

# RELATION BETWEEN INELASTIC DEFORMABILITY AND THERMAL EXPANSION OF GLASS IN ITS ANNEALING RANGE\*

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## ABSTRACT

In accordance with experience concerning the behavior of glass at temperatures within its annealing range, an equation is proposed which relates the various extraordinary heat effects to the inelastic deformability and to the degree of superheating or undercooling. By using this equation in connection with the thermal-expansion curves of a glass within its annealing range, certain constants that are related to the coefficient of viscosity and its changes with temperature and the degree of superheating or undercooling have been determined with reasonable results. Such results make it possible to estimate the inelastic deformability of a glass in its various conditions at all annealing temperatures and are therefore valuable in connection with problems that are encountered in the process of annealing glass. The apparent success achieved in applying the proposed equation to experimental data suggests that the concepts underlying this equation are fundamental and must be considered in any theory concerning the constitution of glass or that of any other extremely viscous liquid.

## I. Introduction

### (1) Superheating and Undercooling with Accompanying Extraordinary Effects in Viscous Liquids

As already pointed out,<sup>1</sup> there is a possibility that the extraordinary heat effects (including the rapid expansion) of glass in its annealing range result because the high viscosity, which increases rapidly as the temperature decreases, causes glass to become considerably superheated or undercooled even when the rates of heating or cooling are very low. Although the phenomena are related in some respects, the superheating and undercooling of glass are not those experienced when melting and crystallization, respectively, are delayed. Rather, they are effects that may be envisioned as possible even in the most fluid liquid at temperatures far above its freezing point if unattainably high heating and cooling rates could be employed. When a liquid is in equilibrium at any given temperature, there is an average statistical relation between its molecules that is unique because any change in temperature, even if infinitesimal, will change it accordingly. Such a change in the average statistical relation, which corresponds to an equilibrium condition, presumably requires many processes or readjustments involving the molecules of the liquid. Although some of these adjust-

ments are completed almost instantaneously, time is undoubtedly an important factor in the development of many others, especially if their progress is affected by viscosity. If the time required for the full development of the sluggish readjustments, that are demanded by a given change in temperature, exceeds the time required to accomplish the temperature change, the liquid can be brought to a temperature in a state of nonequilibrium. Moreover, if the cooling increases the viscosity so greatly that the development of the lagging processes ceases altogether, the liquid (unless reheated) will remain indefinitely in the undercooled state. It may even attain the amorphous solid condition if cooled sufficiently.

When a liquid glass reaches any temperature in a state of nonequilibrium, it might seem improbable that this undercooled or superheated state corresponds closely to an equilibrium condition at some intermediate temperature between the temperature reached and that at which the liquid was in equilibrium when the cooling or heating was initiated. Doubtless there are many cases in which such a correspondence is wanting, but it appears to exist in most glasses if the tests are not too searching. Considerable discussion of this point has been included in a previous paper.<sup>1(a)</sup>

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<sup>1</sup> (a) A. Q. Tool and C. G. Eichlin, "Variations Caused in Heating Curves of Glass by Heat-Treatment," *Jour. Amer. Ceram. Soc.*, **14** [4] 276-308 (1931); *Bur. Stand. Jour. Research*, **6** [4] 523-52 (1931); R. P. 292.

(b) A. Q. Tool, "Analytical Representation Concerning Glass in Its Glass Annealing Range." Extended abstract in Forty-Fourth Annual Meeting Program, The American Ceramic Society, Cincinnati, Ohio, Glass Division Program, p. 13 (April 15, 1942).

(c) A. Q. Tool, "Molecular Strains and Extraordinary Thermal Effects in Glasses." Abstracted in Forty-Fifth Annual Meeting Program, The American Ceramic Society, Pittsburgh, Pa., Glass Division Program, p. 92 (April 15, 1943).

### (2) Equilibrium Curve of a Viscous Liquid

When almost any glass is cooled and heated through its annealing range at a low enough rate, it is always practically in equilibrium on reaching any temperature in that range. By determining the changes in various properties as these treatments proceed, equilibrium curves can be established. A rapid heating or cooling from any temperature at which a glass is in equilibrium causes departures from these curves. If such departures are caused by sufficiently high rates of heating or cooling and if the glass is returned to the initial temperature with equal rapidity and no other lapse of time, the glass is still in practical equilibrium at that temperature. If, however, the initial heating or cooling is comparatively slow, the departures will be

less marked and a rapid return of the glass to its initial temperature will show that it is no longer in equilibrium there. After a few trials in which the same departure is always produced, the glass can be brought rapidly to some other temperature at which it is in practical equilibrium. This temperature will be higher or lower than the initial equilibrium temperature, depending on whether the departure was caused by heating or cooling. It appears, therefore, that in certain respects there has been no marked departure of the glass from the equilibrium sequence that it follows on slow heating and cooling.

### (3) Equilibrium Temperature

In view of experiences just discussed, it has been conjectured that glass, when cooled or heated rapidly in the annealing range, behaves in many respects as a solid material, whereas it behaves as a liquid when the rate of temperature change is low enough. Furthermore, it is inferred that the physicochemical condition or state of a glass is reasonably well known only when both the actual temperature and that other temperature at which the glass would be in equilibrium, if heated or cooled very rapidly to it, are known. This latter temperature has been termed the "equilibrium or fictive temperature" of the glass, and a glass is undercooled or superheated according as the fictive temperature is reached by the actual temperature through heating or cooling, respectively. The difference between these temperatures is obviously a measure of the departure of the glass from equilibrium. In the following discussion, the equilibrium temperature will be designated by  $\tau$  in order to differentiate it from the actual temperature,  $T$ .

As stated earlier,<sup>2</sup> the rate at which equilibrium is approached whenever a superheated or undercooled glass is held at a constant temperature in the annealing range is roughly proportional to the departure of the glass from equilibrium. Moreover, if the departures are of the same magnitude and the temperatures are different, the rates of approach seem to be inversely proportional to the viscosity (which increases exponentially with decreasing temperature). Thus, although equilibrium may be approximated in a few minutes at the upper limit of the annealing range, to attain a similar degree of approximation, even when the initial departure is no greater, may require many months if the treating temperatures are near the lower limit of the range.

### (4) Changes in Equilibrium Temperature and Their Relation to Inelastic Deformability Under Elastic Molecular Strains

Glass is still inelastically deformable to an appreciable extent at temperatures far below its annealing range, especially when it is subjected to considerable loads. At such temperatures and also at temperatures within the lower part of the annealing range, there are

<sup>2</sup> A. Q. Tool, "Relaxation of Stresses in Annealing Glass," *Jour. Research Nat. Bur. Standards*, **34** [2] 199-211 (1945); R.P. 1637; *Ceram. Abs.*, **24** [5] 88 (1945).

See also footnote 1.

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indications that glass has ceased to be a truly viscous liquid and possibly has assumed a plastic nature.<sup>3</sup> That is, whether the loads are of a purely mechanical or a physicochemical character, the number of flow planes appears to decrease rapidly with the temperature unless the loads exceed "minimum" limits which presumably also vary with the temperature and condition of the glass. When flow in a plasticoviscous material is being maintained by stresses of a mechanical or a molecular nature, the viscous flow that has been proceeding unhampered along certain localized flow planes may become completely blocked at any time because of changed molecular relations or it may stagnate in a limited locality because conditions in the immediate or surrounding neighborhood have reduced or eliminated the load, at least temporarily. The resistance in a flow plane that has been blocked may likewise break down because the flow in neighboring planes has unkeyed the block or developed stresses that exceed the breakdown limit. Some readjustments and molecular processes in a glass approaching equilibrium consequently may not only develop much more rapidly than others but may also become completely blocked at low annealing temperatures. The discussion<sup>1(a)</sup> of some peculiarities observed in the exothermic effects yielded by samples of a chilled glass that were only partially annealed at low annealing temperatures was based on this concept of the behavior of glass at low annealing temperatures. Furthermore, according to this concept, any theory based on the assumption that glass is a purely viscous liquid obviously will not be applicable at temperatures below the annealing range. The effects caused by the development of a plastic condition are demonstrated in the following sections. Such effects, however, are simply modifications of the heat effects and density changes that would have occurred if the elastic molecular strains had relaxed because of viscous flow alone.

## II. Approach to Equilibrium

### (1) Differential Equations for Rate of Approaching Equilibrium

According to introductory statements relative to the rate of approaching equilibrium, equation (1) is valid.

$$d\tau/dt = K_T(T - \tau) \quad (1)$$

$K_T$  = factor inversely proportional to viscosity (as long as little change occurs in coefficient of elasticity).  
 $d\tau/dt$  and  $T - \tau$  = time rate of change in equilibrium temp.,  $\tau$ , and departure of this fictive temp. from actual temp.,  $T$ , respectively.

Assuming the empirical relation suggested by Twyman<sup>4</sup> for the dependence of viscosity on temperature in the case of a glass in its annealing range, equation (2) may be used with equation (1).

$$K_T = Ke^{T/k} \quad (2)$$

$k$  = Twyman's constant.

$K$  = (obviously) value of  $K_T$  when  $T = 0$ .

<sup>3</sup> A. Q. Tool and J. Valasek, "Concerning Annealing and Characteristics of Glass," *Bur. Stand. Sci. Paper*, No. 358, 35 pp. (Jan. 31, 1920).

See also footnote 2.

<sup>4</sup> F. Twyman, "Annealing of Glass," *Jour. Soc. Glass. Tech.*, **1**, 61-74 (1917).

Thus,  $K$  is an extrapolated coefficient that relates to the inelastic deformability at  $0^\circ\text{C}$ . Experience indicates that  $K_T$  is approximately the reciprocal of the Maxwellian relaxation time for mechanical stresses and it is consequently extremely small for glass at ordinary temperatures. This apparent similarity between the approach to equilibrium and the relaxation of ordinary elastic strains first suggested that the relaxation of certain elastic molecular strains effects the approach to equilibrium.

