U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1637

Part of Journal of Research of the National Bureau of Standards, Volume 34, February 1945

RELAXATION OF STRESSES IN ANNEALING GLASS

By Arthur Q. Tool

ABSTRACT

An empirical equation representing relaxation of stresses in annealing glass is derived. Although the derivation is based on Maxwell's equation for viscous flow, consideration is also given to the changing viscosity as a glass anneals at a constant temperature. This new equation has been applied to data that were obtained by Adams and Williamson on the relaxation of stresses in annealing glass at various temperatures. It is shown that this equation applies very satisfactorily to their data. Also, it appears to be much more suitable than the reciprocal relation which these authors proposed as a substitute for the wholly unsatisfactory exponential relation that is derived directly from Maxwell's equation. This exponential relation is unsatisfactory simply because it does not take into account the changing viscosity of annealing glass. Finally, the new equation leads to a clearer understanding of the nature and behavior of glass because it does not neglect the change in viscosity.

CONTENTS

I. INTRODUCTION

In procuring data for a previous publication [1],[1] it was noted that the relaxation time [2] of the strains in glass during an annealing at a constant temperature was generally much less when the relative retardations exceeded a thousand millimicrons than when they were under fifty. This should not be the case if the viscosity remains constant as long as the temperature is constant and if the stresses relax according to Maxwell's law. At the time, it was thought possible that the observed results might indicate that glass, even at relatively high annealing temperatures, is appreciably plastic. On further consideration, the degree of plasticity indicated by the results seemed unreasonable, although glass is undoubtedly plastic to a certain degree at very low annealing temperatures. It also seemed improbable that the indicated increase in the relaxation time with decreasing load was the result of observational errors, although the method of measuring

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

[2] In a case in which the stress, F, relaxes according to the relation, $F=F_0e^{-t/\vartheta}$, the constant, ϑ, is the relaxation time and F_0 is the stress when the time $t=0$.

the large relative retardations was comparatively inaccurate. Moreover, a more extensive set of data showing practically the same conditions was obtained by Adams and Williamson [2] at about the same time.

These results show either that Maxwell's law does not apply to the relaxation of stresses in annealing glass, possibly because the glass is plastic, or that the viscosity of an annealing glass at a constant temperature changes and thus causes the factor representing the relaxation time in Maxwell's equation for inelastic flow to be a variable. On finding that Maxwell's equation was inadequate, Adams and Williamson used a reciprocal relation to express the decay of the relative retardation. That this subject is still a matter of some interest is shown by the fact that Weyl and Pincus [3] have recently mentioned the results of Adams and Williamson and their use of the reciprocal relation. For this reason a recently presented theory [4, 5] of the behavior of annealing glass has been applied to their data and the results are presented in this paper.

II. CHANGING VISCOSITY OF ANNEALING GLASS

In any thorough study of annealing glass, it will soon be found that all of the properties of the glass are changed by the annealing, even though the temperature is unchanged. Moreover, it will be found that the properties are a function of the annealing temperature as well as of the actual temperature at which the glass is tested. That is, if the annealing is continued until the equilibrium condition is reached at any annealing temperature, this temperature as well as the standard temperature at which the glass is tested should always be given consideration. Also during an annealing at a constant temperature and before equilibrium is reached, the condition of the glass [3] at any time is always that which approximates an equilibrium condition at a higher or lower temperature which, as the annealing proceeds, continually approaches that of the annealing [6]. This equilibrium, or fictive, temperature, which continually changes while the glass is annealing at an actual temperature, T, will be designated by τ. Furthermore, the time rate of change in τ is always roughly proportional to $T-\tau$ if the annealing is accomplished while T is constant.

If the coefficient of a property of a glass, when τ is constant, can be related reasonably well to the temperature by some expression, such as $D=D_0(1-a(T-T_0)-. . .)$ in the case of density, for example, it will usually be found that a similar expression with different constants relates the coefficient equally well to the fictive temperature, τ, when T is constant. Thus, in the above relation for the change in density with T, the variation in the initial density because of any change in τ is expressed equally well by the relation $D_0=D'_0(1-\alpha(\tau-\tau_0)-. . .)$. As a result of his studies of annealing glass, Twyman [7] concluded that the inelastic deformability (reciprocal of viscosity) of the average glass doubled approximately with each increment of about 8° C in the actual temperature. Consequently, the relaxation time, ϑ, which is closely related to the coefficient of viscosity, should vary approximately according to the expression, $\vartheta=\vartheta_0 e^{-T/k}$ as the temperature changes, if $k=11.5°$ C. That is, although the modulus of elasticity, E, also changes with temperature, its variation is doubtless insignifi-

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[3] Certain glasses behave in an unusual manner, but these are excluded from the present discussion.

