

## STUDIES ON GLASS. VIII

### THE COEFFICIENT OF THERMAL EXPANSION OF BORON TRIOXIDE

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For these studies on glass, which are now being carried on at Stanford University, boron trioxide was selected a few years ago as a typical inorganic, glass-forming material. The results of an extensive study of its heat capacity have been presented in an earlier paper by Thomas and Parks (4). With increasing temperatures, the specific heat at constant pressure was found to undergo an increase of more than 60 per cent between 215° and 270°C. Below this transition region the boron trioxide was a hard glass with a mean atomic heat of 3 to 4 calories, depending upon the temperature and the previous heat treatment of the material; above the transition it was an extremely viscous liquid with an atomic heat approximating the Dulong-Petit value.

In view of these interesting results a number of other physicochemical properties of boron trioxide are now being investigated in this laboratory. In the present paper we shall give some of the data which have been obtained in a study of the cubical coefficient of thermal expansion over the temperature range 100° to 320°C.

#### METHOD AND APPARATUS

The samples of boron trioxide used in this investigation were prepared from Merck's c. p. anhydrous B<sub>2</sub>O<sub>3</sub> (impurities guaranteed to be less than 0.01 per cent). This material was always heated in a platinum crucible for one to two hours at a temperature of about 1200°C. in order to drive off the last traces of water and to eliminate gas bubbles. The molten oxide was next poured into a small cylindrical mold, made out of copper foil, and permitted to cool to room temperature in a desiccator containing phosphorus pentoxide. The copper foil was then stripped from the boron trioxide glass and the latter was smoothed down a little in a lathe. These small cylinders usually contained from 5.5 to 7.5 gm. of oxide, equivalent to 3 or 4 cc. in volume.

A simple dilatometer, with mercury as the dilatometric fluid, was em-

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ployed in the determinations of the coefficient of thermal expansion. It was made entirely out of "tool" steel and consisted essentially of a stout cylindrical can of about 2.0 cm. diameter and 6 cc. capacity. A top fitted into this can by means of a tapered, vacuum-tight joint and was held firmly in position by an adjustable nut. A steel capillary tube, welded through the top, projected upward for a distance of 15 cm. and ended in a small horizontal nozzle; it served as a means of ejecting the excess mercury as the dilatometer was heated to successively higher temperatures and the contents of the steel can underwent expansion.

The large, electrically-heated copper block which Thomas and Parks (4) developed for their specific heat measurements was employed in the present investigation as an adjustable thermostat. The can of the dilatometer was placed within the central cavity of this block with the steel capillary passing upwards through a hole so that the exit nozzle was in the outside air. A small glass weighing bottle then served to collect the mercury droplets as they were expelled at this nozzle during the heating of the copper block between successive steps in temperature.

Measurements of the temperatures were made with calibrated thermocouples in conjunction with a White double-combination potentiometer. A chromel-alumel thermocouple, having one junction fastened to the outside wall of the dilatometer can and the other imbedded in the copper block, served to tell when the dilatometer was at the same temperature as its surroundings. A platinum-platinrhodium thermocouple with one junction on the outside of the dilatometer and the other at 0°C. was used for measuring the actual temperatures to 0.01°C.

The procedure in filling the dilatometer for the expansion measurements was extremely simple. A prepared cylinder of the boron trioxide glass was first placed in position in the dilatometer can, the top was fitted on, and the whole instrument was evacuated to 0.01 mm. by a "Cenco-megavac" oil pump. Clean, freshly heated mercury was then caused to flow into the free space of the dilatometer by raising the level of a mercury reservoir which was connected to the side tube of the evacuating and filling system. The dilatometer and contents were next heated under reduced pressure to over 300°C. in order to remove any possible air bubbles within the instrument, and afterwards a small amount of mercury was introduced as the dilatometer was quickly cooled down to room temperature by quenching in a water or alcohol bath.

After such preparations the dilatometer was placed within the copper block and the latter was heated electrically from 100°C. up to about 300° or 325°C. in seven to ten steps. These steps often covered temperature intervals as large as 32°C., where the boron trioxide was either a hard glass or a very viscous liquid and the expansion coefficient was not changing greatly. On the other hand, the temperature steps within the range

210° to 270°C. were usually kept between 15° and 20°C., as here the coefficient was increasing rapidly. Since boron trioxide is a very poor conductor of heat, it was important to allow sufficient time to elapse at each step for complete equalization of temperature within the sample. Accordingly, in some cases the temperature in the copper block was maintained constant for periods as long as two and a half hours.