On combining equations (1) and (2), expression (3) results,

$$d\tau/dt = K(T - \tau)e^{T/k} \quad (3)$$

Even in the annealing range, equations (2) and (3) yield only a rough fit when they are applied to data procured on an annealing glass. For example,  $d\tau/dt$  will decrease somewhat more slowly with time in an undercooled glass and a little more rapidly in a superheated glass than equation (3) allows. One purpose of this paper is to demonstrate this inadequacy of equation (3) when it is applied to the extraordinary contraction and expansion and to the exothermic and endothermic effects of a glass that is being heated through its annealing range.

That equation (2) and, consequently, equation (3) are inadequate is not surprising since the effect of a changing  $\tau$  on the viscosity is ignored. From experience, the manner in which a property seems to be affected by a change in  $\tau$  is similar to that in which it is affected by a change in  $T$ . It has therefore been assumed in previous cases\* that equation (2) would be more nearly adequate if it had the form of equation (4)

$$K_T = Ke^{T/ae^{\tau/h}} \quad (4)$$

and if  $g$  and  $h$  were analogous to Twyman's constant  $k$ . Equation (3) then becomes (5).

$$d\tau/dt = \hat{K}(T - \tau)e^{T/ae^{\tau/h}} \quad (5)$$

By this means, the inadequacies in expressing the change in  $\tau$  at all ordinary annealing temperatures seem to be removed. More precise data, however, on the changes that are caused in various properties and effects must be procured before a final decision on this point is reached. In any case, equations (4) and (5) obviously are also inadequate as soon as glass ceases to be a purely viscous liquid and assumes a definite plasticoviscous nature; that is, equation (4) does not take into account the possibility that the coefficient of inelastic deformability may depend on the load. Equation (4), moreover, may not be adequate to express the changes in viscosity over wide temperature ranges.

## (2) Equations Modified for Linear Heating or Cooling

In many heating tests,  $T$  is increased at a constant rate, which considerably exceeds that at which  $\tau$  decreases at temperatures below the annealing range even if the initial  $\tau$  value is high. Thus, in the plasticoviscous range of a glass, the relation between  $T - \tau$  and  $T$  diverges comparatively little from a linear one dur-

ing any given test in which the heating rate is relatively high and constant. The absolute value of the factor  $T - \tau$  as it appears in equations (3) and (5) may be thought of as possessing some of the qualities of a mechanical load, especially in its relation to the inelastic deformability of a plasticoviscous glass; that is, as this factor increases, the deformability increases. If the change in the plastic deformability is an exponential function of the load and if the special heating condition mentioned previously is met in any test, then equation (5) should be modified for the plasticoviscous range by introducing the factor,  $e^{(T' - T)/a'}$ . In this exponential factor,  $T'$  is presumably near the upper limit of the range in which the glass is appreciably plastic.

When a glass is being heated or cooled at a constant rate ( $dT/dt = \pm R$ , respectively) instead of being held at a constant annealing temperature, equations (3) and (5) become (6) and (7).

$$d\tau/dT = \pm(K/R)(T - \tau)e^{T/k} \quad (6)$$

$$d\tau/dT = \pm(K/R)(T - \tau)e^{T/ae^{\tau/h}} \quad (7)$$

If  $T$  and  $d\tau/dT$  are given,  $T - \tau$  is definitely determined according to equation (6) and the equation is also easily solved in terms of exponential integrals (equation (8)). If  $y = (T - \tau)/k$  and  $\pm x = (K/R)ke^{T/k}$ , then  $d\tau/dT = \pm xy$  and

$$Ei(\pm x) - Ei(\pm x_0) = ye^{\pm x} \quad (8)$$

because  $dy = ydx = \frac{dx}{x}$ . In this equation,  $x_0$  is the value of  $x$  for some particular temperature,  $T_0$ , at which glass was in equilibrium. For the condition that equilibrium does not exist at  $T_0$ , the right-hand member becomes  $ye^{\pm x} - y_0e^{\pm x_0}$ . The negative sign before  $x$  is obviously used in the case of cooling, and  $y$  is positive or negative, depending on whether the glass is superheated or undercooled.

With respect to equation (7), assigning values to  $T$  and  $d\tau/dT$  leaves  $T - \tau$  indeterminate since, under certain conditions,  $\tau$  may have (from a physical as well as from a theoretical standpoint) either of two values, †

† When  $y$  (or  $(T - \tau)/h$ ) has the value  $+1$ , the product,  $e^{-T/k} d\tau/dT$ , has only one value, the maximum possible. If, in addition,  $d\tau/dT = +1$ , then  $y$  is at a maximum and  $e^{T/k} = Re/Kh$ . Furthermore,  $T = k \ln(Re/Kh)$  is the minimum temperature,  $T_m$ , for which  $d\tau/dT$  can be  $+1$ . That is,  $ye^{-y} < e^{-1}$ , if positive  $y$  is either greater or less than unity, and  $T > k \ln(Re/Kh)$  if  $d\tau/dT = 1$  at the same time.

When  $ye^{-y}$  has a positive value less than  $e^{-1}$ ,  $y$  obviously has a pair of possible values, one greater and one less than unity. If  $T$  is the same in both cases,  $d\tau/dT$  will also be identical and the values of  $y$ , under such conditions, obviously correspond to different heating curves; that is, the larger value corresponds to a curve procured on a comparatively well-annealed sample of glass ( $\tau_0 < T_m$ ) while the lesser corresponds to a curve obtained, under the same standard conditions of test, on a less well-annealed sample of the same glass ( $\tau_0 > T_m$ ). Furthermore, if  $d\tau/dT = 1$  for these values of  $y$ , it follows that the common temperature,  $T$ , for the two cases is greater than  $T_m$ . When the usual heating rate ( $3^\circ$  to  $6^\circ\text{C}$ . per minute) is employed, condition  $y = 1$  and  $d\tau/dT = 1$  will usually occur only if the sample has been moderately well annealed. Since the heat effect (endothermic effect, for instance) is just getting

\* See footnotes 1(c) and 2.

depending on  $\tau_0$ , the initial value of  $\tau$ . Although no simple solution for this relation is available, the course followed by  $T - \tau$  during any heating or cooling is quite definite for any given set of initial conditions. Since  $(1/g) + (1/h) = 1/k$ , as previously shown,<sup>2</sup> equation (7) becomes  $1/x - (h/k)dy/dx = \pm ye^{-y}$  if substitutions\*  $y = (T - \tau)/h$  and  $\pm x = (K/R)he^{T/k}$ , are made. From a practical standpoint, however, neither this nor any of the numerous other forms that can be obtained by various substitutions and transformations seem to possess advantages over equation (7). Although a solution of this equation is lacking, equation (7) as well as equation (8) can be tested by the use of thermal-expansion data and also by a study of their significance with respect to the endothermic and exothermic effects observed in glass.

### (3) Relation of Equilibrium Temperature to Changes in Length

When  $\tau$ , that is,  $T - ky$ , has been computed by means of equation (8) for various temperatures through the use of assumed or determined values for  $k$ ,  $K$ ,  $x_0$ , and  $R$ , the computed results may be compared with experimental data obtained on any property that is subject to the extraordinary changes observed when a glass is heated or cooled through its annealing range. The linear thermal-expansion curves may be used, for example, although it is difficult to determine precisely the expansivities for those values of  $T$  and  $\tau$  that are in that part of the practical annealing range where softening begins. Apparently, no great errors are introduced by assuming that the linear expansivities ( $a$  for varying  $T$  and constant  $\tau$ , and  $\alpha$  for varying  $\tau$  and constant  $T$ ) are approximately constant throughout the annealing range and have values that can be determined with reasonable precision near the lower limit and sometimes even throughout the lower half of that range. Thus, it appears that the linear expansion

(† footnote concluded from page 242)

per unit length through the annealing range is expressed approximately by equation (9),

$$(L - L_0)/L_0 = a(T - T_0) - \alpha(\tau - \tau_0) \quad (9)$$

if  $L_0$  is the length of the glass sample when  $T = T_0$  (a temperature usually chosen at some point within or just below the annealing range that may or may not be the one for which  $x = x_0$  and  $\tau = \tau_0$ ). The use of equation (9) in conjunction with equation (7) is considered in section III.

## III. Application of Equations to Thermal Expansion Data

### (1) Thermal-Expansion Curves

In a progress report, the writer<sup>1(b)</sup> showed the inadequacy of equations (6) and (8) by applying them to experimental expansion data. Although not indicated definitely, much of the discrepancy between experimental and computed results could be eliminated by assuming that the viscosity of glass is affected by changes in  $\tau$  much as it is by changes in  $T$ . A résumé of that report and a fuller discussion of the effect of changes in  $\tau$  are presented here.

The expansion data used were obtained on two samples of a borosilicate crown of the usual kind employed in thermometers that are graduated to temperatures exceeding 500°C. One of the samples was treated at a high temperature (approximately 850°C.) and cooled rapidly in moving air in order to prevent  $\tau$  from falling below 650°C. The cooling rate of this treatment in fact was such that the red glow of the small sample in a comparatively dark room disappeared in about 5 seconds. The other sample was treated for several weeks at 500°C. in order to reduce  $\tau$  to that temperature. Each sample consisted of three small pyramids of a type that is suitable for expansion measurements by the interferometric method and that makes very rapid cooling possible after treatments at high temperatures. The expansion measurements extended from room temperature to the softening point near 620°C. and were made by Saunders according to the weighted-spacer method which he has described.<sup>5</sup>

The portions of the resulting expansion curves between 260° and 620°C. are shown in Figs. 1 and 2 (curves (1) and (1')). The relative placement of the two expansion curves (curve of the chilled sample above that of the annealed) was determined by making them practically coincide at about 615°C. where both samples were just entering the range of slight but noticeable softening. The  $\tau$  values of the two samples in this range were presumably almost equal, and the values of  $T - \tau$  were doubtless not much greater than a degree since the heating rate used in these tests was only 3°C. per minute; that is, within the range of appreciable softening, it is difficult to maintain  $T - \tau$  at values exceeding 1 degree unless the rates of heating or cooling are exceptionally high. In other words, if deformation of the samples had not taken place, the ex-

under way when  $d\tau/dT$  is unity, the beginning of the endothermic (or rapid expansion) effect in a moderately annealed sample apparently often occurs at a somewhat lower temperature than in the less or the more thoroughly annealed samples. Examples of series of curves that present this appearance are found in Figs. 4 and 8 of a previous publication.<sup>1(c)</sup>

For the chilled and annealed samples that were used in the expansion tests described in this paper, the temperatures at which  $d\tau/dT$  equaled unity were estimated to be 586° and 578°C., respectively. When  $T_m$  was computed by using the values found for  $k$ ,  $h$ , and  $K$  (or  $R/K$ ), the value 577.5°C. was obtained.

