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Expansion Effects of Annealing Borosilicate Thermometer Glasses

By Arthur Q. Tool and James B. Saunders

The expansivity of many glasses can be increased almost 10 percent by increasing the equilibrium temperature from 150 to 200 deg C above the lowest such temperature attainable by long annealing treatments in the lower part of the annealing range. By changing the equilibrium temperatures of a number of the better known borosilicate thermometer glasses, the increase in expansivity per degree increase in equilibrium temperature was found to be about 2.4×10^{-9} at 100° C. Also, it was found that the average values of the change in volume per degree Centigrade change in the equilibrium temperature approximated 7.8×10^{-5} when the volumes were measured at room temperature. As these effects concern the performance of thermometers, the results obtained are used to demonstrate their relation to certain ice point fluctuations that are observed in thermometers. It is shown that under particularly adverse conditions the ice point reading may be changed by as much as 30 deg C. Under more normal conditions of use, this source of error is considerably diminished, but it still remains important in precise work. Also, small changes in the value of the graduations anywhere along the stem may result from changes in the expansivity of the glass as its equilibrium temperature is changed by use at temperatures in the annealing range.

I. Introduction

The expansivity and specific volume of all glasses can be changed appreciably by heating the glasses to temperatures within their annealing ranges. In thermometer glasses these changes can be quite important, because their development by heating a thermometer into the annealing range of its glass often raises or lowers its ice point by several degree intervals on the scale graduated on the stem. Such a treatment may also cause a measureable change in the scale length of the degree intervals. These effects are the result of a shift in the equilibrium temperature of the glass. As long as a thermometer is not heated to its annealing range, appreciable shifts of this nature are never induced. The graduations of many thermometers extend to temperatures that are well within the annealing range of the glass from which the thermometers are made. For instance, thermometers made from borosilicate glasses that are similar to the old and once well-known Jena 59^{III} have often been graduated to 520° C, although these glasses can be annealed at temperatures as low as 450° C [1, 2].[1]

Annealing one of these thermometers for a long period of time at 450° C reduces the specific volume and the expansivity of the glass to about the lowest values obtainable without employing impractical annealing schedules. Treatments of this kind considerably increase the stability of the glass and, if the ice point and calibration are

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[1] Figures in brackets indicate the literature references at the end of this paper.

determined while the glass is in this stable condition, the thermometer functions well as long as it is not heated above 450° C. In fact, it can be heated for short periods to temperatures near 520° C without seriously affecting its calibration. However, continuous use at temperatures near and above 500° C ultimately increases the expansivity and specific volume. These changes cause an appreciable ice point lowering and a slight reduction in the distance between the ice and boiling points. Most of these conclusions can be deduced from an earlier investigation by H. C. Dickinson [2] on the stabilization of thermometers made of a borosilicate glass.

To learn something more of the magnitude and effect of the changes caused in the expansivity and specific volume of thermometer glasses by heat treatment, a number of such glasses were investigated. Those discussed in this paper include some glasses used in thermometers for the determination of temperatures above 450° C.

II. Sources of Glasses

The data reported in this paper were obtained on samples of Jena 59^{III}, similar Corning borosilicate glasses, Jena 2954 ^{III}, and a glass that is designated by the number 172 and is used for thermometers indicating temperatures that greatly exceed the highest point safely registered by ordinary borosilicate thermometers. Since fresh samples of Jena 59 ^{III} were unavailable, samples of this glass were procured from old thermometers. From the appearance of these thermometers, their bulbs seemed to have been blown from the capillary tubing of the stem. Consequently, all tests on this type of glass were made on the stem glass, but the results are considered as representative of the bulb glass also. Of the Corning glasses, that designated by G80 was obtained directly from the Corning Glass Works. Although this glass was supposed to be similar to the capillary tubing used for stems of borosilicate thermometers, it was in the form of ordinary tubing with an outside diameter of about 10 mm. Capillary and bulb tubing of the Corning borosilicates were obtained from the Taylor Instrument Co., and are designated as glasses TS and TB, respectively. Capillary and bulb tubing of the Jena 2954^{III} were supplied by the Fisch-Schurman Corporation and are designated as glasses JS and JB. The capillary tubing of glass 172 was submitted by the Precision Thermometer and Instrument Co. The samples of bulb tubing were generally so thin walled and small in diameter that suitable test specimens were prepared from them with difficulty.

III. Thermal Expansion Tests

The first step in an investigation of the effects caused by heat treatment is the location of the annealing ranges of the glasses to be tested. The annealing range can be determined from graphs showing the linear thermal expansion of a glass as a function of temperature. Figures 1, 2, and 3 show such graphs for expansions determined by an interferometric method. The upper third of the annealing range (see fig. 3) corresponds approximately to the temperature range that extends upward from a temperature *A* (the approximate beginning of the rapid expansion range of a glass on heating) and ends at a temperature *B* (the beginning of noticeable inelastic deformation under light stress). The location of the temperatures A and B is an easy matter if thermal expansion curves are obtained on annealed glasses by the interferometric method. All details for obtaining such curves have been fully discussed in a previous paper [3]. A desirable

