CONCERNING THE ANNEALING AND CHARACTERISTICS OF GLASS

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CONTENTS

I. INTRODUCTION

To anneal glass quickly and efficiently is one of the many problems met in its production. The purpose of annealing is to avoid or remove all stresses which might be permanent, and injurious after the glass is in use. The harmful effects produced by such stresses are the variations in the refractive index, which cause double refraction, and the tendency of the glass to warp or break.

The problems which arise in annealing glass for different uses may differ in particular cases but in general they are much the same. The actual annealing procedure is often varied materially, depending upon the degree of annealing required, on the nature of the glass, and the character of the pieces. Consequently, to plan the most efficient process, it is necessary to consider all the factors entering into the particular annealing problem. For this purpose, a thorough knowledge of the general nature of glass is important. Furthermore, it is desirable to develop and standardize a number of simple tests which will make it possible to determine the points at which changes in the annealing procedure

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can be made to advantage.   This paper is the result of an investigation concerning the characteristics of glass in the usual annealing range and some of the general problems met in annealing.

Three necessary factors enter into any process for annealing glass—the temperature at which it is annealed, the corresponding period of annealing, and the corresponding rate and mode of cooling.   For brevity's sake these factors will be referred to as the "annealing temperature," the "annealing time," and the "cooling procedure."   The annealing temperature is the constant and uniform temperature at which any stresses that may exist in the glass are allowed to relax.   The period during which the glass is held at this temperature is the annealing time.   During this time, temperature uniformity and constancy are extremely important.   The length of the annealing time is determined by the magnitude of the initial stresses, the chosen standard of annealing and the relaxation time.   The cooling procedure is important since, if the cooling is not controlled properly, it will lead to reintroduction of permanent stresses while the glass is hardening, or to breakage, due to temporary stresses, after it has hardened sufficiently.

As intimated, the above factors may be varied considerably, but there is some definite treatment of any particular piece of glass which will give the desired results most quickly and efficiently.   The range of temperature, however, within which it is practicable to anneal any particular type of glass is narrow. If the temperature is too low, the stresses will relax too slowly, consequently a much longer total time will be required to obtain the desired degree of annealing, although a higher initial cooling rate is permissible.   If the temperature is too high, the danger of deforming the glass or changing its character is increased.   The initial cooling, also, must be slow, and very accurately controlled to prevent the reintroduction of permanent stresses.   The length of the annealing time and the subsequent rate of cooling depend on the annealing temperature selected, and on the degree of annealing desired.

For ordinary glassware in which the chief consideration is to remove danger of breakage, Twyman[1] considers that stresses as large as one-twentieth of the breaking stress are allowable. Where double refraction must be avoided, as in certain optical instruments, or where deformations due to slow relaxation of stresses are harmful, as in optical instruments or thermometers,

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[1] F. Twyman, Trans. Soc. Glass. Tech., 1; 1917.

the requirements are more exacting; but for these cases there seems to be a lack of reliable tests and specifications on the allowable magnitude of the stresses. In view of this uncertainty good practice would seem to demand that the stresses should be reduced to a minimum, especially for the best grade of instruments. The following measurements by Zschimmer and Schulz[2] give an approximate idea of what this minimum might be. They found that an especially well-annealed plate gave an average relative retardation of one-third millimicron per centimeter thickness. This plate was 24 cm in diameter and 3.9 cm thick, and was intended for a telescope lens. A normally annealed plate of approximately the same dimensions gave three times this retardation.

The stresses which correspond to this double refraction will be different for glasses of different compositions. In dealing with the ordinary small pieces, the stresses can be removed to such an extent that their effects are evident only with the most sensitive tests.

II. ANNEALING TEMPERATURE, AND SOME CHARACTER-ISTICS IN THE ANNEALING RANGE

Various arbitrary methods have been suggested for the purpose of determining a suitable annealing temperature. The majority of these involve tests which determine at what temperature the rate of deformation of loaded rods reaches a certain standard value. In such determinations the dimensions of the rods and the manner of loading must be taken into account. There are also a number of optical methods all of which are quite similar. These involve observations on the rate at which the double refraction decreases at various temperatures, or determinations of the temperature at which it disappears in a reasonable time.

In the present investigation, the working range of temperature at which several kinds of glass should be annealed has been determined by a number of these methods. A discussion of some of the methods used and the results obtained follows.

1. OPTICAL METHOD

Results obtained by one of the optical methods are shown in Table 1. The annealing temperatures (column 7) determined by this method (which will be designated method I) indicate the maximum temperature at which the annealing should ordinarily take place. The "upper limits" (column 8) are temperatures that may be used to remove large stresses quickly, if this should

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[2] Zschimmer u. Schulz, Ann. d. Phy., 42, p. 345; 1913.

appear necessary, but it is considered inadvisable to hold the glass at this temperature for any length of time owing to the consequent deformation or possible changes in the character of the glass. In addition, as already stated, special precautions must be taken in the cooling procedure when such high annealing temperatures are employed.

TABLE 1.—Critical Ranges in Various Glasses

Number	Name [a]	Critical range in glass				Annealing range by optical method: Method I	
		On cooling		On heating			
		A' $\pm 15°$ C	B' $\pm 10°$ C	A $\pm 10°$ C	B $\pm 5°$ C	Annealing temperature $\pm 15°$ C	Upper limit $\pm 15°$ C
		°C	°C	°C	°C	°C	°C
B. S.76	Dense flint	435	495	460	490	....	....
B.S.110	Medium flint................	405	480	455	485	460	510
B.S.188	Light flint	445	525	485	525	485	510
B.S.145	Barium flint.................	470	550	520	560	515	550
B.S.20	Light crown	450	525	495	525	480	530
B. S. 94	Borosilicate crown	475	560	515	565	525	550
K. 266	Borosilicate crown	500	585	545	585	525	550
B.S. 87	Light barium crown	520	590	575	605	570	610
B.S. 124	Heavy barium crown	530	610	575	630	605	625
	Pyrex tubing.................	....	....	520	670	....	....
Approximate formula B_2O_3..........		....	....	240	285	....	....
0.13 Na_2O, 1B_2O_3..................		....	....	340	375	....	....
0.28 Na_2O, 1B_2O_3..................		....	....	415	445	....	....
0.44 Na_2O, 1B_2O_3..................		....	....	450	480	....	....

[a] For composition, see Williams and Rand, J. Am, Ceram. Soc. 2, p. 422.

The method by which these points were determined simply consisted of observing samples of the glass placed between crossed nicols and heated in an electric tube furnace. The samples were in the form of cylinders about 2 cm in diameter and 5 cm long, or prisms approximately 2 by 2 by 5 cm, and were polished on both ends. The glass was heated at a rate that was reduced to a constant value of about 2° C per minute when approaching the anticipated annealing range. A Pt—Pt,Rh thermocouple was used to determine the temperature. During heating the intensity of the restored light, which was partly, if not wholly, due to temperature gradients caused by the heating, was observed. The double refraction so produced remained quite constant during the constant rate of heating until the "annealing temperature" was reached. At this temperature a perceptible diminution in the intensity of the light began. This showed that the stresses were

already relaxing at a fairly rapid rate. As the temperature rose
still higher the intensity decreased at a constantly increasing rate
until it had practically vanished at the "upper limit." At this
latter temperature any sudden change in the heating or cooling
was observed to produce very little double refraction. This
showed that the glass deformed very quickly relieving the stresses
caused by changes in the temperature gradients.

The choice of the "annealing temperature" and the "upper
limit" as fixed points in the annealing range is made, because
these points can be reproduced to within a few degrees centigrade
on reproducing the conditions, provided care is taken to insure
that the thermocouple measures the actual temperature of the
glass. The best arrangement for measuring the temperature in
these tests is to place the couple in a small hole along the axis
of the cylinder, but this precaution is unnecessary if low heating
rates are employed and if there is a good thermal contact between
the couple and the surface of the glass. When rapid heating is
employed considerable discrepancies will be observed, arising
from the difference in temperature between the center of the
cylinder and the surface. On heating at a rate of 20° C per
minute, this difference may be as large as 20°. The increase in
the thermal expansivity in this range, as will be shown later, also
becomes a disturbing facter when the rates are large.

One of the chief elements of arbitrariness in the choice of these
temperatures, especially the lower one, lies in the fact that if the
glass is badly strained, the relaxation of the large stresses is
perceptible at a much lower temperature. If several rings
are visible in the interference figure, the double refraction may
begin to decrease perceptibly almost 100° C lower than if fairly
well annealed glass were employed. Such temperatures are in
most cases too low for annealing. Hence it is advisable to use
well annealed or only slightly strained specimens in these tests.
The greater part of the stresses will then be due to the temperature
gradient produced by heating.

When the annealing temperature was chosen at or slightly
below the point where these small stresses began to diminish
perceptibly, as determined by method I, a number of experiments
indicated that one or two hours were sufficient to anneal the glass
to such an extent that only a very little evidence of double refrac-
tion remained. This annealing time does not include the time
required for establishing temperature equilibrium nor for subse-
quent cooling.