If equation (8) were applicable, there should be no  $T_m$  above which the maxima of the endothermic effects must be reached and consequently they would not be confined to a limited range. Experience shows that the temperature range in which these maxima occur is limited even if the treatment of a glass is varied greatly.

\* In making these substitutions, the identity  $e^{T/k} / e^{T/h} = e^{T/k} / k e^{(T - T)/h}$  is used. When appearing, however, in an exponent as in this case,  $T - \tau$  (although its magnitude is presumably proportional to certain molecular strains) cannot be considered as necessarily having an effect analogous to that of a mechanical load in its relation to inelastic deformations.

<sup>5</sup> J. B. Saunders, "Improved Interferometric Procedure with Application to Expansion Measurements," *Jour. Research Nat. Bur. Standards*, **23** [1] 179-95 (1939); *R. P.* 1227; *Ceram. Abs.*, **18** [11] 306 (1939).

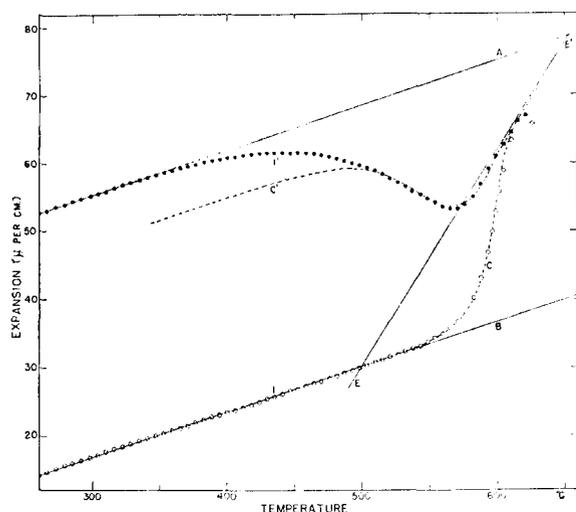


Fig. 1.—Comparison of computed and experimentally determined thermal-expansion curves for a borosilicate thermometer glass; 1 and 1', experimental curves for annealed sample (circles) and chilled sample (dots), respectively; A and B, tangents to curves 1' and 1, respectively, at points near 300°C.; EE', approximate thermal-expansion curve of glass when it does not depart from equilibrium because heating and cooling rates are very low; C and C', computed thermal-expansion curves (broken lines) corresponding to 1 and 1'. These curves were computed in accord with equation (7), and the departure of C' from 1' below 500°C. results presumably because equation is inapplicable while a glass is in its viscoplastic stage.

pansion curves presumably would have practically coincided with the equilibrium curve from this point upward. This curve, represented by the line EE', intersects the expansion curve of the annealed sample at 500°C. because up to that point there was no appreciable change in the  $\tau$  value of that sample. If the heating rate from this point had been made very low, the resulting expansion curve on the annealed sample would have coincided approximately with EE' from 500°C. until the temperature of appreciable deformation was reached. A line (such as EE') representing the sequence of equilibrium conditions in terms of change in length undoubtedly should be somewhat curved, but, in this purely demonstrational presentation, relatively minor details of this nature will be ignored for the purpose of simplicity.

## (2) Method of Estimating Expansivities

Between 300° and 500°C., the expansivity of the annealed sample was found to be about 0.066 ( $\mu$  per cm. per °C.); below this range, the average was less than 0.063. The expansivity of a severely chilled glass usually increases a few percent at atmospheric temperatures, but the expansivity of the chilled sample at 300°C. was also about 0.066 in the same units. If a line coinciding with the expansion curve of the chilled glass and having this slope (0.066  $\mu$  per degree) is extended to high temperatures, it intersects EE' at 653°C., which is presumably the initial value of  $\tau$  in the chilled sample and also its value during the earlier steps of the expansion test and until the equilibrium condition of

the sample begins to change appreciably as it appears to have done immediately above 340°C. This temperature is about 150° below the lower limit of the practical annealing range of this glass and is, therefore, far below the range in which purely viscous flow is presumed to be possible.

If the relative placement of the two curves is approximately correct, the difference (653° to 500°) between the initial  $\tau$  values of the two samples produces a difference in length of 38.4  $\mu$  per cm. This corresponds to a linear expansivity of 0.251  $\mu$  per cm. per degree change in  $\tau$ . In the usual units, this value also corresponds to a volume expansivity of  $0.75 \times 10^{-4}$  for a change of one degree in  $\tau$ , and it is about 0.7 as large as the value found by testing a borosilicate optical glass. The sum,  $0.251 + 0.066 = 0.317$ , is presumably  $10^4$  times one third the volume expansivity of the glass when it behaves as a liquid within its annealing range, that is, when this particular glass follows its equilibrium curve (line EE').

## (3) Determination of Equilibrium Temperatures

Knowing the expansivities and the initial  $\tau$  values, it is a simple matter to compute the  $\tau$  value at any temperature,  $T$ , from the expansion curves. Thus, for the chilled glass,  $\tau = 653^\circ - [0.066(T - 300^\circ) - (L_T - L_{300})/L_{300}]/0.251$  (see equation (9)) and, for the annealed glass, the expression is the same except that 500° replaces 653°C. In Fig. 3 (curve (1), circles, annealed; curve (1'), dots, chilled glass), the  $\tau$  values so obtained are plotted against  $T$ .

## (4) Insufficiency of Equation (8) Which Relates Viscosity to Actual Temperature Only

In view of the temperature range involved and the form of the  $\tau$  curve for the annealed glass, it is comparatively easy to select values for  $K$  and  $k$  that make it possible to compute, by means of equation (8), a curve that follows the experimental curve moderately well. By introducing the  $\tau$  values so computed into equation (9) and thus transforming to expansions again, the computed results shown in Fig. 2 (curve (2)) were procured. To delay the beginning of the rapid expansion to the point indicated by the experimental curve, it was necessary in computing these  $\tau$  values and expansions to assume that  $K_T$  possessed the value unity (reciprocal of one hour) at a rather high temperature (560°C.). It was then necessary to assign a rather high value (15 degrees) to  $k$  in order to prevent the expansion from developing too rapidly when  $T - \tau$  reached the rather large values indicated by the experimental results. As a result, when this difference became comparatively small at high temperatures, the rate of expansion was too low as a comparison of curves (2) and (1) in Fig. 2 indicates. When the values assigned to  $K$  and  $k$  were used to compute (2') for the chilled sample, the contraction effect that accompanies a decreasing  $\tau$  was displaced to temperatures that were far too high, since its range almost coincided with that of the rapid expansion of the annealed sample. As a matter of fact, such a result is to be expected because, in the development of equation (8), the viscosity at any temperature was always

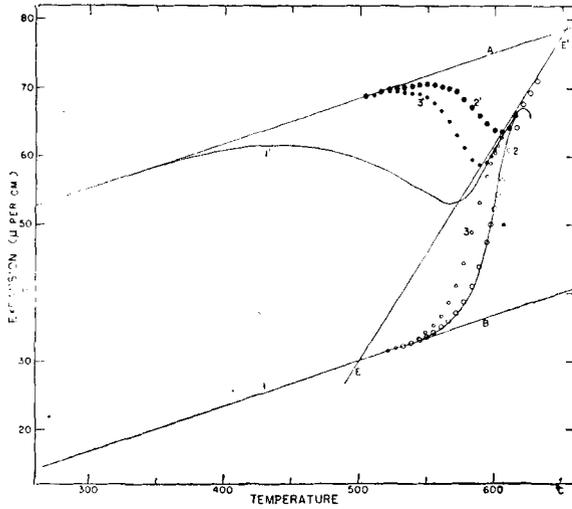


FIG. 2.—Comparison of thermal-expansion curves determined experimentally and computed in accord with equation (8); curves 1, 1', A, B, and EE' reproduced from Fig. 1; 2 and 2' (large circles and large dots, respectively), correspond to curves 1 and 1', computed on assumption that necessary constants were  $k = 15$  degrees,  $K = e^{-37.3}$ , and  $T_1 = 560^\circ\text{C}$ . and also that initial  $\tau$  values were  $500^\circ\text{C}$ . and  $653^\circ\text{C}$ . for annealed and chilled samples, respectively; 3 and 3' (small circles and small dots, respectively), similarly computed except constants were  $k = 13.57$  degrees,  $K = e^{-40.1}$ , and  $T_1 = 544.1^\circ\text{C}$ . This comparison of experimental and computed curves indicates that equation (8) is unsatisfactory, probably because viscosity varies as equilibrium temperature changes.

