification was observed when V_t was greater or less than 25.845 cm³. No other crystalline phases of silica were found in the specimens examined.

(3) Infrared Absorption of Partly Annealed Silica Glass

Five specimens with V_0 ranging from 23.409 to 23.482 cm³ were annealed for periods of from 15 minutes to 10 hours at 500°C to yield V_t of 24.547 to 25.069 cm³. The infrared absorption from 2 to 34μ was examined. No variation in the spectra was observed. The results were identical to those shown in Figs. 7 and 8 of Part I of this series.

(4) Annealing of Boron Oxide Glass

The limited results on boron oxide glass at 25°C are shown in Fig. 8. Since the densification was carried out at 25° and 75°C, and annealing at atmospheric pressure occurred at 25°C, the values of V_0 are uncertain. The annealing was again described by equation (1) as for vitreous silica.

IV. Discussion

(1) Previous Work on Silica Glass

For silica glass densified in the rigid state, Bridgman and Simon[3] found that when a specimen of $\Delta\rho/\rho$ = 17.5% was heated at 430°C for 1 hour, $\Delta\rho/\rho$ became 7.9%. On the other hand, Cohen and Roy[4] reported that when a sample of $\Delta\rho/\rho = 4\%$ (calculated by the present writer from the reported refractive index of 1.475) was heated at 600°C for a week, no annealing was observed. The present results are in agreement with the single observation of Bridgman and Simon.[3] The apparent absence of annealing observed by Cohen and Roy possibly was due to the thermal history of the sample in question. According to these workers,[5] the experimental procedure adopted in the densification was to release the pressure first before the temperature was lowered. Thus the sample must have remained at an elevated temperature and atmospheric pressure for some finite time. Figure 2 in the present paper shows that large volume relaxation occurred even after only 1 to 2 minutes at 500° or 700°C. The reported refractive index of 1.475 corresponds to a molar volume of 26.183 cm³. In Fig. 4, for instance, the annealing rates at such large molar volumes are seen to be extremely slow after the first 10 or 15 minutes. It is thus likely that the single sample examined by Cohen and Roy was already partly annealed and had a specific volume corresponding to the later stage of annealing as shown in Fig. 3(*A*) or in Fig. 4(*C*).

(2) Anomalous Volume Flow at Low Temperatures

In Figs. 1 through 4 and in Table I, it is shown that silica glass densified in the *rigid* state can undergo rapid and large volume flow at temperatures far below the softening temperature, i.e., again in the *rigid* state. It is well-known that both oxide glasses and organic polymers will exhibit volume flow near the glass transition temperature. Thus, if Fig. 9 represents the volume/temperature relation of any glass-forming system and T_g' the apparent glass transition temperature, a specimen kept at a temperature somewhere along AB will undergo volume shrinkage with time and approach an equilibrium volume along AC.[6] Alternately, a specimen heated rapidly from some lower temperature to a higher temperature near T_g' may have an initial volume somewhat below AC. A positive volume flow toward AC will then occur until equilibrium is attained. These rates of approach

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[3] P. W. Bridgman and I. Simon, "Effect of Very High Pressures on Glass," *J. Appl. Phys.*, **24** [4] 405–13 (1953); *Ceram. Abstr.*, **1953**, September, p. 168*g*.

[4] H. M. Cohen and Rustum Roy, "Effects of Ultrahigh Pressures on Glass," *J. Am. Ceram. Soc.*, **44** [10] 523–24 (1961).

[5] H. M. Cohen and Rustum Roy, "Effects of Ultrahigh Pressure on Glass," Symposium on Physics and Chemistry of High Pressure. The Society of Chemical Industry, London, June 27–29, 1962; preprint, pp. 31–37.

[6] See, for example, J. D. Mackenzie, "General Aspects of the Vitreous State"; Chapter 1 in Modern Aspects of the Vitreous State, Vol. I. Edited by J. D. Mackenzie. Butterworth, Inc., Washington, D. C., 1960. 226 pp.; *Ceram. Abstr.*, **1961**, August, p. 201*f*.