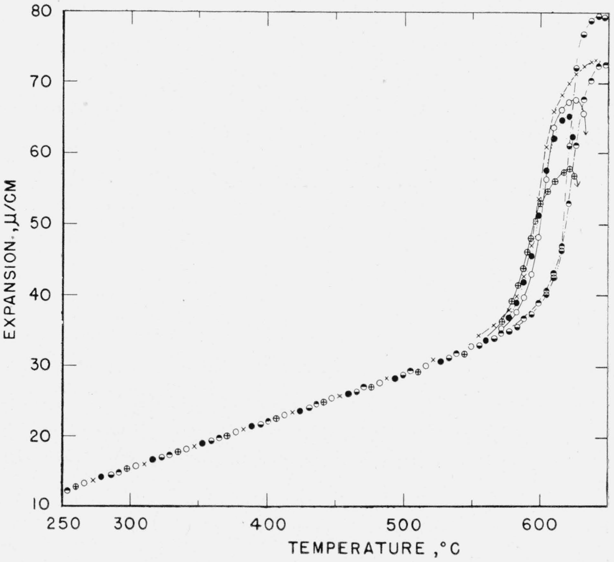

FIGURE 1. *Expansion curves of annealed thermometer glasses.*

Glasses annealed for 30 days at 500° C. Curves TS, TB, and G80 represent expansions of Corning thermometer glasses, and curves 59^{III}, JS, and JB represent expansions for Jena glasses. ○, TB; ●, TS; ⊕, G80; ×, 59^{III}; ◒, JS; ◓, JB.

form of test specimen is either a ring- or T-shaped spacer placed between the interferometer plates. However, with one exception, the nature of the above-mentioned glass samples made it necessary to use three tripod spacers in this investigation.

As received, most of the glasses were indifferently annealed. After procuring preliminary thermal expansion curves on the glasses in this condition, it was estimated that a treatment of 30 days at 500° C should be sufficient to bring six of the seven glasses to equilibrium at that temperature. It appeared that a corresponding temperature for glass 172 exceeded 650° C. Samples of the six glasses were then subjected to the treatment that seemed necessary to establish equilibrium at 500° C. This treatment was followed by rapid cooling to room temperature from which the expansion tests began. The thermal expansion curves shown in figure 1 for the six glasses resulted from these tests. These curves show that the annealing ranges of the Jena 2954^{III} glasses, JB and JS, are about 20 deg C higher than those of the other four glasses. This is obvious because of the relative positions of the beginning points, A, of the rapid expansion (see table 1). The curves also show that the interferometrically determined deformation points, B, of all six glasses lie between 600° and 650° C. These results for B made it apparent that it would be useless to attempt to cool any of the six glasses so rapidly from any treating temperature above 625° C that a condition of equilibrium corresponding to the treating would be maintained.

TABLE 1. *Temperatures determined in locating annealing ranges*

Glass	Temperatures			
	°*C* C[a]	°*C* D[a]	°*C* A[b]	°*C* B[c]
TS	443	[a] 567	[b] 583	[c] 621
TB	435	569	590	626
JS	449	575	610	644
JB	449	578	609	646
59^{III}	448	571	585	642
G80	448	563	572	622
172	665	715	730	795

[a] Temperatures at which contraction of chilled samples began and ended, respectively.

[b] Temperatures at which rapid expansion of annealed samples began according to a graphical determination demonstrated in figures 3.

[c] Temperatures at which inelastic deformation appeared according to a rather similar graphic determination. At these temperatures, the rate of deformation approximated that of thermal expansion.

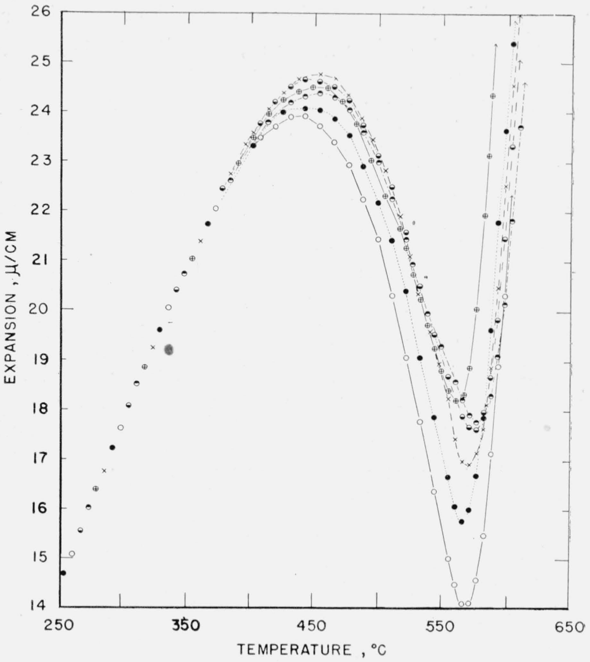

FIGURE 2. *Expansion curves of chilled thermometer glasses.*

Glasses cooled rapidly from 800° C. Designations for curves are explained under figure 1 and in text. ○, TB; ●, TS; ⊕, G80; ×, 59^{III}; ◒, JS; ◓, JB.

To gain more information concerning the lower limit of the practical annealing range, undercooled samples of the six glasses were prepared by heating them to 800° C and cooling them as rapidly as possible in air. Such a treatment probably left the samples in an undercooled condition corresponding to equilibrium at undetermined temperatures not far below 700° C. The thermal expansion curves in figure 2 were obtained on these samples. These curves show the contraction that takes place as the equilibrium temperature [4] of a severely undercooled glass decreases while being heated through its annealing range. The temperature C at which the contraction begins marks the approximate lower limit of the annealing range. Accordingly, it appears that all six of the glasses can be brought to equilibrium at temperatures as low as 450° or 475° C, provided they are subjected to heat treatments that continue for several months at such temperatures. This estimate of the time required to establish equilibrium at low annealing temperatures is based on previous experience with other glasses under similar conditions. Similar experience has also shown that the necessary duration of treatments for establishing equilibrium at various temperatures within the annealing range increases by a factor approximating 2 for each 8 deg C decrease in temperature. In procuring the data on the change in expansivity as the equilibrium temperature is changed, the periods of treatment at the various annealing temperatures were determined in accord with this experience. They ranged from about 4 months at low annealing temperatures to less than an hour above the upper limit of the annealing range.

In figure 3, curves similar to those in the previous figures are presented for glass 172. In this case, the undercooled sample was heated to 1,000° C before chilling and the well-annealed sample was treated 23 weeks at 650° C.