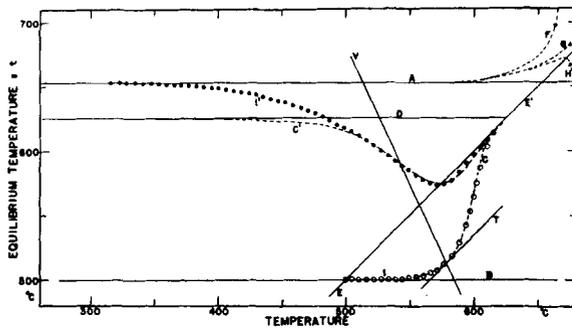


FIG. 3.—Curves relating to changes in equilibrium temperature as glass is heated or cooled; curves 1 and 1' (circles and dots, respectively), equilibrium temperatures computed in accord with equation (9) from corresponding experimental curves 1 and 1' of Fig. 1; C and C' (broken lines), equilibrium temperatures that correspond to curves C and C' of Fig. 1 and computed by a step-by-step method based on equation (5); B, A, and D, tangents ( $d\tau/dT = 0$ ) to equilibrium temperature curves 1 and C, 1', and C', respectively, at points near  $300^\circ\text{C}$ .; EE', trend of equilibrium temperature (slope  $d\tau/dT = 1$ ) when glass remains in constant equilibrium because rate of heating (or cooling) is very low; T (parallel to EE'), tangent to curves 1 and C when degree of superheating (or  $T - \tau$ ) reaches maximum; V, one of family of curves indicating conditions for constant viscosity; F, G, and H, approximate courses that would be followed by equilibrium temperature during cooling if cooling rates ( $30^\circ$ ,  $37.5^\circ$ , and  $40^\circ\text{C}$ . per second, respectively) from comparatively high temperatures prevented equilibrium temperature from falling below  $653^\circ\text{C}$ . when  $T$  became zero.

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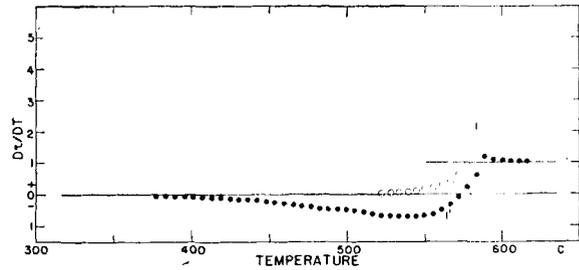


FIG. 4.—Slopes of equilibrium temperature curves 1 and 1' (Fig. 3) at various actual temperatures.

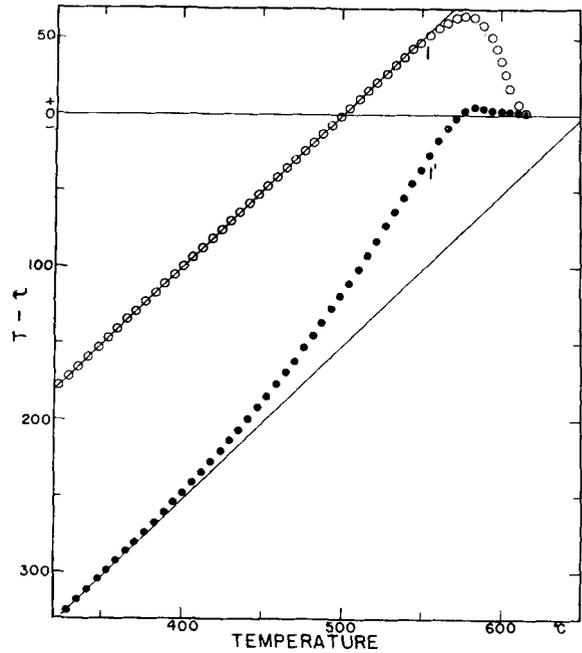


FIG. 5.—Degrees of undercooling and superheating ( $T - \tau$ ) indicated by curves 1 and 1' in Figs. 1 and 3.

presumed to be the same regardless of the value of  $\tau$ . Consequently, unless there is a large difference in the absolute magnitude of the values of  $T - \tau$  in the two cases, the contraction of the chilled sample and the rapid expansion of the annealed sample will begin at about the same temperature. The maximum rates of contraction and expansion in these cases will also be attained at temperatures that are not materially different.

### (5) Determination of Constants in Equation (7) Which Relates Viscosity to Actual and Equilibrium Temperatures

Since differential equation (7) has not been solved explicitly for  $\tau$  (except in the form of series suitable only for relatively narrow ranges in  $T/g$ ), the foregoing simple procedure cannot be used in applying this equation to experimental data. If, the slopes,  $d\tau/dT$ , are sufficiently well known at three well-separated points in the annealing range, the constants,  $g$ ,  $h$ , and  $K/R$ , can be determined. Having made such determinations, it

is possible to compare computed values for the ratio  $(d\tau/dT)/(T - \tau)$  at various temperatures with the similar ratios that can be obtained by using the slopes (Fig. 4) and departures from equilibrium (Fig. 5) that are both obtained from curves 1 and 1' in Fig. 3. The relative error in the slope determinations from these curves unfortunately is large over much of the range of the extraordinary heat effects and, in some cases (especially throughout the range of the superheating of chilled specimens), the relative errors in determining  $T - \tau$  are also rather large. The data obtained for  $d\tau/dT$  and  $T - \tau$  (Figs. 4 and 5) are considered to be adequate for the purpose since this paper is purely a demonstrational presentation without pretense of high precision.

The three ranges in which these data seemed to be comparatively good were near the respective temperatures (1), that at which  $d\tau/dT = 1$ ; (2) that, at which this slope attained a maximum in the case of the superheated annealed sample; and (3), that near the temperature at which the slope reaches a minimum (maximum negative value) in the case of the under-cooled chilled sample. Letting  $p$  and  $d$  symbolize slope  $(d\tau/dT)$  and departure from equilibrium  $(T - \tau)$  and the subscripts  $c$  and  $a$  indicate the chilled and annealed samples, respectively, data in the first two cases were (1),  $p_a = 1.00$ ,  $T_a = 578.0^\circ\text{C}$ .,  $\tau_a = 513.0^\circ\text{C}$ ., and  $d_a = 65.0$  degrees; and (2),  $p_a = 5.37$ ,  $T_a = 603.0^\circ\text{C}$ .,  $\tau_a = 578.0^\circ\text{C}$ ., and  $d_a = 25.0$  degrees. In the third case, data at a point chosen near that of the minimum were (3),  $p_c = -0.72$ ,  $T_c = 542.9^\circ\text{C}$ .,  $\tau_c = 589.7^\circ\text{C}$ ., and  $d_c = -46.8$  degrees. Use of the first and third of these sets of data with equation (7) gives the result  $h/g = (\tau_c - \tau_a)/(T_a - T_c) = 2.185$ .\* On using this ratio in connection with the second set of data, it follows that  $g = 19.78$ ,  $h = 43.22$ , and  $k = 13.57$ . This value of  $k$  is rather high, but it is by no means so extreme as the value 15 that appeared necessary in the case of equation (8).

In using the value found for  $h/g$  in connection with the second set of data, advantage was taken of the fact that  $p_a = 5.37$  was presumably a maximum. At such a point,  $dp/dT = 0$ , and thus, on differentiating equation (7), it follows that for this condition  $h = (p + h/g)d/(p - 1)$  and that  $p = (1 + d/g)/(1 - d/h)$ . These equations also hold for a minimum in  $p$ . The fourth set of data was chosen at a point where such a minimum appeared to be and was as follows: (4),  $p_c = -0.73$ ,  $T_c = 540.0^\circ\text{C}$ .,  $\tau_c = 591.6^\circ\text{C}$ ., and  $d_c = -51.6$  degrees, and it was found that the expression relating  $p$  and  $d$  was reasonably well satisfied by these data without changing  $h$  and  $g$ .

Having determined  $g$  and  $h$ , any of these sets of data can be used to determine  $K/R$  and also  $T_1/k$  if  $T_1$  symbolizes the temperature for which the glass, when

\* By introducing two sets of data (such as the first and third presented above into equation (7)) and by equating the logarithms of the ratios of the corresponding members of the two resulting equations, a rearrangement of the result yields  $h/g = (\tau_3 - \tau_1)/(T_1 - T_3) + (h/(T_1 - T_3)) \ln(p_1 d_3 / p_3 d_1)$ . In this case, the third set of data was taken at a point such that  $p_1/d_1 = p_3/d_3$  approximately. The logarithmic term consequently disappeared.

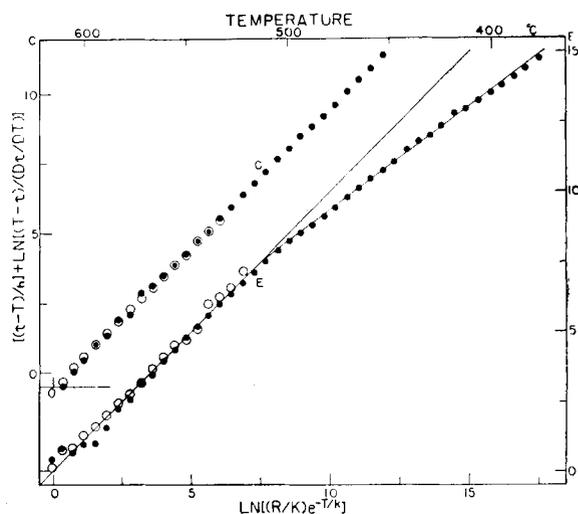


FIG. 6.—Test of degree to which changes in equilibrium temperature satisfy equation (7); curve  $E$ , tests of results (curves 1 and 1' in Figs. 3, 4, and 5) derived from thermal-expansion data (curves 1 and 1' in Fig. 1), ordinates on right; curve  $C$ , tests of data derived from curves  $C$  and  $C'$  in Fig. 3 (displaced ordinates on left); circles and dots, annealed and chilled glass, respectively, in both cases.

in equilibrium ( $T = \tau$ ), has a relaxation time,  $1/K_T$ , equaling 1 hour. That is,  $K = (pR/d)e^{-T/k} / e^{-\tau/h} = e^{-T_1/k}$ . Since  $R = 180^\circ$  per hour ( $3^\circ$  per min.), the two values for  $K$  are  $K_a = e^{-40.20}$  and  $K_c = e^{-40.05}$  if the second and fourth sets of data are used. The corresponding values for  $T_1$  are  $545.6^\circ$  and  $543.5^\circ\text{C}$ . Two such sets of data should give the same values for  $K$  and also for  $T_1$  if equation (7) is applicable regardless of the treatment received by the glass; the fair agreement found here exceeds what should be expected in view of the unreliability of the  $d$  and  $p$  determinations. There is the probability, moreover, that  $R$  varied more than was apparent during the tests.

