

"FRACTURE STRENGTH OF COMMERCIAL SODA - LIME - SILICA GLASS FROM A  
-100°C to 700°C"

by

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**ABSTRACT**

Apparatus for conducting high speed tensile tests is described and fracture strength values on etched soda-lime-silica glass rods (Kimble Std. Flint, R-6) from -100°C to 700°C are reported. The time for fracture varied from 0.5 to 2.8 milliseconds, depending on the level of fracture stress. The results showed the glass rods to have a maximum strength at 100°C, after which there was a significant decrease in strength as the temperature was increased. The average room temperature strength was 266,300 p.s.i., rising to 343,200 p.s.i. at 100°C, and falling off to 53,800 p.s.i. at 700°C. On conducting a series of controlled experiments at 400°C, the heat treatment damage was found to:

1. increase with time
2. relate only to the surface
3. be permanent
4. occur in a vacuum as well as in air

The increase in strength was thought to be due to an increase in the surface energy of the glass due to the physi-absorbed surface water

being driven off. Several possible causes for the heat treatment damage of both glass fibers and etched glass are discussed.

The strength of unetched soda-lime-silica glass was found to remain more or less constant, 60,000 p.s.i., up to 700°C. Thus, it was concluded that the effect of temperature on the stress corrosion of glass becomes negligible for short fracture times.

Thesis Supervisor: A. R. Cooper, Jr.

Title: Professor of Ceramics

## TABLE OF CONTENTS

	Page
ABSTRACT	ii
LIST OF FIGURES	vi
LIST OF TABLES	vii
LIST OF PLATES	viii
LIST OF SYMBOLS	ix
ACKNOWLEDGEMENTS	x
I. INTRODUCTION	1
II. LITERATURE SURVEY	
A. Introduction	3
B. Static Fatigue	5
C. Atomistic Theories	9
D. "Intrinsic" Strength of Glass	12
E. Effect of Water on Glass Surface	21
III. PLAN OF WORK	25
IV. DESCRIPTION OF APPARATUS AND MATERIALS USED	
A. Apparatus	26
B. Sample Preparation	34
V. DISCUSSION OF WORK DONE	
A. Results	37
B. Discussion of Results	54
VI. CONCLUSIONS	59
VII. RECOMMENDATIONS	60

	Page
VIII. BIBLIOGRAPHY	61
IX. APPENDIX	
A. Details of Experimental Data	64
B. Statistics	69

## LIST OF FIGURES

<u>Number</u>	<u>Title</u>	<u>Page</u>
1.	Effect of Temperature on the Breaking Stress of Glass	4
2.	Stress-time Characteristics of Glass Rods in Bending at Various Temperatures	7
3.	Stress-time Characteristics of Glass Under Various Atmospheric Conditions	7
4.	Load Cell Circuit	29
5.	Strength versus Temperature of Etched Glass	44
6.	Strength of Etched Glass at Room Temperature	46
7.	Logarithm of Strength versus Inverse of Absolute Temperature for Etched Glass	47
8.	Strength versus Temperature of Unetched Glass	49

## LIST OF TABLES

<u>Number</u>	<u>Title</u>	<u>Page</u>
I	Otto's Results on Glass Fibers	13
II	Physical Properties of Soda-Lime-Silica Glass	35
III	Viscous Flow Measurements	42
IV	Loading Rate	43
V	Variation of the Averages	45
VI	Below Room Temperature Tests	48
VII	Tensile Tests at 400°C - 2 minutes	50
VIII	Tensile Tests at 400°C - 30 minutes	50
IX	Sample Heated to 400°C (2 minutes), Cooled to 100°C, and Tested	51
X	Sample Heated to 400°C (2 minutes), Cooled, Reetched, Heated to 100°C and Tested	51
XI	Tensile Tests at 100°C	52
XII	Sample Heated to 400°C (30 minutes), Cooled, Reetched, Heated to 100°C and Tested	52
XIII	Sample Heated to 400°C, Cooled and Tested at Room Temperature Under Atmospheric Conditions	53
XIV	Strength versus Temperature of Etched Glass	65
XV	Strength versus Temperature of Unetched Glass	67

## LIST OF PLATES

<u>Number</u>	<u>Title</u>	<u>Page</u>
1	An Overall View of Tensile Testing Apparatus	27
2	Loading Trace of Oscilloscope Sweep Speed, 2 millisec/cm	30
3	Loading Trace of Oscilloscope Sweep Speed, 5 sec/cm	30
4	View of Furnace, Icebox, and Sample	33
5	Etching Apparatus	33



## LIST OF SYMBOLS

$\sigma$	Tensile strength
$\bar{\sigma}$	Average tensile strength
$S$	Standard deviation of a given set of strength values
$\bar{S}$	Pooled standard deviation
$\mu$	Micron

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## I. INTRODUCTION

The increasing use of glass as a structural material emphasizes the importance of its behavior under stress and the conditions governing its failure. Although the effect of temperature on the mechanical strength of metals has been fully investigated, there still remains a large amount of controversy as to the variation in strength of glass as a function of temperature. In all of the previous experiments, the investigators were confronted with the problem of the great sensitivity in the observed strength values to the variation in the surface condition of the glass studied; and consequently, these investigators have measured the temperature dependence of surface flaws. Thus, the theories proposed for the strength-temperature dependence of glass have been macroscopic in nature rather than microscopic. It would, therefore, be instructive to conduct experiments on the strength of a "flawless" glass as a function of temperature in order to clarify the question as to the true strength-temperature dependence of glass.

B. Proctor<sup>(34)</sup> has shown that by purely surface treatments, etching with hydrofluoric acid, large pieces of ordinary commercial glass may be given strengths as high as 500,000 p.s.i., similar to those obtained with fine glass fibers. This is in very good agreement with the observations made by Tichane and Carrier<sup>(41)</sup>. They found that by etching soda-lime glass with hydrofluoric acid, a surface finish that approaches that of a freshly fractured surface can be obtained.