2. MEASUREMENTS OF RETARDATION

The rapid disappearance of the double refraction as the upper limit was approached seemed to make a more careful investigation desirable. Consequently an apparatus for measuring the ellipticity of the polarized light was used instead of a simple analyzing nicol. This apparatus consisted of a Stokes[3] elliptic analyzer modified by the addition of a Brace[4] elliptic half shade and a Jellet split nicol. A detailed description of this modified analyzer and the methods of taking the observations[5] and making the various calculations[6] have been published elsewhere. In order to use this method it was necessary to employ monochromatic light, and to place diaphragms on the end surfaces of the cylinder. These diaphragms were so placed that their openings, 2 mm in diameter, were within 1 mm of the circumference of the cylinder and on that radius of the cylinder which made an angle of 45° with the plane of polarization. This was a position of maximum ellipticity. The plane polarized monochromatic light entering the cylinder was practically parallel. The emergent light was elliptically polarized and for all small effects it was found that, on proper adjustment, one of the axes of the ellipse always fell very nearly the 45° plane. The light was homogeneous enough to permit fairly accurate settings for relative retardations as large as one-half wave. For small retardations the measurements were accurate to one-thousandth of a wave length.

The observations necessary for the calculation of the retardation δ are the complementary settings C and C' of the compensator and N and N' of the nicol for a matched field. When any rapid changes were taking place in the relative retardation while the glass was being heated or cooled, the observations were taken at intervals of one to three minutes. They were then plotted against time or temperature, as seemed most advantageous. The resulting curves were used for the calculation of the retardation at regular temperature or time intervals. A set of such observations, for example, was made on a cylinder of medium flint which had been comparatively well annealed. The cylinder was held at 275° C until its temperature was steady and uniform. It was then heated at a rate of 7° C per minute, the double refraction being measured until it had entirely disappeared at the high tem-

[3] G. Stokes, 9, Phil. Mag. (4), **2**, p. 420; 1851.
[4] D. B. Brace, Phys. Rev.,**18**, p. 70; 1904.
[5] Tool, Phys. Rev., **31**, p. 1: 1910.
[6] L. B. Tuckerman jr, Univ. of Nebr. Studies, **9**, No. 2; April, 1909.

peratures above the usual annealing range. Fig. 1 shows the form of the curves obtained when these observations were plotted. The relative retardations between the tangential and radial components which were computed from these curves are shown in Fig. 2. This relative retardation is indicated as positive when the radial component was retarded with respect to the tangential component.

The curve indicates that the double refraction shows a distinct rise to a maximum just before it begins to fall rapidly. It does
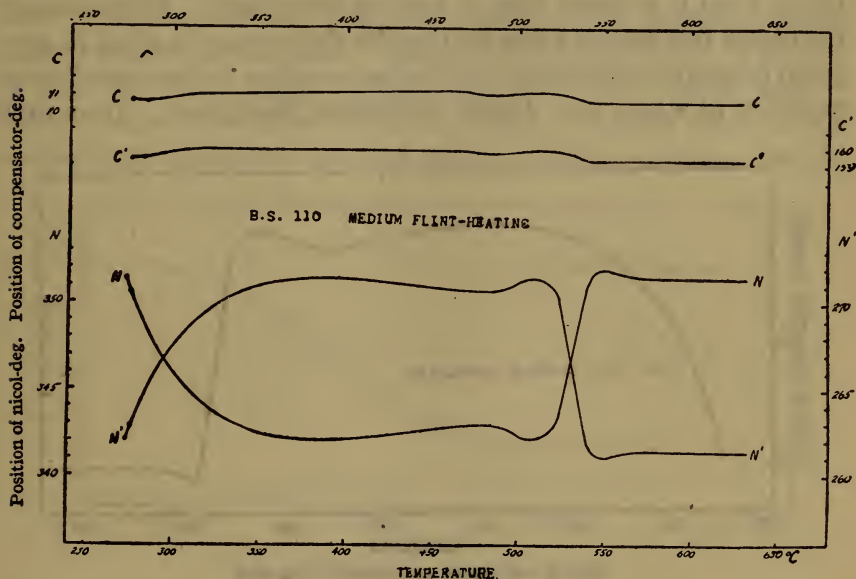

FIG. 1.—*Nicol and compensator settings with elliptic analyzer*

not, as might be expected, approach zero asymptotically, but crosses to negative values for a time, and then, after reaching a minimum, it gradually approaches zero again. This peculiar action at these temperatures is an indication of an interesting transformation that takes place near the annealing temperature range in glasses. Other manifestations of this effect lie in an apparent increased absorption of heat which has been observed in this laboratory,[7] as well as by M. So,[8] and in the increased thermal expansivity observed by C. G. Peters.[9] The form of this curve shows clearly that there is a rapid decrease in the ellipticity at these temperatures, and indicates that the cause of the

[7] Tool and Valasek, Meeting of Am. Phys. Soc., Baltimore; December, 1918.
[8] M. So., Proc. Tokyo Math. and Phys. Soc.; September, 1918.
[9] C. G. Peters, Meeting of Am. Phys. Soc., Baltimore; December, 1918.

definiteness of the "annealing temperature" and the "upper limit" of the annealing range, when the standardized method previously described is used, is to be found not only in the rapidly increasing mobility of the glass, but also in its changing thermal expansivity. In this connection it should be stated that a large difference in temperature between the center and the surface of the cylinder is necessary in order to obtain these curves with pronounced maxima and minima. Consequently, the surface temperatures at which the stresses become zero are much higher than if a slower rate of heating were used. Furthermore, the higher rate allows a shorter time for the stresses to relax in any given temperature interval. This also increases the measured temperature at which the double refraction disappears. Thus any
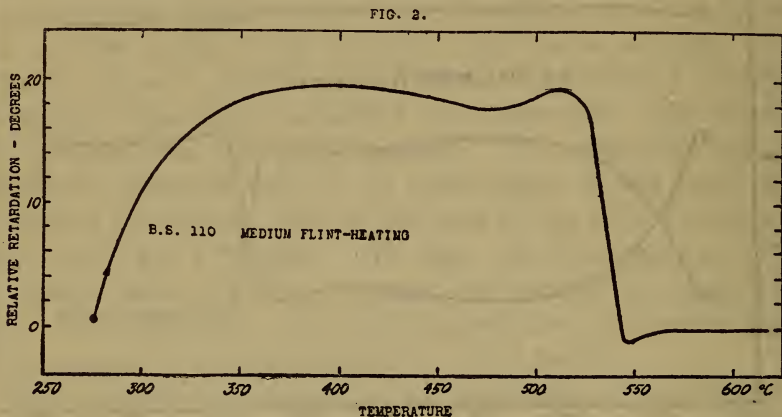
FIG. 2.

FIG. 2.—*Relative retardation on heating*

discrepancy between the temperatures for the disappearance of the double refraction as taken from the curve in Fig. 2 and the results by method I are accounted for.

The necessity for using large rates of heating and large differences in temperature in order to obtain curves showing a measurable maximum or minimum, is evident when the nature of this effect is considered. The explanation is clear when it is remembered that with rapid heating the outer surface of the cylinder reaches the temperature of increased rate of expansion (see Fig. 9) considerably ahead of the center. This increases the stresses and consequently the ellipticity of the transmitted light. When the center has reached this temperature, the surface is much hotter, and the stresses are, therefore, relaxing much more rapidly in the outer layers. This causes the stresses in the central portion to change from tension to compression. At the surface a re-

versal also takes place, but it is from compression to tension. A small temperature difference would not show this effect pronouncedly, but would merely change the slope of the ellipticity or retardation curve, without producing either a measurable maximum or a negative retardation. When such a procedure as that in method I is followed, this effect caused by the change in thermal expansivity, merely increases the sharpness of the disapperance of the restored light, and consequently the definiteness of the points determined.

In a similar manner the retardations were measured while cooling through this region. One of the resulting curves is shown in Fig. 3. The cooling started well above the "upper limit," Table 1, where the glass was soft enough to adjust itself to the temperature gradients due to cooling without showing double
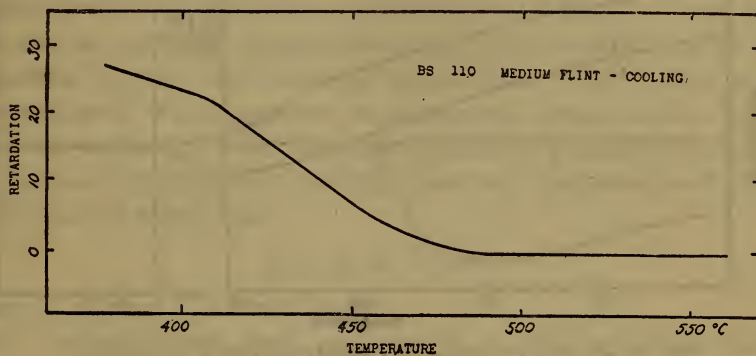

FIG. 3.—*Relative retardation on cooling*

refraction. An inspection of the curve shows that approximately at the "upper limit" the glass became double refracting, giving a positive retardation, the retardations rising first at an increasing rate, and then at a decreasing rate as the cooling proceeded. This decreasing rate is due partly to the decreased thermal expansivity and partly to the diminished rate of cooling at lower temperatures.

