

# Viscosity and the Extraordinary Heat Effects in Glass

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In accordance with experience concerning the behavior of glass at temperatures within its annealing range, an equation is proposed that 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.

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# I. Introduction

## 1. Superheating and Undercooling with Accompanying Extraordinary Effects in Viscous Liquid

As already pointed out [1, 2, 3],<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, since 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 adjustments 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. That is, in the case of heating, the liquid can be superheated and, in the case of cooling, it can be undercooled. 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.

<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

When a liquid glass reaches any temperature in a state of nonequilibrium, it might, on first thought, 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 is included in a previous paper [1].

## 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 such 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, it will be found that the glass is still in practical equilibrium at that temperature. However, if the initial heating or cooling is comparatively slow, the departures will be less marked and a very 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, it will be found, nevertheless, that 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, according as a heating or a cooling caused the departure. 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 such as those just discussed, it has been conjectured that glass, when

cooled or heated very 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. Obviously, the difference between these temperatures is 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 in previous papers [1, 2, 3, 4], 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, it seems that the rates of approach are, in addition, 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, reaching 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**

Especially when subjected to considerable loads, glass is, to an appreciable extent, still inelastically

deformable at temperatures far below its annealing range. At such temperatures and also at temperatures within the lower part of the annealing range there are indications that glass has ceased to be a truly viscous liquid and possibly has assumed a plastic nature [4, 5]. That is, whether the loads are of a purely mechanical or a physicochemical character, it appears that the number of flow planes decreases 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 plastico-viscous material is being maintained by stresses of either 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. Likewise, the resistance in a flow plane that has been blocked may break down because the flow in neighboring planes has unkeyed the block or developed stresses that exceed the breakdown limit. As a consequence, some readjustments and molecular processes in a glass approaching equilibrium may not only develop much more rapidly than others, but some may also become completely blocked at low annealing temperatures. The discussion [1] 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, it is obvious that any theory based on the assumption that glass is a purely viscous liquid 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 pages. However, such effects are simply modifications of the heat effects, density changes, etc., that would have occurred if the elastic molecular strains had relaxed because of viscous flow alone.

## II. The Approach to Equilibrium

### 1. Differential Equations for the Rate of Approaching Equilibrium

According to the introductory statements relative to the rate of approaching equilibrium,

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

In this relation  $K_T$  is a factor that is inversely proportional to the viscosity as long as there is little change in the coefficient of elasticity, and  $d\tau/dt$  and  $T - \tau$  are, respectively, the time rate of change in the equilibrium temperature,  $\tau$ , and the departure of this fictive temperature from the actual temperature,  $T$ . Assuming the empirical relation suggested by Twyman [6] for the dependence of viscosity on temperature in the case of a glass in its annealing range, it appears that

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

In this expression,  $k$  is Twyman's constant, and  $K$  is obviously the value of  $K_T$  when  $T=0$ . Thus,  $K$  is an extrapolated coefficient that relates to the inelastic deformability at  $0^\circ$  C. Experience indicates that  $K$  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 eq 1 and 2, the expression

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

results. Even in the annealing range, eq 2 and 3 yield only a very 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 somewhat more rapidly in a superheated one than eq 3 allows. One purpose of this paper is to demonstrate this inadequacy of eq 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 eq 2 and, consequently, eq 3 are not adequate is not surprising as the effect of a changing  $\tau$  on the viscosity is ignored. From experience it seems that the manner in which a property is affected by a change in  $\tau$  is very similar to that in

which it is affected by a change in  $T$ . For this reason it has been assumed in previous cases [3, 4] that eq 2 would be more nearly adequate if it had the form

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

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

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

By this means the above-mentioned inadequacies in expressing the change in  $\tau$  at all ordinary annealing temperatures seem to be removed. However, more precise data 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, it is obvious that eq 4 and 5 are also inadequate as soon as glass ceases to be a purely viscous liquid and assumes a definite plastico-viscous nature. That is, eq 4 does not take into account the possibility that the coefficient of inelastic deformability may depend on the load. Moreover, this equation 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 that considerably exceeds that at which  $\tau$  decreases at temperatures below the annealing range even if the initial  $\tau$ -value was high. Thus, in the plastico-viscous range of a glass, the relation between  $T - \tau$  and  $T$  diverges comparatively little from a linear one during 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 eq 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 plastico-viscous 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 above is met in any test, then eq 5 should be modified for the plastico-viscous range by introducing the factor  $e^{(T' - T)/g'}$ . 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, eq 3 and 5 become

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

and

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

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

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

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

With respect to eq 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,<sup>2</sup> 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