In view of these recent reports, it was thought that a study of the variation in strength of etched soda-lime-silica glass with temperature would help clarify the controversy as to the true strength-temperature dependence of glass without the complication introduced by pre-existing surface flaws. Another advantage of this method is that by reetching

a sample that has been heat treated, it can be determined whether the temperature effect is surface or internal. To reduce the effect of stress corrosion, apparatus for high speed tensile testing, fracture time 0.5 to 2.8 milliseconds, was used.

Strength versus temperature of unetched soda-lime-silica glass was measured in order to compare with the results obtained from the etched glass and those of previous investigators. Other special tests were made in the hope that additional information regarding the temperature effect on glass strength would be found. The time dependence was obtained by comparing results obtained by holding a specimen at 400°C for intervals of two and thirty minutes before fracturing. To check whether the temperature effect is permanent or not, samples were tested at 100°C after they were heated previously to 400°C. By heat treating a sample at 400°C in a vacuum before testing under atmospheric conditions, the temperature effect of the atmosphere was hoped to be eliminated.

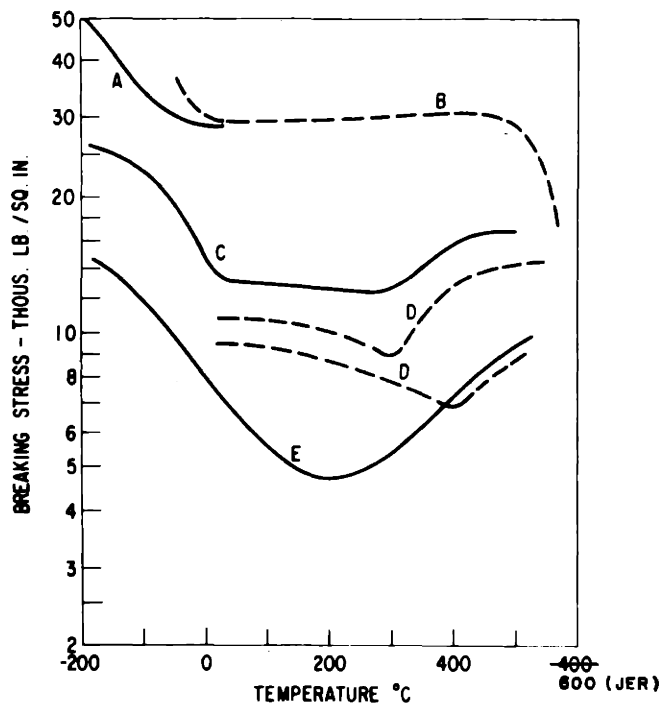
## II. LITERATURE SURVEY

### A. Introduction

From theoretical reasons and experimental evidence, one would expect the strength of matter to decrease with increasing temperature. Thermal motion helps to sever the bonds between the atoms under tension. Thus, it was not surprising when evidence was presented by several investigators that the breaking stress of glass tends to increase at temperatures below 0°C (Figure 1). However, from Figure 1 it can be seen that the results from experimental studies of the effect of increasing temperature on the strength of glass are not consistent. In all of these studies, the investigators were using a glass that has on the surface pre-existing flaws or cracks that act as stress concentrators. Thus, they measured more the influence of temperature on these flaws rather than the intrinsic strength of glass; and, therefore, the theories proposed by these investigators were in terms of these microcracks on the glass surface. Thus, the increase in strength at the low temperatures was attributed to a reduction in the rate of chemical attack of the microcracks with decreasing temperature rather than a decrease in thermal motion of the atoms.

Vonnegut and Glathart<sup>(44)</sup> thought that the decrease in strength with increasing temperature was due to an increase in chemical attack of the glass by water. The increase in strength at 200°C was attributed to the decrease in surface adsorption of the atmospheric water. They concluded that the primary cause of strength variation of glass is the variation in the activity of adsorbed moisture on the surface of the glass. They suggested that experiments should be made "over the same temperature range in high vacuum, in the absence of adsorbed films."

Smekal<sup>(36)</sup> described his decrease in strength up to 150°C as due



**Figure 1. Effect of temperature on the breaking stress of glass (after Charles):**

- A. Fibers, 0.008 to 0.016 inch diameter in tension (Onnes and Braak).**
- B. Bars, window glass in bending (Jones and Turner, Holland).**
- C. Fibers, 0.052 inch diameter in tension (Smekal).**
- D. Strips, soda-lime glass in bending (Gregorius).**
- E. Rods, 1/4 inch diameter soda-lime glass in bending; load duration 10 seconds (Vonnegut and Glathart).**

to the increase in thermal energy produced by temperature. The increase in strength at 150°C was explained by the "healing" of the microcracks which outweighs any increase in thermal motion or chemical reactivity. The "healing" process consists of a rounding out of the sharp edges which would make the flaw less dangerous.

Jones and Turner<sup>(24)</sup> believed that the chemical attack of glass was counter balanced by the temperature "healing" effect; and thus, no significant change was found in the strength of glass as a function of temperature. Jones<sup>(23)</sup> pointed out that even though there is not good agreement between the results of various workers as to the form of the variation with temperature of the strength of glass, all results indicate that the strength is more or less maintained up to the annealing range of glass.

#### B. Static Fatigue

The variation in magnitude of the reported strengths in Figure 1 are probably due to variations in specimen size, forming temperature, degree of abrasion, and chemical composition of the glass studied. The reasons for the discrepancy of the variations of strength with temperature have not been fully investigated, although certain experimental work suggests that the loading time has a definite influence on this characteristic. Thus, it would be instructive to investigate some of the results in static fatigue since the variation in loading times among the different investigators could very well explain the discrepancies in the strength of glass versus temperature.