cant when compared to the very rapid change in the coefficient of viscosity, $\eta = E\vartheta$. If the changes in the relaxation time with T and τ can be expressed reasonably well by similar relations, it follows that $K = 1/\vartheta = K_0 e^{T/g} e^{\tau/h}$ should express approximately the value of the reciprocal of the relaxation time for different values of T and τ. If a glass is cooled or heated so slowly that it never departs materially from the equilibrium condition, $T = \tau$, it follows that $k = gh/(g+h)$, provided it is assumed that Twyman's empirical relation was based on measurements on deformations that developed almost entirely while the glass was never far from equilibrium. A study of his experiments suggests that this assumption is applicable, since the deformations which he observed almost certainly were developed mainly at comparatively high annealing temperatures at which τ never departs materially from T unless the cooling rate is quite high. That is, the deformations were developed mainly before the glass departed from the equilibrium curve of its liquid form.

If the expression for $1/\vartheta$ is introduced into Maxwell's equation for inelastic flow [1, 2], a modification, $dF/dt = EdS/dt - K_0 F e^{T/g} e^{\tau/h}$, is obtained that should apply reasonably well to the development of inelastic deformation in stressed glass, provided the variations in E with T and τ are not too great.

As it has been observed [8] that the manner in which temperature affects the velocity of approach by any coefficient (density, refractivity, etc.) to its equilibrium value is roughly the same (provided the coefficient has a given displacement from its equilibrium value regardless of the temperature) as the manner in which temperature affects the mobility of the glass, it seems that the viscosity governs the rate of these approaches. Consequently, it appears that

$$d\tau/dt = K_0 (T - \tau) e^{T/g} e^{\tau/h} \qquad (1)$$

should represent approximately the velocity of the change in τ as both T and τ change. In part at least, this differential equation allows for the lack of strict proportionality between $d\tau/dt$ and $T - \tau$ in an annealing glass at a constant temperature. Its solution (in terms of exponential integrals)

$$Ei(y) - Ei(y_0) = -K_0 e^{T/k} t \qquad (2)$$

(if T is constant and if $y = (T - \tau)/h$ and y_0 is its value when $t = 0$) applies rather satisfactorily to data on the changes in τ as they are derived from experimental results on the varying coefficients of an annealing glass.

If a glass is cooled very rapidly from temperatures well above the annealing range, τ is very high when atmospheric temperatures are reached, and if the cooling is particularly severe, it may be more than 50° C above the temperatures at which the rapid expansion and endothermic effects become appreciable; whereas, if a glass is cooled very slowly so that it can follow its equilibrium curve as a liquid throughout the annealing range and possibly to even lower temperatures, τ may be reduced as much as 70° to 90° C below the beginning points of the heat effects mentioned. Somewhere in the range 10° to 40° C below these points, the relaxation time is approximately 1 hour, and the point at which $K = 1$ is, therefore, roughly the midpoint of the range of possible values of τ in glass at ordinary temperatures. That is, without exceptional treatments, the possible range of τ-values in the average glass is about 140° C, and when the glass is in equilibrium ($T=\tau$) at a temperature near the midpoint of this range, the viscosity coefficient, $\eta=E\vartheta$, (ϑ expressed in seconds) should be approximately 2.2×10^{15} if $E=6\times 10^{11}$ at such temperatures. This assumed value for E is only slightly less than the average value for a number of glasses [9] at ordinary temperatures. Consequently, the above estimate of the value of η is presumably rather high, since E undoubtedly decreases appreciably as the temperature approaches the annealing range. Although η has been determined experimentally [10, 11] at temperatures that are so low that they probably were near the upper limits of, or were well within, the annealing ranges of the glasses tested, the results cannot safely be compared with the above estimate because no auxiliary determinations on the locations of the rapid expansion ranges were made. However, the η-values for the lowest temperatures used in these experimental determinations ranged from 10^{13} to 10^{16}.

If a slowly cooling glass follows its equilibrium curve throughout the range of temperatures corresponding to the range of τ-values that may exist even after ordinary temperatures are reached and also if $k=10°$ C, the η-values for this interval of cooling will range, according to the above estimate for the midpoint value, from 2×10^{12} to 2×10^{18} approximately. However, if the glass is cooled so rapidly through this temperature interval that τ does not change, and if $g=h=20°$ C, the initial η-value on reaching the lower limit of the temperature interval will be about 2×10^{15}, and any stresses in the glass will begin to relax almost as rapidly as they would have relaxed if the glass were in equilibrium at the midpoint. However, the decrements in the relaxations as time progresses will be greatly different in the two cases. Moreover, if the glass after being brought to equilibrium at the lower limit of the temperature interval is heated so rapidly to the upper limit that τ does not change, the initial η-value will again be that of the glass in equilibrium at the midpoint of the interval. (These values for g, h, and the resulting η, although they are not improbable, were introduced merely as aids in conceiving the effects of a varying or unvarying τ.) Effects of this nature, which are the result of the previous history of the glass, were noted and studied by the authors of the reports cited.