<sup>2</sup> 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  $e^{-1}$ , it is obvious that  $y$  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, moreover, it is obvious that the values of  $y$ , under such conditions, correspond to different heating curves. That is, the larger value corresponds to a curve procured on a comparatively well-annealed sample of glass ( $\tau_0 < T_m$ ), whereas 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  $6^\circ$  C/min) is employed, it will be found that the condition  $y = 1$  and  $d\tau/dT = 1$  usually occurs when the sample has been moderately well annealed. Since the heat effect (endothermic effect, for instance) is just getting under way when  $d\tau/dT$  is unity, it often appears that the beginning of the endothermic (or rapid expansion) effect in a moderately annealed sample occurs at a somewhat lower temperature than in either less or more thoroughly annealed samples. Examples of series of curves that present this appearance are found in figures 4 and 8 of a previous publication [1].

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

If eq 8 were applicable, there would 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.

heating or cooling is quite definite for any given set of initial conditions. Since  $(1/g) + (1/h) = 1/k$ , as previously shown [4], eq 7 becomes  $1/x - (h/k)dy/dx = \pm ye^{-y}$  if substitutions,<sup>3</sup>  $y = (T-\tau)/h$  and  $\pm x = (K/R)he^{T/k}$ , are made. However, from a practical standpoint, neither this nor any of the numerous other forms that can be obtained by various substitutions and transformations seem to possess advantages over eq 7. Although a solution of this equation is lacking, it as well as eq 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 eq 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. For example, the linear thermal expansion curves may be used, 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. It appears that 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 per unit length through the annealing range is expressed approximately by

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

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

<sup>3</sup> In making these substitutions, use is made of the identity  $e^{T/ke^{T/h}} = e^{T/k}e^{-(T-\tau)/h}$ . However, when appearing 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 that is analogous to that of a mechanical load in its relation to inelastic deformations.

### III. Application of Equations to Thermal Expansion Data

#### 1. Thermal-Expansion Curves

In a progress report [2] made to the Glass Section at the Cincinnati meeting of the American Ceramic Society in 1942, the inadequacy of eq 6 and 8 was shown by applying them to experimental expansion data. It was also pointed out, although not shown definitely, that much of the discrepancy between experimental and computed results could be eliminated by assuming that the viscosity of glass is affected by changes in  $\tau$  very much as it is affected by changes in  $T$ . In the following, a résumé of that report and a fuller discussion of the effect of changes in  $\tau$  are presented.

The expansion data used for this purpose were obtained on two samples of a borosilicate crown that was of the usual kind employed in thermometers that are graduated to temperatures that exceed  $500^{\circ}\text{C}$ . One of the samples was treated at a high temperature (approximately  $850^{\circ}\text{C}$ ) and cooled rapidly in moving air in order to prevent  $\tau$  from falling below  $650^{\circ}\text{C}$ . In fact, the cooling

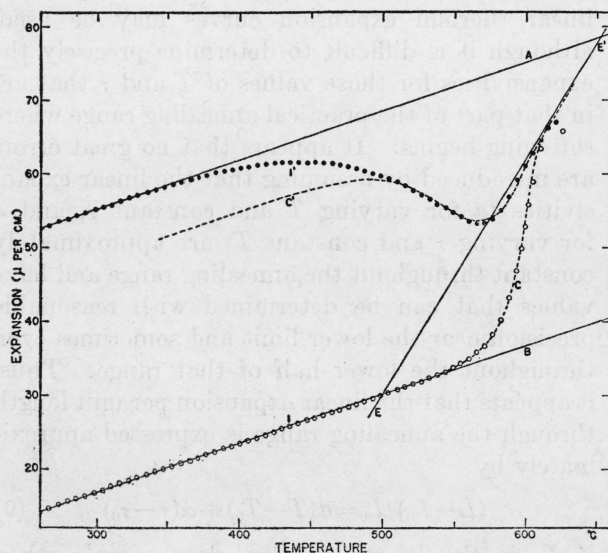


FIGURE 1.—Comparison of computed and experimentally determined thermal-expansion curves for a borosilicate thermometer glass.

1 and 1', Experimental curves for an annealed sample (circles) and a chilled sample (dots), respectively; A and B, tangents to curves 1' and 1, respectively, at points near  $300^{\circ}\text{C}$ ; EE', the approximate thermal-expansion curve of the glass when it does not depart from equilibrium because the 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 eq 7, and the departure of C' from 1' below  $500^{\circ}\text{C}$  results presumably because the equation is inapplicable while a glass is in its visco-plastic stage.

rate of this treatment 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  $500^{\circ}\text{C}$  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  $620^{\circ}\text{C}$  and were made by James B. Saunders according to the weighted-spacer method that he has described [7].