After these constants are determined for a glass, the relaxation times,  $1/K_T$ , can be obtained for all conditions and temperatures in the annealing range. Even the viscosity coefficients,  $\eta$ , can be estimated if the elastic modulus,  $E$ , is known within reasonable limits, that is,  $\eta = E/K_T$ .

## (6) Testing Applicability of Equation (7)

(A) *First Method*: From equation (7), it is apparent that a straight line should result if  $\ln(d/p) - d/h$  is plotted against  $\ln(R/K) - T/k$ . That is, as long as the viscosity varies approximately as assumed (and also provided the relation between it and the extraordinary expansion and contraction is that assumed), there should be within the annealing range no departures from this straight line that are not ascribable to uncertainties in the data. For this test, the  $p$  and  $d$  values from Figs. 4 and 5 and the  $h$ ,  $k$ , and  $K$  (average) values given in section (5) were used. (Since the rate of heating was  $180^\circ\text{C}$ . per hour,  $R = e^{5.193}$  and  $\ln(R/K) = 45.320$ .)

The results of this test are shown by curve  $E$  in Fig. 6. Between  $600^\circ$  and  $500^\circ\text{C}$ ., the departures from a straight line are reasonably small except in a

few cases in the range where the chilled glass became superheated and the procurement of data without very large relative errors was impossible. Beginning, however, near 500°C. and extending to lower temperatures, there is a steadily increasing departure from a straight line by the results for the chilled glass. The sense of the departure indicates that  $d\tau/dt$  at temperatures below the annealing range has absolute values (at least when  $\tau - T$  is large) that are greater than they would have been if the deformability had continued to decrease with decreasing temperature according to its manner of decrease within the annealing range. That is, the relatively distended glass of the chilled sample collapses under heavy loads more readily at these relatively low temperatures than would have occurred if it had retained an almost purely viscous character with a viscosity coefficient that continued to decrease with  $T$  and  $\tau$  as in the annealing range. This result was expected because experience in attempts at establishing equilibrium conditions at such relatively low temperatures led to the conclusion that the rate of collapse at these temperatures is no longer roughly proportional to the load, as in the annealing range, but decreases so much more rapidly as the collapse progresses that (in the case of a glass approaching equilibrium at a constant temperature) the product of  $e^{(\tau - T)/h}/(T - \tau)/dt$  decreases rapidly (instead of remaining constant as it would if the glass were purely viscous) as  $(\tau - T)$  becomes small. That is, when a glass is at a temperature such that it is definitely plastic, this product exceeds or falls short of  $Ke^{\tau/k}$  in magnitude according as the physicochemical "load" (as represented by  $T - \tau$ ) is large or small.

(B) *Second Method:* Since Fig. 6 indicates that the chilled sample did not behave as required by equation (7) until 500°C. was exceeded, it becomes a matter of interest to determine approximately how much lower than 653°C. the initial  $\tau$  value would have been if the glass had behaved according to that equation throughout the heating. Such a determination can be made by laborious step-by-step computations.

If the temperature is constant, equation (5) can be written in the form  $e^{-z}dz/z = -Ke^{\tau/k}dt$ , in which  $z = (\tau - T)/h$ . The solution of this for any interval of time,  $\Delta t$ , for instance, is  $Ei(-z_1) - Ei(-z_0) = -Ke^{\tau/k}\Delta t$ , in which  $z_0$  and  $z_1$  are the values of  $z$  at the beginning and end of the time interval. Consequently, the  $\tau$  value reached by a treatment at  $T_0$  is  $\tau_1 = hz_1 + T_0$ . Assuming the temperature to be changed so sharply from  $T_0$  to  $T_0 + \Delta T$  at the end of this first step that  $\tau_1$  is unchanged, it follows that  $e^{\tau_0/k}$  is changed to  $e^{(\tau_0 + \Delta\tau)/k}$  and that  $z_0$  is changed from  $(\tau_0 - T_0)/h$  to  $z_1 - \Delta T/h$  for the second step in which the glass is treated for an interval,  $\Delta t$ , at an increased temperature. If  $z_2$  is the  $z$  value reached at the end of the second time interval, the  $\tau$  value reached is  $\tau_2 = hz_2 + T_0 + \Delta T$ , and after  $n$  such step-by-step treatments,  $\tau_n = hz_n + T_0 + (n - 1)\Delta T$ .

By making  $\Delta T/\Delta t = R$  the rate of heating in degrees per hour, this exponential integral equation becomes equation (10).

$$Ei(-z_1) = Ei(-z_0) - (K/R)e^{\tau/k}\Delta T \quad (10)$$

Using equation (10) in the step-by-step computation (1946)

and choosing some point  $(T_0, \tau_0)$  on the experimental curve as the initial condition produces a computed curve which passes through this initial point and approximates a curve that satisfies equation (7), and the smaller  $\Delta T$  is made the closer will be the approximation. Intervals ranging from 0.5 to 6 degrees were tried. In some ranges, large intervals can be used without developing the progressively increasing error too much, but when  $\tau$  is changing rapidly, intervals smaller than the least used would have improved the results obtained. The intervals used in computing curves (C) and (C') in Fig. 3 were 0.5 and 1 degrees, and  $T_0$  and  $\tau_0$  were 516° and 608.4°C., for the chilled sample, and 530° and 500°C. for the annealed sample. The computed curves and the  $\tau$  curves derived directly from the experimental data therefore intersect at these points. These computed curves, (C) and (C'), indicate in both cases that the glass at temperatures above 516°C. behaved very nearly as equation (7) requires.

When the previously employed test (made by plotting  $\ln((d/p)e^{-t/h})$  against  $\ln((R/K)e^{-\tau/k})$ ) was applied to these computed curves, the results shown by curve (C') in Fig. 6 were obtained. In view of the fact that intervals no smaller than one-half degree were used, these results are as satisfactory as could be expected, and they indicate that the computed curves, (C) and (C') (Fig. 3), throughout most of their courses are not far from curves that fully satisfy equation (7).

### (7) Evidences of Plasticity

In Fig. 3, the trend of curve (C'), compared with that of curve (1') at temperatures below the annealing range, suggests that 653°C. is about 28° higher than the initial  $\tau$  value required if equation (7) had expressed reasonably well the behavior of the chilled sample at temperatures below as well as within the annealing range. In accord with previously expressed surmises, this difference between the actual and required initial  $\tau$  values is presumably the result of the failure of equation (7) to take into account the increased mobility of plastic glass when subjected to very large loads. In this connection, curve (E) of Fig. 6 indicates that those points obtained below 516°C., where  $T - \tau$  is almost proportional to  $T$ , would have been aligned approximately with those obtained above that point if the abscissas for the lower of these ranges had been computed by means of the expression  $\ln(R/K) - T/k - (513 - T)/52.6$ . It is to be presumed that the values of the constants  $T'$  and  $g'$  of this added term (513° and 52.6° in this particular case) depend, at least, on the initial  $\tau$  value and the rate of heating. In view of previous mention that an added term containing such constants might be indicated under certain conditions, the manner in which the results below 516°C. depart from the basic straight line suggests that the deformability of glass in its supposedly plasticoviscous condition is actually an exponential function of the load as well as of the temperature. This possibility merits further investigation.

This discussion of the possible characteristics of this particular glass at temperatures below 516°C. must not be taken as a suggestion that it undergoes some sudden

and definite change at that point. It is more probable that all changes that take place in ordinary glasses while heating or cooling do so gradually over a considerable temperature range. That is, this point for the upper limit of the plastic range has about the same significance as the softening point or the point chosen as the beginning of the rapid expansion range.

#### (8) Use of Equation (7) in Determining Cooling Curves

The magnitude of the cooling rate that produced an initial  $\tau$  value of 653°C. was a matter of some curiosity. Approximations to cooling curves (as shown in Fig. 3) were therefore computed by the step-by-step method,\* and it was assumed that  $\tau$  had fallen to 653°C. by the time  $T$  had fallen to 550°C., below which there had been no further appreciable change in  $\tau$ . It was thought that the cooling rate might have been about 40° per second, since it appeared that the sample in cooling from 850°C. had lost all redness in about 5 seconds. The cooling curve procured for that rate suggests, however, a lower rate since it indicates a crossing of the equilibrium curve at a temperature slightly above 670°C. rather than at 850°C. When a rate of 30° per second was used in the computation, the resulting curve began at about 655°C. to diverge from the equilibrium curve instead of continuing to

\* Equation (8) can be used to determine directly a rate of cooling that is definitely lower than the required rate to produce a given  $\tau$  value ( $\tau'$ ) when  $T$  becomes zero. When  $T$  reaches zero,  $x = Kk/R$  and is very small unless  $R$  has a very low value. Consequently,  $e^x = 1$  and  $Ei(-x) = \ln(Kk/R) + \gamma$  approximately. (Euler's constant =  $\gamma = 0.5772$ .) Thus, equation (8), for cooling from an equilibrium temperature,  $T_0$ , to zero degrees becomes  $-\tau'/k = \ln(Kk/R) + \gamma - Ei(-x_0)$  which, since  $x_0 = (Kk/R)e^{T_0/k}$ , may be changed so as to become  $[(T_0 - \tau')/k] - \gamma = \ln x_0 - Ei(-x_0)$ . From this equation,  $x_0$  is easily determined approximately when the left-hand member is known and adequate tables of exponential functions and integrals are available. Thus,  $R$  is known if  $T_0$  and the necessary constants of the glass are known. Moreover,  $x_0$  is so large, when the starting temperature,  $T_0$ , is high and  $R$  is not too great, that  $Ei(-x_0)$  is negligible. Consequently, for such cases,  $R = Kke^{\gamma + \tau'/k}$ . Using the values previously found for  $K$  and  $k$  and assuming that equilibrium was established when cooling began at a starting point near 850°C., it is apparent that  $x_0$  is large for this case and that  $R = 19.9^\circ$  per second approximately. Thus, a rate computed in this manner and known to be too low, is about one half that indicated by the step-by-step computation described previously.