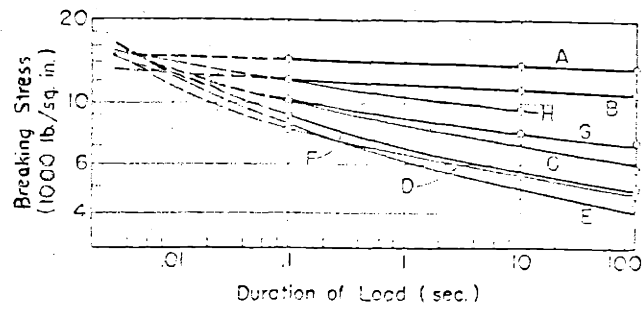
Charles<sup>(5)</sup> in his report on the static fatigue of glass has described the failure of glass with pre-existing flaws in terms of stress, time of load duration, and temperature. He further proposed a mechanism for the chemical attack of glass by water that can lead

to the growth of a microcrack until the Griffith criterion for failure of brittle materials is satisfied, or to a rounding out of the flaw to make it less dangerous. The level and time of the applied load dictates whether the flaw will propagate or round out. From his experimental data on the static fatigue of soda-lime glass he concluded the following:

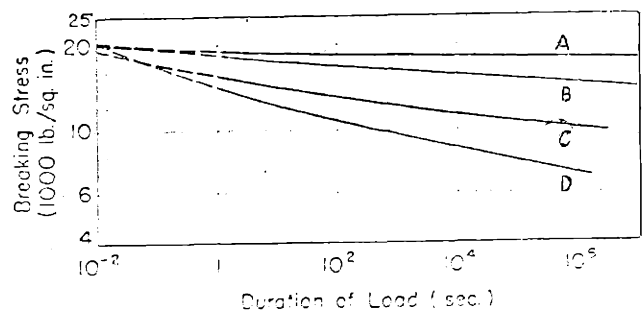
1. No delayed failure effect is observed at  $-170^{\circ}\text{C}$ ; and therefore, no apparent flaw growth occurred at this temperature. Kropschat and Mikesell<sup>(26)</sup> also observed this effect of decreasing fatigue with decreasing temperature down to  $-197^{\circ}\text{C}$ , after which fatigue becomes negligible. Both believed that this effect was due to a reduction in chemical attack with decreasing temperature.
2. Delayed failure became most pronounced in saturated water vapor at a temperature around  $150^{\circ}\text{C}$ .
3. Accelerated corrosion behavior at temperatures above  $150^{\circ}\text{C}$  led to a continuous reduction of the delayed phenomena in saturated water vapor. At  $240^{\circ}\text{C}$  the enhanced macroscopic corrosion etched out the original surface flaws and quickly converted the glass rods, for all intents and purposes, from specimens subject to delayed failure in the ordinary sense.

Vonnegut and Glathart<sup>(44)</sup> have reported experimental work which shows the stress-time effect in atmosphere to be a function of temperature (Figure 2). At very low temperatures of  $-100^{\circ}\text{C}$ , and also at elevated temperatures of  $+400^{\circ}\text{C}$  or higher, the relative reduction of breaking stress with time is materially less than at room temperature. When these curves are extrapolated to much shorter time intervals, they all tend to coincide, within the limits of experimental accuracy, at a





**Figure 2. Stress-time characteristics of glass rods in bending at various temperatures (from Shand):**  
 (A)  $-187^{\circ}\text{C.}$ , (B)  $-85^{\circ}\text{C.}$ , (C)  $+20^{\circ}\text{C.}$ , (D)  $+112^{\circ}\text{C.}$ ,  
 (E)  $+200^{\circ}\text{C.}$ , (F)  $+300^{\circ}\text{C.}$ , (G)  $+420^{\circ}\text{C.}$ , (H)  $+520^{\circ}\text{C.}$



**Figure 3. Stress-time characteristics of glass under various atmospheric conditions (from Shand).** (A) Atmospheric pressure  $< 10^{-5}$  mm. Hg with prior heat-treatment in vacuum, (B) atmospheric pressure  $< 10^{-1}$  mm. Hg with prior heat-treatment in vacuum, (C) atmospheric pressure  $< 10^{-5}$  mm. Hg without heat-treatment in vacuum, (D) full atmospheric pressure, with and without prior heat-treatment in vacuum. Note: For rods given vacuum pretreatment and tested in air with moisture and  $\text{CO}_2$  removed, the breaking stresses were of same order of magnitude as for curve (A).

fracture time of several milliseconds. As Shand<sup>(35)</sup> pointed out, these observations have greater significance on noting the results of Baker and Preston<sup>(3)</sup>, and Gurney and Pearson<sup>(16)</sup>.

Baker and Preston<sup>(3)</sup> found that the strength in vacuum was about the same as in air at a  $10^{-2}$  second loading period, being 25,000 p.s.i. in vacuum compared to 20,000 p.s.i. in air. Thoroughly baked out glass in a high vacuum was reported to have a tensile strength fairly independent of the time of loading, up to 10 seconds. It was found that glass is 20 percent stronger when dry than when wet, and two to two and one-half times as strong when baked in a vacuum. It was believed that the strength loss was due to a chemical attack of the flaws in the glass by water and possibly by some gasses such as carbon dioxide. Also, autoclaving tests showed that glass is rapidly etched by water at higher temperatures, similar to that of etching with hydrofluoric acid. The soda-lime rods increased in strength from 13,000 to 27,400 p.s.i. by etching in an autoclave for 4 hours under 600 p.s.i. steam pressure. It is interesting to note that Mould<sup>(28)</sup> also reported that water will etch the glass surface; and consequently, improve its strength. He found the strength of grit blasted glass increased from 9,470 to 12,340 p.s.i. upon immersion in liquid water at room temperature for 24 hours.