The portions of the resulting expansion curves between  $260^{\circ}$  and  $620^{\circ}\text{C}$  are shown in figures 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  $615^{\circ}\text{C}$ , where both samples were just entering the range of slight but noticeable softening. In this range the  $\tau$ -values of the two samples were presumably almost equal, and the values of  $T-\tau$  were doubtless not much greater than a degree, as the heating rate used in these tests was only  $3\text{ deg C/min}$ . 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 expansion curves presumably would have practically coincided with the equilibrium curve from this point upward. This curve is represented by the line EE', and it intersects the expansion curve of the annealed sample at  $500^{\circ}\text{C}$  because up to that point there was no appreciable change in the  $\tau$ -value of that sample. However, 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  $500^{\circ}\text{C}$  until the temperature of appreciable deformation was reached. Doubtless a line (such as EE') representing the sequence of equilibrium conditions in terms of change in length should be somewhat curved; but in this purely demonstrational presentation, relatively minor details of this nature will be ignored for the purpose of simplicity.

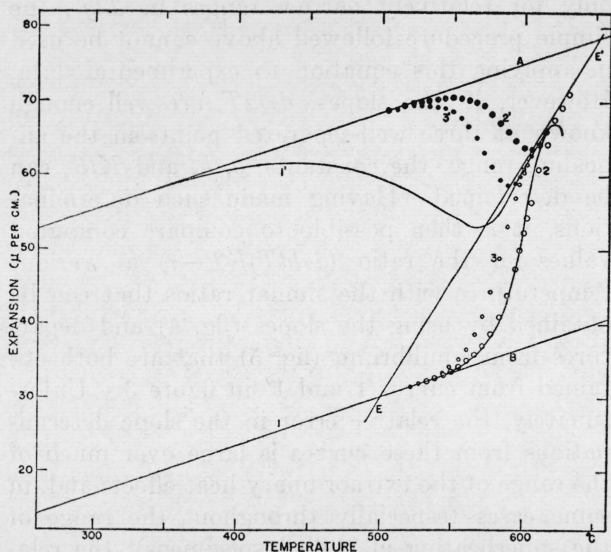


FIGURE 2.—Comparison of thermal-expansion curves determined experimentally and computed in accord with equation 8.

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

## 2. Method of Estimating Expansivities

Between  $300^\circ$  and  $500^\circ\text{C}$  the expansivity of the annealed sample was found to be about  $0.066$  ( $\mu/\text{cm}/\text{deg C}$ ), but below this range the average was less than  $0.063$ . Although the expansivity of a severely chilled glass is usually increased a few percent at atmospheric temperatures, the expansivity of the chilled sample also appeared to be about  $0.066$  at  $300^\circ\text{C}$ . If a line coinciding with the expansion curve of the chilled glass and having this slope ( $0.066 \mu/\text{deg}$ ) is extended to high temperatures, it intersects EE' at  $653^\circ\text{C}$ , 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 began to change appreciably—as it appears to have done immediately above  $340^\circ\text{C}$ . This temperature is about  $150$  deg 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.

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If the relative placement of the two curves is approximately correct, the difference ( $653$  to  $500$  deg) between the initial  $\tau$ -values of the two samples produced a difference in length of  $38.4 \mu/\text{cm}$ . This corresponds to a linear expansivity of  $0.251$  ( $\mu/\text{cm}/\text{deg C}$  change in  $\tau$ ). In the usual units, this value also corresponds to a volume expansivity of  $0.75 \times 10^{-4}$  for a 1-deg change 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 of 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,  $\tau = 653^\circ - [0.066(T - 300) - (L_T - L_{300})/L_T]/0.251$  (see eq 9) and, for the annealed glass, the expression is the same except that  $500^\circ$  replaces  $653^\circ\text{C}$ . In figure 3 (curve 1, circles, annealed; curve 1', dots, chilled glass), the  $\tau$ -values so obtained are plotted against  $T$ .

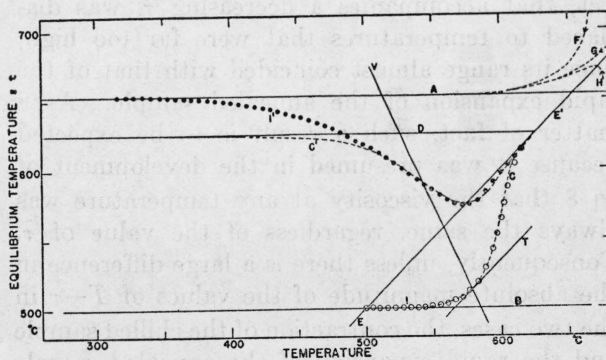


FIGURE 3.—Curves relating to changes in the equilibrium temperature as a glass is heated or cooled.