III. EQUATION FOR THE RELAXATION OF STRESSES IN UNANNEALED GLASS

In a severely chilled piece of glass, the value of τ may be very high, and the residual stresses, which comprise a balanced system and which are the result of the temperature gradients that existed as the glass passed through the annealing range, may approach the breaking limit of the glass. The high value of τ and of these stresses are maintained without appreciable decay at ordinary temperatures because the viscosity is so extremely high; but, when the glass is reheated, the viscosity is so reduced, as the annealing range is approached, that τ and the average absolute magnitudes, F, of the stresses immediately begin to decrease at an appreciable rate.

Usually, stressed glasses are double refracting unless the stresses are the same at all points and in all directions. Except in certain limited portions, this uniformity of the stresses is never met in glass strained by chilling. If the strained piece of glass has some simple geometrical form, such as a rectangular prism, it is usually possible to pass a beam of plane polarized light through it along a path which makes it possible to bisect, throughout most of the path at least, the angle between the directions of principal stresses with that of the plane of polarization. Because of the photoelastic action of most glasses, the component oscillation in the direction of one principal stress is retarded (or accelerated) in its velocity of propagation relative to the component in the other direction. This relative retardation, δ, (usually measured in millimicrons, mμ, per centimeter of path) is proportional to the average difference between the principal stresses, which usually vary both in sign and magnitude along the path. That is, it does not measure the maximum difference nor does it give a certain indication of the average magnitude of the stresses, particularly, if those seldom used paths along which one principal stress is always practically zero are excepted. Moreover, as the stresses decay in an annealing glass, δ will not be a certain indicator of the rate of decay unless care is taken to preserve the pattern of the stress distribution throughout the time required for the test.

Under suitable conditions it may be assumed [4] that δ and F are proportional throughout an annealing test. That is, as in the case of the elastic modulus E, it will be assumed that the changes in the photoelastic constant with τ and T are insignificant compared to the changes in η with τ and T. Moreover, experience indicates that δ may also be considered as proportional to the average absolute value of $\tau - T$, which is usually large and positive in a severely chilled glass if T is not too high. That is, $x=\delta/\delta_0=F/F_0=(\tau-T)/(\tau-T)_0$ if the conditions at any time t are compared to the conditions at the time from which t is measured. On writing $A=(\tau-T)_0/h$ and substituting hAx for $\tau-T$ in eq 1, the relation, $d(Ax)/dt=-(K_0e^{T/k})\,Axe^{Ax}$, is obtained for annealing at a constant temperature. The solution of this differential equation is

$$Ei(-Ax)-Ei(-A)=-K_0e^{T/k}t=-K_Tt, \qquad (3)$$

since $x=1$ when $t=0$. Clearly, K_T is the value of the reciprocal of the relaxation time that will be reached provided the annealing is continued until $\tau=T$. In certain cases this condition exists from the beginning and Maxwell's equation, $dF/dt=-K_TF$, applies. (In the case of a balanced system $dS/dt=0$, since the sum of the elastic and inelastic strains remains constant.) That is, in view of the assumed proportionality of F and δ,

$$\ln(\delta/\delta_0)=K_Tt. \qquad (4)$$

Moreover, in exceptional cases, T exceeds the average value of τ In such cases A is negative.

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[4] No doubt this assumption merely approximates the actual relation between the relaxing stresses and the changing fictive temperature. In regard to this relation, it will be noted that the density changes that accompany the changes in τ will react on the stresses if τ-gradients exist in the glass. That is, appreciable τ-gradients doubtless are present in any severely strained glass, and the accompanying differential density changes should as a rule hasten the relaxation. This follows because the highest values of τ and the consequent highest rate in its decrease are presumably near the surface where the compressive stresses approach a maximum. The comparatively large increase caused in the density by the decrease in τ in the region of these stresses should reduce them to a greater extent than the tractions in the interior are enhanced by lesser increases in density.