Table II. Comparison of $t_{1/2}$, the Observed Times in Which (V_∞ − V_0) Decreased by 50%, and τ_v, the Calculated Relaxation Times for Volume Viscosity, Assuming that E^*_v = 150 Kcal per Mole

V_0 (cm³)	Temp. (°C)	$t_{1/2}$ (minutes)	τv (minutes)
24.634	900	$<10^{-2}$	10^6
24.318	800	$<10^{-1}$	10^8
25.922	800	$<10^{-2}$	10^8
24.527	700	$<10^{-2}$	10^{11}
25.636	700	$<10^{-2}$	10^{11}
25.601	600	20	10^{15}
26.495	500	<1	10^{20}

to equilibrium at any temperature not far removed from T_g' may be represented by an equation of the type

$$\frac{1}{V}\frac{dV}{dt} = \pm \frac{F}{\eta_v} \tag{4}$$

where η_v is a volume viscosity and F is some driving force for the process. F has been discussed in the form of $(T-T)$, where T is the so-called "fictive" temperature, by Tool[7] or $(n_t - n_e)$, where n_t and n_e refer to the refractive indices at time t and at equilibrium respectively, by Collyer.[8]

It is evident from the volume/temperature relation for silica in Fig. 9 that the present annealing kinetics are not governed by the same driving force nor the same volume viscosity of equation (4). The arrows in Fig. 9 represent the magnitude of the volume change at that particular temperature in the time shown. The solid arrows indicate that the temperature of annealing was similar to the temperature at which the specimen was densified. The dashed arrows represent annealing temperatures which were higher or lower than the temperature of densification. Thus specimen M, for instance, was densified at 500°C to a specific volume of 23.5 cm³. After annealing at atmospheric pressure at 500°C for 10 hours, the specific volume had become 25.1 cm³. Specimen N, on the other hand, was compressed at 400°C to give a V_0 value of 24.6 cm³. Its specific volume became 26.9 cm³ after an annealing of 1 hour at 900°C. Thus, irrespective of V_0, annealing temperature, or preparation history, all the specific volumes of the densified specimens tended to approach that of the uncompressed silica glass with time rather than that along *AD*.

No measurement of η_v for fused silica is available. It is known, however, that for many other glass-forming systems, the magnitudes of η_v and η_s are similar, η_s being the shear viscosity. The ratio η_v/η_s is not highly sensitive to temperature. The corresponding relaxation times, τ_v and τ_s, and activation energies, E^*_v and E^*_s, and their temperature dependencies apparently are also similar.[9,10] Now

$$\tau_s \approx \eta_s/G \tag{5}$$

where G is the modulus of rigidity. Since $G \approx 10^{11}$ cgs units and η_s is approximately 10^{13} poises at T_g, $\tau_s \approx 100$ seconds. The shear viscosity of fused silica is 10^{13} poises at approximately 1200°C and E^*_s is 170 to 180 kcal per mole.[11] It is assumed that $\tau_s \approx \tau_v$ and $E^*_s \approx E^*_v$ and therefore $\tau_v \approx 1$ minute at 1200°C. The values of τ_v at lower temperatures can thus be estimated from

$$\tau_v = \tau_0 \exp\,(E^*_v/RT) \tag{6}$$

It is unlikely that the value of 180 kcal per mole for E^*_s will decrease with decreasing temperature, especially for the densified glasses since V_0 is much less than V_∞. Nevertheless, a conservative value of 150 kcal per mole was used to obtain the values of τ_v in Table II. Higher values obviously are obtained if E^*_v is assumed to be 180 kcal per mole. Since the annealing behavior of the densified glasses was extremely complex, it is difficult to define unambiguously a single relaxation time for comparison with τ_v. The observed times in which $(V_\infty - V_0)$ had decreased by 50%, $t_{1/2}$, were arbitrarily chosen for this purpose and are listed in Table II. It is evident that τ_v and $t_{1/2}$ correspond to totally different volume flow mechanisms.