These positive retardations, which became evident while the glass (medium flint) was becoming rigid, were due to the differences in density that were incorporated in the glass at the high temperatures where the glass was soft. The temperature at which the retardation becomes evident coincides closely with that corresponding to the point B' on the cooling curve showing the apparent heat evolution for medium flint. (For the significance of the point B', see p. 549, Table 1 and Figs. 6 and 7.) There is

also a suggestion of a discontinuity in the slope of the curve at a somewhat lower temperature which approximately corresponds to A', the end of the apparent heat evolution. Between the temperature at which this change in slope of the retardation curve occurs and that at which the retardations first become evident, it would also appear that the slope of the curve is steeper than the small change in the cooling rate would warrant. Therefore it seems evident that the form of retardation curve obtained on cooling through this region is modified by the changes in the thermals expansivity and allied effects which accompany some molecular transformation which takes place in that temperature range where the glass ceases to deform readily under small stresses. As in the case of the curves obtained on
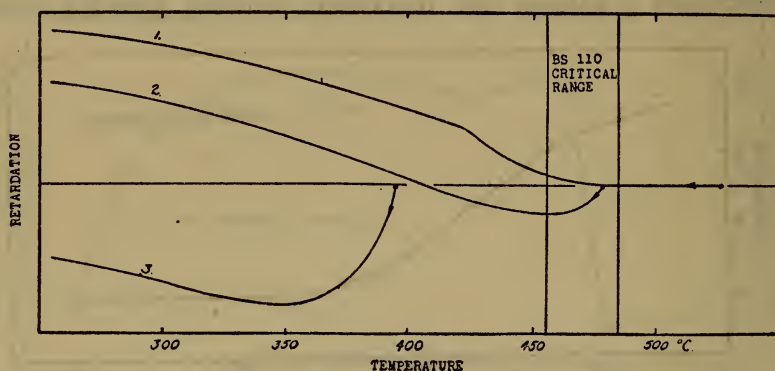

FIG. 4.—*Relative retardation on cooling from various temperatures*

heating, it would appear that the change in the thermal expansivity is the most potent factor producing the anomalous character of the curves for the retardation observed on cooling.

If similar determinations of the retardations evident on cooling are carried out when the starting point is below the "upper limit," there will be no initial stage in the curve where the double refracton remains practically zero. The retardations will, however, immediately become negative, as indicated in the curves *2* and *3*, Fig. 4 (based on qualitative observations), then cross over to positive values at some point that depends on the starting temperature and on the cooling rate, and will remain permanently positive after temperature uniformity has been reached. For a well-annealed sample, and a starting temperature below that at which the glass loses its rigidity, this negative retardation will not change sign, and will become zero only when temperature uniformity is again established.

The initial negative retardations on these curves show that the glass is not soft enough to adjust itself wholly, in the time allowed, to the cooling gradients. The magnitude of the maximum negative retardation will, therefore, depend, for any one sample, on the distance of the starting point below the "upper limit" and on the rate of cooling. The magnitude of the positive retardation finally remaining is approximately the difference between this maximum negative retardation and the retardation which the same cooling rate would have produced in the glass at a temperature where it was quite rigid. The amount of permanent double refraction depends, therefore, on the plasticity or viscosity of the glass at the starting temperature and on the rate of cooling. This phase of the subject has been investigated by Zschimmer and Schulz,[10] who used a somewhat similar method to determine the residual double refraction for a certain mode of cooling. They found that the increment of retardation is inversely proportional to the difference between the starting temperature θ and some other temperature θ_0 which appears to correspond closely to the "upper limit" of method I. If S denotes a quantity proportional to the retardation introduced by cooling from any temperature θ, then their equation states that:

$$(S_0 + S)(\theta_0 - \theta) = C$$

where S_0, θ_0, and C are constants.

For temperatures near and above θ_0 the equation ceases to hold, and in the latter case the retardation obtained by cooling at a given rate remains constant. The curves in Figs. 2, 3, and 4, taken in conjunction with the data of Zschimmer and Schulz, show clearly the advisability of annealing at the lowest temperature possible without unnecessarily increasing the annealing time, and in all cases below the temperature θ_0, which corresponds closely, as stated above, to the "upper limit" determined by method I.

3. CRITICAL RANGE

The peculiar manner of the disappearance of the stresses observed when studying the effect of rapid heating upon the results obtained by method I led to an investigation of the apparent heat absorption, and the thermal expansion in this range. To determine whether any heat effect accompanied the softening of the glass, a differential thermocouple method[11], [12] was used. (See diagram of

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[10] Zschimmer u. Schulz, loc. cit.
[11] Burgess and Le Chatelier, Measurements of High Temperatures, 3 ed., p. 383.
[12] G. K. Burgess, this Bulletin, 5, p. 199; 1908.

apparatus, Fig. 5.)   One of the junctions of a Pt,Rh—Pt—Pt,Rh differential couple was placed in a small piece of the glass under investigation and the other in a neutral body.   A third wire of platinum leading down to the junction in the glass made it possible to determine the temperature of the glass as well as the difference in temperature between the two junctions of the differential couple.   A number of neutral bodies were used, the most convenient being fine alundum, which was packed tightly about the junction.   The other junction was introduced into the glass either by fusion or by placing it in a small hole drilled into the sample, or by packing finely powered glass around it.   The
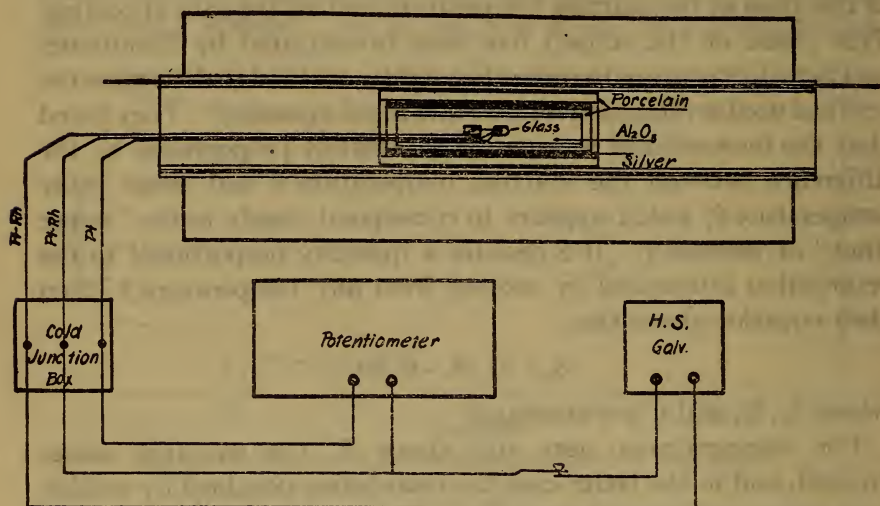

Fig. 5.—*Diagram of apparatus for determining critical range*

last method is by far the easiest to manipulate.   The mass of glass used was varied from approximately 1 to 50 g and caused only minor variations in the result.

The glass and neutral body were usually packed in a small porcelain tube with fine alundum powder as the packing material. The porcelain container was then placed in a heavy silver tube which served to equalize the temperature and, consequently, to reduce the differential readings due merely to unequal heating. The silver tube with its contents was then heated in an electric tube furnace at a constant rate.   After some trials in which rates varying from $\frac{1}{2}$ to 10° per minute were tried, a uniform rate of 4° C per minute was adopted.   A galvanometer deflection of 1 cm corresponded to approximately 0.4° C temperature difference. The temperature of the glass was determined in the usual way by

a thermocouple and a potentiometer. The galvanometer and potentiometer circuits were supplied with the necessary keys and switches so that readings on the two instruments could be taken without interference.

In the curves shown in Fig. 6 the galvanometer deflections are plotted against the temperature of the glass. The observations were made 4 to 8° apart, and the errors of observation are less than the width of the curves. In every case it will be seen that the glass shows an increased absorption of heat on heating, while on cooling there is evidence of a decrease in evolution of heat in passing through the same region. The temperature range covered by the phenomenon is twice as great for cooling as it is for heating, and moreover the limits on cooling are not so sharply defined. This is often the case with similar effects in other materials. These effects are not necessarily true endothermic or exothermic transformations as these terms are usually interpreted, but for the sake of brevity they will be referred to as heat absorptions and evolutions.