Gurney and Pearson<sup>(16)</sup> concluded from their results (Figure 3) and from Baker and Preston's<sup>(3)</sup> that approximately 20,000 p.s.i. could be interpreted as the strength of glass when free from atmospheric attack, either because no atmosphere was present or because the time for fracture was too short for appreciable attack to take place. They further concluded that some of the delayed fracture must be due to atmospheric constituents contained in the surface layers of the glass because:

1. With vacuum of  $10^{-5}$  mm Hg delayed fracture was observed without baking but not with baking.
2. Short time loading strength after a month in a high vacuum without baking did not reach the short time loading strength of glass baked for 48 hours in a vacuum.

Shand<sup>(35)</sup> on reviewing these experimental observations drew two inferences from them. The first is that with decreasing fracture time the effect of the ambient atmosphere decreases, until for periods of a few milliseconds, the effect disappears completely. The second is that for these very short fracture times, the breaking stresses should become independent of temperature. These inferences indicate, that for short fracture times, the temperature effect on the stress corrosion of glass becomes negligible. In support of this, Kingery and Pappis<sup>(25)</sup> showed that the impact strength of soda-lime-silica glass showed little variation up to 500°C.

### C. Atomistic Theories

There is, however, a large group of theories that approach the problem of the fracture of glass from an atomistic viewpoint, rather than a macroscopic one. Charles<sup>(5)</sup> in his survey on the strength of glass summarizes these concepts which evaluate the probabilities of certain atom combinations or atom group combinations leading to fracture. Under zero stress, the rates of formation and dissociation of these combinations are assumed equal, so that, over long periods, no change in the system is apparent. The application of a mechanical stress is considered to bias the backward and forward rates of formation of these entities so that the probability of degeneration of the system, by the formation of those special atom arrangements which could define a crack, becomes appreciable during normal time durations.

Cox<sup>(7)</sup> further pointed out that the probability, even if small, cannot be neglected in view of the large number of opportunities for the occurrence of the event which the rapid interchange of energy and the number of atoms provide. Also, such a discontinuity under a stress could presumably cause a stress enhancement that may become cumulative. Furthermore, Cox stated, any local change in state of the glass could provide such a discontinuity, even if it is less favorable in enhancing the stress, than an actual crack or void. The activation energy involved in this process may be smaller than first thought since there is ample evidence to support the fact that configurational changes in glass are characterized by a small activation energy.

These "atomistic" theories may generally be applied to a pre-existing crack to govern its rate of change with time, or to a "flawless" material, to describe the generation and propagation of cracks. All of these concepts are derived from the same basis in statistical mechanics and the resulting expressions, describing crack initiation and growth, are remarkably similar. In general, the rate of combination of events favorable to crack initiation or growth is expressed as an exponential function involving a term in which an activation energy is modified either by a product function of stress Poncelet<sup>(33)</sup> (1948) and Taylor<sup>(39)</sup> (1947)

$$\frac{dN}{dt} = A \exp \left[ -f(\sigma) \frac{Q}{kT} \right] \quad (1)$$

N = number of atom combinations leading to crack propagation

t = time

A = constant

f(σ) = function of applied stress

Q = activation energy necessary to form a specific atom combination

$T$  = absolute temperature

$k$  = Boltzman's constant

or by an additive function of stress Cox<sup>(7)</sup> (1948), Fisher<sup>(12)</sup> (1948), Holloman<sup>(20)</sup> (1948), Gibbs and Cutler<sup>(15)</sup> (1951).

$$\frac{dN}{dt} = A \exp \left[ -Q - \frac{\phi(\sigma)}{kT} \right] \quad (2)$$

$\phi(\sigma)$  = an energy function of stress

Most of these authors have applied their formulae, with varying degrees of success, to the case of glass fracture at room temperature. It is thought that the macroscopic processes, atmospheric attack, viscoelastic deformation, flow, etc., which are involved in failure, need not be explicitly described for their influence is reflected in the value of  $Q$  (a characteristic zero stress activation energy).

Both Charles<sup>(4)</sup> and Jones<sup>(23)</sup> conceded that at higher temperatures, where the fluidity of the glass permitted appreciable reorganization, these theories may have some justification. At lower temperatures, however, they expressed skepticism in the validity of these expressions in describing fracture. Jones failed to see how a thermal fluctuation could be regarded as precipitating fracture since the period of a single thermal oscillation or even a number of closely associated, oscillations is negligibly small in comparison with both the short and long times of measurements. Further he pointed out that these expressions all showed a characteristic zero strength at  $0^{\circ}\text{K}$  where the strength would be expected to be the highest.

Charles expressed skepticism in that the expressions described more the effect of temperature on a system rather than stress and yet the experiment, designed or quoted to illustrate the applicability of the theories, are invariably isothermal. The important generalizing feature of this approach is that a stress should strongly modify the

temperature dependence of the process involved. He showed experimentally that the temperature dependence of the failure process was not solely dependent upon the applied stress by describing failure in terms of stress, time and temperature. Also, he pointed out that crack propagation is not a direct function of temperature, as the theory predicts. Dimmick and McCormick<sup>(8)</sup> even found a negative dependence of crack propagation on temperature.

#### D. "Intrinsic" Strength of Glass

All of the previous investigators have used a glass with known pre-existing flaws. It would be instructive to study the results of experiments made on glass that is considered to have a more "flawless" surface so that one can obtain a better understanding of the more "intrinsic" strength of glass i.e. the strength of glass without stress concentrators.