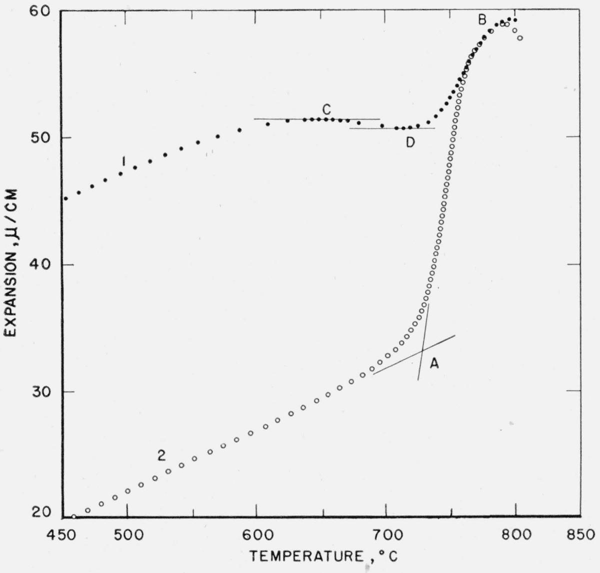

Figure 3. *Expansion curves of thermometer glass 172.*

Curve 1, glass cooled rapidly from 1,000° C. Curve 2, glass annealed for 23 weeks at 650° C. Points C and D represent beginning and end, respectively, of the contraction shown by chilled sample. The respective points A and B approximately represent the beginning of rapid expansion and of appreciable deformation shown by annealed sample.

Figure 3 is also used to show something of the significance of the temperatures A, B, and C and to show how they are determined. The determination of a temperature D is also demonstrated; this is the temperature that marks the end of the contraction of a chilled glass as it is being heated through the annealing range. In some respects, D as well as A appears to mark the beginning of the rapid expansion effect. However, D is in the region of undercooled glass, whereas A is in the region of superheated glass. At D, the contraction caused by a decreasing equilibrium temperature is just balanced by the normal expansion caused by an increasing actual temperature. At A, the expansion caused by an increasing equilibrium temperature adds appreciably to the normal expansion.

The temperature A can be determined only from expansion curves for samples that have been moderately or well annealed. Its value depends somewhat on the degree of annealing and also on the rate of heating. Temperature B is little affected by the degree of chilling or annealing, but it is affected by the rate of heating and the character of the contact points between the sample and the interferometer plates. Temperatures C and D are both affected by the rate of heating and by differences in the effectiveness of the chilling. Consequently, repeated observations show considerable variations. Despite the various causes for deviations in the determined values of A, B, C, and D, these temperatures are very useful in locating the annealing range and in devising annealing procedures.

IV. Change in Expansivity as Equilibrium Temperature Changes

For determining the change in expansivity as the equilibrium temperature of the six first-mentioned glasses was changed, treating temperatures, usually at 25- or 30-deg intervals, from 450° (or 475°) to 630° C. were chosen. At each of these temperatures the samples were held for periods that were deemed sufficient to establish equilibrium. The samples were then cooled rapidly to room temperature. Rapid cooling is unnecessary from low-treating temperatures, but it is necessary in cooling from high-treating temperatures if the downward drift of the equilibrium temperature is to be prevented. Since rapid cooling from the treating temperatures has no harmful effects on expansion measurements below the annealing range, the same cooling procedure was followed in all cases of heat treatment.

After these treatments, expansion curves from room temperature to 250° C. were obtained on the samples (see curve 1, fig. 4, for a typical curve). The tests were stopped at 250° C., because heating to that point certainly did not affect the equilibrium condition of the glass. This certainty made it possible to use both heating and cooling data in determining the expansivity and also to repeat the test on a sample as many times as repetition seemed necessary.

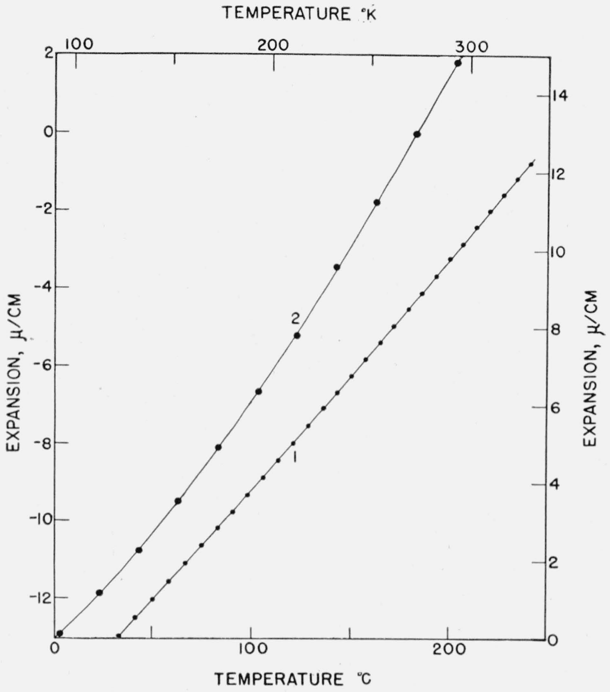

FIGURE 4. *Comparison of experimental and computed linear expansion data.*

Solid lines and dots represent computed and experimental data, respectively. Curve 1, glass annealed for 6 months at 475° C., ordinates on the right and abscissas in degrees Centigrade at bottom of figure. Curve 2, experimental points based on expansivity data obtained by H. G. Dorsey on crown glass tubing, ordinates on the left and abscissas in degrees Kelvin at top of figure.