The temperatures at the beginning A and the maximun B on the curves for the heat absorption on heating and at the maximum B' and the end A' on the curves showing a heat evolution on cooling were determined as shown in Fig. 7. They are given for a number of glasses in Table 1. This table shows that the temperature range within which a rapid softening of the glass occurs, as determined by method I, corresponds within reasonable limits to the range between A and B. It would appear, therefore, that the heat absorption and the rapid softening of the glass are allied phenomena, and that it should be possible to determine the annealing range by means of the heat absorption. Tests on a number of glasses in this laboratory support this view. Since in most cases it is advisable to carry out the whole process of annealing below the temperatures where the glass becomes too soft, it appears that the region of this heat absorption must be considered as defining the upper limit of the annealing range. The experimental errors in determining this region are in most instances much smaller than those in determining the annealing range by other methods. Considering both accuracy and convenience, it may be said to be one of the best methods for this purpose. In the case of certain opaque or colored glasses it is especially advantageous. This method for determining the annealing range will be referred to as method II.
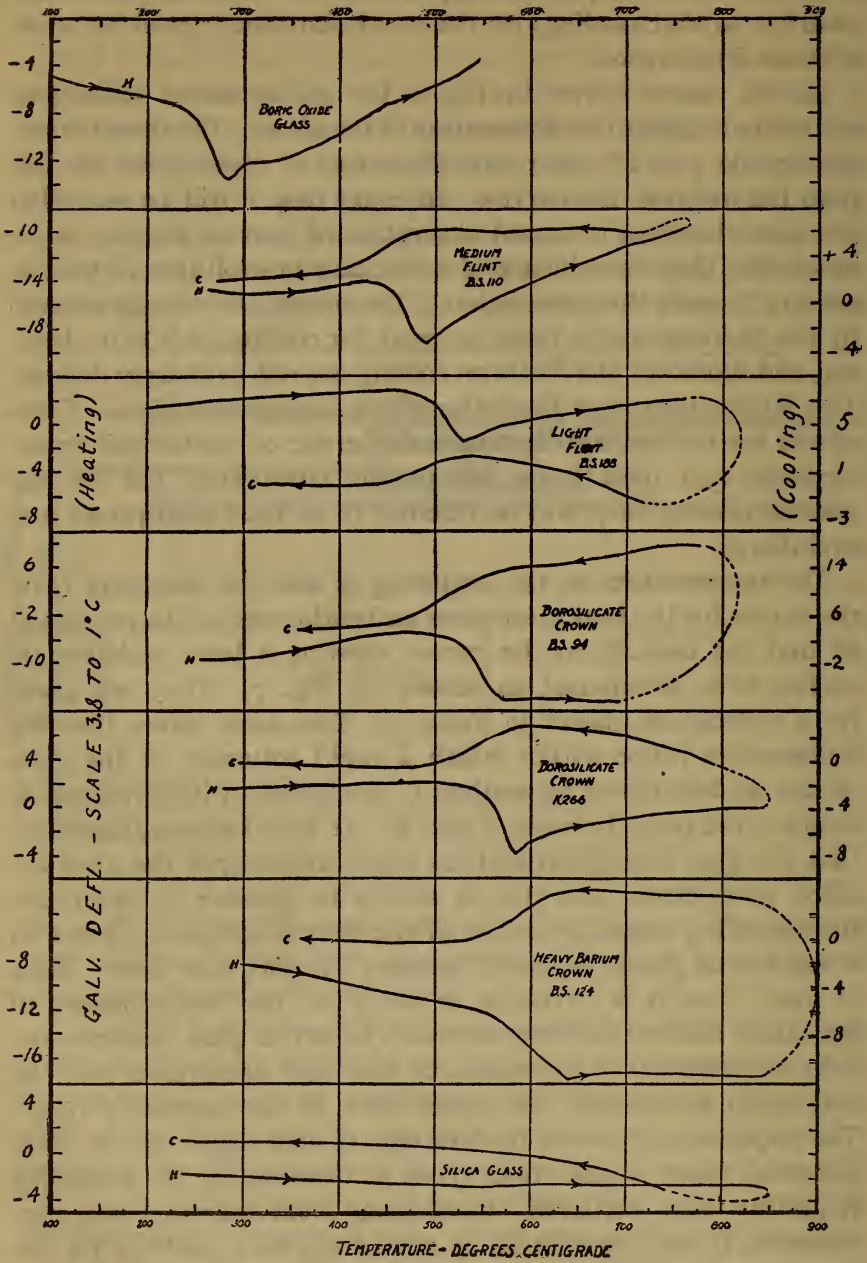
FIG. 6.—*Critical range by differential thermocouple*

The location of this heat effect was also determined by the use of
the "inverse time" method of Osmond.[13]   This method employs
only one couple, and involves the measurement of the time that it
takes the sample to rise through successive short and equal steps
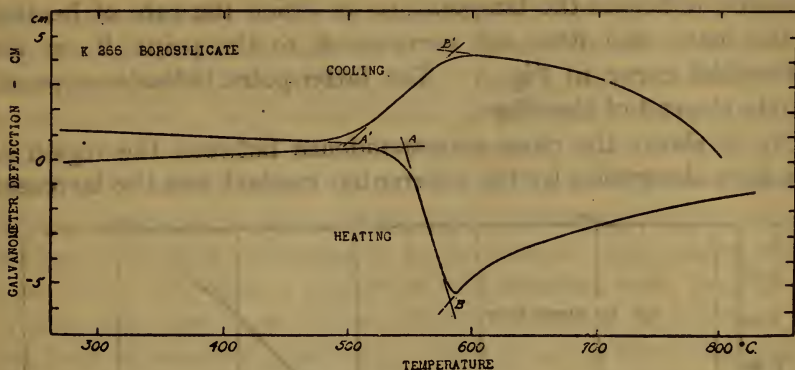of temperature.   The time interval is best measured on a chrono-

FIG. 7.—*Determination of critical range from curves by differential thermocouple*

graph but can be determined by a stop watch or, as tests have
shown, even by an ordinary watch if great care is exercised.
The temperature measurements must be accurate to within one-
half degree centigrade.   In the glass factory it would probably be
easiest to prepare the sample by dipping the end of the thermo-

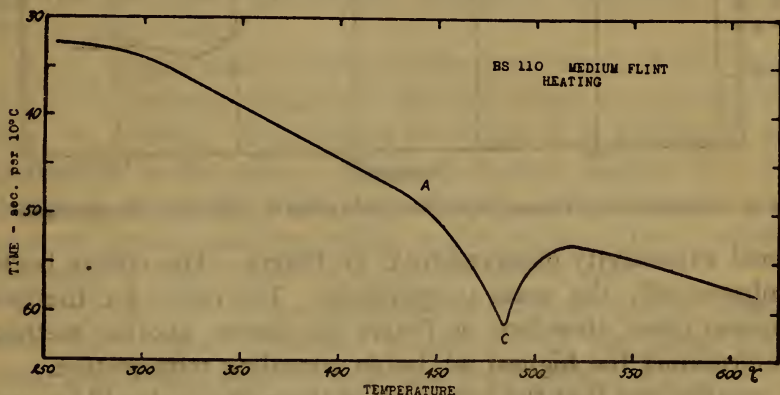FIG. 8.—*Critical range by inverse rate method*

couple into the molten glass and taking out a very small
amount.   With the proper apparatus the location of this heat
effect, and hence the approximate annealing temperature, could
be determined before the pot had solidified.   A base metal couple
should be sufficient for this purpose.   Fig. 8 shows a curve,

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[13] Burgess, loc. cit.

obtained by this method, in which an iron-constantan thermo-couple, a stop watch, and a Leeds and Northrup type K poten-tiometer were employed. The point *A* on this curve indicates the beginning of the effect on heating, and is identical with the same point obtained by the differential method. The cusp *C*, however, indicates the temperature at which the rate of heating is the least, and does not correspond to the point *B* on the differential curve in Fig. 7. The latter point indicates approxi-mately the end of the effect.

Fig. 9 shows the close correspondence between the region of this heat absorption by the differential method and the increased
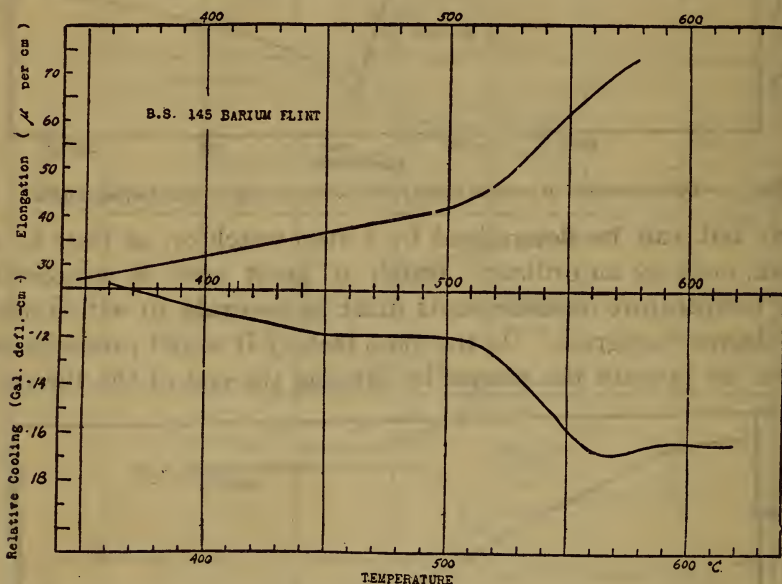
FIG. 9.—*Comparison of thermal expansion and curves by differential thermocouple*

thermal expansivity observed by C. G. Peters. The effects begin at substantially the same temperature. The curve for thermal expansion gives, therefore, as Peters has shown, another method of determining the highest advisable annealing temperature.