1 and 1' (Circles and dots, respectively), equilibrium temperatures computed in accord with eq 9 from the corresponding experimental curves 1 and 1', figure 1; C and C' (broken lines), equilibrium temperatures that correspond to curves C and C' of figure 1 and were computed by a step-by-step method based on eq 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 the equilibrium temperature (slope  $d\tau/dT=1$ ) when glass remains in constant equilibrium because the 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 a maximum; V, one of a family of curves indicating conditions for constant viscosity; F, G, and H, approximate courses that would be followed by the equilibrium temperature during cooling if the cooling rates ( $30, 37.5,$  and  $40 \text{ deg C}/\text{sec}$ , respectively) from comparatively high temperatures prevented the equilibrium temperature from falling below  $653^\circ\text{C}$  when T became zero.

#### 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 eq 8, a curve that follows the experimental curve moderately well. By introducing the  $\tau$ -values so computed into eq 9 and thus transforming to expansions again, the computed results shown in figure 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 1 hour) at a rather high temperature ( $560^\circ\text{C}$ ). Furthermore, it was then necessary to assign a rather high value (15 deg) to  $k$  in order to prevent the rapid 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 (fig. 2) indicates. Moreover, 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 it was presumed in the development of eq 8 that the viscosity at any temperature was always 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. Also, the maximum rates of contraction and expansion in these cases will be attained at temperatures that are not materially different.

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

As differential eq 7 has not been solved explicitly for  $\tau$  (except in the form of series suitable

only for relatively narrow ranges in  $T/g$ ), the simple procedure followed above cannot be used in applying this equation to experimental data. However, if the slopes,  $d\tau/dT$ , are well enough 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 then 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 figure 3. Unfortunately, the relative error in the slope determinations from these curves 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. Nevertheless, it is considered that the data obtained for  $d\tau/dT$  and  $T-\tau$  (figs. 4 and 5) are adequate for the purpose, because 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) at which  $d\tau/dT=1$ , (2) at which this slope attained a maximum in the case of the superheated annealed sample, and also (3) near the temperature at which the slope reaches a minimum (maximum negative value) in the case of the undercooled 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, the 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  $d_a=65.0^\circ\text{C}$ ; and (2),  $p_a=5.37$ ,  $T_a=603.0^\circ\text{C}$ ,  $\tau_a=578.0^\circ\text{C}$ , and  $d_a=25.0^\circ\text{C}$ . In the third case, the data at a point chosen near that of the mini-

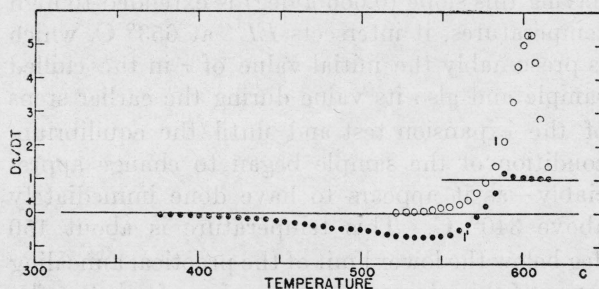


FIGURE 4.—Slopes of the equilibrium temperature curves 1 and 1', figure 3, at various actual temperatures.



imum were (3),  $p_c = -0.72$ ,  $T_c = 542.9^\circ \text{C}$ ,  $\tau_c = 589.7^\circ \text{C}$ , and  $d_c = -46.8$ . Use of the first and third of these sets of data with eq 7 gives the result  $h/g = (\tau_c - \tau_a)/(T_a - T_c) = 2.185$ .<sup>4</sup> 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 for eq 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 eq 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)  $p_c = -0.73$ ,  $T_c = 540.0^\circ$ ,  $\tau_c = 591.6^\circ$ , and  $d_c = -51.6^\circ$ , 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  $T_1/k$

<sup>4</sup> By introducing two sets of data (such as the first and third presented above) into eq 7 and by equating the logarithms of the ratios of the corresponding members of the two resulting equations, a rearrangement of the result yields  $h/g = (\tau_c - \tau_a)/(T_1 - T_a) + (h/(T_1 - T_a)) \ln(p_1 d_3/p_3 d_1)$ . In the above case the third set of data was taken at a point such that  $p_1/d_1 = p_3/d_3$  approximately. Consequently the logarithmic term disappeared.