IV. APPLICATION OF THE EQUATION TO EXPERIMENTAL DATA

To procure data that have the required accuracy for thoroughly testing eq 3 or any other proposed expression concerning the decay of the double refraction in annealing glass is not an easy matter. In the first place, sizeable pieces of glass are usually considered necessary for the tests. Consequently, temperature gradients of considerable magnitude are likely to be present at the time of testing unless exceptional care is taken. These gradients make the effective temperature of the glass rather uncertain. Also, they cause the stresses to relax more quickly in some parts of the glass than in others. Through this differential action, the double refraction pattern is gradually changed, and, as a result, δ may actually increase for a time if the observations are made along some possible paths through the glass. In the second place, K changes so rapidly with temperature that the temperature range available for the tests is rather limited. That is, the decay is so rapid at the upper limit of the range that much of the double refraction effect has disappeared before the glass can be heated to that point; while it is so slow at the lower limit that the tests are extremely tedious unless the strains are large. As a result, the observations obtained in a test at high temperatures are usually few in number and made when δ is small, whereas those obtained at low temperatures, although comparatively numerous, are made when δ is very much larger. In view of the dependence of K on τ, data of this sort will yield values for k that are too large by varying degrees if the simple Maxwellian equation is used. Moreover, because of the limited range available, the temperature intervals between tests designed for the determination of k are often scarcely more than double the possible errors in the temperature determinations.

Presumably, because of the effect of a changing fictive temperature, τ, Adams and Williamson found that eq 4 was inapplicable to their data and, therefore, proposed the reciprocal relation

$$1/\delta - 1/\delta_0 = A't. \qquad (5)$$

Consequently, to test the relative applicability of eq 3, 4, and 5 to the decay of double refraction in annealing glass, they were applied to the data obtained by Adams and Williamson (page 622, reference 2) on a light flint while it was being annealed at 300° C. The experimental data and resulting computed curves are shown in figure 1.

In fitting these data, eq 3 has the obvious advantage of an additional constant. In arriving at tentative values for the three constants, δ_0, A, and K_T, required in using this equation, the method followed was essentially, (a) the drawing of a smooth curve that seemingly approximated the trend of the experimental data, (b) the choosing of three trial points on this curve in order to obtain two equations for the purpose of eliminating K_T, and finally (c) the search for a value of A that would satisfy the equation resulting after the elimination. A few trials will yield such a value if an adequate table of exponential integrals is used. In the case of the above-mentioned data for a light flint, the first and third trial points coincided, respectively, with the first and eleventh experimental points, while the second was near the third experimental point. These trial points yielded the values

5.56 and 6.97×10^{-5} for A and K_T, respectively, and the computed curve resulting from the use of these constants is that designated by A in figure 1. Since this curve fits the experimental data reasonably well, a betterment was not attempted.

As Adams and Williamson pointed out, eq 5 does not yield a reasonable fit for these particular experimental data, and eq 4 is even less satisfactory as curves B and C, respectively, indicate. In computing these curves, only two trial points are required to determine tentative values for δ_0 and A' in one case and δ_0 and K_T in the other.

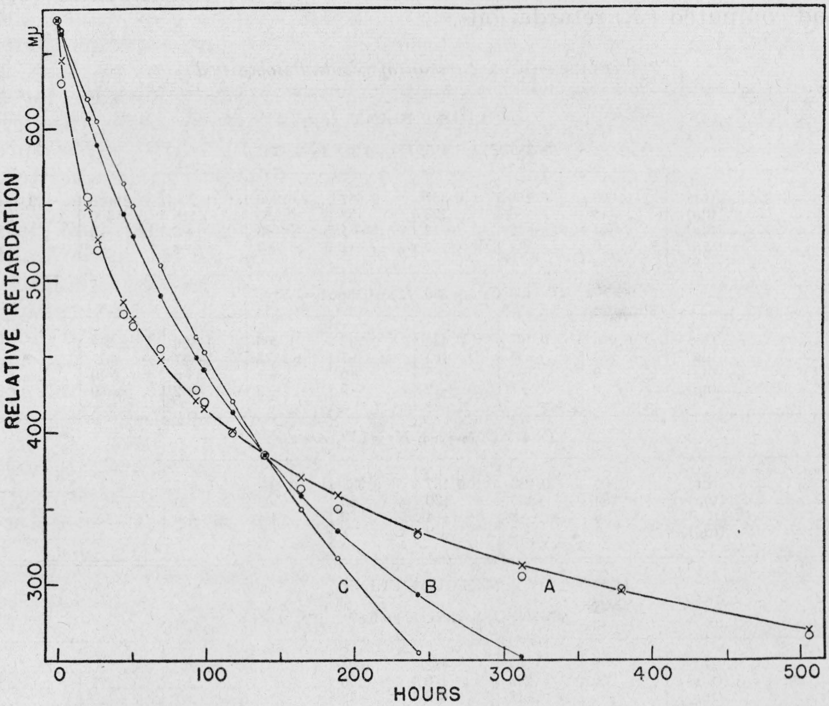

FIGURE 1.—*Decay of double refraction in light flint annealing at 300° C.*

Curve A: Circles, experimental data by Adams and Williamson; crosses, points computed by equation 3.
Curve B: Points computed by equation 5.
Curve C: Points computed by equation 4.