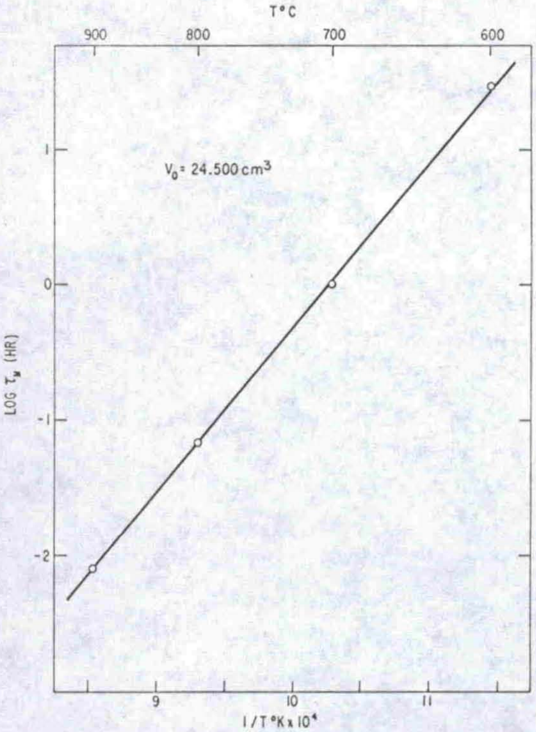

Fig. 10. Relation between apparent Maxwell relaxation time, τ_M, and $1/T$ for densified silica glass of V_0 = 24.500 cm³.

An alternative consideration is τ_M, the Maxwell relaxation time, defined as the time in which the stresses have decreased to $1/e$ of their original value. In Fig. 10, log τ_M for a specimen of V_0 = 24.500 cm³ is shown as a function of $1/T$ for the temperature range 600° to 900°C. From the slope, an apparent energy of activation for this process, E^*_a, of 55 kcal per mole is evaluated. This is to be compared with the value of 180 kcal per mole for E^*_s. The values of τ_M are of course also many orders of magnitude smaller than τ_v of Table II. It must be stressed that the presently observed annealing kinetics are not Maxwellian in nature. The use of τ_M is purely an arbitrary means for purpose of comparison.

(3) Comparison with Other Known Flow Processes Under Stress

Since shear plays an important role in the densification of oxide glasses in the rigid state (see Part I of this series), the subsequent annealing process might be regarded as the release of "frozen-in" internal stresses. A comparison of other

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[7] A. Q. Tool, "Relation Between Inelastic Deformability and Thermal Expansion of Glass in Its Annealing Range," *J. Am. Ceram. Soc.*, 29 [9] 240–53 (1946).

[8] P. W. Collyer, "Study of Time and Temperature Effects on Glass in Annealing Range," *J. Am. Ceram. Soc.*, **30** [11] 338–44 (1947).

[9] R. O. Davies and G. O. Jones, "Irreversible Approach to Equilibrium in Glasses," *Proc. Roy. Soc.* (*London*), **A217**, 26–42 (1953).

[10] Nishio Hirai and Henry Eyring, "Bulk Viscosity of Liquids," *J. Appl. Phys.*, 29 [5] 810–16 (1958).

[11] J. D. Mackenzie, "Viscosity-Temperature Relation for Network Liquids," *J. Am. Ceram. Soc.*, 44 [12] 598–601 (1961).

properties such as delayed elasticity is thus desirable. Under a constant applied stress, the development of strain is given by[11]

$$\text{Strain} = \alpha + \beta t + \gamma f(t) \tag{7}$$

where α is the instantaneous strain, βt is the irrecoverable viscous flow in time t, and γ is the so-called delayed elasticity. On removal of the applied stress, α is instantly and totally recovered and the fraction N of the total delayed elasticity which has developed at the time of the removal of the stress is also recovered according to the same decay function of time, $f(t)$. Delayed elasticity has been observed in vitreous silica at 25°C and that $f(t)$ is of the form $\log t$.[13] Although there appears to be an apparent similarity between this and the presently observed annealing given by equation (1), it is unlikely that the two processes are identical. The ratio γ/α, for instance, is only 0.001 for silica glass at room temperature. For other oxide glasses also, $\gamma/\alpha < 0.03$ at $T < (T_g - 300°)$. The ratio of the volume shrinkage due to densification for silica glass to the compressibility at room temperature, however, is as much as 0.5 (see Part I).

Another process which would appear to be related to the present annealing is that of the "cold flow" of organic polymers at temperatures much below T_g.[14] There are, however, at least two distinct observable differences. First, no substantial density variation is encountered in cold flow. Second, recovery occurs only when the cold-drawn polymer is annealed at temperatures near T_g. The two processes are therefore considered to be dissimilar.