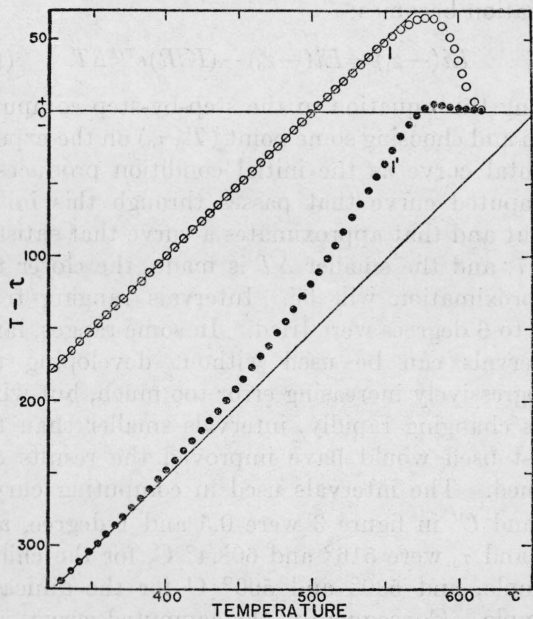


FIGURE 5.—Degrees of undercooling and superheating ( $T - \tau$ ) indicated by curves 1 and 1' in figures 1 and 3.

if  $T_1$  symbolizes the temperature for which the glass, when in equilibrium ( $T = \tau$ ), has a relaxation time,  $1/K_T$ , equaling 1 hour. That is,  $K = (pR/d)e^{-T/g}e^{-\tau/h} = e^{-T_1/k}$ . Since  $R = 180 \text{ deg/hr}$  (3 deg/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 eq 7 is applicable, regardless of the treatment received by the glass, and the fair agreement found here exceeds what should be expected in view of the unreliability of the  $d$ - and  $p$ -determinations. Besides, there is the probability 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 the Applicability of Equation 7

### (a) First Method

From eq 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 that 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 figures 4 and 5 and the  $h$ ,  $k$ , and  $K$  (average) values given above were used. (Since the rate of heating was 180 deg/hr,  $R = e^{5.193}$  and  $\ln(R/K) = 45.320$ .)

The results of this test are shown by curve  $E$  in figure 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. However, beginning near  $500^\circ \text{C}$  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

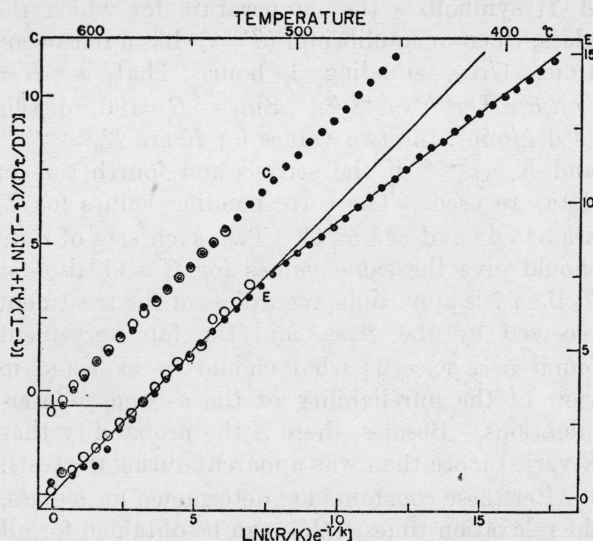


FIGURE 6.—Test of the degree to which changes in equilibrium temperature satisfy eq 7.

*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 the right. *C*, tests of data derived from curves *C* and *C'* in figure 3 (displaced ordinates on the left). (Circles and dots, annealed and chilled glass in both cases.)

(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 under heavy loads collapsed more readily at these relatively low temperatures than it would have collapsed 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  $e^{(\tau-T)/h}/(T-\tau)$  and  $d(T-\tau)/dt$  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  $Ke^{T/k}$  in magnitude according as the physicochemical “load” (as represented by  $(T-\tau)$ ) is large or small.

## (b) Second Method

As figure 6 indicates that the chilled sample did not behave as required by eq 7 until  $500^\circ\text{C}$  was exceeded, it becomes a matter of interest to determine approximately how much lower than  $653^\circ\text{C}$  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, eq 5 can be written in the form  $e^{-z}dz/z = -Ke^{T/k}dt$ , in which  $z = (\tau - T)/h$ . The solution of this for any interval of time,  $\Delta t$ , for instance, is  $Ei(-z_1) - Ei(-z_0) = -Ke^{T/k}\Delta t$ , 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, now that the temperature is 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  $e^{T_0/k}$  is changed to  $e^{(T_0 + \Delta T)/k}$  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, the above exponential integral equation becomes