In order to compute the expansivity at any desired temperature, attempts were made to fit various formulas to the data. These formulas included the usual parabolic and cubic equations but the best results were obtained by using the equation

$$\Delta L = A + BT + CT \ln T \qquad (1)$$

In this equation, ΔL is the expansion per unit length caused by heating from some absolute temperature T' to another absolute temperature T, and A, B, and C are constants, although A naturally depends on the choice of T'. The expression for the slope of the expansion curve is

$$dL/dT = B + C(\ln T + 1) = C \ln(T/T_0) \qquad (2)$$

In eq 2, the absolute temperature T_0 is that at which dL/dT becomes zero.[2] As is well known, this condition for maximum density is found in vitreous silica at a temperature that is not far above −100° C. Below this temperature, the expansivity is negative, because the glass increases in length as temperature decreases. Every glass probably reaches a minimum specific volume at some low temperature that may be even nearer absolute zero. This temperature T_0 at which the expansivity is zero has its analogues in the temperatures at which the temperature coefficients of refractivity become zero. These temperatures, at which the refractivities reach a minimum, range from atmospheric temperatures downward [6]. Thermal expansion is an important factor but not the only one in determining the temperature coefficients of refractivity. This is obvious because increasing the density of a glass by cooling would increase the refractivity if no other factor were involved. Consequently, the temperatures for minimum volume and for minimum refractivity are by no means the same. Moreover, the temperature for minimum refractivity varies with the wavelength of the refracted light.

Equation 1 was fitted to the expansion data by means of the so-called method of averages. As an example of the results, a computed curve, together with the observed results is presented as curve 1 in figure 4. The constants, B and C of eq 1, which were obtained by this computation were introduced into eq 2 for computing the expansivity at any temperature at which the glass might behave as a solid. Samples of computed results for a wide temperature range are shown by the linear expansivity curves in figure 5.

The linear expansivities (cm/cm °C) shown in figure 6 were computed for 100° C (373.2° K) and plotted as functions of the equilibrium temperatures of the glass samples. The temperature, 100° C, was chosen, because it was reasonably remote from the limits, room temperature, and

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[2] The slope of the expansion curve becomes zero at some low temperature, which according to eq 2 is given by the relation $\ln T_0 = -(B/C) - 1$. Using the values obtained for B and C as a result of the computations required in fitting experimental data of curve 1 in figure 5, it was found that $T_0 = 16.2$°K. Because of the range of the extrapolation, a value so computed has limited significance. By using the same method of analysis on expansivity data obtained by Dorsey [5] on a crown glass, a value $T_0 = 32.0$°K was obtained. As his data extended downward to 93°K, the range of extrapolation is considerably less in this case. For results based on his data see curves 2, figures 4 and 5.

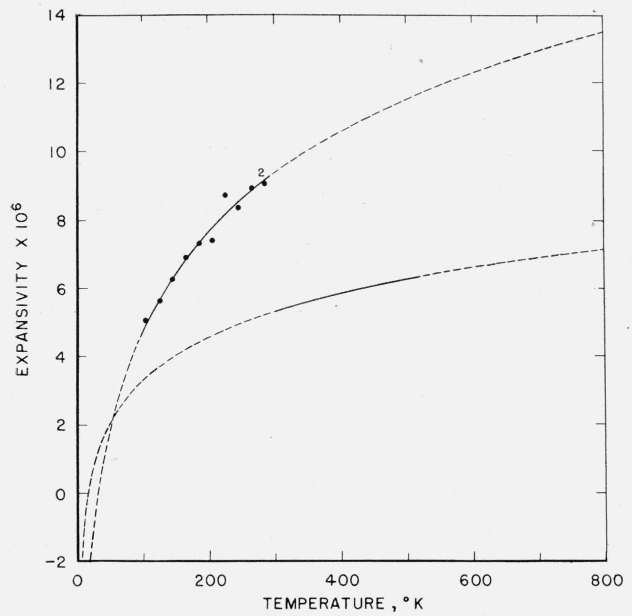

Figure 5. *Computed linear expansivities for wide range of temperatures.*

Curve 1, computed linear expansivities corresponding to curve 1 of figure 4. Curve 2, computed expansivities corresponding to curve 2 of figure 4. Solid parts of curves cover temperature ranges of the experimental data. Broken parts of curves represent extrapolated results computed for temperatures ranging from 10°K to points near or within the annealing ranges of the glasses. Dots plotted along curve 2 indicate Dorsey's results.

250° C., of the range used for the expansion tests. As many thermometers made from these glasses are ungraduated from 5° to some point between 200° and 300° C., the range of the tests approximately coincides with this ungraduated range. However, the temperature used in this investigation for expansivity determinations is a matter of little importance, because the only purpose of the investigation was to learn to what extent the expansivity at some standard temperature is changed by making definite changes in the equilibrium temperature. It was not intended to attempt the more difficult study of the manner in which changing the equilibrium temperature effects the increase in expansivity as the temperature of the glass is increased. Furthermore, this last-mentioned change in expansivity is of relatively little importance as far as thermometers are concerned.

The change caused in the expansivity at 100° C by changing the equilibrium temperature 150 deg C was found to be nearly 6 percent of the average expansivity. This finding agrees reasonably well with some results obtained on other glasses. In view of results obtained in this laboratory, it appears that the expansivity of most glasses can be increased almost 10 percent by increasing the equilibrium temperature from 150 to 200 deg C above the lowest such temperature attainable by long annealing treatments.