The calculation of the coefficient of expansion of the boron trioxide from the weights of the mercury ejected between successive temperatures was simple. At an initial temperature,  $T_1$ , the volume of the mercury in the dilatometer plus the volume of the oxide sample was equal to the volume of the dilatometer itself; or in equation form we have

$$\left(\frac{1}{d_1}\right)W_1 + V_{1(\text{oxide})} = V_{1(\text{dilatometer})} \quad (1)$$

where  $d_1$  and  $W_1$  represent, respectively, the density and weight of the mercury in the dilatometer. At a higher temperature,  $T_2$ , we may similarly write

$$\left(\frac{1}{d_2}\right)W_2 + V_{2(\text{oxide})} = V_{2(\text{dilatometer})} \quad (2)$$

The weight of mercury which is ejected from the dilatometer in heating from  $T_1$  to  $T_2$  is, of course,  $W_e = W_1 - W_2$ . By making use of this fact and subtracting the first equation from the second, we then obtain

$$\Delta V_{\text{oxide}} = \Delta V_{\text{dilatometer}} - \left(\frac{1}{d_2} - \frac{1}{d_1}\right)W_1 + \frac{W_e}{d_2} \quad (3)$$

The volume increase of the dilatometer over the temperature ranges of this study was first determined in two independent series of measurements, which were carried out in the absence of a boron trioxide sample. The necessary data for the density of mercury at the various temperatures were taken from the Landolt-Börnstein "Tabellen" (2).

From the values of  $\Delta V_{\text{oxide}}$  (obtained by equation 3) the cubical coefficient of expansion,  $\alpha$ , may be evaluated. By definition

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p$$

However, for the rather small temperature steps employed in the present investigation  $\frac{\Delta V_{\text{oxide}}}{\Delta T}$  approaches  $\left(\frac{\partial V}{\partial T}\right)_p$ ; and accordingly we have employed here the approximation

$$\alpha = \frac{2}{V_2 + V_1} \left( \frac{\Delta V_{\text{oxide}}}{T_2 - T_1} \right) \quad (4)$$

which will not involve us in any great error.

#### EXPANSION DATA

Expansion determinations were made upon several different boron trioxide samples in the course of our investigation, but naturally a number of these measurements were rather preliminary in character. In the present connection we shall restrict ourselves for the purposes of brevity to a consideration of the data for the last two samples studied.

TABLE 1  
*The cubical coefficient of expansion of boron trioxide*

UNANNEALED		PARTIALLY ANNEALED		CAREFULLY ANNEALED	
Sample 1, under various conditions					
<i>degrees C.</i>	$\alpha$	<i>degrees C.</i>	$\alpha$	<i>degrees C.</i>	$\alpha$
113.1	0.41 ( $10^{-4}$ )	122.1	0.48 ( $10^{-4}$ )	123.7	0.52 ( $10^{-4}$ )
139.7	0.37 ( $10^{-4}$ )	156.9	0.55 ( $10^{-4}$ )	157.4	0.60 ( $10^{-4}$ )
166.7	0.17 ( $10^{-4}$ )	188.1	0.55 ( $10^{-4}$ )	184.4	0.83 ( $10^{-4}$ )
193.7	-0.17 ( $10^{-4}$ )	213.3	0.83 ( $10^{-4}$ )	204.4	1.08 ( $10^{-4}$ )
217.8	-0.73	234.8	3.98	222.8	3.45
234.9	2.19	256.6	5.70	247.5	5.61
251.1	5.84	286.5	6.25	275.7	6.05
269.1	6.00				
290.3	6.16				
310.0	5.84				
Sample 2, under various conditions					
122.1	0.40 ( $10^{-4}$ )	120.6	0.56 ( $10^{-4}$ )	114.2	0.54 ( $10^{-4}$ )
152.3	0.19 ( $10^{-4}$ )	152.9	0.59 ( $10^{-4}$ )	143.4	0.49 ( $10^{-4}$ )
180.4	-0.19 ( $10^{-4}$ )	177.8	0.71 ( $10^{-4}$ )	171.8	0.59 ( $10^{-4}$ )
204.9	-1.07 ( $10^{-4}$ )	198.3	0.85 ( $10^{-4}$ )	199.6	1.18 ( $10^{-4}$ )
229.4	0.55 ( $10^{-4}$ )	217.1	1.62 ( $10^{-4}$ )	226.9	4.35 ( $10^{-4}$ )
250.2	4.10	233.1	4.64 ( $10^{-4}$ )	250.0	6.13
270.0	6.22	249.1	6.64 ( $10^{-4}$ )	270.0	5.92
293.8	6.35				

Sample 1 contained 6.3 g. of the oxide. After its installation in the dilatometer it was first heated to about 325°C. and then quickly cooled by quenching the dilatometer in water. The results of a series of expansion measurements made upon the material in this condition are given in the first part of table 1 under the heading "unannealed." The sample was next cooled from 300°C. down to room temperature at the rate of about 5°C. per hour. The subsequent series of expansion measurements

appears in the first section of table 1 under the heading "carefully annealed." Finally, the sample was cooled from 300°C. to room temperature at the rate of 25°C. per hour, after which the data for the "partially annealed" material were obtained.