It was decided that the beginning of these effects should be con-sidered as the upper limit of the annealing range. The advan-tage to be gained by the more rapid disappearance of the stresses at higher temperatures seems to be outweighed by the necessary precautions to be observed on cooling through this region with-out reintroducing additional strain. As already indicated, this difficulty is not due to the softness of the glass alone, but also to the marked changes in the thermal expansivity and other con-

stants, which accompany radical changes in the molecular group-ings of the glass. In addition, such molecular changes may ex-pedite certain deleterious effects, such as crystallization during the annealing and slow cooling.

The exact nature of these changes in the molecular groupings is not to be explained without a further and thorough investigation of the subject. It appears, however, that they are accompanied either by a small, but definite, absorption of heat on heating, and a corresponding, but less well-defined, evolution of heat on cool-ing; or, by a change in the thermal conductivity; or, some other property of such a character as to produce an apparent absorp-tion or evolution of heat. The usual magnitude of the relative heating or cooling with respect to the neutral body amounted to 2 or 3° C. Although a number of experiments were carried out to determine the exact nature of this effect, its explanation has not been established positively. Neither has it been determined whether this heat absorption results merely from a change in the specific heat[14] or something which might be considered as a heat of chemical solution or reaction, or a latent heat of change in state.[15] The possibility of a change in the specific heat or con-ductivity caused by the relaxation of the internal stresses was considered, but no relation between the magnitudes of the stresses and the heat effect was found. Moreover, powdering the glass did not alter results.

M. So, whose observations corroborated those on the absorp-tion while heating, apparently did not notice the corresponding effect on cooling. He ascribes the effect to a melting of some component in the glass. However, it may suggest the rapid change in properties which characterize a substance not too far removed from conditions which would admit of the coexistence of phases in equilibrium at a transformation point.

In order to determine whether the transformation was connected with the complex chemical composition of the usual glasses, some simple borax glasses were made up with proportions rang-ing from pure boric-acid glass to fused borax. The curves were quite similiar to those obtained on the common glasses, but the absorption occurred in different regions. The temperature ranges for the absorption are given in Table 1 under the heading "Crit-ical range."

It was considered that, even in stable glasses, the transforma-tion might be associated with or followed by a slight crystalliza-

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[14] W. P. White, Am. Jour. Sci., 47; January, 1919.   [15] M. So, loc. cit.

tion.   Usually such crystallization effects are too small to be observed easily.   Consequently it seemed desirable to investigate a case where a marked crystallization does occur.   Some observations were made, therefore, on the unstable sodium metasilicate glass made as described by Guertler.[16]   According to Guertler this glass shows a large evolution of heat due to crystallization when it softens.   The heating curves presented in Fig. 10 show
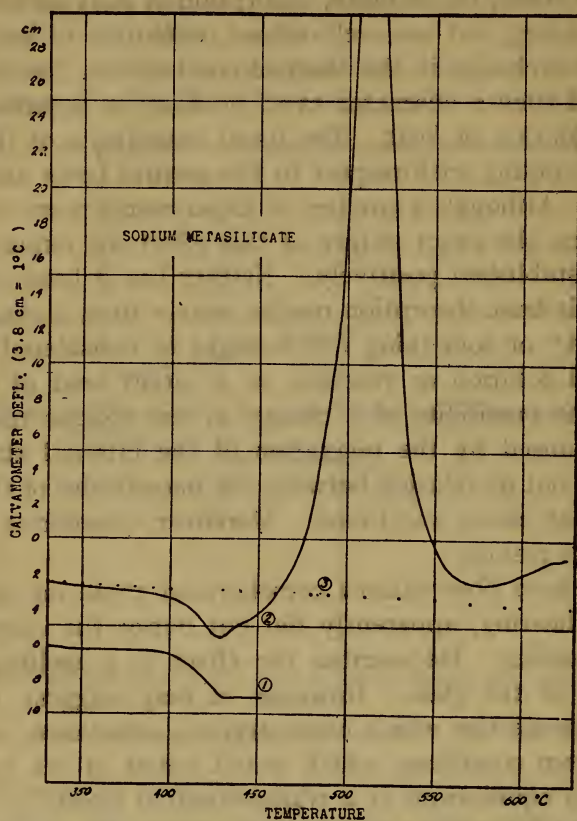
FIG. 10.—*Heating curves on sodium metasilicated with differential thermocouple*

that this exothermic transformation in sodium metasilicate glass occurs soon after but not coincident with the apparent endothermic effect on heating.   Curves *1*, *2*, and *3* in this figure were taken in this sequence on the same sample.   They show that the glass can be heated for a short time beyond the first transformation without changing its properties to any great extent, although the slight difference between curves *1* and *2* would lead one to infer that some crytallization had occurred during the first heat-

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[16] Guertler, Zeits fur. Anorg. Chem., **40**, p. 8268: 1904.

ing. On continued heating the glass became crystallized, giving the second curve, and when heated again gave the smooth curve shown as *3*. This latter curve was continued until melting occurred, which was above 1000° C. It would appear, from curves *1* and *2*, that for this glass at least there is no danger of crystallization when it is held for a short period of time at temperatures near and possibly even somewhat above the first or endothermic transformation. Further investigation showed that the presence of a few crystals caused crystallization to begin sooner than if a perfect glass had been used, but in no case did it occur until after the first transformation. A more thorough study of the tendency of the ordinary glasses to crystallize in this region seems desirable, since in practice this tendency has sometimes been found to interfere with the free choice of an annealing temperature.

Tests made on some of the optical glasses from this Bureau indicated that such glasses were too stable to show sufficient crytallization within the time available, hence no relation could be established between the tendency toward crystallization and the apparent endothermic transformations which they show when heated. Crystallization of the ordinary glasses seems to be greatly accelerated by impurities [17] [18] or dissolved gases, as has been demonstrated. It appears that the most active substances in this respect are the chlorides and sulphates that occur as impurities in potash. The general composition of the glass and the temperatures used in its manufacture are other factors that affect the tendency toward devitrification. It has been demonstrated that the injurious effects of impure chemicals often can be ameliorated by the proper control of the melting temperature. It would therefore be of interest to determine whether these impurities affect the endothermic transformation on heating.

III. ANNEALING TIME

The results outlined above all point to the desirability of as low an annealing temperature as is consistent with the efficient and rapid removal and prevention of permanent stresses. In order to employ such low "annealing temperatures" efficiently it is necessary to obtain some information concerning the "annealing time" required, and the rate of relaxation of the stresses at various temperatures. This leads to the consideration of methods for the determination of Maxwell's "relaxation time" for stresses

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[17] Cauwood and Turner, J. Soc. Glass Tech., **1**, pp. 87–96; 1917.
[18] Fenner and Ferguson, J. Am. Ceram. Soc., **1**, pp. 468–76; 1918.

in viscous media. A number of such methods have been in use, and they are, perhaps, the best means available to determine the most satisfactory annealing time and temperature. These methods may be divided into two classes, of which the first to be considered deals with the rate of deformation of the glass under an external force, and the second, with the rate at which the glass loses its double refracting power. Of the first class, the methods commonly used consist of bending, twisting, or stretching strips or rods. Of these the latter two are to be considered the most satisfactory except in those cases where the preparation of the samples is difficult.

The methods of the second class vary only in the manner in which the double refraction is measured. When the stresses are large, this may be done by determining the rate of disappearance of the interference rings in a badly strained cylinder of glass. When they are small, the retardation may be measured by some such instrument as the Stokes analyzer described previously.

The theory and equations necessary for the determination of the relaxation time are discussed thoroughly in articles by Maxwell,[19] Zschimmer and Schulz,[20] and Twyman.[21]

Some of the discussions will be given here, merely that the symbols used may be clearly defined. Maxwell's equation on which all these measurements are based states that:

$$\frac{dF}{dt} = E\frac{dS}{dt} - \frac{F}{T}$$

where F, S, and t are respectively the stress, strain, and the time, while E is the elastic coefficient involved and T is a constant called the "relaxation time."

According to the value of T and its variation with the magnitude of the stress, the body will show the properties of elasticity, plasticity, or viscosity. These terms are used by different authors in different senses, and even the same author is not always consistent. This uncertainty is, in a large measure, due to the present incomplete knowledge of the subject, but the following discussion may serve tentatively to distinguish between these terms.