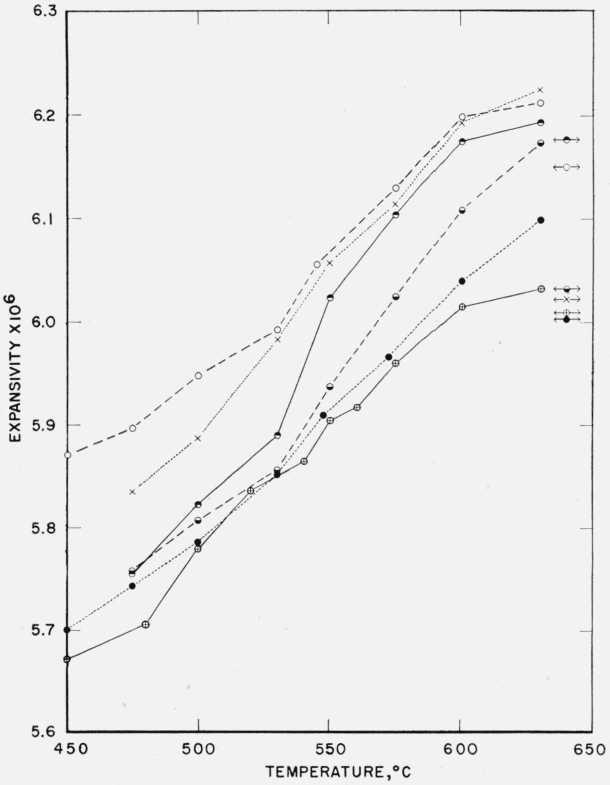

Figure 6. *Changes caused in linear expansivity by changing the equilibrium temperature.*

Computed linear expansivities for 100° C are plotted against the temperature of annealing treatment. Expansivities of the original or untreated glasses are indicated by the double arrows at the upper right of the figure. A treatment of 1 hr. was ample to establish equilibrium at 600° C. At 500° C. a treatment approximating 30 days usually seemed necessary. Some of the glasses appeared to require treatments of almost 6 months duration at 475° C. It is unlikely that equilibrium was established in any of the glasses at 450° C., as even 475° C is a very low annealing temperature for most of them. After some tests, it seemed that treatments of a year or more might be required to approximate equilibrium in the bulb glasses at the lower temperature. ○, TB; ●, TS; ⊕, G80; X, 59^{III}; ◒, JS; ◓, JB.

When the tests were repeated several times on any sample without changing its equilibrium temperature, it was found that the spread of the results seldom exceeded ½ of 1 percent, or about 3×10^{-8}(cm/cm°C). However, when the results obtained on samples treated at different temperatures are considered, it is obvious that errors in the determinations of the treating temperatures and uncertainties concerning the adequacy of the treatments will become apparent. These factors seemed to increase the uncertainty of a single determination to at least 1 percent when determining the expansivity of a sample after any particular treatment. As this uncertainty is about one-seventh of the change caused in expansivity by reducing the equilibrium temperature to the extent of 100 deg C, the failure of the results to indicate smooth curves when presented as in figure 6 is easily understandable.

Because of the irregularity of the results, neighboring points for the same glass were joined by straight lines merely to distinguish more clearly between the results obtained on the various glasses. The results as presented in figure 6 show that the expansivities of the stem glasses (JS, TS, and G80) are generally lower than those of the bulb glasses (59^{III}, JB, and TB). The expansivities of the glasses JS and JB are respectively the highest and lowest of the two groups. This fact indicates that there is less difference between these two glasses than there is between T_S and T_B. As far as can be determined from the results, the increase in the expansivity as the equilibrium temperature increases is roughly linear and not greatly different for the six glasses. Apparently, the equilibrium temperature coefficient of the expansivity (the change in linear expansivity per degree Centigrade change in the equilibrium temperature) is about 2.4×10^{-9}.

According to the tests made on glass 172, the linear expansivity of this glass at 100° C increased from about 3.5×10^{-6} to about 3.7×10^{-6} as the equilibrium temperature was increased from 650° to 800° C. The expansivity of the glass as received was about 3.6×10^{-6}, which was found to be the value that corresponded to an equilibrium temperature approximately 750° C. The equilibrium temperature coefficient of the linear expansivity appeared to be somewhat less than 1.1×10^{-9} for this glass.

V. Volume Change Caused by Annealing

As already stated, a glass expands or contracts whenever it is held at an annealing temperature that differs from the equilibrium temperature established by the preceding annealing treatment. Any such contraction or expansion caused by heating a thermometer into the annealing range of its glass not only results in a corresponding raising or lowering of the reading for the ice point but also for any other temperature. Whenever a thermometer is both poorly annealed and graduated into the annealing range, these changes in readings may be quite large. Holding the temperature of such a thermometer for a considerable time at low annealing temperatures but still within the range of the graduations causes a contraction that results in an ice point rise that may be equivalent to 30° C or more according to the graduated scale. The lower limit of the annealing range of glasses similar to the Jena 16^{III} glass [3] is near 350° C, and that for glasses similar to the Jena 59^{III} is somewhat below 450° C. Thermometers made of these glasses are sometimes graduated to temperatures that are 70° C above these limits, and they are therefore subject to considerable ice point changes if used frequently within the annealing ranges.

In view of these considerations, measurements were made on the volume change caused by changing the equilibrium temperatures of the glasses. For these measurements, the equilibrium temperature of samples from each glass, excepting glass 172, was established at 500° C. For other samples of the same glasses, this temperature was established at 620° C. At the lower temperature, a treating period exceeding 2 months was employed to establish what appeared to be a close approach to equilibrium. At the other temperature, a period of only a few hours appeared to be sufficient for the same purpose, but it was necessary to cool very rapidly in order to prevent a downward shift of the equilibrium temperature.

The volume change caused by increasing the equilibrium temperature from 500° to 620° C was determined for the six glasses by obtaining expansion curves for both samples of each glass and by treating these curves as shown in figure 7. In this interferometric method of measuring the volume change caused by heat treatment, the expansion curves for the samples were determined from room temperature to 578° C. Then, measurements both on the expansion of the annealed sample and on the contraction of the chilled sample were continued at this temperature as equilibrium was approached. These measurements were continued until it seemed that no further significant change would take place.

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[3] For a discussion of the properties and compositions of Jena 16 III and 59 III see H. Hovestadt, Jena Glass (English translation, MacMillan and Co., Limited, London (the MacMillan Co., New York) 1902).