The trial points used in these cases were the first and third of those used previously.

In addition to this test at 300° C, Adams and Williamson determined the decay of double refraction in a light flint at three higher temperatures that are within the upper half of the annealing range. Table 1 presents the residuals (R_3) obtained through the use of eq 3 and also those (R_5) obtained by Adams and Williamson through the use of eq 5. In applying the first of these equations to their data, it usually was endeavored to balance approximately the positive and negative residuals both in magnitude and distribution, also to make those residuals as few as possible which exceeded an assumed maximum probable error of $\pm 5 m\mu$ in the δ-determinations. In only a few cases was it necessary to depart markedly from these aims, provided the results on ordinary crown are excepted.

For simplicity in applying eq 3, the observed initial relative retardation was chosen as the value of δ_0. The ratios $x=\delta/\delta_0$ for the remaining observations were then multiplied by various trial values for A and corresponding sets of values for K_Tt and K_T were computed. The A-value that yielded a spread that seemingly approximated the minimum possible in the K_T-values and the average of its set of K_T-values were then used to compute values of δ and the residuals $(\delta_e-\delta_c)$ for the various times of observation. Usually it was necessary to adjust these A- and K_T-values a few times in order to procure more satisfactory sets of differences between the experimental (δ_e) and computed (δ_c) retardations.

TABLE 1.—*Comparison of residuals obtained*

LIGHT FLINT

$T=385$°C, $\delta_0=415$, $K_T=0.21$, $A=2.93$

t (hr)	0.000	0.183	0.367	0.567	0.800	1.200	1.600	2.333
δ (mμ)	415	280	223	188	155	118	100	80
R_5 (mμ)	−15	+16	+12	+4	+3	+3	−5	−7
R_3 (mμ)	0	−4	−2	−1	+3	+8	−1	−2

$T=400$°C, $\delta_0=280$, $K_T=0.60$, $A=1.53$

t (hr)	0.000	0.167	0.433	0.733	1.000	1.500	2.317	
δ (mμ)	280	195	135	97	72	47	27	
R_5 (mμ)	+9	−1	−8	−6	+1	+6	+10	
R_3 (mμ)	0	+1	−2	−2	+2	+2	0	

$T=415$°C, $\delta_0=293$, $K_T=1.74$, $A=1.5$

t (hr)	0.000	0.083	0.167	0.333	0.467	0.667		
δ (mμ)	293	185	130	80	58	40		
R_5 (mμ)	+6	−8	−4	0	+4	+6		
R_3 (mμ)	0	−2	+2	+1	0	−3		

MEDIUM FLINT

$T=306$°C, $\delta_0=356$, $K_T=0.87 \times 10^{-4}$, $A=4.3$

t (hr)	0	267	483	1004				
δ (mμ)	356	205	170	130				
R_5 (mμ)	−5	+18	+3	−18				
R_3 (mμ)	0	0	+1	0				

$T=374$°C, $\delta_0=594$, $K_T=0.042$, $A=2.75$

t (hr)	0.000	0.533	0.950	1.533	3.017	4.500	6.083	
δ (mμ)	594	465	409	349	261	228	192	
R_5 (mμ)	−16	+18	+19	+21	+13	−10	−10	
R_3 (mμ)	0	−3	−3	+3	+11	−4	−4	

$T=390$°C, $\delta_0=573$, $K_T=0.24$, $A=2.00$

t (hr)	0.000	0.333	0.917	1.417	2.000	2.333		
δ (mμ)	573	378	253	190	160	130		
R_5 (mμ)	−5	+13	0	+4	−7	+6		
R_3 (mμ)	0	+4	−1	+5	−9	+2		

$T=406$°C, $\delta_0=350$, $K_T=0.53$, $A=2.27$

t (hr)	0.000	0.167	0.333	0.667	1.000	1.500		
δ (mμ)	350	205	160	103	80	52		
R_5 (mμ)	−5	+12	−1	0	−4	−3		
R_3 (mμ)	0	+6	−2	+2	−3	−1		

In particular, the results obtained on ordinary crown at 450° C offered exceptional difficulties, since there is evidence of a serious temperature change after the eleventh hour of this test. As a matter of fact, the authors state that most of the measurements on this glass were of a preliminary nature and, from their remarks, it may be assumed that some of the results possibly are affected by considerable errors in the temperature determinations. Furthermore, most of the relative retardations were determined by an inferior method in the case of this glass.