It is desirable occasionally to estimate a minimum for the rate at which a glass in equilibrium at some temperature,  $T_0$ , can be cooled to room temperature without material change in  $\tau$  from  $\tau_0 = T_0$ . In such a case,  $R$  must be so large that  $x_0$  becomes very small. It then becomes obvious, on expanding  $Ei(-x_0)$  in the above equation for determining  $x_0$ , that  $T_0 - \tau' = kx_0$  approximately and that  $R = Kk^2e^{T_0/k}/(T_0 - \tau')$ . That is, if equation (8) were applicable,  $R$  is the minimum rate necessary to prevent  $\tau_0 - \tau'$  from exceeding some small assigned value. If  $k$  is replaced by  $g$ , and  $K$  by  $Ke^{T_0/h}$ , the result is that which would have been obtained if equation (7) had been used for the same purpose and on the assumption that  $\tau$  varied so little that  $e^{\tau/h}$  could be treated as a constant. The ratio of these results for  $R$  is  $g^2/k^2$  and the smaller result, at least, is much lower than required, but such computations aid in estimating the cooling rates required to obtain desired  $\tau$  values.

approach it. That is, this rate was much too low unless, a higher rate preceded it, for example, from 850° to about 660°C. Without using very small intervals in the computation, it also appears that a rate of 37.5° per second is somewhat too low. Thus, it seems that the probable average rate of cooling in the chilling treatment was slightly under 40° per second (see curves (F), (G), and (H) in Fig. 3).

### IV. Application of Equations to Endothermic and Exothermic Effects

#### (1) Relation of Heat Effects to Inelastic Deformability

As previously stated,† the manner in which strain is dissipated in annealing glass and the character of the exothermic and endothermic effects, observed when chilled and annealed glasses are heated, suggest the gradual development and disappearance of a degree of plasticity in glass as cooling and heating, respectively, proceed within and especially below the practical annealing range. As in the case of the expansion effects, so also in that of the endothermic effect, the degree of plasticity that develops within the useful annealing range can apparently be ignored. At unusually low and, for most purposes, impractical annealing temperatures, it seems necessary to assume the existence of a considerable degree of plasticity in seeking an explanation for the progressive changes which appear in the exothermic effect of samples of a glass that, subsequent to a severe chilling from a high temperature, have been annealed for different periods of time at a very low annealing temperature. Curves showing such effects have previously been presented,<sup>1(a)</sup> and the progressive changes are believed to indicate that some molecular readjustments leading to equilibrium conditions develop rather readily at low treating temperatures while others develop very slowly or not at all until the glass is subjected to higher treating temperatures. Such differences in the rates of development are easily explained if it is assumed that only a portion of the flow surfaces normally available at temperatures in the annealing range are still open at lower temperatures for viscous flow while other portions are either entirely closed or are practically so unless exceptional loads are applied.

Careful consideration will show that the heat generated by the flow, as the elastic molecular strains (which are excessive because of superheating or undercooling) are relaxed, is probably negligible compared with the observed heat effects. These considerations then lead to the conclusion that the observed heat effects are the result of a rapidly changing specific heat as the equilibrium temperature changes.

#### (2) Experimental Conditions in Determining Heat Effects

For understandable reasons, the actual conditions that exist in obtaining curves which show exothermic and endothermic effects are always different from the idealized conditions assumed in discussing the methods

† See Tool, footnote 2, and Tool and Valasek, footnote 3.

of test. Generally, the test sample is assumed to be so small that any temperature gradients within it while heating or cooling at a considerable rate can be neglected. Actually, this condition is seldom approximated and, as a result, the observed heat effects are blunted and spread over a temperature range that is somewhat too broad.

In tests of this kind, the well-known differential-thermocouple method is commonly used. One hot junction of this couple is in the test sample, while the other is either in the wall that supplies the heat to the heating sample and that supposedly conforms to an isothermal surface or it is in a so-called neutral body that is enclosed, in contact with the sample, by the same isothermal wall. There is also, supposedly, no transfer of heat from one of these junctions to the other that would appreciably affect the magnitude of the heat effects that are sought. These ideal conditions at best are only approximated and, as a result, any improvement in the test conditions usually accentuates the effects as they are shown by heating curves.

### (3) Relation Between Heat Effects and Changes in Equilibrium Temperature

If  $T$  is the temperature of the test sample at any instant and if the simultaneous temperature of the isothermal wall is  $T_w$ , the rate of heat (II) supply to the sample is  $dH/dt = A(T_w - T)$ . Under idealized conditions, the factor  $A$  is the product of the area and the so-called external conductivity of contact between sample and wall. If the sample weighs 1 gm., the rate of its heat absorption equals this rate of supply and is  $s''dT/dt + \sigma d\tau/dt$  in the case of glass. In this expression,  $\sigma$  is the heat absorbed per degree increase in  $\tau$  and  $s''$  is the normal specific heat. Both of these coefficients, like the expansivities, are functions of  $\tau$  and  $T$ . Thus,  $s'' = s(1 + bT + \beta\tau) = s' + s\beta\tau$  serves as a first approximation for the change in the specific heat with these temperatures. In the second form of this approximation,  $s'$  is presumably independent of  $\tau$  and is, consequently, the same for all samples of a glass whether chilled or annealed. The normal specific heat of a material represents (in the case of heating) both the energy required to increase the thermal agitation and that to expand the material against the so-called intrinsic pressure that results from the molecular attractions. Increases in  $\tau$  do not affect the thermal agitation but are normally accompanied by expansions which generally reduce the intrinsic pressure somewhat, since a separation of the molecules usually reduces their mutual attraction. Consequently,  $\sigma$  represents only an energy of separation and  $\beta$  is normally negative.

By equating the heat supplied to that absorbed and by introducing the first approximation for  $s''$ , the relation,  $T_w - T = (R/A)(s' + s\beta\tau + \sigma d\tau/dT)$ , is obtained and, for the neutral body, which presumably has no peculiar characteristics in the temperature range of the tests, the corresponding equation is  $T_w - T_n = (R_n/A_n)s'_n$  if  $R$  and  $R_n$  are the heating rates of the sample and neutral body, respectively. It is helpful in practice if  $s'_n = s'$ , and  $A_n = A$ , approximately. In such a case, equation (11) results.

$$T - T_n = (R/A) (s' (-1 + R_n/R) - s\beta (\tau - \tau_a) - \sigma d\tau/dT) \equiv G \quad (11)$$

In this equation,  $\tau_a$ , the  $\tau$  value for a very well-annealed sample, is introduced because  $\tau$  never can be reduced to zero in ordinary glasses.

In the following discussion,  $G$  represents the experimental results found for  $T - T_n$ . Ordinarily these experimental results are greatly affected by gradients and consequently seldom approximate the values that  $T - T_n$  should have under ideal conditions. For example, in testing a well-annealed sample,  $T - T_n$  should approximate zero throughout the range between the temperature at which a steady heating condition is first established and that at which the endothermic effect begins. This is obvious because  $R_n = R$ ,  $\tau = \tau_a$ , and  $d\tau/dT = 0$ . However,  $G$  may have a fairly large value that is either positive or negative, depending on the characteristics of the heating furnace and the manner of packing the sample and neutral body. When proper care is taken, the disturbing gradients do not change materially between the time a steady condition is first developed and that at which granular samples show a considerable degree of sintering. Since a disturbing degree of sintering seldom takes place below temperatures that are well above those required for the completion of the endothermic effect, a second steady condition of heating is usually developed. In these ranges of steady heating, the  $G$  values change slowly and only because  $A$ ,  $s'$ , and  $\sigma$  change slightly as  $T$  (and also  $\tau$ , when the second steady condition is reached) increases. Thus, when the results for  $G$  are plotted against  $T$ , the curves show two distinct levels, one preceding and the other following the heat effects. If these levels are represented by  $G_1$  and  $G_2$ , repeated tests on identical samples show that  $G_1 - G_2$  does not vary greatly if proper precautions are taken. For this reason,  $G$  will be considered to represent properly  $T - T_n$  plus an error that is practically constant and can be neglected at least as long as only differences in the determinations of  $G$  for a single test are considered.

When several samples of a glass are tested, they will all have attained approximate equilibrium when the second level is reached and the several curves can properly be made to coincide approximately in this region, although the  $G_2$  values may be quite different because of the errors mentioned. Because the variation in  $G_1 - G_2$  is usually small in the case of identical samples, the initial levels of the curves will then almost coincide unless there is a wide spread in the initial  $\tau$  values of the several samples. That is, when the spread is not large, the effect of the differences in the initial  $\tau$  values is often masked by the errors in determining  $G_1 - G_2$ , but this masking is insufficient to hide the effect of differences as large as those found between the  $\tau$  values of severely chilled and well-annealed samples (Fig. 7, curves (27) and (38), see also Tool and Eichlin, Fig. 8, footnote 1(a)).