The end points of the resulting expansion curves for the chilled and annealed samples were then made to coincide at B, as shown in figure 7, which presents results obtained on glass JS. By this construction, the change in length at room temperature caused by the 120° C difference in equilibrium temperature between the two samples is given by the difference in the ordinates of curves 1 and 2 at room temperature. According to figure 7, the change in length for this pair of samples was 32 μ for a sample 1 cm long. In terms of volume change, this result is equivalent to 0.96 percent for a 120° C change in equilibrium temperature.

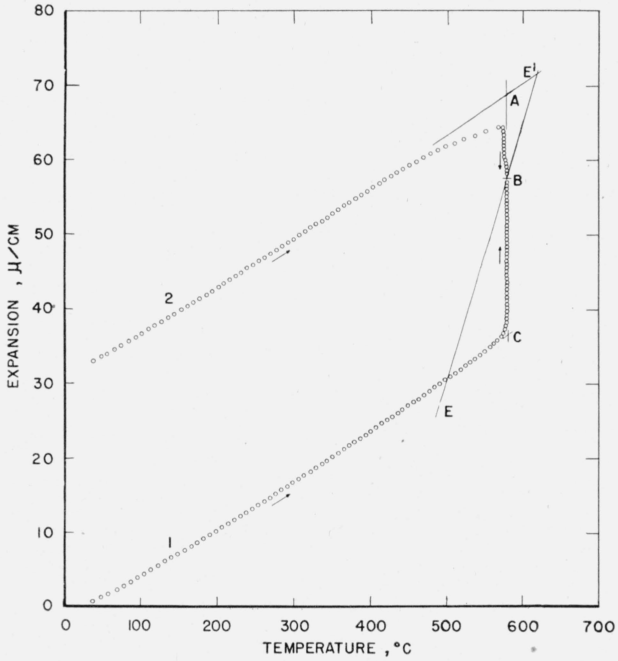

FIGURE 7. *Change in length as glass is held at constant annealing temperature.*

Expansion curves of glass JS when heated to and held at temperature 578° C. Curve 1, sample previously annealed until equilibrium was established at 500° C. Curve 2, sample previously treated and chilled to establish and maintain a condition of equilibrium at 620° C. Curve EE', length-temperature equilibrium curve, which presumably represents the expansion curve that the annealed sample would have followed had it been heated at a very low rate from 500° to 620° C.

The corresponding change in length at 578° C can be estimated by extrapolating curve 2 from a point near 400° C to point A and with a slope slightly greater than that between 300° and 400° C and also by extrapolating curve 1 from 500° C to point C. The difference in the ordinates of A and C gives an approximation for the change in length at 578° C when the change in equilibrium temperature is 120° C. When the curves were extrapolated as shown in figure 7, it was found that this difference was also 32 μ. In view of the larger expansivity of chilled glass compared to annealed glass, it appears that a somewhat larger value should have been obtained for the change in length at 578° C. Possibly, the estimated value at 578° C is no larger in this case, because the slope of the extrapolation of curve 2 from 400° C to point A was not made large enough.

For most glasses, the change in length while being annealed is practically proportional to the change in equilibrium temperature. In other words, any increase in the equilibrium temperature of a sample in equilibrium at 500° C should produce about the same change in length as the same increase would produce if the sample were in equilibrium at 600° C. Because of this near proportionality, the equilibrium curve (represented in fig. 7 by line EE') may be considered to approximate a straight line, over a range of about 100° C, to the same degree that curves 1 and 2 approximate straight lines over an equal range in the neighborhood of 200° C. For the same reason, the ratio $(620-578)/(578-500)$ approximates the ratio AB/BC.

As the equilibrium temperature of an annealed glass does not change materially until it is exceeded by the actual temperature, the equilibrium curve must intersect curve 1 of the annealed sample at 500° C. It must also pass through point B, which was obtained when the glass reached equilibrium. Line EE' in figure 7 represents the approximate course of such an equilibrium curve. Also, if the curvature of the equilibrium curve is very slight as supposed, continuing it as a straight line beyond B should cause it to intersect the line AE' at 620° C. When expansion curves, obtained on samples that are in equilibrium at such different temperatures, meet the demands of such constructions, confidence in the determinations of the volume changes by the interferometric method is enhanced. The results obtained by this method on six glasses are shown in table 2.

For five of the glasses, the volume change as determined by this interferometric method for a 120° C difference in equilibrium temperature ranged from 0.94 to 1.05 percent. As the departure from an average does not exceed the uncertainty of such results, it seems that the probable volume change for all of these five samples is approximately 1 percent.

TABLE 2. *Volume changes caused by a change of 120 deg C in equilibrium temperature*

Glass	Method of testing	Percentage of volume change
G80	Interferometric	0.95
	Archimedean	.91
59^{III}	Interferometric	1.05
TS	Interferometric	0.98
	Archimedean	.97
TB	Interferometric	1.02
JS	Interferometric	0.94
	Archimedean	.95
JB	Interferometric	.84
	Archimedean	.86
	Pycnometer	.82

For the sixth glass, Jena 2954 ^{III} bulb, all results obtained by the interferometric method were lower, and averaged 0.84 percent. As this tubing was less than 3 mm in diameter and very thin walled, it was difficult to construct spacers for the interferometer that were entirely satisfactory. Because it was feared that the unsatisfactory spacers affected the results adversely, larger spacers were made by fusing the glass into large beads. The results remained the same. As a further check on the results obtained, determinations of the change in volume for a 120° C change in equilibrium were also made on some of the glasses by finding the apparent loss of weight when the samples were weighed in a liquid of known density. These determinations were made by E. L. Peffer of the capacity and density laboratory of this Bureau. His results are listed in table 2 as being obtained by the Archimedean method. Determinations on the glass JB were also made by the pycnometer method. No determination of this volume change was made for glass 172.

From an average of the results given in table 2 for the change caused in a unit volume by a change of 120° C in equilibrium temperature, it appears that the average volume change per unit volume per degree change in this temperature is near 7.8×10^{-5}. According to density data presented in a previous paper [7], the same equilibrium temperature coefficients for some optical glasses range from 4.8×10^{-5} to 12.4×10^{-5}.