Sample 2 was very similar to the preceding one, although it had been prepared from a different batch of boron trioxide. In this case the expansion coefficients for the unannealed condition were obtained after the dilatometer and contents had been heated to 325°C. and quenched in a large beaker of ethyl alcohol. The heat treatments of the sample prior

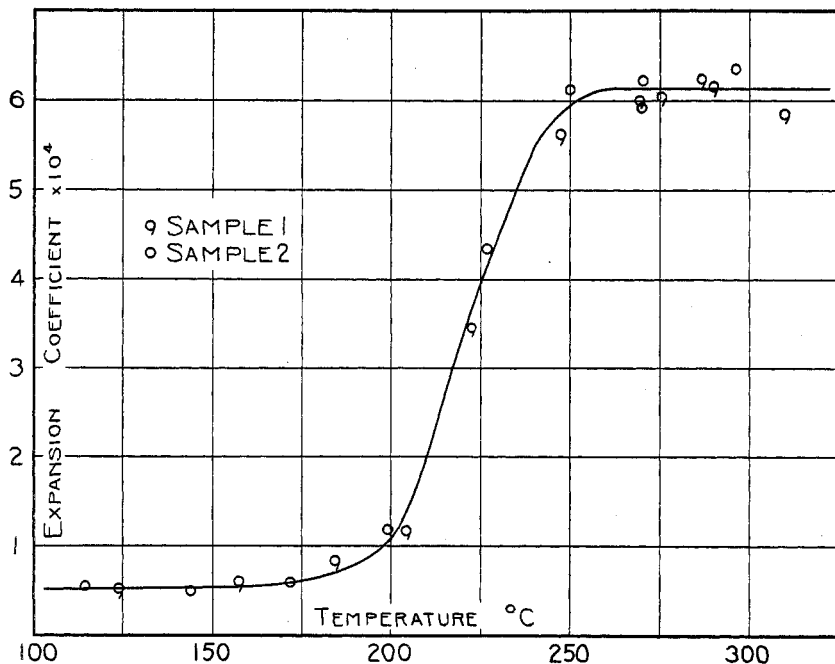


FIG. 1. SHOWING THE EXPANSION DATA FOR THE TWO SAMPLES IN THE CAREFULLY ANNEALED CONDITION

to the "carefully annealed" and "partially annealed" determinations were practically the same as in the case of sample 1. All these data appear in table 1.

In our judgment the experimental error incidental to our method of measuring the coefficient of expansion should be under 5 per cent in all cases. Any deviations between different series of data which appreciably surpass this figure should be attributed to differences in the heat treatment of the samples either prior to or during the measurements. A comparison of our various results therefore serves to bring out the great variability of the boron trioxide in the region below 260°C., where, as it

cools, the oxide begins to change over from an extremely viscous liquid<sup>2</sup> to a hard, glassy condition.

The glasses, after they have been "carefully annealed," undoubtedly represent fairly close approaches to internal equilibrium and accordingly the expansion coefficients obtained in this connection for the two samples are in good agreement. Likewise, the influence of strains and previous thermal history is relatively unimportant in the viscous liquid above

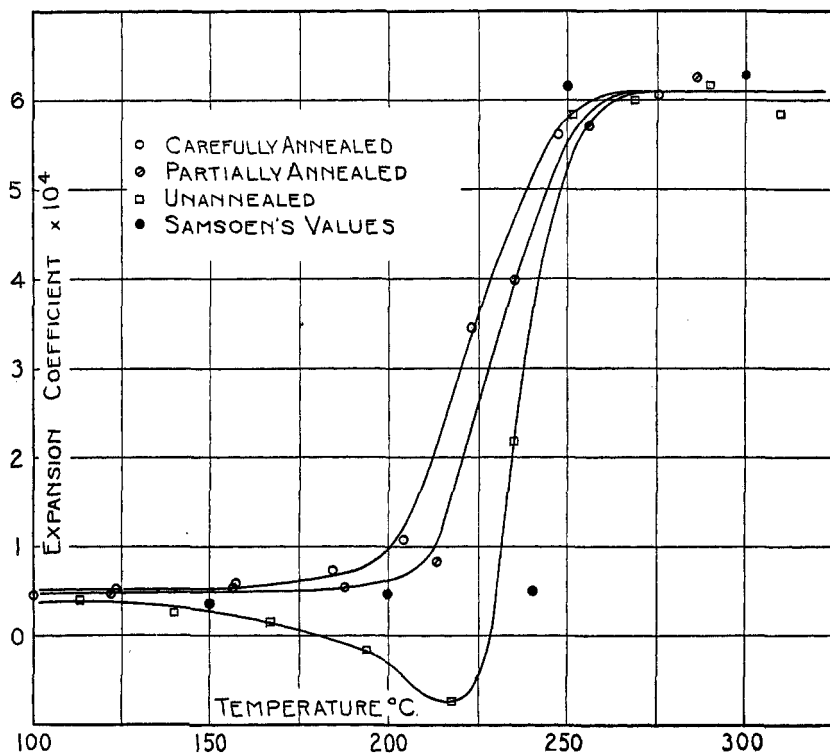


FIG. 2. SHOWING THE EXPANSION DATA OBTAINED FOR SAMPLE 1 FOLLOWING VARIOUS DEGREES OF ANNEALING

270°C., and so in this region the results of all determinations, regardless of previous treatment, are practically within the limits of experimental error. These findings are represented graphically in figure 1.