When T is infinite the above equation represents the behavior of a perfectly elastic body. For a large number of the common rigid bodies this condition is approximated until very large forces, which are said to exceed the elastic limit and to approach the

[19] J. C. Maxwell, Phil. Mag. (4), **35**, p. 129; 1868.   [21] F. Twyman, loc. cit.
[20] Zschimmer and Schulz, loc. cit.

limit of rupture, are applied. For many materials T ceases to be extremely large for comparatively small stresses. In other words, such materials have low elastic limits. Under stresses, whose magnitude lies between the elastic limit and the breaking stress, materials are plastic. Hence those materials with low, finite elastic limits are usually considered plastic bodies. For a plastic condition T the relaxation time generally varies with the stress. It may be practically constant, however, if the variations of the stresses are confined within certain limits. When the elastic limit is zero and T is independent of the stress, the material may be termed "viscous." In a truly viscous material T is independent of the stresses even when these are indefinitely small. In general, when T is extremely large, the material is elastic; when T is a function of the stress, the material is plastic; and when T is independent of the stresses, even when they become indefinitely small, the material is viscous. It is to be noted that this conception of "viscous" bodies does not identify "viscosity" with the "internal friction" which is characteristic of all substances.[22][23] Generally there is no sharp line of demarcation between the elastic, plastic, and viscous conditions, and they merge gradually into each other. Most solids, such as metals or glass, may exhibit any or all of these properties depending on the manner in which they are tested. For that reason they may be termed elastico-plastico-viscous materials. Certain theories concerning molecular aggregations and their action in solids are often helpful in explaining these characteristics and the various elastic aftereffects. A number of such theories have been advanced, one of which is the Maxwell-Butcher [24] theory. It has been employed by certain investigators as an aid in discussing the properties of glass.

1. MEASUREMENT OF THE RELAXATION TIME BY AN APPLIED LOAD

When F in Maxwell's equation is constant as in the methods of the first class, which employ a glass body under a constant external load, the following solution is obtained:

$$ET = F \left/ \frac{dS}{dt} \right.$$

Here ET has the dimensions of a coefficient of viscosity. In the strip-bending experiment, for example, F and $\frac{dS}{dt}$ may be de-

[22] Thomson and Tait, Nat. Phil., 1, art. 741.
[23] Love, Math., Theory Elast., Cambridge, 2 ed., p. 115.
[24] Butcher, Proc. London Math. Soc., 8, p. 103; 1876.

termined by observation and the value of ET calculated. It is not possible to determine T unless E is known, and this is an inherent weakness of this method when T is desired. The elastic coefficient is not very easily determined at the temperatures employed, and is usually assumed to be approximately the same as at ordinary temperatures, although probably it changes considerably in the critical range. When values for T (expressed in hours) are calculated for several temperatures on the assumption of some constant value for E, they will be found to satisfy the equation given by Twyman:

$$T_\theta = T_o \, e \, \frac{\theta_o - \theta}{k}$$

In this, T_θ and T_o are the relaxation times at temperatures θ and θ_o, while k is a constant depending on the nature of the glass. The constant k may be determined from observations on the variation of the rate of bending with the temperature.

The methods of this type used in this laboratory consisted of stretching thin rods or bending strips of glass. The former was used only occasionally to check the results obtained by bending. The latter method was very similar to that described by Twyman except that in most cases the strip rested on two supports instead of being clamped at one end. The method of support did not appear to affect the results. When the two supports were used, they consisted of small smooth porcelain tubes. The strips tested were approximately 50 mm. long, 4 to 10 mm. wide, and 1 to 2 mm. thick. The loads varied from 15 to 500 gms. and were always large enough to make the weight of the strip negligible in the calculations. The strip was heated in an electric tube furnace and observed with a long-focus micrometer microscope. The temperature of the strip could be determined within $\pm 2°$ C and held constant for a considerable length of time to within one-half of 1 degree. Observations on the rates of bending were taken at four or five points in an average range of 40° C without changing the load. The logarithms of the rates plotted against the corresponding temperatures fell on a straight line as required by Twyman's equation. The slope of this line determines k.

The bending method gave very consistent values for both ET and k when the observations were repeated. The values of k for the different glasses tested varied from 10 to 13. (See Table 2.) The average value was such that, roughly speaking, ET doubled for every 8° C drop in temperature. As the temperature was

increased k seemed to increase somewhat.   It must also increase
for lower temperatures since otherwise the glass would be more
rigid at room temperature than the experiments of Zschimmer and
Schulz would indicate.

TABLE 2

Name	Method	Range °C	k	$T_{500}a$
				Hours
Borosilicate	Bend	535–585	11.4	....
Do	....do	555–590	11.5	2.1
Do	....do	605–640	11.6	....
Do	....do	600–660	12.6	....
Do	Optical	510–535	10.3	8.5
Light flint	Bend	475–530	12.3	.0094
Do	Stretch	500–545	11.9	.0114
Do	Optical	440–490	11.7	.067
Dense flint	Bend	485–530	10.2	.0059

a T_{500} extrapolated by Twyman's equation when necessary.

The values assumed for E were as follows:

$$\text{Borosilicate} - E = 7500 \text{ kg } /\overline{mm}^2$$
$$\text{Light flint} - E = 6500 \text{ kg } /\overline{mm}^2$$
$$\text{Dense flint} - E = 6000 \text{ kg } /\overline{mm}^2$$

Contrary to expectation the values obtained for ET by varying
the load from 15 to 250 g were constant within the experimental
error.   Moreover the values for T, on assuming E to be the same
as at room temperature, were about one-sixth as large as those
obtained by the optical method for a retardation of 10 to 15°,
or approximately 15 to 23 millimicrons.   That this discrepancy
could be due entirely to assuming a wrong value for E is extremely
doubtful.   A more plausible explanation lies in the fact that the
bending experiments as they were carried out necessitated the
use of higher temperatures and greater stresses than could be em-
ployed successfully in the more accurate measurements by the
optical methods.

2. MEASUREMENT OF THE RELAXATION TIME BY AN OPTICAL METHOD

For applying the optical methods (that is, methods of the
second class) Zschimmer and Schulz assumed that the deforma-
tion or S remained constant while the stresses causing double re-
fraction relaxed.   This assumption would appear to be inade-
quate, at least for bodies of limited dimensions under no external
constraint.   Solving Maxwell's equation on this assumption,
however, gives

$$F = F_o e^{-\frac{t}{T}}$$
$$\text{or } t = T \log_e \frac{F_o}{F} .$$

If it is assumed that F is proportional to the retardation δ, which Pockels[25] has shown to be the case for externally applied forces, then

$$T = t/\log_e \delta_0/\delta$$

In these equations F_0 and δ_0 are the initial stresses or retardations while F and δ are the corresponding quantities after a time t. When these quantities are measured the relaxation time T may be computed, or if $\log_e \delta$ is plotted against time, then T may be found from the slope of the resulting curve. If T is constant for all stresses, this curve should be a straight line. This was not found to be the case, however, when this method was used. In fact, T appeared to increase quite materially as the stresses and the resulting double refraction decreased. This was to be expected if the glass was plastic.

The retardations were measured with the Stokes analyzer while the strained cylinder of glass was being annealed at a constant temperature. The temperature could be kept constant within a few tenths of a degree for several hours. Some of the resulting observations are summarized in Table 2.

When T was determined for the same magnitude of retardation at different temperatures, it was found that Twyman's empirical equation connecting θ and T was satisfied. Some of the computed values of the exponent k in this equation are also given in Table 2.

In order to obtain values for T when the retardations were large, some observations were made on the rates at which the rings in a badly strained cylinder disappeared. A very large variation of T with the magnitude of the double refraction was evident. When two or three rings were visible the value of T was the same as obtained by bending a strip. This would indicate that the difference in the magnitude of the stresses was a factor in causing the discrepancy between the two methods. It is possible, also, that the assumption of a constant strain is relatively a closer approximation for larger strains. However, the entire question of the distribution of the stresses, the magnitudes of the elastic coefficients involved, and of the manner in which glass deforms is unsettled. It is worthy of note in this connection that Zschimmer and Schulz using an optical method found that, at room temperatures, the average retardations in pieces with large strains would show a perceptible decrease after one month, while

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[25] F. Pockels, Ann. der Physik, 7, p. 745; 1902.

the small average retardations in samples with less strain actually increased after the same period of time. If this same condition exists at higher temperatures, it might well cause the above described variation in T with the magnitude of the double refraction and the discrepancy in the results obtained for the relaxation time by the two methods.

The values in Table 2 are only a few collected from tests to determine the annealing time, and are given to illustrate the points discussed and to emphasize the necessity of a more thorough investigation of the manner in which the stresses relax while the glass is being annealed. For such an investigation the methods for determining T and k should be far more refined than is required for general testing. The determination of these constants over a wide range of temperatures is especially desirable. An interference method would undoubtedly be of advantage in determining the rate of deformation at low temperatures and under small loads.