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

Using this equation in the step-by-step computation and choosing some point  $(T_0, \tau_0)$  on the experimental curve as the initial condition produces a computed curve that passes through this initial point and that approximates a curve that satisfies eq 7, and the smaller  $\Delta T$  is made, the closer the approximation will be. 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 figure 3 were 0.5 and 1 degree, and  $T_0$  and  $\tau_0$  were  $516^\circ$  and  $608.4^\circ\text{C}$ , for the chilled sample, and  $530^\circ$  and  $500^\circ\text{C}$  for the annealed sample. Consequently, the computed curves and the  $\tau$ -curves derived directly from the experimental data intersect at these points. These

computed curves,  $C$  and  $C'$ , indicate in both cases that the glass at temperatures above  $516^\circ\text{C}$  behaved very nearly as eq 7 requires.

When the previously employed test—made by plotting  $\ln((d/p)e^{-d/h})$  against  $\ln((R/K)e^{-T/k})$ —was applied to these computed curves, the results shown by curve  $C$  in figure 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 eq 7.

## 7. Evidences of Plasticity

In figure 3 the trend of curve  $C'$  when compared to that of curve  $1'$  at temperatures below the annealing range suggests that  $653^\circ\text{C}$  is about 28 deg higher than the initial  $\tau$ -value required if eq 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 eq 7 to take into account the increased mobility of plastic glass when subjected to very large loads. In this connection, curve  $E$  of figure 6 indicates that those points that were obtained below  $516^\circ\text{C}$ , where  $T-\tau$  is almost proportional to  $T$ , would have been alined 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 ( $513^\circ$  and  $52.6^\circ$  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  $516^\circ\text{C}$  depart from the basic straight line suggests that the deformability of glass in its plastico-viscous condition is 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  $516^\circ\text{C}$  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

Since the magnitude of the cooling rate that produced an initial  $\tau$ -value of  $653^\circ\text{C}$  was a matter of some curiosity, approximations to cooling curves (as shown in fig. 3) were also computed by the step-by-step method<sup>5</sup> and on the assumption that  $\tau$  had fallen to  $653^\circ\text{C}$  by the time that  $T$  had fallen to  $550^\circ\text{C}$ , below which there had been no further appreciable change in  $\tau$ . It was thought that the cooling rate might have been about 40 deg/sec, since it appeared that the sample in cooling from  $850^\circ\text{C}$  had lost all redness in about 5 sec. However, the cooling curve procured for that rate suggests a lower rate, because it indicates a crossing of the equilibrium curve at a temperature slightly above  $670^\circ\text{C}$  rather than at  $850^\circ\text{C}$ . When a rate of 30 deg/sec was used in the computation, the resulting curve began at about  $655^\circ\text{C}$  to diverge from the equilibrium curve instead of continuing to approach it. That is, this rate

<sup>5</sup> 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  $T$  reaches 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, eq 8, for cooling from an equilibrium temperature,  $T_0$ , to zero degrees becomes  $-\tau'/k = \ln(Kk/R) + \gamma - Ei(-x_0)$  which, since  $x_0 = (Kk/R)e^{\tau_0/k}$ , 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  $R = Kke^{\tau'/k}$ . Using the values previously found for  $K$  and  $k$ , and assuming that equilibrium was established when cooling began at a starting point near  $850^\circ\text{C}$ , it is apparent that  $x_0$  is large for this case and that  $R = 19.9$  deg/sec, approximately. Thus, a rate computed in this manner and known to be too low, is about one-half of the rate indicated by the step-by-step computation described above.

Occasionally it is desirable 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  $R = Kk^2 e^{\tau_0/k} / (T_0 - \tau')$ . That is, if eq 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  $Ke^{1/h}$ , the result is that which would have been obtained if eq 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 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.

was much too low unless a much higher rate preceded it from 850° to about 660° C, for instance. Without using very small intervals in the computation, it also appears that a rate of 37.5 deg/sec

is somewhat too low. Thus, it seems that the probable average rate of cooling in the chilling treatment was slightly under 40 deg/sec. See curves *F*, *G*, and *H* in figure 3.

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

### 1. Relation of Heat Effects to Inelastic Deformability

As previously stated [4, 5], 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 for 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. However, 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 [1], and the progressive changes are believed to indicate that some molecular readjustments leading to equilibrium conditions develop rather readily at low treating temperatures, whereas 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 to the heat effects observed.