In addition to the light flint, Adams and Williamson also tested a medium flint not only at points restricted mainly to the upper half of the annealing range but also at a temperature, 306° C, which is far below that range as it is limited by normal practice. For this reason, the results obtained by applying eq 3 to the data on medium flint also are included in table 1. In the case of both of these glasses it will be noted that the averages of the residuals resulting from the use of eq 3 usually are less than one-half the averages of the residuals obtained by Adams and Williamson from the use of eq 5. Usually, this experience was repeated when eq 3 was applied to data for the seven other glasses which these authors tested. Consequently, the residuals for these remaining glasses are not presented. However, the natural logarithms of the values for K_T are indicated in all cases in figure 2.

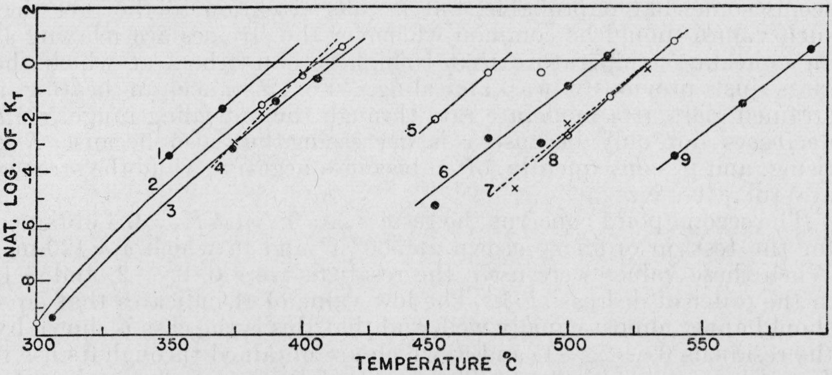

FIGURE 2.—*Natural logarithms of K_T for various glasses at various temperatures.*

The values of K_T were computed by equation 3 from data obtained by Adams and Williamson for various glasses annealing at various temperatures.

Curve 1, extra-heavy flint; 2, light flint; 3, medium flint; 4, heavy flint; 5, barium flint; 6, ordinary crown; 7, borosilicate crown; 8, light barium crown; 9, dense barium crown.

V. REMARKS CONCERNING THE VALUES OBTAINED FOR A, K_T, AND k

When δ_0 was large and the testing temperature was comparatively low, the values found for A ranged from 5.6 to 3, whereas, when δ_0 was relatively low and the testing temperature was high, they ranged from 1.5 to -0.6. Otherwise the A-values were intermediate and came in the order anticipated except in a few cases, such as the values obtained from the tests on medium flint at 390° and 406° C (see table 1). However, such reversals should not be uncommon, since a glass in equilibrium at any point in the upper half of the annealing range can be cooled sharply enough to be as severely strained as a glass that has been cooled less sharply from a higher temperature but still sharply enough to prevent a too great recession in τ.

With regard to small values of A, two minor points observed while applying eq 3 to these data deserve mention. The first is concerned with the paucity of data on light barium crown in the test at 540° C. Two observations are sufficient to yield a value for K_T or A' if eq 4 or 5 is used, but are inadequate for the determination of A and K_T of eq 3. Since 162 mμ is not a very large value for δ_0 (in view of the 7.5-cm path in this case), it seemed possible that eq 4 might be adequate, but its use yielded the result $K_T=1.38$, which is somewhat out of line with the values of K_T (0.066 and 0.264) that were obtained from the results of the tests at 500° and 516° C, respectively. That is, these results indicate that a better value for K_T at 540° C is 2.1, although the introduction of this value yields the result $A=-0.565$ when eq 3 is applied to the data obtained at 540° C. Since this temperature is not particularly high, a negative value for A, in this case, seems somewhat improbable, but it calls attention to the fact that such values should be common whenever the stresses are relaxing at an annealing temperature that is higher than others at which the glass just previously was annealing. For instance, in heating a strained glass at a moderate rate through the annealing range, $\tau-T$ decreases not only because τ is decreasing but also because T is rising, and it, consequently, often becomes negative while the stresses are still rather large.

The second point concerns the results $A=0.2$ and $K_T=0.4$ obtained for the test on ordinary crown at 500° C and in which $\delta_0=120$ mμ. When these values were used, the residuals were 0, 0, -2, and $+1$, in the order of decreasing δ. The low value of A indicates that eq 4 should apply almost equally well, and that this is the case is shown by the residuals 0, $+2$, -1, and 0, which are obtained through its use if K_T is given the value 0.45. The corresponding residuals obtained by Adams and Williamson are $+3$, -6, -2, and $+10$. In this case also, the number of observations is unsatisfactory and the testing temperature, 500° C, is scarcely high enough to cause a close approach to the condition, $(\tau-T)_0=0$, ordinarily; but the result calls attention to the fact that eq 4 alone applies if A approximates zero.