On the other hand, the glasses in the "unannealed" and "partially annealed" conditions yielded results of poorer reproducibility below 260°C. In particular, the coefficients of expansion for the unannealed glasses run decidedly below those for the carefully annealed and even assume various

<sup>2</sup> We have been able to make viscosity measurements upon boron trioxide down to 267°C., at which temperature  $\eta = 2 (10^{11})$  poises.

negative values between 180° and 230°C. In other words, there is actually a decrease in the volume of the glass sample within this range. Such behavior, of course, makes the subsequent rise as the viscous-liquid condition is approached even more rapid than in the case of a carefully annealed glass. The data for the "partially annealed" glasses, as might have been expected, generally lie between those for the "unannealed" and "carefully annealed" conditions. Curves for the three sets of data thus obtained in the case of sample 1 are shown in figure 2.

Some measurements of the coefficient of thermal expansion of boron trioxide within this temperature range have also been made by Samsoen (3). The values reported by him have been included for comparative purposes in figure 2 where they are represented by the solid dots. His results below 200°C. and above 260°C. are in good agreement with some of our determinations. However, between these two temperatures he obtains a much sharper transition in the expansion coefficient than we have ever found in any of our samples.

#### DISCUSSION

The results of this study show that for boron trioxide the cubical coefficient of thermal expansion in the viscous-liquid state is more than ten times that for the glass and that between these two states there is a transition<sup>3</sup> extending over a temperature range of about 50°C. Thus these expansion phenomena parallel those found by Thomas and Parks (4) in their study of the specific heats of this substance. They are also in thorough agreement with the results of some expansion measurements of an optical glass reported by Berger (1). In view of such findings it seems to us quite clear that a glass must be considered in a separate category from the undercooled viscous liquid from which it is formed.

The very marked influence of the rate of cooling from the liquid to the glassy states is also a noteworthy feature. Probably no actual glass can be considered as being in a condition of true thermodynamic equilibrium at a temperature much below its softening region; the attainment of such an equilibrium might require the lapse of almost infinite time. However, our boron trioxide glasses which were formed by careful annealing were probably not greatly removed from a condition of internal equilibrium or, in other words, they represent a good approach to stable glasses. On the other hand, the glasses which were produced by quenching the dilatometer in water or alcohol represent substances which are in a state of great strain or, we might say, which are greatly removed from the condition of internal equilibrium at lower temperatures. It is interesting to

<sup>3</sup> It must be realized that the coefficients of expansion reported here are mean values over temperature intervals. Such values tend to smooth out the curve and to decrease the sharpness of the change.

note that the volumes of such glasses are appreciably larger than those for the annealed, as the comparative data (table 2) for the volumes of the two samples under various conditions show.

The volumes of the unannealed glasses at room temperature are almost as great as those of the carefully annealed at a temperature within the transition region. Thus in the unannealed glass there must be a tendency for the material to undergo internal changes in the direction of a smaller volume. Nevertheless, the effects of such a tendency cannot become very noticeable at temperatures far below the softening region of the glass because the velocity of the shift toward the equilibrium point is bound

TABLE 2  
*The volume of the glass samples at room temperature*

CONDITION	SAMPLE 1	SAMPLE 2
Unannealed.....	cc. 3.419	cc. 3.425
Partially annealed.....	3.384	3.379
Carefully annealed.....	3.373	3.366

to be extremely low where molecular translation is infrequent. However, as the temperature of the unannealed glass approaches the softening region and the frequency of translational motion of the molecules in the structure increases markedly, this tendency of the internal equilibrium to shift towards a smaller volume predominates for a time over the general expansion tendency of the material and produces the negative values of the coefficient of expansion between 180° and 230°C.

#### SUMMARY

By use of a small dilatometer with mercury as the dilatometric fluid the coefficients of thermal expansion of two samples of boron trioxide have been measured between 100° and 325°C. with a probable experimental error of less than 5 per cent. The coefficient for the viscous liquid was found to be more than ten times that for the glassy state. The character of the expansion coefficient-temperature curves below 260°C. depended greatly upon the extent of the annealing during the initial formation of the glass.

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