Otto's results<sup>(31)</sup> on glass fibers (.0004 inches in diameter) show that strength steadily decreases with increasing temperature; fracture time was approximately 30 seconds. The strength decreased from 500,000 p.s.i. at room temperature to 150,000 p.s.i. at 600°C. If the fiber is heated to a certain temperature and then tested at room temperature, the strength is lower than that originally recorded for that temperature. If the fiber is heated, cooled to room temperature, then reheated to the same temperature and tested, the strength is intermediate between that obtained originally for that temperature and the room temperature strength of the fiber that was heat treated. If Otto heats a fiber to 649°C, holds for 30 minutes, then draws the diameter from .0004 inches down to .0002 inches, cools to 538°C, and tests, the strength is 550,000 p.s.i. His other results are as given in Table 1.

TABLE 1.

Testing Condition	Strength p.s.i.
Air, 50 per cent relative humidity	500,000
Distilled water	500,000
1:1 Molar ratio of methyl alcohol and water	500,000 *
Dry methyl alcohol	Up 15 per cent
Vacuum	Up 15-18 per cent
Liquid nitrogen	Up 60 per cent

\* Mould<sup>(28)</sup> also reported that the strength of abraded glass in dry methyl or isopropyl alcohol is 40 per cent greater than in distilled water. With the addition of water to the alcohol solution, his fatigue curve for the glass became parallel to that for distilled water, and as the water content increases, the curves shifted down toward the water curve.

Otto explained his results in terms of an adsorbed water layer on the surface of the glass. On heating the fiber, this layer reacted with the fiber to cause some sort of damage. Otto has found that even the slightest disturbance to the surface of his fibers, lowered their strength; even, etching in hydrofluoric acid which normally strengthens glass. On heating but testing at room temperature, a still lower strength is recorded because more adsorption of water on the glass surface is possible. If the sample is reheated, the heating causes more severe damages; and therefore, the strength is lower than that originally obtained for that temperature. However, this strength is above the room temperature strength because the reduction in the adsorbed layer offsets the damage done by it. By drawing his fiber at  $649^{\circ}\text{C}$ , he created new surfaces that do not have a chance to absorb any further water since the fiber was only cooled to  $538^{\circ}\text{C}$  and "healed" the damaged surface by rounding out any defects produced by the adsorbed water. Thus, he observed a significant increase in strength because there is no water present to react with these new surfaces. His other results, cited previously, substantiate his argument that the adsorbed water layer causes the damage.

Holloway<sup>(21)</sup>, as reported to Charles, presented results that clearly demonstrated that glass fibers exhibit extraordinarily high strengths, 522,000 p.s.i., if ordinary atmosphere is excluded during preparation and testing. Further, his results confirmed the expectation that the effect of atmosphere becomes more pronounced the higher the level of testing strength.

Thomas<sup>(40)</sup> found that the breaking stress of a glass fiber is constant (coefficient of variation  $\pm 0.85$  per cent) provided the drawing temperature of the molten glass is sufficiently high to



permit a fiber of uniform diameter to be produced. The strength of the fibers as formed was 530,000 p.s.i. Further, he found that the room temperature strength of glass fibers decreased on annealing at temperatures as low as 100°C, and the rate of decrease in strength increased with an increase in annealing temperature. A constant value in strength was reached after holding the fiber at an annealing temperature for a period of time, 2 hours at 300°C and immediately at 600°C. Also, the strength of the fibers decreased with an increase of relative humidity and with an increase in time of exposure at room temperature. Dry air was found to cause little reduction in strength within the first 24 hours; after which, there was a gradual reduction to 86 per cent of original strength after 128 days. Exposures in vacuum had no effect on strength up to 28 days. Exposure to 100 per cent relative humidity had more drastic effects, 70 per cent reduction in strength after 128 days. He concluded that no damage is done to the glass surface by moisture attack since the reduction in strength would be expected to be greater than that observed. He believed that the moisture penetrated into the outer layers of the fibers, forming a weak layer of glass which does not contribute to the strength of the fiber, but which has no bad flaws so that cracks are not started prematurely from the weak surface.

Hillig<sup>(18)</sup> with experiments on fire-polished pure fused quartz glass rods of 0.5 to 3.0 mm diameter recorded a median strength of 700,000 p.s.i. at -195°C. At room temperature the glass was about half as strong. He found that the slightest mechanical damage lowered the strength drastically. Merely placing a finger upon the specimens reduced the strength to 50,000 p.s.i. Testing the fiber under water had no apparent effect on strength; however, the presence of hydrofluoric acid lowered the strength substantially.

Very recently it has been suggested that the damage done on annealing a glass fiber is a result of surface devitrification. This theory was first proposed by Aslanova<sup>(2)</sup>. She found that glass fibers of various chemical compositions decreased in strength up to 70 per cent on heat treatment. Fibers of alkaliglass began to lose strength at 100°C, alkali-free aluminoborosilicate glass at 300°C, and quartz glass at above 600°C; but she did not state the length of time of heat treatment. She showed that the strength of the fibers was restored after the surface layer had been removed by etching with hydrofluoric acid or alkali solution. On comparing electron-diffraction patterns of the fibers before and after heat treatment, the lines in the electron-diffraction pattern were found to sharpen after the heat treatment. All of the electron-diffraction patterns of fibers heat treated at 400-600°C contained rings or spots. She thought that this indicated an increase of crystallite size. Interpretation of the electron-diffraction patterns of fibers from alkali-free borosilicate glass showed that a number of the lines are due to low temperature cristobalite with a tetragonal lattice. She thought that crystals of various and possibly mixed compositions are formed in this glass from heat treating since not all the lines in the pattern corresponded to the cristobalite lattice. Thus, she concluded that the damage done on annealing glass fibers is due to surface devitrification. It should be pointed out that she found that heat treatment had no effect on the strength of massive glass and only a slight effect on the strength of thick fibers. Correspondingly, massive glass gave a much weaker diffraction pattern after heat treatment. This would indicate that the pre-existing flaws in massive glass remain of prime importance even after heat treatment.