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 that show exothermic and endothermic effects are always very different from the idealized conditions assumed in discussing the methods of test. Generally, it is assumed that the test sample is 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, whereas 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. Also, supposedly, there is 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. At best, these ideal conditions 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 ( $H$ ) sup-

ply to the sample is  $dH/dt=A(T_w-T)$ . Under idealized conditions, the factor  $A$  in this relation is the product of the area and the so-called external conductivity of the contact between sample and wall. If the sample weighs 1 gram, the rate of its heat absorption equals this rate of supply and is  $s''dT/dt+\sigma d\tau/dt$  for 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 expended in expanding 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 that 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 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  $'_n=s'$ , and  $A_n=A$  approximately. In that case, it follows that

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

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, these 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. As 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 very 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 it will be considered that  $G$  properly represents  $T-T_n$  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 just 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

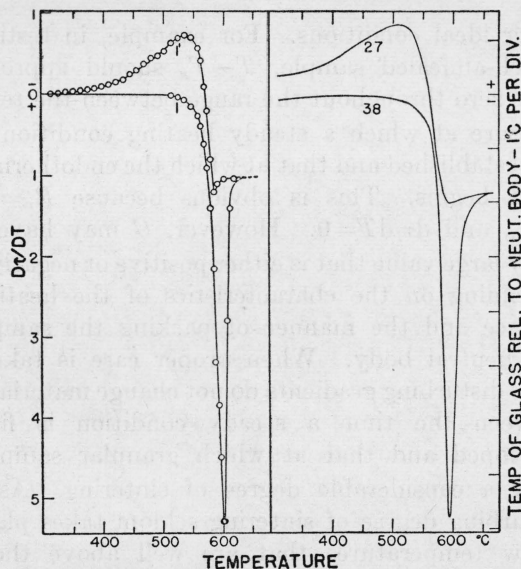


FIGURE 7.—Exothermic and endothermic effects.

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

well-annealed samples (fig. 7, curves 27 and 38). (See also ref. 1, fig. 8.)

The significance of the difference between the initial levels of these curves is at once apparent from eq 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 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 as  $\beta$  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 very 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 (exo-

thermic effects), which are observed in chilled glasses only, and their minima (endothermic effects), which are very pronounced in all annealed glasses. During the endothermic and exothermic effects,  $(R_n/R) - 1$  takes on small positive and negative values, respectively. Consequently, in both cases, the effect of the  $s'$ -term, eq 11, is to detract somewhat from the effect of the  $\sigma$ -term. However, as when developing the approximate relation,  $G_1 - G_2 = R\sigma/A$ , the  $s'$ - and  $\beta$ -terms, being relatively small, may again be neglected for simplicity. Then, if the values obtained for  $T - T_n$  at the peaks of the endothermic and exothermic 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  $G_4 - G_1 = -(R\sigma/A)(d\tau/dT)_{\max}$  roughly approximate actual conditions. As estimated from curves 27 and 38 in figure 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  $-8.0$  deg C, respectively. Consequently,  $(d\tau/dT)_{\min} = -0.55$ , and  $(d\tau/dT)_{\max} = 4.4$ . When compared to the respective values  $-0.73$  and  $5.37$  found from the expansion curves of the thermometer glass, these values obtained from the differential heating curves of the borosilicate optical glass appear rather low. However, this result is to be expected since experimental conditions prevent the heating curves from showing the full magnitude of the heat effects.

If the full magnitude of the endothermic effect and the corresponding change in  $\tau$  could be well determined (especially in the case of a thoroughly annealed glass), it seems that 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 percent or more in error, gave the result  $s''/\sigma = 140/8$ . In arriving at the estimate of 140 deg as the value of  $\tau_4 - \tau_1$ , it was considered that the initial equilibrium temperature,  $\tau_1$ , of the sample that yielded curve 38 was probably somewhat below 460° C and that  $\tau_4$  was not far below 600° C, because the difference between the actual and equilibrium temperatures is not great when the endothermic effect reaches its maximum.

As the heating rate in obtaining the heating curves under consideration was about 6 deg/min, it follows that  $\sigma/A = (G_1 - G_2)/R = 1.8/0.1$  and, from this result and the above ratio, that  $s''/A =$

315. Thus, for any probable value of  $s''$  at temperatures in the annealing range, the order of  $A$  appears to be in the neighborhood of  $10^{-3}$ . This rough approximation is not a wholly improbable value, since  $A$  (instead of possessing its idealized significance in these tests) was concerned with the conduction of heat from some undermined surface in the furnace through a wall that was of uncertain area and was composed of a thin layer of burned asbestos paper and an undetermined thickness of granular glass or alundum. However, this uncertainty is of minor significance, as the chief purpose of introducing the very rough approximations, that were obtained as described in the immediately preceding paragraphs, is to give a clearer picture of the significance of the curves that result 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

Besides the reproduced curves 27 and 38 (which were obtained by tests in which  $R=6$  deg/min), figure 7 also contains curves obtained for comparison by plotting the data, shown in figure 5 for  $d\tau/dT$ , according to the manner and scale used in plotting the experimentally determined differential heating curves. Although the two glasses were unlike, the treatments that they had received 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 and  $-8$  deg, 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. However, when the difference in the heating rates is considered, it is seen that the factor in this case has very little definite significance, 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 deg.