The significance of the difference between the initial levels of these curves is at once apparent from equation (11) when it is considered that  $d\tau/dT$  is approximately zero and unity in the ranges of the first and second levels, respectively. To make this significance more apparent, it will be assumed that the change in  $A$  with

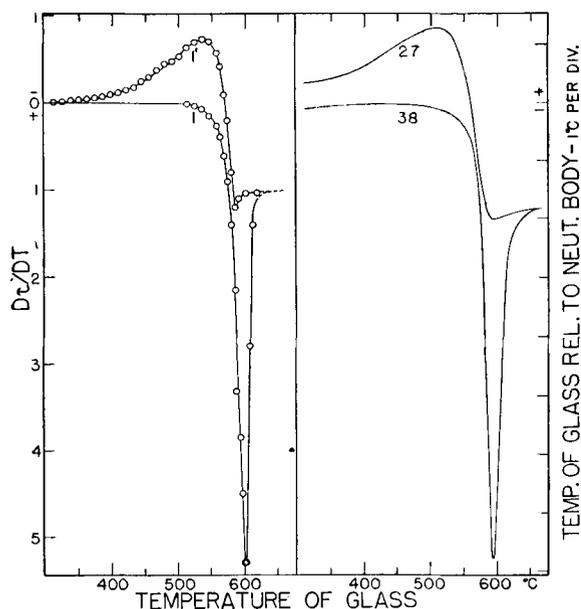


FIG. 7.—Exothermic and endothermic effects; curves 27 and 38, observed effects on heating chilled and annealed samples, respectively, of borosilicate optical glass; curves 1 and 1' indicate approximately the heat effects which, according to curves 1 and 1' in Fig. 1 and curves 1 and 1' in Fig. 4, should be found for annealed and chilled samples of borosilicate thermometer glass if decrease in specific heat with increasing equilibrium temperature were insignificant. Separation between curves 27 and 38 below 400°C. is mainly the result of comparatively low specific heat when  $\tau$  is high.

temperature is negligible. In that case,  $G_1 - G_2 = (R/A)(s\beta(\tau_2 - \tau_1) + \sigma)$ , since  $R_n/R = 1$  at both levels. Thus by neglecting the relatively small  $\beta$  term, the difference between the levels is approximately  $R\sigma/A$ , but since  $\beta$  is negative, there is some increase in  $G_1 - G_2$  as the initial  $\tau$  value,  $\tau_1$ , is increased and thereby causes the  $\beta$  term to decrease. The  $\tau$  value,  $\tau_2$ , is that of the temperature at which all of the various curves, when plotted to show the results of a series of tests, are brought into coincidence in the range of the second level. Unless  $R$  is very low or the glass has been chilled severely,  $\tau_2$  is greater than  $\tau_1$ .

When  $d\tau/dT$  reaches its maximum negative and positive values in the temperature range between the first and second levels, the heating curves (as plotted) attain, respectively, their maxima (exothermic effects), which are observed in chilled glasses only, and their minima (endothermic effects), which are very pronounced in all annealed glasses. During the exothermic and endothermic effects,  $(R_n/R) - 1$  takes on small negative and positive values, respectively. Consequently, in both cases, the effect of the  $s'$  term (equation (11)) is to detract somewhat from the effect of the  $\sigma$  term. The  $s'$  and  $\beta$  terms, again being relatively small, may be neglected for simplicity. Then, if the values obtained for  $T - T_n$  at the peaks of the exothermic and endothermic effects are designated by  $G_3$  and  $G_4$ , respectively, it follows that  $G_3 - G_1 = -(R\sigma/A)(d\tau/dT)_{\min}$  and  $G_4 - G_1 = -(R\sigma/A)$

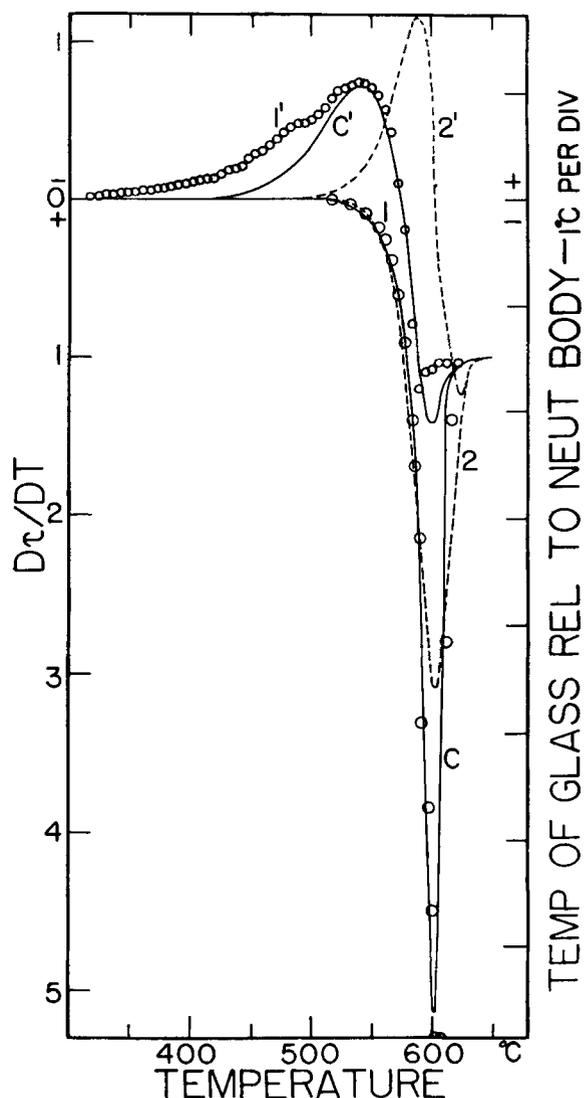


FIG. 8.—Comparison of computed exothermic and endothermic effects; curves 1 and 1', (large and small circles, respectively) same as 1 and 1' of Fig. 7; curves C and C', computed effects in accord with computed curves C and C' of Figs. 1 and 3; failure of equation (7) to account for plasticity of glass below annealing range presumably causes divergence between C' and 1' below 500°C.; curves 2 and 2' (broken lines) computed heat effects in accord with curves 2 and 2' in Fig. 1. Wide divergence between these curves and 1 and 1' presumably caused by failure of equation (8) to account for both plasticity of glass below 500°C. and decrease in viscosity as equilibrium temperature increases.

$(d\tau/dT)_{\max}$  roughly approximate actual conditions. As estimated from curves (27) and (38) in Fig. 7, it appears that the three differences,  $G_1 - G_2$ ,  $G_3 - G_1$ , and  $G_4 - G_1$  are about 1.8, 1.0, and  $-8.0^\circ\text{C}$ ., respectively. Consequently,  $(d\tau/dT)_{\min} = -0.55$ , and  $(d\tau/dT)_{\max} = 4.4$ . When compared with the respective values  $-0.73$  and  $5.37$  found from the expansion curves of the thermometer glass, the values obtained from the differential heating curves of the borosilicate

optical glass appear rather low. This result, however, is to be expected since experimental conditions prevent the heating curves from showing the full magnitude of the heat effects.

If the magnitude of the endothermic effect and the corresponding change in  $\tau$  could be accurately determined (especially in a thoroughly annealed glass), it should be possible to determine the ratio  $s''/\sigma$ , since the relation between the relative cooling of the glass and the change in  $\tau$  should be expressed approximately by  $s''(G_1 - G_4) = \sigma(\tau_4 - \tau_1)$ , in which  $\tau_4$  is the magnitude of  $\tau$  when the relative cooling reaches its peak. A rough estimate which could be 30% or more in error gave the result  $s''/\sigma = 140/8$ . In arriving at the estimate of 140 degrees as the value of  $\tau_4 - \tau_1$ , the initial equilibrium temperature,  $\tau_1$ , of the sample that yielded curve (38) was considered probably to be somewhat below 460°C. and  $\tau_4$  not far below 600°C., since the difference between the actual and equilibrium temperatures is not great when the endothermic effect reaches its maximum.

Since the rate of temperature increase in obtaining the heating curves under consideration was about 6 degrees per minute, it follows that  $\sigma/A = (G_1 - G_2)/R = 1.8/0.1$  and, from this result and the foregoing ratio, that  $s''/A = 315$ . Thus, for any probable value of  $s''$  at temperatures in the annealing range,  $A$  appears to be in the order of  $10^{-3}$ . This value is an approximation only but is within reasonable limits, since the conduction of heat from an undetermined surface in the furnace through a wall of uncertain area composed of a thin layer of burned asbestos paper and an undetermined thickness of granular glass or Alundum must be considered in evaluating  $A$ . This uncertainty is of minor significance, however, since the chief purpose of introducing the rough approximations is to give a clearer picture of the significance of the curves resulting from this rather complicated type of test which, although excellent in a qualitative sense, does not lend itself to precise determinations.

#### (4) Estimated Heat Effects Based on Equilibrium Temperatures Obtained from Thermal-Expansion Curves

In addition to the reproduced curves (27) and (38) (which were obtained by tests in which  $R = 6^\circ$  per minute), Fig. 7 also contains curves obtained for comparison by plotting the data, shown in Fig. 5 for  $d\tau/dT$ , according to the manner and scale used in the experimentally determined differential heating curves. Although the two glasses were unlike, the treatments were not too dissimilar. Consequently, it seemed that their observed exothermic and endothermic effects should have had about the same magnitude if the heating rates had been the same. To make  $G_3 - G_1$  and  $G_4 - G_1$  approximate  $1^\circ$  and  $-8^\circ$ , respectively, for the synthetic curves (right-hand scale of Fig. 7), it was necessary to multiply the values of  $d\tau/dT$  by 1.48. This factor corresponds to  $R\sigma/A$ , since  $d\tau/dT$  is zero in the range of the first and unity in that of the second level. When the difference in the heating rates is considered, the factor in this case has little definite sig-

nificance, since halving the heating rate changes the magnitude of the heat effects appreciably. Nevertheless, a survey of the heating curves obtained on a number of ordinary glasses indicates that the average magnitude of  $G_1 - G_2$  is near  $1.5^\circ$ .

In preparing curve (1'), the  $s\beta(\tau_2 - \tau_1)$  term was neglected. As a result,  $G_1 - G_2$  is the same for both synthetic curves, (1) and (1') (Fig. 7); that is, the decrease in  $s''$  (at low temperatures) as  $\tau_1$  is increased was ignored. In all other respects, the two sets of curves, experimental and synthetic, are quite similar in form.

In Fig. 8, the synthetic differential heating curves (2) and (2') (for chilled and annealed samples, respectively) correspond to the curves with similar designations in Fig. 2, and are replicas of those shown before the Glass Division in 1942.<sup>1(b)</sup> As then, these curves are now presented to show that the form of the exothermic effect, if the viscosity of glass depended only on the actual temperature, would not be that of the experimentally determined effect. It is also apparent that the exothermic and endothermic effects of a chilled sample would then occur, contrary to experience, exactly within the temperature range of the endothermic effect of a well-annealed sample. In plotting these curves,  $d\tau/dT = \pm xy$  (see equation (8)) was also multiplied by the factor 1.48 to bring them into conformity with the other curves of Fig. 7.