Cornlissen, et al<sup>(6)</sup> investigated the effect of heat treatments of various durations on pristine (modified) photosensitive glass rods, especially at 550 and 650°C. Heat treating at 650°C resulted in a very rapid fall in strength (364,000 to 85,400 p.s.i.) within 1 minute, after which the strength remained constant for about 1 hour before decreasing again to 28,450 p.s.i. after 16 hours. It was noticed that this second decrease in strength was accompanied by a visible crystallization process that started at the glass surface and became more intensive after a lapse of time. The heat treatments carried out at 550°C showed similar characteristics as those at 650°C. A very rapid decrease in strength within the first minute to 85,400 p.s.i. but remaining constant for 8 hours before slightly decreasing again to 81,000 p.s.i. They did not attribute the initial decrease in strength to surface devitrification but stated that it might be due to the same cause as that of soda-lime glass which was described in a report by Cornelissen, J. and Zylstra, A.L. that is to be published.

Ernsberger<sup>(11)</sup> used an ion exchange technique for defecting microcracks on a "flaw-free" surface of acid etched sheet glass. By using controlled experiments and examining photomicrographs, he identified three classes of surface imperfections that would cause strength impairment:

1. invisible fissures originating in the grinding operation
2. microabrasions
3. devitrification nuclei

He found on heat treating plate glass the ion exchange technique could detect incipient devitrification down to heat treating temperatures of 400°C, but not below. He pointed out from the photomicrographs that the devitrification nuclei were a source of surface microcracks,

these can act as stress concentrators. He, further, found that the incidence of devitrification nuclei are controlled chiefly by surface contamination. Clean pristine glass, heat treated in a clean container to protect the surface from dust, was found to be extremely resistant to the nucleation of devitrification. By comparison he showed that the residue of evaporation of a droplet of tap water (190 ppm total solids) initiated devitrification with only a mild heat treatment, 1 hour at 650°C.

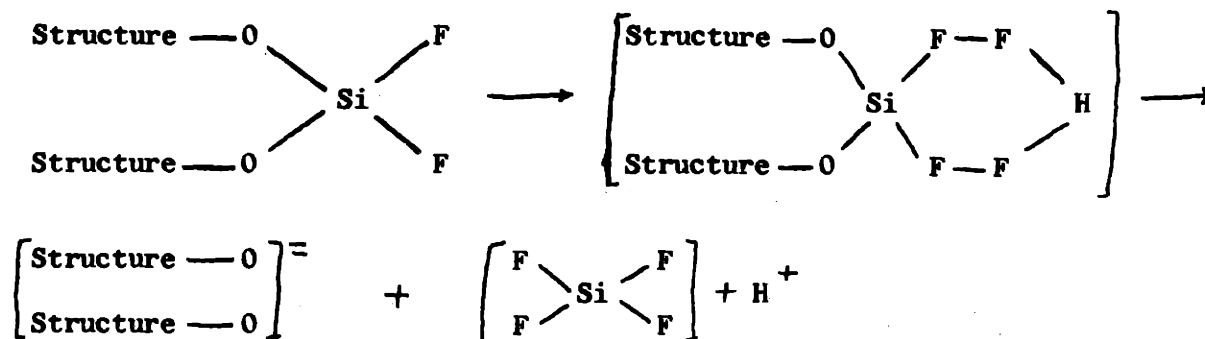
Encouraged by previous investigators (11), (27) who obtained improvements in the strength of bulk glass by only surface treatments, Proctor (34) investigated the effect of etching glass with hydrofluoric acid. He measured the variation of bending strength with depth of dissolved surface layer for various size soda, pyrex, and fused silica rods. The etching mechanism was described as one that removed the surface cracks by rounding out the crack bottoms so that stress concentration by microcracks is reduced and the strength of the sample is increased. This result can be predicted from the fact that the small radius of curvature at the crack tip has a lower chemical potential and solubility than the flat sides. The chemical mechanism described for the etching process is as follows:

The first step is the replacement of a surface layer of hydroxyl groups by fluorine atoms,



This satisfies the electron-neutrality requirements of the surface layer but there is a secondary co-ordination deficiency for the silicon atom which is remedied by further fluorine adsorption, pre-

ferably with the bifluoride ion. Finally the silicon moves over into the  $\text{SiF}_4$  group and detaches itself from the main structure,



Fresh hydrogen ions attach themselves to the oxygens on the structure and the  $\text{SiF}_4$  co-ordinates two more fluorine ions to form  $\text{SiF}_6$  ion in solution.

It was found that on etching the strength increased rapidly until a critical depth was reached. With further etching, however, the increase in strength was much more gradual. Maximum strengths of about 500,000 p.s.i. were recorded for the 8 mm diameter soda glass rods with the mean strengths rising to almost 400,000 p.s.i. The critical depth for these glass rods was about  $3 \times 10^{-2}$  cm. On varying the size of the soda glass rods, he found that for 3 mm diameter rods, the increase in strength with etching was much more rapid than that for the 8 mm rod, being  $1.5 \times 10^{-2}$  cm from the surface. The mean strengths for the 3 mm rods rose to about 320,000 p.s.i.; but limitations in the bending apparatus limited the testing of these rods beyond the removal of  $2.5 \times 10^{-2}$  cm. With the larger 10 mm diameter rods, the increase in strength was both less rapid and less marked than that of the 3 mm and 8 mm rods. The mean strength rose to about 250,000 p.s.i. with a critical depth of  $6 \times 10^{-2}$  cm.

Proctor<sup>(34)</sup> conducted tensile tests after drawing down a 4 mm diameter rod to 1/2 to 1/4 mm diameter. The rise in strength with etching was even more rapid than that for the 3 mm diameter rod.

Mean strengths rose to about 320,000 p.s.i. with little removal of surface material.