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 figure 8 the synthetic differential heating curves 2 and 2' (for chilled and annealed samples, respectively) correspond to the curves with similar designations in figure 2, and are replicas of those shown before the Glass Section at the previously mentioned Cincinnati meeting of the American Ceramic Society [2]. 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. Also, it is apparent that, contrary to experience, the exothermic and endothermic effects of a chilled sample would then occur exactly within the temperature range of the endothermic effect of a well-annealed sample. In plotting these curves,  $d\tau/dT = \pm xy$  (see eq 8) was also

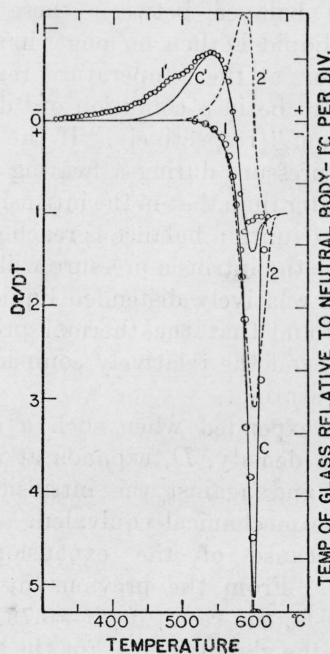


FIGURE 8.—Comparison of computed exothermic and endothermic effects.

1 and 1', (Large and small circles, respectively) same as 1 and 1' of figure 7; C and C', computed effects in accord with computed curves C and C' of figures 1 and 3. The failure of eq 7 to account for the plasticity of glass below the annealing range presumably causes the divergence between C' and 1' below 500°C. 2 and 2', (broken lines) computed heat effects in accord with curves 2 and 2' in figure 1. The wide divergence between these curves and 1 and 1' presumably is caused by the failure of eq 8 to account for both the plasticity of the glass below 500°C and the decrease in the viscosity as the equilibrium temperature increases.

multiplied by the factor 1.48 to bring them into conformity with the other curves of figure 7.

Curves  $C$  and  $C'$  correspond to the similarly designated curves in figures 3 and 1. 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 quite small, there are two pressures to be considered in relation to liquids, (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 the 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 that 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 [11] 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/cm.<sup>2</sup>

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 [3], this is the same order of magnitude as that of values that have been mentioned as possible for the intrinsic pressure of water [8]. 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 very excessive compactions and distentions 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 [9] (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 [3], chain- or ring-like molecules [10] and some other forms of extended molecular structures that often have been discussed as possibilities (for references, see [10, 11]) 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. However, the rate of alteration 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, respectively.

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. Furthermore, the structures gradually become permanent and probably attain a considerable elasticity of form if the cooling is extended to temperatures considerably below the practical annealing range. At this stage the liquid is overly distended 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. However, it seems 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. Furthermore, the expansivity of the vitreous solid 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 [12].

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 the other of the pressures becomes temporarily the greater in limited elements of the whole volume of liquid.

## VI. Conclusion

Practically speaking, glass at temperatures within and above its annealing range is a purely viscous liquid that is easily undercooled or superheated because its viscosity is so very high. However, 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 plastico-viscous material.

Although 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, a glass expands when the equilibrium temperature increases as well as when the actual temperature rises, and lowering either temperature increases the viscosity very rapidly.

Ordinarily, the equilibrium temperature 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 immediately lower range within which glasses take on a plastic character.

The rate at which the equilibrium temperature changes is proportional to the degree of under-

cooling (or superheating) and also to the inelastic deformability. Moreover, for the same departure from equilibrium, the rate increases very rapidly as the inelastic deformability is increased by raising the actual temperature. As this deformability also increases as the equilibrium temperature increases, the manner of approaching equilibrium from an undercooled condition differs somewhat from the manner of approach from a superheated condition at the same actual temperature.

In approaching equilibrium from an undercooled condition, a glass contracts and evolves heat, whereas it expands and absorbs heat in approaching equilibrium from a superheated condition. The rates at which these heat effects develop depend on the rate of approaching equilibrium and are therefore also 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. It is found that 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. As the equation 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 plastico-viscous 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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