3. APPLICATION OF RELAXATION TIME

Although the constancy of T and k must be questioned, in the case of the former when the force is varied, and of the latter when the temperature range is very large, still they are of great value in estimating the annealing time and determining a cooling procedure. If the initial stresses are to be reduced by holding at some constant annealing temperature until they are any fraction F/F_o, for example, one-tenth of their original value, then the time required to anneal will be:

$$t_1 = T \, log_e \, F_o/F = 2.3 \, T$$

When due allowance is made for the variation of T with the stress, a very fair approximation to the annealing time can be obtained. Furthermore, the time required for the stresses to decrease to $(\frac{1}{10})^n$ of their initial magnitude will be equal to $n \times t_1$ hours. In order to obtain t_1 for successive drops of $10°$ in the annealing temperature, it is necessary only to multiply by a constant derived from Twyman's equation. Thus

$$t_{(\theta-10)} = t_\theta \times e^{\frac{10}{k}}$$

Assuming an average value of $k = 11.3$ this would give the relation:

$$t_{(\theta-10)} = 2.4 \, t_\theta$$

In arranging the annealing schedules, for small articles at least, usually it was found desirable to choose an annealing tem-

perature somewhat below the beginning of the heat absorption. Schedules beginning at temperatures much higher or much lower were usually found to be less efficient. Some experiments on a piece of badly strained light flint illustrate this. The location of the beginning of the heat absorption was at 485° C. It was found that 10 days at 430° C were required to obtain the same reduction of stresses that could be obtained in one-half hour at 485° C. On the other hand, it could be cooled very rapidly from the lower temperature without reintroduction of permanent strain, while from 485° C the cooling rate during the first 30 or 40° required much more accurate control to obtain the same result. There is apparently some temperature, with the corresponding method of cooling, that gives the most efficient procedure. For small pieces this temperature appears to be 10 to 20° C below the critical range.

It is of the utmost importance that the temperature of the glass should be as uniform as possible, especially in the annealing range. The introduction of strains in homogeneous glass is due solely to temperature gradients. Whether these are due to rapid or unsymmetrical cooling, or to a lack of temperature uniformity while annealing, is immaterial. Stresses due to the latter cause may be larger and more harmful, inasmuch as they may be very irregularly distributed. The importance of temperature uniformity can not be overemphasized, since the lack of it is the chief source of difficulty in annealing glass. This is especially the case when fine annealing is attempted. Temperature control, such that there are no disturbing fluctuations in, or uncertainties concerning the actual temperature which the glass attains, is absolutely necessary to insure successful annealing. Unless these conditions are met, certain devices which are used to determine whether the temperatures which existed in a lehr or kiln have been satisfactory will give misleading indications. Such devices usually consist of a rod or tube of the glass to be annealed, supported horizontally but free to bend. The suitability of the temperature conditions which existed is determined from the amount this rod deformed during its passage through the lehr with the glass which was being annealed. Unless the temperature control and distribution were satisfactory, the indication derived from the amount of deformation will have no meaning, since a very unsatisfactory temperature condition might have produced the same bending. With proper pre-

cautions such devices may be of value, although examining the product itself in a reflection polariscope would be as easy and would give more reliable information.

IV. COOLING PROCEDURE

Certain generalizations concerning cooling can be made, but the process can not be completely defined without a knowledge of the conditions to be met. A different cooling procedure will have to be followed for every change in the kind of glass and in the size or shape of the article. In any case where all the conditions are known it is possible, however, to specify with considerable accuracy what should be a good cooling procedure. The efficiency of the procedure must be determined by the expense and time required to produce a satisfactory product.

As an example of a mode of cooling which proved very satisfactory from the standpoint of laboratory experience, the following experimental cooling procedure is given. The glass was light flint and the maximum size of the pieces was approximately 2 by 6 by 8 cm. The cooling followed an annealing period of about two hours, during which the glass was held at a constant uniform temperature of 475° C, or 10 to 15° below the critical range. After various trials it appeared that satisfactory results could be obtained by a cooling rate that had reached 5° C per hour at 460° C and which was increasing in such a way that it doubled for every 10° C drop thereafter until the natural cooling rate of the furnace was reached at approximately 420° C. This method of cooling is practically that suggested by Boys,[26] Twyman,[27] and English and Turner [28]. The previously mentioned measurements by Zschimmer and Schulz on the double refraction shown by annealed glass were the basis for considering the results satisfactory. The time consumed was also taken into account.

Doubtless the cooling rate could have been further increased at the lower temperatures since experiments on similar blocks showed that a much more rapid rate of cooling at 200° C did not introduce serious permanent double refraction. Increasing the rate must, however, in any case be discontinued after it becomes large enough to produce stresses approaching the elastic limit.

For large pieces of the same glass, the rate at any temperature must be much lower. In the case of the simpler types of solids

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[26] Boys, Nature, **98**, p. 150; 1916.
[27] Twyman, loc. cit.
[28] English and Turner, J. Soc. Glass Tech., **2**, p. 90; 1918.

such as the sphere, a statement of the relation between the rate of cooling and the size may be made when the cooling is approximately linear. Linear cooling means equal changes of surface temperature in equal time intervals. If the pieces are not very large and the rate of cooling is not changing rapidly, the method of cooling discussed above may be considered to be linear at any instant; that is, the temperature distribution inside the piece of glass approximates that of linear cooling. For linear cooling of a sphere the difference between the surface temperature and the mean temperature is proportional to the square of the radius. The tangential stresses at the surface, which are the largest stresses in the sphere, are proportional to this difference in temperature, and, consequently, to the square of the radius. The cases of the slab and cylinder are very similar, and it may be said that the maximum stresses present are roughly proportional to the square of the least dimension. If, then, the cooling may be considered linear in effect at any instant, the rate of cooling at any given temperature should be inversely proportional to the square of the least dimension.

In the case of very large pieces it may be necessary to reduce the annealing temperature, and correspondingly to increase the annealing time in order to shorten the extremely long period of cooling that otherwise would be necessary. Large blocks of glass for optical purposes naturally take a longer time to anneal because of the more rigid requirements as to double refraction.

The mode of cooling just discussed is based on the increasing rigidity of the glass as it cools. Above the critical range the glass may be considered to have changed from a plastic to a nearly viscous state, the elastic limit for a large part of the molecular aggregates being practically zero. As the cooling proceeds through the critical range the glass loses its viscous nature very rapidly, and below this range may be considered practically as a plastic body. It is in the temperature region where the glass is predominately plastic, but still viscous enough to allow the relaxation of small stresses, that annealing should take place. Unless the annealing temperature is chosen too low, all stresses, no matter how small, will disappear in a reasonable time as measurements on the double refraction will show. These stresses disappear completely, due to the fact that the glass still retains to a certain extent its viscous character.

At lower temperatures the relaxation time rapidly increases, and the glass becomes more and more rigid, losing much of its

plasticity and becoming like an elastic substance; accordingly when the glass is being cooled from its annealing temperature, the rate, which initially must be relatively low, may be increased as the glass cools without adding materially to the amount of permanent strain. The manner of increasing the cooling rate is based partly on the assumption that Twyman's relation still holds for a considerable distance below the critical range. Although the measurements by Zschimmer and Schulz would indicate that the glass in the cooling range grew rigid more slowly, with decreasing temperature, than this relation demands, still it appears that it adequately represents the conditions so far as the first 100° C of cooling is concerned.

In the preceding discussion of the annealing procedure it was found convenient to use certain concepts and methods of discussion which involve one of the various molecular theories devised to explain the continuous change of a body from a viscous fluid to an elastic solid. For discussing the behavior of glass the Maxwell-Butcher theory seemed especially convenient. According to this theory, metals and many other materials, including glasses, which are elastico-plastico-viscous, are composed of various types of aggregates, molecules or groups of molecules, which can be divided into two classes. Aggregates of the first class will deform under forces so small that they have no sensible magnitude, and those of the second class will require a finite force before disorganizing. The second class may again be separated into groups having different disorganization limits, or, in other words, different elastic limits. When the body consists chiefly of groups of the first class, it will behave as a viscous substance. When, however, groups of the second class predominate, the deformation will appear to be elastic for small loads applied for a short time, and plastic for loads exceeding the elastic limit. Now if the disintegration limits of any of the groups vary with the temperature, the elastic limit, the plasticity, and the viscosity will show variation. In the case of glass, as the temperature is raised the magnitude of the stresses necessary to cause the disintegration of many of the groups becomes small, and the glass becomes quite plastic. This is the condition that exists for some 50° C, or more, below and throughout the critical range. At higher temperatures the disintegration limits of many groups become practically zero, and these aggregates then belong to the first class. The glass then behaves much like a viscous fluid.

Whether the characteristics of the glass will be predominately elastic, plastic, or viscous will, accordingly, depend on the temperature, the magnitude of the load, and the time of its application. In the case of the plastico-viscous type of deformation, the relaxation time should under certain conditions be practically independent of the load. These considerations show that, in the bending experiment, a condition may well have existed that caused the relaxation time to remain independent of the load, since the manner of conducting these experiments necessitated the application of rather large stresses at relatively high temperatures in order to obtain measurable rates of bending. These stresses may easily have exceeded the majority of the disorganization limits at those temperatures. On the other hand, the measurements by the optical method were carried out at relatively low temperatures, and for small stresses. The glass was predominately plastic for these conditions, hence as the retardations decreased the relaxation time continually became larger. The two methods can hardly be expected to agree when employed under such different states of aggregation in the glass, and with forces of unlike magnitudes applied in a radically dissimilar manner. The optical method could not be employed in the critical range because the double refraction disappeared so rapidly that time was not available to take sufficient observations. It would appear, therefore, that this view concerning the character of such solids explains in part the discrepancy between the results as obtained by the two methods. Moreover, it is apparent that these characteristics must be taken into account if the cooling method chosen is to be efficient. As glass appears to be always slightly viscous, there always will be a slight residual strain after cooling.