The compression and subsequent annealing of a borosilicate glass was studied by Anderson.[15] The largest $\Delta\rho/\rho$ values were about 0.2% whereas the minimum $\Delta\rho/\rho$ values of the present work were 2.0% and the maximum close to 20%. The annealing of the borosilicate glass is satisfactorily described by $\Delta\rho/\rho = c\ [1 - \exp(-t/\tau)]$. Present observed data for both SiO_2 and B_2O_3 glasses are not compatible with such a relation. The presence of metal ions in the borosilicate glass must give rise to further differences in the annealing behavior.

(4) Annealing of Boron Oxide Glass

Bridgman and Simon[3] first observed that the density of boron oxide glass densified in the rigid state decreased with time at 25°C. After about 50 days, a specimen showed a decrease of $\Delta\rho/\rho$ from 3.4 to 2.2%. Heating at 100°C resulted in a further decrease to 1.5% within a day. From the very limited experimental data, the activation energy for the annealing between 25° and 100°C was evaluated by Bridgman and Simon from

$$E = k(1/T_1 - 1/T_2)^{-1} \log (r_2/r_1) \tag{8}$$

where r is the initial rate of density decrease obtained approximately from tangents drawn to the annealing/time curves. A surprisingly low value of 1.3 kcal per mole was obtained for E. Although, as Bridgman and Simon remarked, this was only a crudes etimate, the magnitude of E did illustrate the uncommon nature of the annealing process. When a similar method was used in the present study for vitreous silica with $\Delta\rho/\rho$ from 2 to 18%, the plots of $d(\log r)/d(1/T)$ for the first 15 minutes of annealing over any 200° temperature intervals between 300° and 900°C were not linear. The best straight lines, however, also yielded abnormally low values of E of from 1 to 10 kcal per mole.

Table III. Comparison of Apparent Rate Constant b of Equation (1) for B_2O_3 and SiO_2 Glasses at Approximately Equivalent Volumes and Temperatures

	B_2O_3		SiO_2	
	(1)	(2)	(1)	(2)
Annealing temp. (°K)	298	298	773	973
T/T_g	0.59	0.59	0.53	0.66
$(V_\infty - V_1)$	1.790	1.915	2.127	1.627
b	0.34	0.34	0.20	0.30

From Fig. 8, assuming equation (1) to be valid, the apparent "rate constant" b for the two specimens of B_2O_3 glass is 0.34. In Table III, the values of b for two specimens of SiO_2 glass with the nearest available $(V_\infty - V_1)$ values and equivalent temperatures defined by T/T_g are seen to be 0.20 and 0.30. The approximate equality of b of equation (1) and E of equation (8) for B_2O_3 and SiO_2 glasses is indicative of the similarity of the annealing process of these materials.

(5) Tentative Model

It has been suggested that when oxide glasses with random *network* structures such as GeO_2, B_2O_3, and SiO_2 are highly compressed, entanglement of parts of the network may occur (see Part I of this series). When the pressure is removed, total elastic recovery is no longer possible, especially when shear stresses have been applied. The presently observed (*a*) large volume flow at temperatures as low as 200°C for silica glass and 25°C for boron oxide glass, (*b*) magnitudes of the apparent relaxation times and activation energies, and (*c*) tendency for the specific volume of all the compressed glasses to reapproach that of the uncompressed material (Fig. 9), are all in support of the molecular entanglement model. It has been demonstrated in Sections (2) and (3)

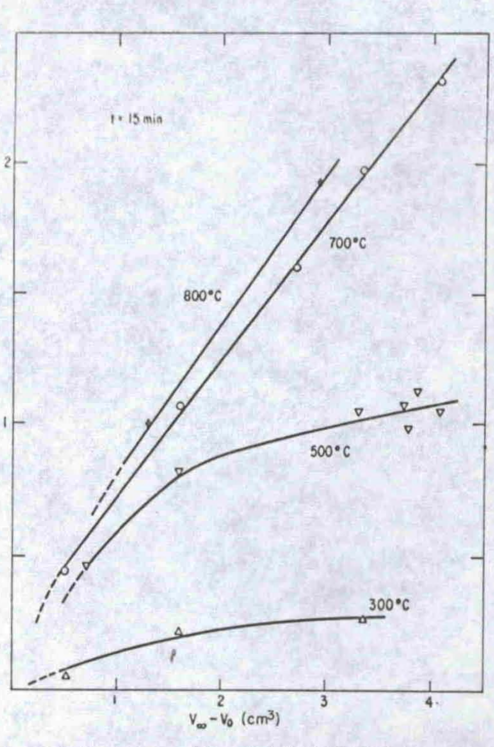

Fig. 11. Relation between $(V_t - V_0)$ for initial 15 minutes of annealing and the driving force $(V_\infty - V_0)$ for densified silica glass.