Although it would be quite difficult, if the testing temperatures were in the upper half of the annealing range, it is still possible to so manipulate the chilling treatments and the reheating to the annealing temperatures that the values of $(\tau-T)_0$ are known, at least approximately, in tests such as these that are being discussed. In that case, when A is determined, h becomes known. Unfortunately, it is impossible to determine the h-values for any of the glasses tested by Adams and Williamson because there is nothing in their data to indicate the values of τ_0.

When the natural logarithms of the values found for K_T are plotted as ordinates against the temperatures of the tests, as in figure 2, the result is much the same as that shown by Adams and Williamson in a similar presentation of the relation that their A'-values bore to the same temperatures. Since the lines representing the trend of the plotted points in figure 2 were located graphically, judgment played a considerable role in their positions, curvature and slopes. Since they are all approximately straight, these lines indicate that the k-values of the glasses do not change materially within the annealing ranges. Consequently, since the relaxation time, $\vartheta=1/K_T$, has been expressed in hours, $k=(T-T_1)/\ln K_T$ approximately if the relaxation time is 1 hour at T_1. In preparing these curves and computing the following values of k, only two determinations of $\ln K_T$ were ignored. These were the results derived from the data on barium flint and on ordinary crown at the temperature 490° C in both cases. These results were ignored because it seemed possible that errors of 20° were made in recording the temperatures.

The values obtained for k are as follows: 11.8° C, extra heavy flint; 12.6°, light flint; 10.2°, heavy flint; 12.8°, medium flint; 11.6°, barium flint; 13.4°, ordinary crown; 10.5°, borosilicate crown; 10.6°, light barium crown; and 12.9°, dense barium crown. Although the probable errors in these determinations are undoubtedly large, the average of the k-values is 11.8° C, which agrees closely with Twyman's experience. From the change in the constant A', Adams and Williamson obtained an average value for their constant, $M_1=(\log_{10}e)/k$, that approximates 0.33. This corresponds to a k-value approximating 13.2°. However, presumably for the purpose of simplifying the computations in preparing their sample annealing schedules, they gave $p=(\log_{10}2)/M_1$ the value 10°, in a relation which is essentially $A'=A'_0 2^{(T-T_0)/p}$, rather than 9.1°, which their average value for M_1 indicates or the value, 8°, which was found by Twyman. Comparatively few if any of the optical glasses ordinarily produced have a k-value as high as 14.4°, which corresponds to $p=10°$. This rather high value for p suggests that the annealing times computed by Adams and Williamson are too short and particularly so for the comparatively low annealing temperatures. However, it must be considered that they were merely demonstrating a method of preparing annealing schedules and were not recommending schedules that could be used for all of the glasses that may be included in the types tested. This is obvious, since it is well known that the upper limits of the ranges of suitable annealing temperatures for the various glasses that may be included within a single type often cover a range of 50° C or more.

Dimensionally, both K and $A'L$, when L represents the length of the light path in glass, are time reciprocals and are directly related to the fluidity of the glass. The minute was the time unit used by Adams and Williamson in making their observations. Consequently, at the temperature T at which $1/A'L$ becomes 1 minute, $M_2=M_1T=(T\log_{10}e)/k$. Such temperatures, T, are far above the annealing range and are high enough to cause considerable deformation in a short time. Within the annealing range, the hour is a suitable unit for measuring the relaxation time, $\vartheta=1/K$. In that case, the temperatures, T_1, at which $K=1$ and $\ln K=0$, are suitable for annealing optical blanks that are not too large. These temperatures can be determined from figure 2 and are as follows: 390° C, extra-heavy flint; 407°, light flint; 405°, heavy flint; 413°, medium flint; 475°, barium flint; 513°, ordinary crown; 532°, borosilicate crown; 532°, light barium crown; and 585°, heavy barium crown. As the annealing temperatures of pieces of glass with a thickness of 2 cm, Adams and Williamson recommended the following corresponding temperatures: 382° C, 408°, 407°, 418°, 494°, 514°, 541°, 552°, and 592° C.

Finally, the results obtained for K at very low temperatures, in the cases of the light and medium flints, indicate that k decreases appreciably from its magnitude at ordinary annealing temperatures whenever a glass is cooled to temperatures near or below the lower limit of its practical annealing range. That is, the K-values obtained for these glasses indicate that curves representing $\ln K$, as in figure 2, should become appreciably steeper at very low annealing temperatures. Such a decrease is to be expected, since it seems probable that there is a continual decrease in the available flow planes as a glass cools through these low temperatures and gradually changes from a highly viscous liquid condition to an elastic solid condition in which it shows no more viscous and plastic deformability than many crystalline solids. It will be noted, however, that glasses that have been cooled very rapidly from high temperatures should show, because of their high τ-values, a much greater inelastic deformability than well annealed glasses. In fact, it should be possible to chill fine threads of glasses or plastics, especially those with very low annealing ranges, so severely that they will anneal at atmospheric temperatures until τ decreases sufficiently to raise the viscosity and plasticity beyond that possibility.