Proctor<sup>(34)</sup> further found that neither variations in the concentration and composition of the etching solution, nor changes in the initial condition of the glass surface had a significant effect on the strengths which were obtained on etching. However, on annealing the glass rods, he found a significant lowering of unetched strengths, but no differences between the etched strengths of unannealed etched rods and rods that were annealed before etching.

Proctor<sup>(34)</sup> reported a large amount of scatter in his results, the coefficient of variation being about 30 per cent for a given set of rods. He said that it was probably due to unidentified flaws that could come from:

1. surviving the etching process
2. introduced during etching
3. distributed through the bulk of the glass

He indicated that the last cause is the most likely and gives it as a possible reason as to why higher strengths were not obtained with the soda glass. He stated that there is some evidence from electron microscopy that glasses may contain widely distributed internal discontinuities of the size of some tens of angstroms. He suggested that these "weakly bonded regions" emerging at the surface are attacked by the atmosphere to produce more effective stress raising flaws. This could happen before stressing by a simple corrosion mechanism or, as discussed by Charles<sup>(5)</sup>, in connection with fatigue. In the first case, the strength should be a function of the atmospheric history between manufacturing and testing, and, in the second case, a function of rates and conditions of loading.

To investigate more thoroughly the internal discontinuities

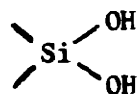
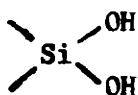
mentioned by Proctor<sup>(34)</sup>, it would be helpful to review a very comprehensive article by Statton and Hoffman<sup>(37)</sup> on the "Structure in Silicate Fibers as Shown by Small-Angle Scattering of X-Rays." They found that a relatively high inhomogeneity in electron density existed in practically all the samples studied. These inhomogeneities were interpreted as voids of sub-microscopic size (20 to 500 angstroms) in which the Si-O-Si network does not fill all the space. The size distribution of these voids shifted toward smaller dimensions when the samples were annealed, showing a compaction of the glass. These voids were elongated into ellipsoids or cracks by the spinning operation; the greater the windup speed, the greater this elongation in the direction of the fiber axis. When these fibers were chemically attacked, these ellipsoids were etched into a more spherical shape. This indicates that elongated voids are at the surface of the fiber and sealed spherical holes are in the interior. Changes in chemical composition of the melts produced varying amounts and elongation of the voids.

#### E. Effect of Water on Glass Surface

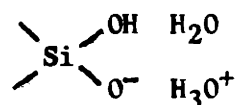
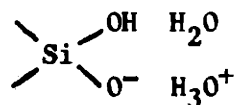
As can be seen from previous investigators, the surface of glass and its reaction with water play a very important and complicated role in the strength of glass. Thus, it would be instructive to investigate further the relationship between water and the glass surface. Iler<sup>(22)</sup> stated that the surface of silica is covered with a monolayer of hydroxyl groups termed "bound water". When silica is heated up to 500° to 600°C, this layer is partly removed, and part of the surface is left in a dehydrated oxide condition which will not physically adsorb water or methyl red dye as does the hydrated surface. This surface will re-

hydrate only slowly on exposure to water. He further stated that aged glass (1 or 2 years) is covered with a hydrated layer many molecules (about 100 angstroms) thick. This description of the surface is in very good agreement with that of Weyl<sup>(46)</sup> and Todd<sup>(42)</sup>.

Weyl<sup>(46)</sup> in his treatise on the surface chemistry of glass illustrated how water absorbs on the surface of glass. The water chemisorbs on the glass in the form of the OH ions by breaking the Si-O bonds:



However, the secondary charges of Si are still left unsatisfied so that more water is physi-absorbed on subsequent layers.



Todd<sup>(42)</sup> found that the gas evolved from soda-lime glass at temperatures below the softening point is primarily water. On heating the glass in a vacuum, a rapid evolution of gas (primarily water) occurred upon first heating, followed by an evolution which became increasingly persistent as the bake out temperature approached the softening point of glass. From the facts that the amount of water evolved at temperatures at and below 300°C increased with ageing of the glass and that the gas sources could be largely removed by etching the surface with 1 per cent hydrofluoric acid, indicate



that this water resided at the surface, probably in the form of a layer of hydrates. He also pointed out that since his isotherms for temperatures at and below 300°C approached different limiting values, the hydrated layer must be complex in structure; since, if only a single molecular species were involved, these isotherms would all approach the same limit only at different rates. He found that the water evolved from a unit surface at a constant temperature above 300°C is linear with respect to the square root of the time of bake out. He concluded that above 300°C the surface gases are rapidly and completely removed, and thus, the diffusion of water from the interior of the glass is of primary importance at these higher temperatures.

Tichane and Carrier<sup>(41)</sup> made electron micrographs of replicas of a weathered soda-lime glass surface before and after various chemical and fire polishing treatments. These micrographs were compared with an electron micrograph of a replica of a freshly fractured soda-lime glass surface which was used as a typically smooth surface. Using this comparison, they found the smoothest surfaces were produced by hot dilute solutions of hydrofluoric acid, sodium citrate, phosphoric acid, and ethylene diaminetetracetate. On the other hand, short treatments with hot solutions of distilled water, nitric acid, and citric acid did little, other than to remove the gross weathering products from the glass surface.

Haller<sup>(17)</sup> compared the geologic hydration of obsidian, the hydration of obsidian artifacts, the water vapor adsorption of vitreous silica. From these results he interpreted the adsorption mechanism as the diffusion of water into the glass,  $10^{-8} \text{ gm cm}^{-2}$

day<sup>-1/2</sup>, accompanied by an irreversible change in the glass structure. He described the mechanism as one of ion exchange. The net effect being the migration of protons into the glass and the migration of alkali ions out of the glass. In the absence of a suitable diffusion sink or in the absence of mobile cations in the glass structure, the mechanism of the interaction between water and glass is that of a diffusion of all constituents of the water into the glass, without the counter diffusion of any glass constituents.