VI. Rate of Expansion at Constant Temperature

In an earlier paper [8], it was suggested that the exponential integral equation

$$Ei(y) - Ei(y_o) = -Kte^{T/k} \qquad (3)$$

approximately represents the progress of density changes at constant annealing temperatures. In this equation, t represents time and $Ke^{T/k}$ is constant if the temperature T remains constant. For a linear expansion as the equilibrium temperature increases, the arguments y and y_o of the exponential integrals represent $(L_\infty - L)/CL_o$ and $(L_\infty - L_o)/CL_o$, respectively. In these expressions, L is the length at any time t, and L_∞ and L_o are the lengths when t is infinite and zero respectively. The constant C is the product of the equilibrium temperature coefficient of expansion (slope of curves in fig. 6), and a constant h which is related to Twyman's constant k appearing in eq 3.[4] The change in thermometer readings with time as a thermometer is held at an annealing temperature T is therefore a function of the change in the argument y with time.

As the expansions are generally computed in terms of microns per centimeter length at room temperature, and as the total expansion in heating from room temperature to points in the annealing range seldom reaches 100 μ, the length L_0 at the beginning of a treatment at a constant annealing can be assumed to be 1 cm or 10^4 μ without introducing appreciable error. As indicated in the above citation, the other constants ($Ke^T/^k$, $L_\infty - L_0$, and C) can be determined by approximation methods and subsequent adjustments.

By following the method outlined in connection with eq 3, curve 1 (as indicated by a continuous line) in figure 8 was obtained. The dots lying along this line are observed points and correspond to the points that are in line with and between the points B and C in figure 7. This correspondence between expansion and time is known, because the time was recorded for each observation during the annealing periods in which the

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[4] According to Twyman's empirical equation concerning the change in the viscosity of a glass as the temperature changes, $K_T = Ke^{T/k}$ is the reciprocal of the relaxation time at any temperature T, if K is the extrapolated value of K_T for $T=0$. The relation between the presumably constant temperature intervals k and h is shown in a previous publication [4]. The interval h has a significance only when the equilibrium temperature changes.

data used for curves such as 1 and 2 in figure 7 were procured. The data for curve 2 in figure 8 were computed by means of the logarithmic equation

$$\ln\,(L_{\infty}-L)-\ln\,(L_{\infty}-L_0)=Kte^{T/k}, \qquad (4)$$

and on the assumption that the curve must coincide with the experimental data at two points at least. As usual, the results obtained by the use of eq 3 are more satisfactory than those obtained by the use of eq 4.

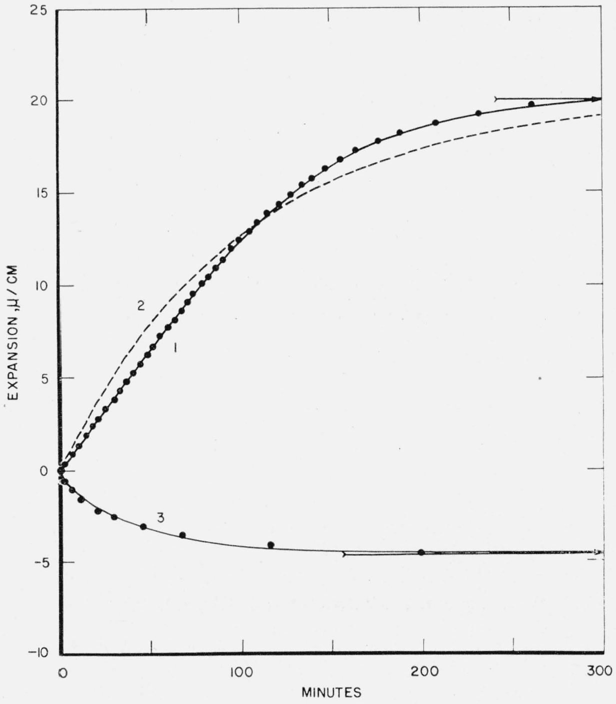

Figure 8. *Experimental and computed linear expansions and contractions (microns per centimeter) at a constant annealing temperature.*

Curve 1, solid line represents computed results, dots represent experimental points corresponding to points on curve 1 between C and B in figure 7. Curve 2, presents results computed on the assumption that the expansion is a logarithmic function of time. Inset curve 3, computed and experimental results corresponding to points on 2 between A and B in figure 7. At infinite time, curves 1 and 3 are tangent to fletched lines.

After computing curve 1 (fig. 8), the same values for the constants (CL_0 and $Ke^{T/k}$) were used to compute curve 3 of figure 8. This curve represents the approach of the chilled sample to equilibrium at 578° C after that temperature was approximated in the test yielding curve 2 of figure 7. However, the time of observation was recorded for the last ten observations only. Consequently, the first five points showing the vertical drop of curve 2 (fig. 7) are not represented in curve 3 (fig. 8). For curve 3 as for curve 1, the value assumed for $L_{\infty}-L_0$ is indicated by a fletched line to which the curve becomes tangent after an infinite time.

VII. Relation of Results to Performance of Thermometers

To simplify the discussion of the relation between the performance of thermometers and the data obtained on the borosilicate glasses tested, it will be assumed that the bulbs alone are affected by annealing or by occasional heating into the lower part of the annealing range of the glass. It will also be assumed that all second-order effects resulting from changes in the actual and equilibrium temperatures are relatively negligible when compared to the first-order effects. Generally, the uncertainties introduced by these assumptions are less than those resulting from uncertainties in the data procured on expansivity and volume changes.