VI. CONCLUSION

When a glass is cooled very slowly from high temperatures, it continues to behave as a liquid throughout the annealing range and apparently to even lower temperatures if the cooling rate is extremely low. Naturally, its properties, including viscosity, all change accordingly, that is, their temperature coefficients are generally much higher than when the glass or plastic behaves as a solid at temperatures far below the annealing range.

When the cooling rate is comparatively high, the glass departs from the equilibrium curve of its liquid condition at temperatures that are determined by the rate and nature of the glass. These temperatures of departure will be above the usual annealing range if the rate is exceptionally high. If the rapid cooling is continued after such departures, the glass begins to behave as a solid even before the annealing range is left behind. That is, even within the annealing range, a glass, although greatly undercooled, will react temporarily as a solid to comparatively sudden temperature changes.

Far below their annealing ranges, glasses and many of the so-called plastics behave as solids; but, when they are reheated, they drift toward the equilibrium curves of their liquid conditions as soon as the annealing range is reached. When the undercooling is considerable and the rate of reheating is comparatively low, this drift is very marked and often begins 50° C or more below the lowest annealing temperatures. Drifts of this kind are accompanied by large contraction and exothermic effects, which practically cease as soon as the equilibrium curve of the liquid condition is neared.

If the heating is continued after the equilibrium curve is reached, the glass becomes superheated, and this superheating will be quite large if the heating rate is high enough and the prior cooling rate was comparatively low. However, the rising temperature ultimately reduces the viscosity so greatly that the glass or plastic returns rapidly to the equilibrium curve, and this return is accompanied by large "rapid expansion" and endothermic effects.

When the rate of reheating is much higher than the prior rate of cooling, the drift while the glass is in an undercooled condition is quite negligible, and the curve followed by a glass or plastic while in its solid condition at comparatively low temperatures continues beyond the point at which it intersects the curve of the equilibrium condition. This point or temperature of intersection has been referred to in previous papers by such terms as the "effective annealing," "equilibrium," or "fictive" temperature of the glass while it is in the particular solid condition corresponding to a particular intersection point. This temperature, which can be varied at will over a wide range by reheating the glass, was termed the fictive temperature because it is, in most cases, at least as effective in determining the properties of a glass as the actual temperature.

Although most of the properties of glass are affected considerably by any large change in the fictive temperature, any rise or fall in it causes an exceptionally marked decrease or increase, respectively, in the viscosity and, consequently, greatly affects the relaxation of any stresses that may be in the glass. This leads to an interesting situation, since the fictive temperature is usually changing continually even when the stresses are relaxing at a constant real temperature.

Based on experience, an empirical expression was proposed previously for the relation between the time rate of change in this temperature and the magnitudes of it and the real temperature. In this report, this expression has been used in connection with Maxwell's equation for the development of inelastic deformation (that is, for the flow in stressed visco-elastic materials) in order to obtain an expression for the relaxation of stresses in an annealing glass. The resultant expression has been applied to the data obtained by Adams and Williamson on the stress relaxation at different annealing temperatures and for different kinds of glasses, and it has been found to fit experimental data better than previously suggested expressions fit them.

VII. REFERENCES

[1] A. Q. Tool and J. Valasek, Sci. Pap. BS **15,** 537 (1920) S358.
[2] L. H. Adams and E. D. Williamson, J. Franklin Inst. **190,** 597, 835 (1920).
[3] W. A. Weyl and A. G. Pincus, J. Applied Phys. **14,** 37 (1943).
[4] A. Q. Tool, Bul. Am. Ceramic Soc. **21,** 13 (Apr. 15, 1942).
[5] A. Q. Tool, Bul. Am. Ceramic Soc. **22,** 92 (Apr. 15, 1943).
[6] A. Q. Tool and C. G. Eichlin, J. Am. Opt. Soc. **8,** 419 (1924).
[7] F. Twyman, J. Soc. Glass Techn. **1,** 61 (1917).
[8] A. Q. Tool and C. G. Eichlin, BS J. Research **6,** 523 (1931) RP292; J. Am. Ceramic Soc. **14,** 276 (1931).
[9] H. Hovestadt, Jena Glass, English Ed., p. 158 (The Macmillan Co., New York, N. Y., 1902).
[10] V. H. Stott, E. Irvine, and D. Turner, Proc. Roy. Soc. [A] **108,** 154 (1925); J. Soc. Glass Techn. **9,** 207 (1925).
[11] H. R. Lillie, J. Am. Ceramic Soc. **14,** 502 (1931); J. Am. Ceramic Soc. **16,** 619 (1933).

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