Since the selection of the cooling procedure depends on the ultimate strains introduced, it is necessary to determine their magnitude, or rather the magnitude of the stresses which accompany them. For such a determination there is no really good method. Practically the only one available is the study of the double refraction. This method is unsatisfactory in the first place because no reliable investigations have been published which specify the allowable double refraction for any kind of optical glass, and secondly because the different kinds of glass show different amounts of double refraction under the same stress. There are, in fact, very heavy lead glasses that show no double refraction under stress, while still heavier glasses exhibit an effect opposite in sign to that of the common types. In most, if not all glasses, both com-

ponents of the light, resolved in and perpendicular to the direction of the pressure, are retarded. With the exceptions noted above, the electric component vibrating perpendicular to the direction of the pressure is retarded by the greater amount. Under tension both components are accelerated. Neuman,[29] Pockels,[30] Zschimmer, and Schulz,[31] and others[32] have investigated this subject quite thoroughly, both from theoretical and experimental standpoints. They have, also, disscussed in some detail the relation these double refraction effects bear to the chemical composition. This aspect of the subject, however, is not well enough understood to be of any great aid in testing. Consequently such standards as have been established are purely arbitrary. It may be possible to establish more definite standards by specifying the relation between the double refraction due to permanent strain and that produced by a standard pressure on a standard specimen of the same glass. Only a careful investigation will show whether such a method is feasible. At present it is only possible to state that, in annealing glass for optical purposes, it is advisable to remove the stresses as completely as possible, and to bring about a symmetrical distribution of those stresses which cannot be removed in the time available. This latter can be accomplished only when the temperature distribution over the surface is uniform during annealing. It is not difficult to anneal small pieces so that the double refraction is imperceptible under ordinary methods of testing.

It is often of advantage to know something of the magnitude and distribution of the stresses in the body during cooling. The theory of these thermoelastic stresses has been thoroughly developed by Neuman,[33] Hopkinson,[34] Rayleigh,[35] and others.[36] They have also given the equations for the stresses in a number of cases under certain conditions of heat flow. These equations are quite interesting, and are in a number of cases important in testing. In the case of annealing, however, they do not give the distribution of stresses since they all assume that the stresses depend only on the existing temperature differences. In the actual process of annealing and cooling the stresses are continually relaxing at various rates through viscous and plastic flow, so that those present

[29] Neuman, Pogg. Ann., 54, p. 449; 1841.
[30] F. Pockels, Ann. d. Phys., 7, p. 745; 1902.
[31] Zschimmer and Schulz, loc. cit.
[32] Kerr, Phil. Mag. (5), 126, p. 321; 1888.
[33] F. E. Neuman, Vorles. uber d. Theorie d. Elast. d. fest Korper, Leipsig; 1885.
[34] Hopkinson, Mess. of Math., 8, p. 168; 1879.
[35] Rayleigh, Phil. Mag. (6), 1, p. 169; 1901.
[36] The publication in the near future of a collection of these formulas is contemplated.

at any time depend not only on the temperature distribution then present but on the whole previous history of the annealing. These equations do, however, lead to a better understanding of the manner in which the strains are produced in glass by different modes of cooling. They also make it possible to gain an approximate idea of the stresses during any process of heat treating.

V. CONCLUSIONS

In summarizing the annealing procedure, it is evident that the first step is to determine a suitable "annealing temperature." This may be done by the use of method I, or still better, by determining the beginning of the critical range (method II). With the proper apparatus (described on p. 551) this latter determination is simple and preferable. If it is used, the annealing temperature should usually be chosen 10 or 20° C below the beginning of critical range.

The next step requires the determination of the "annealing time" corresponding to the chosen "annealing temperature." This is most easily done by studying the rate of deformation of loaded rods of glass. In this way the "relaxation time," and hence the "annealing time" for any degree of annealing, can be approximated in the manner discussed.

A study of the change of the relaxation time with temperature aids in determining the proper rate and mode of cooling. Since, for a certain temperature interval below the critical range, the relaxation time increases very rapidly with decreasing temperature, the rate of cooling, which initially must be very small, may be increased gradually to a certain maximum. This maximum and the rate at any given temperature depends on the size and other characteristics of the object to be annealed. A cooling procedure which appears satisfactory for small pieces is discussed under "cooling."

Since the rate of cooling must be reduced materially in annealing large pieces, consideration must be given to the fact that the slow cooling in the upper range allows the thermoelastic stresses to act for a much longer time. This makes it seem advisable to anneal at a lower temperature where the relaxation time is larger. In this case the annealing time must be increased according to Twyman's equation. For example, if the annealing temperature is reduced 20° C, the annealing time should be increased by a factor of at least 4 and possibly 8. The cooling may then begin at a much more rapid rate.

The procedure outlined here can serve at best only as a guide, since in actual practice the conditions are entirely different from those which exist in a laboratory. The chief causes of poor results in practice are without doubt the lack of temperature uniformity, fluctuations in the temperature during the annealing period, and too rapid or irregular cooling in the upper part of the cooling range. It is essential that the glass take on the required temperature for the required time while annealing, and that it does not merely pass through air heated to that temperature. In cooling, care must be taken that the heat flow is not chiefly through one part of the surface, especially when the body is somewhat extended.

VI. SUMMARY

Certain methods for determining the annealing range were tested, and the "annealing temperatures" obtained are given for a number of optical glasses.

The critical temperature range for these glasses was determined. In this range there is an apparent absorption of heat on heating, and a corresponding evolution of heat on cooling. In this range there is, also, a marked change in a number of the properties of glass. For most optical glasses, at least, it was found advisable to anneal at a temperature somewhat below this range.

Some of the methods available for determining the relaxation time, and consequently the "annealing time," were tested. The manner in which the relaxation time varies with the temperature was investigated, also, and some results on representative glasses are given.

A cooling procedure which proved very satisfactory in the laboratory is discussed. Mention is also made of the factors which must be considered in cooling the glass and in testing the final product.

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1906	Dickinson	Bull. Bur. Stand	2	189
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1912	Zschimmer	Zeits. f. Instk	33	303
1916	Boys	Nature	98	150
1917	Twyman	Soc. Glass Tech., Tr. (1917)	1	
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VISCOUS AND PLASTIC DEFORMATION

Year	Author	Reference	Volume	Page
1868	Maxwell	Phil. Mag (4)	35	129
1876	Butcher	Proc. London Math. Soc	8	103
1892	Voigt	Ann. d. Phys	47	671
1901	Reiger	Phys. Zeits	2	213
1904	Trouton & Andrews	Phil. Mag	7	347
1911	Bingham	Am. Chem. Journ	45	264
1914	Guye	Arch. d. Sci. Phys. et Nat	37	301

DOUBLE REFRACTION

Year	Author	Reference	Volume	Page
1843	Neumann	Ab. d. Konig Ak. d. Wissen		112
1850	Stokes	Phil. Mag. (4)	2	420
1880	Macé de l'Epinay	Ann. chim et Phys	19	5
1888	Kerr	Phil. Mag	26	321
1891	Schott	Zeits f. Instk	11	330
1903	Czapski	Wied Ann	42	319
1904	Brace	Phys. Review	18	70
1908	König	Ann d. Phys	4	1
1908	Wright	Am. Jour. Sci	26	370
1909	Tuckerman	Univ. of Nebr. Studies (No. 2)	9	
1910	Tool	Phys. Review	31	1
1914	Wright	Jour. Wash. Acad. Sci	4	594
1914	Filon	Proc. Roy. Soc	A 89	587

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1879	Hopkinson	Mess. of Math	8	168
1885	Neuman	Theorie der Elasticität (Leipzig)		112
1894	Winkelman & Schott	Ann. d. Phys	51	745
1901	Rayleigh	Phil. Mag. (6)	1	169
1914	Schulz	Sprechsaal	47	460, 478
1919	Williamson	Proc. Wash. Acad. Sci	9	209

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1904	Guertler	Zeits. für Anorg. Chem	40	268
1905	Zschimmer	Zeits. für Elektrochem	11	628
1912	Kroll	Zeits. für Anorg. Chemie	77	1
1914	Brockbank	Trans. Am. Ceram. Soc	15	600
1915	Quincke	Ann. d. Phys	46	1025
1916	Langmuir	J. Am. Chem. Soc	38	2244
1917	Canwood and Turner	J. Soc. Glass Tech	1	87
1917	Tillotson	J. Ind. Eng. and Chem	9	937
1918	Tool and Valasek	Meet Am. Phys. Soc., Baltimore		
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1918	So	Proc. Tokyo Math. and Phys. Soc		
1918	Fenner and Ferguson	J. Am. Ceram. Soc	1	468
1918	Schulz	Verh d. Dent. Phys. Ges	20	24
1919	Bowen	J. Am. Ceram. Soc	2	261
1919	Williams and Rand	J. Am. Ceram. Soc	2	422

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