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[12] G. O. Jones, "Viscosity and Related Properties in Glass," *Rept. Progr. Phys.*, **12**, 133–62 (1948–49) (published 1949).

[13] J. B. Murgatroyd and R. F. R. Sykes, "Delayed Elastic Effect in Silicate Glasses at Room Temperature," *J. Soc. Glass Technol.*, **31** [141] 17–35T (1947); *Ceram. Abstr.*, **1948**, February, p. 31*e*.

[14] See, for example, A. Staverman and F. Schwarzl, "Cold-Drawing of Polymers"; pp. 158–64 in Die Physik der Hochpolymeren; Bd. IV, Theorie und molekulare Deutung technologischer Eigenschaften von hochpolymeren Werkstoffen. Edited by H. A. Stuart. Lange & Springer, Berlin, 1956. 696 pp.

[15] O. L. Anderson, "Effect of Pressure on Glass Structure," *J. Appl. Phys.*, **27** [8] 943–49 (1956); *Ceram. Abstr.*, **1957**, January, p. 6*c*.

in the foregoing that the present annealing process is not equivalent to that encountered in delayed elasticity, annealing near T_g, and cold-drawing of polymers.

According to equations (2) and (3),

$$\frac{dV}{dt} = \frac{B(V_\infty - V_t)}{t(1 - A \log t)} \tag{9}$$

$$= \frac{B(V_\infty - V_0)}{tC} \tag{10}$$

where $A = (10^{-2}\, e^{0.003T})$, $B = A/2.303$, and $C = 1.0053/1 + 5.3 \times 10^{-3}\, e^{0.006T}$. These empirical constants were evaluated only in an approximate manner. Both $(V_\infty - V_t)$ and $(V_\infty - V_0)$ may be regarded as a driving force for the volumetric approach to equilibrium. In Fig. 11, a plot of $(V_t - V_0)$ is shown versus $(V_\infty - V_0)$ for the initial 15 minutes of annealing for densified silica glass. $(V_\infty - V_0)$ is approximately equal to $(V_\infty - V_t)$ in this interval of time. The nonlinearity of the 500° and 300°C plots is indicative of the inadequacy of equations (2) and (3). At any temperature, however, the increase of volume flow with the increasing driving force $(V_\infty - V_0)$ is clearly established.

(6) Devitrification of Silica Glass at Low Temperatures

The growth of α-cristobalite in silica glass at temperatures as low as 500°C has not been previously reported. Even assuming that a barrier to nucleation is absent, the formation of discernible amounts of α-cristobalite at 500°C is not explicable by simple crystal-growth phenomena. The growth rate in the absence of catalyzing agents is given by[16]

$$u = [\Delta H(T_m - T)/3\pi a^2 \eta_s T_m] \tag{11}$$

where ΔH is the heat of fusion, T_m is the melting temperature, and a is a "jump" distance. The calculated growth rate of α-cristobalite in vitreous silica at 1400°C is approximately 10μ in 10 hours. In the presence of catalyzing impurities, the observed growth rates may be larger by a factor of 2000.[16] Since the shear viscosity, η_s, is exponentially dependent on temperature, the growth rate must also decrease accordingly when the temperature is lowered. If a conservative value of 150 kcal per mole is adopted for the activation energy for viscous flow, the calculated growth rate at 500°C, inclusive of an enhancing factor of 2000, is only 2×10^{-14} A in 10 hours. Since sufficient α-cristobalite was actually formed in this time to be discernible by eye and identifiable by X-ray analysis, the observed devitrification cannot be the result of impurity-catalyzed growth alone. It is likely that the shear stresses present in the network constitute an important factor in this anomalous crystallization at low temperatures.

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[16] N. G. Ainslie, C. R. Morelock, and D. Turnbull, "Devitrification Kinetics of Fused Silica"; pp. 97–107 in Symposium on Nucleation and Crystallization in Glasses and Melts. Edited by M. K. Reser, Geraldine Smith, and Herbert Insley. The American Ceramic Society, Inc., Columbus, Ohio, 1962. 123 pp.