Curves (C) and (C') correspond to the similarly designated curves in Figs. 1 and 3. These curves were obtained from the values of  $d\tau/dT$  that were procured by the previously described step-by-step computations, and they show a definite approach to the form and relative placement of the experimental curves. They also closely resemble the synthetic heating curves (Fig. 7) that were derived more directly from the expansion data, except that much of the heat developed in the plastic range is not represented. That is, the dependence of the viscosity on  $\tau$  both broadens the exothermic effect and displaces it somewhat toward temperatures below those of the endothermic effects of annealed glasses, even if plasticity is not taken into account.

## V. Speculative Discussion

In addition to the external pressure which is comparatively small, two pressures to be considered in relation to liquids are (1) the thermal pressure arising from the collisions of the thermally agitated molecules and (2) the so-called "intrinsic pressure" arising from the mutual attraction of the molecules. On the average, these opposed pressures are equal when a liquid is in an equilibrium condition at any temperature. Cooling or heating a viscous liquid rapidly from a temperature at which equilibrium has been reached disturbs the balance between these pressures because the liquid is then no longer in an equilibrium condition at the temperature reached and may be said to be in a condition of "distension" or "compaction," respectively. If the change in thermal pressure during a heating or cooling is always greater than that in the intrinsic pressure, it follows that (until a balance is reached between

the pressures) the intrinsic pressure will gradually compress the relatively distended liquid after an undercooling and the thermal pressure will gradually expand the relatively compacted liquid after a superheating.

The work expended when such a compacted liquid with a density,  $D$ , expands at a constant temperature and against the intrinsic pressure,  $P$ , equals the mechanical equivalent of the heat absorbed because of the expansion; thus,  $Pdv = JD\sigma d\tau$ . From the previous discussion of expansion tests, the result,  $dv/d\tau = 0.75 \times 10^{-4}$ , was obtained for the glass tested. For the same glass,  $D = 2.5$  approximately, and according to the previous very rough estimate,  $\sigma = s''/17.5$ . Although  $s''$  for this glass is unknown, it appears from a summary<sup>6</sup> of the results of a number of investigations that the specific heat for the average glass at temperatures in its annealing range is somewhat in excess of 0.2. On the basis of these rough values,  $P = 1.6 \times 10^{10}$  dynes per sq. cm.; that is the intrinsic pressure of glass in its annealing range, appears to exceed  $1.5 \times 10^4$  atmospheres and, as previously pointed out,<sup>1(c)</sup> this is the same order of magnitude as that of values that have been mentioned as possible for the intrinsic pressure of water.<sup>7</sup> If it becomes possible to obtain really dependable values for the intrinsic pressure of glasses and other viscous liquids by this or other means, the values will be of considerable interest since this theoretical pressure is closely related to surface tension and to certain other properties. It is also to be hoped that speculations of this sort may help in those theories that are based on X-ray studies of glass. This hope rests on the assumption that the excessive compactions and distensions found in extremely viscous liquids when superheated and undercooled are in some comparatively simple manner concerned with the character and size of the larger molecules in these liquids.

Such molecules not only add to the viscosity and thus hamper the readjustments of smaller molecules to temperature changes but, when present in relatively large numbers, probably form comparatively extended frameworks<sup>8</sup> (supermolecules) that also become too compacted (or distended) whenever the temperature is rapidly raised (or lowered) and that are delayed in correcting this incompatibility by the viscosity and plasticity to which they presumably contribute so greatly. As previously pointed out,<sup>1(c)</sup> chain- or ring-like molecules<sup>9</sup> and some other forms of extended molecular structures that often have been discussed as possibilities\* might easily be subject to such incompatibilities whenever there is a temperature change.

Within the annealing range, these extended lattice-

like structures formed from simpler molecules are presumably unstable in the sense that they (individually but not on the average if equilibrium exists) are being continually altered in form and size by the thermal agitation of the components. The rate of alteration, however, is presumably so low that the structures not only change comparatively little during a rapid heating or cooling over even considerable temperature intervals but also persist in a compacted or distended state for appreciable periods after the end of the heating or cooling.

As the thermal agitation decreases in a cooling liquid, the persistence of such structures presumably increases rapidly and the rate of increase doubtless parallels that at which the viscosity increases. The structures, moreover, gradually become permanent and probably attain a considerable elasticity of form if the cooling is extended to temperatures considerably below the practical annealing range. The liquid is overly distended at this stage and the intrinsic pressure exceeds considerably the thermal pressure. Consequently, much of the contraction on cooling consists of something akin to an elastic compression in which the structural members suffer various excessive elastic distortions or molecular strains.

As the thermal pressure decreases toward zero on continued cooling, the elastic resistance of the structures becomes a greater and greater factor in balancing the intrinsic pressure. It seems, however, that their elastic coefficients should also be increasing quite rapidly at very low temperatures. In that case, the increase in compression per degree decrease in temperature decreases, and the increase in the elastic coefficients may even be sufficient at low temperatures to cause the strains, that have been building up, to diminish. The expansivity of the vitreous solid, furthermore, may become negative if the expansion caused by this diminution in strain more than offsets the contraction which accompanies the decreasing thermal pressure. That is, many, if not all, vitreous materials may yield expansivity curves that, in this respect, resemble the expansivity curve of vitreous silica at very low temperatures.<sup>10</sup>

The compacted condition as caused by rapid heating can be produced to an appreciable degree only in the annealing range. In this condition, the excessive thermal pressure may also be regarded as the cause of elastic molecular strains; that is, the excess of the thermal over the intrinsic pressure is balanced by the elastic resistance of molecular structures to distortion. Even after equilibrium is established, molecular strains are doubtless present and continually varying about an average as one after another of the pressures become temporarily the greater in limited elements of the whole volume of liquid.

## VI. Conclusions

Practically speaking, glass at temperatures within and above its annealing range is a purely viscous liquid that is easily undercooled or superheated because its

<sup>6</sup> G. W. Morey, *Properties of Glass*, pp. 212-18 and 531-39. Amer. Chem. Soc. Monograph Series, Reinhold Publishing Corp., New York, N. Y., 1938. 561 pp.; *Ceram. Abs.*, **18** [2] 48-49 (1939).

<sup>7</sup> H. S. Taylor, *Treatise on Physical Chemistry*, Vol. I, pp. 141-43. D. Van Nostrand Co., New York, 1925.

<sup>8</sup> A. Q. Tool and C. G. Eichlin, "Variations in Glass Caused by Heat-Treatment," *Jour. Amer. Ceram. Soc.*, **8** [1] 1-17 (1925); p. 13.

<sup>9</sup> E. Preston, "Structure and Constitution of Glass," *Jour. Soc. Glass. Tech.*, **26** [14] 82-107T (1942); *Ceram. Abs.*, **21** [11] 233 (1942).

\* See Morey, footnote 6, and Preston, footnote 9.

<sup>10</sup> R. B. Sosman, *Properties of Silica*, pp. 352-67. Chemical Catalog Co., New York, 1927; *Ceram. Abs.*, **7** [7] 505-506 (1928).

viscosity is so very high. At temperatures far below its annealing range, glass behaves as an elastic solid although there is an intermediate range in which it possesses the characteristics of a plasticoviscous material.

While the condition of an undercooled glass is not one of equilibrium at the actual temperature of that glass, it usually corresponds to one of equilibrium at some temperature within the annealing range and, if the actual temperature is raised quickly enough to that point, the glass will be practically in equilibrium there. A corresponding relation exists between the condition of a superheated glass and some equilibrium temperature within the annealing range. The degree of undercooling (or superheating) is measured by the difference between the actual and equilibrium temperatures.

The properties of a glass are affected not only by changes in the actual temperature but also by changes in the equilibrium temperature. Thus, the expansion of a glass increases when the equilibrium temperature is increased as well as when the actual temperature rises, and lowering either temperature increases the viscosity very rapidly.

The equilibrium temperature ordinarily changes at a perceptible rate only when the actual temperature exceeds the lower limit of the annealing range, but, if the degree of undercooling is very high as in quenched glasses, it decreases at appreciable rates even when the actual temperature is in the temperature interval immediately below the annealing range and within which glasses take on a plastic character.

The rate at which the equilibrium temperature changes is proportional to the degree of undercooling (or superheating) and also to the inelastic deformability. For the same departure from equilibrium, the rate also increases very rapidly as the inelastic deformability is increased by raising the actual temperature. Since this deformability also increases as the equilibrium temperature is increased, the manner of change in properties is somewhat different when equilibrium is approached from an undercooled condition than when it is approached from a superheated condition at the same actual temperature.

A glass contracts and evolves heat when equilibrium

is approached from an undercooled condition, but it expands and absorbs heat when equilibrium is approached from a superheated condition. The rates at which these heat effects develop depend on the rate at which the difference between actual and equilibrium temperatures is decreased and they are therefore controlled by the inelastic deformability.

In view of the foregoing conclusions, an equation has been proposed that relates these various rates to the inelastic deformability. This equation is applicable to experimental data on the extraordinary expansion and contraction effects and on the exothermic and endothermic effects of glass in its annealing range. Since it is based on the concept that glass is a purely viscous liquid, it is not applicable to data on changes taking place while a glass is within its plasticoviscous stage in which the inelastic deformability increases with the load.

By using this equation in connection with the usual expansion curves that are obtained by heating a glass to temperatures just above its annealing range, reasonable results are found for constants that are related to the coefficient of viscosity and its changes with the actual and equilibrium temperatures. These constants would make it possible to determine this coefficient if the modulus of elasticity were known for the glass at these high temperatures.

The behavior of glass at temperatures within and immediately below its annealing range indicates that the various heat effects appear because the balance between the average intrinsic pressure (which arises from the molecular attractions) and the average thermal pressure (which arises from the thermal agitation) is disturbed during superheating and undercooling. This disturbance of the normal balance of the pressures in a liquid causes elastic molecular strains that are abnormal. When such abnormal elastic strains exist in a glass within its annealing range, they relax gradually at rates that are governed by the inelastic deformability which also governs the rates of relaxation of ordinary strains in annealing glass.

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