With regard to the thermometer used as an example for the discussion, it will be considered that the borosilicate glass of which it was made possesses the average expansion coefficients for this type of glass. It will also be considered that the glass was thoroughly annealed at 450° C before graduating the stem and making the calibration. According to results that are exemplified by the curves presented in figures 5 and 6 for linear expansivity, it appears that the average volume expansivity in the temperature range from 0° to 100° C approximates 16.4×10^{-6} for a borosilicate thermometer glass in such a condition. Furthermore, according to data and an equation appearing in the International Critical Tables [9], it appears that the corresponding average coefficient is about 182.5×10^{-6} for the volume expansion of mercury. Consequently, for each unit volume of the bulb, a volume of mercury averaging approximately 166.1×10^{-6} will be forced into the capillary of the stem for every degree Centigrade rise in temperature. This result of the differential expansion is the average volume of the capillary between the degree graduations in the range from 0° to 100° C, if the volume of the bulb is unity.

The expansivity and specific volume of the glass are increased appreciably if the thermometer is used or treated in such a manner that its equilibrium temperature is raised from 450° C to some other temperature, such as 500° C. According to the results of the previously described tests, the increases in volume and volume expansivity are, respectively, 7.8×10^{-5} and $3\times2.4\times10^{-9}$ per degree increase in equilibrium temperature. For a 50-deg increase, the changes in volume and volume expansivity are therefore 3.9×10^{-3} and 3.6×10^{-7}, respectively. Moreover, the average volume expansivity between 0° and 100° C becomes 16.8×10^{-6}. This increase in expansivity reduces the volume of mercury forced into the capillary to 165.7×10^{-6} per unit volume of the bulb and per degree rise in temperature. However, if the original volume of the bulb were unity, the 50-deg C increase in the equilibrium temperature increases the bulb volume to 1.0039. The product of this volume and the new differential expansivity, 165.7×10^{-6}, is about 166.4×10^{-6}. In other words, increasing the equilibrium temperature of the bulb glass of a completed thermometer increases the volume of mercury forced into the capillary for each degree rise in temperature. This increase is sufficient to cause a noticeable effect in those parts of the stem that are unaffected by usage or heat treatment.[5]

To demonstrate the relative importance of the ice-point lowerings, produced by these changes in volume and expansivity, it will be assumed for the moment that no volume change took place at 500° C during the treatment that raised the equilibrium temperature from 450° C to that point. That is, only the change in expansivity is supposed to have taken place. However, in such a case, the volume of the bulb is reduced at all temperatures below 500° C. At 0° C, this reduction amounts to $500\times3.6\times10^{-7}$ or 180×10^{-6}, provided the increase in expansivity persists throughout the range, 500° to 0° C. Consequently, the increase in the expansivity of the glass probably causes an ice-point lowering that somewhat exceeds 1 deg C.

Compared to this ice-point shift, the one caused by the neglected volume change is far more important. According to the value given above for this change, it causes an ice-point lowering or depression that approximates $3.9\times10^{-3}/1.66\times10^{-4}$, or 23.5° C. Consequently, the total effect of increasing the equilibrium temperature by 50 deg C is probably an ice-point lowering of 24+ deg C.

Many thermometers of borosilicate glasses of the kind tested have been graduated to 520° C. In such cases, it is easily possible to increase the equilibrium temperature from 450° to 520° C. As the change in volume at constant actual temperature is approximately proportional to the change in equilibrium temperature, it follows that the volume change produced by an increase of 70 deg C. will cause a lowering or depression of 33+ deg C in ice point and that the total effect will approximate 35 deg if the effect caused by the change in expansivity is added. As already indicated, negative depressions or elevations of this order have been obtained by annealing poorly annealed thermometers at temperatures that were low enough to require treatments approximating 3 weeks in duration before equilibrium was established. Such cases are exceptional and merely show that the maker failed for some reason to age the thermometers for a sufficient time at a suitable annealing temperature.

Under normal conditions of usage, ice-point shifts of the magnitudes found in this demonstration are not likely to develop in properly annealed thermometers. However, it is difficult to avoid small effects whenever a thermometer is graduated to and used at temperatures that can be regarded as low or medium annealing temperatures. In such cases, frequent ice-point determinations or their equivalent should be made. The calibration of the thermometer can then be adjusted in accord with the results of such checks.

VIII. Summary

The changes caused in expansivity by changing the equilibrium temperature of some borosilicate thermometer glasses were determined in this investigation. For some of these glasses that are

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[5] In normal usage, a considerable portion of a thermometer stem is immersed and thus receives about the same treatment as the bulb. Consequently, the volume of the capillary per degree of the graduations on the immersed portion of the stem is changed to about the same percentage as the volume of the bulb, provided the glass and the initial conditions are the same for both immersed parts. Hence, the average volume of the capillary between degree graduations on the immersed portion of the stem is increased from the original value, 166.1×10^{-6}, to 166.8×10^{-6}. In other words, a degree change in the temperature of the bulb is indicated as slightly less than a degree on the scale of the immersed portion of the stem, whereas it is indicated as slightly more than a degree on the scale of the unaffected part. For a change of 100 deg in the reading, these discrepancies amount to a few tenths of a degree.

commonly used in thermometers, the increase in expansivity per degree increase in equilibrium temperature was found to be about 2.4×10^{-9}.

The changes in volume per degree change in equilibrium temperature were also determined for some of the glasses. A method of determining these changes from expansion curves for two or more differently treated samples is demonstrated. The average value of the changes approximated 7.8×10^{-5} per unit volume.

Measurements were made on the time rates of expansion and contraction while the glasses were being held at constant temperature in their annealing ranges. It is demonstrated that a previously proposed equation that involves exponential integrals applies satisfactorily to the experimental results of these measurements.

A discussion of the relation of the various results to the performance of mercury glass thermometers is included. In this discussion, it is shown that the volume and expansivity changes resulting from changes in equilibrium temperature are sufficient to account for ice-point elevations observed when poorly annealed thermometers are used at moderately high annealing temperatures.

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