Parikh<sup>(32)</sup> measured the surface tension of a commercial soda-lime-silica glass in various atmospheres in the temperature range of 450° to 700°C. He concluded that the surface tension remained constant between these temperatures, but found a linear relationship between the depression of surface tension and the polarity of the molecules in the test atmosphere. Nonpolar gases, such as dry air, nitrogen, hydrogen and helium have very little influence on the surface tension of the soda-lime-silica glass studied; whereas, polar gases, such as water vapor, sulphur dioxide, ammonia, and hydrogen chloride lower the surface tension by varying amounts. Water vapor was found to exhibit the most pronounced effect, causing a lowering from 315 to 205 dynes cm<sup>-1</sup> for a vapor pressure of 16 mm Hg.

### III. PLAN OF WORK

After reviewing previous literature, it was decided that high speed tensile tests should be performed on etched, commercial soda-lime-silica glass as a function of temperature. It was decided to slightly modify the rapid loading equipment, used in the testing of the dynamic properties of rubbers<sup>(1)</sup>, for the tensile testing of glass at temperatures from  $-100^{\circ}\text{C}$  to  $+700^{\circ}\text{C}$ .

In order to insure breakage at one point, glass rods were to be locally necked down by the use of a gas-air torch while the sample was being rotated in a glass lathe. It was decided to only etch the glass rods in this local necked region; therefore, apparatus that rotated the specimen on rollers, while hydrofluoric acid was dropped on to the necked region, was constructed. The smallest diameter of the necked down regions were to be measured by means of a microscope fitted with a micrometer eyepiece.

#### IV. DESCRIPTION OF APPARATUS AND MATERIALS USED

##### A. Apparatus

In Plate 1 an overall view of the tensile apparatus is presented. The basic apparatus was originally built by the Research Plastics Laboratory for the very rapid elongation of rubber samples. High speed loading was accomplished by a gas piston operated by nitrogen pressure. The piston is enclosed in a two-way gas cylinder, in which the pressure can be rapidly switched from one side of the piston to the other by the action of a solenoid valve. The solenoid is actuated by a foot switch for the convenience of the operator of the equipment. The lower, movable plate of the apparatus is first raised by gas pressure being applied below the piston - the sample is then inserted. The sample is broken by switching the gas pressure to the top side of the piston. The base plate is thus pushed down suddenly against a large metal stop, which is fitted with a rubber bumper to minimize the shock.

The gas piston was operated at a nitrogen tank pressure of 125 p.s.i. Calibration of the equipment has shown that about 7 pounds of force is exerted by the piston for each p.s.i. gas pressure, indicating an effective piston area of about 7 square inches. A gas pressure of 125 p.s.i. would thus represent about 875 pounds of force exerted by the piston.

The top holder of the sample was attached to a dynamic load cell by hardened steel pins. The design of load cells of this type was described in a previous report<sup>(10)</sup>. An oscilloscope recorded the impulse from the load cell. The electrical circuit that connected the load cell to the oscilloscope was found to have an excess of electrical

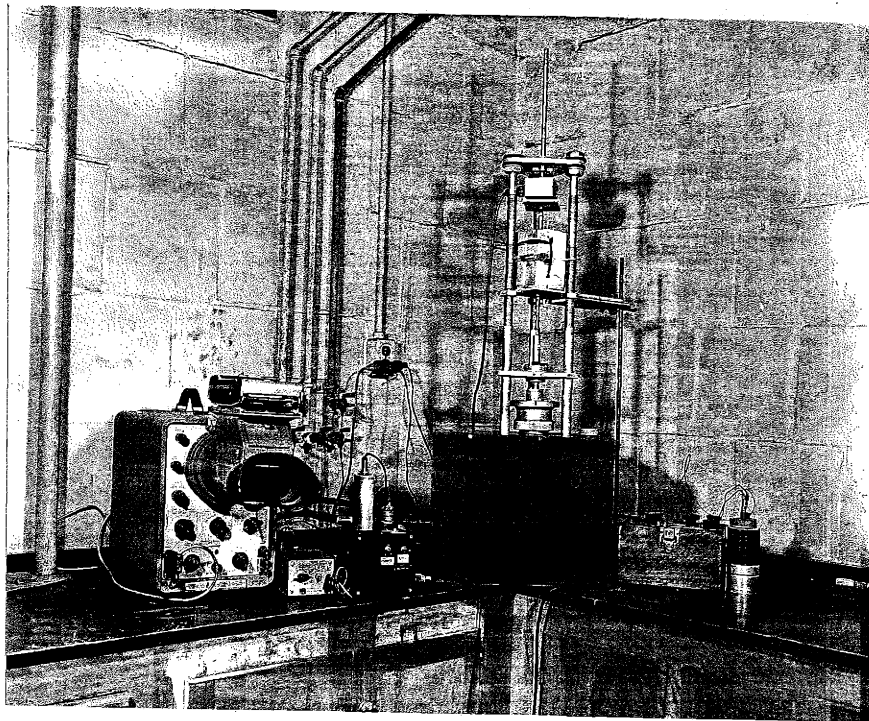


Plate 1

An Overall View of the Tensile Testing Apparatus

noise which made accurate measurements impossible. Therefore, a new circuit was built and is shown in Figure 4. Placing a weight on the load cell caused a voltage change across the strain gage bridge that was measured on the oscilloscope. The push button switch was used to short circuit the oscilloscope input to insure a zero calibration on the oscilloscope. The strain gage bridge could then be balanced to the zero calibration by adjusting the helipot. To make calibrating the equipment more convenient from day to day, it was decided to place a known resistor across one of the strain gages. Thus, by comparing the voltage change caused by the resistor and a known weight, the resistor could be calibrated. The vibrator was connected in series with the resistor in order to facilitate the measuring of the voltage change caused by the resistor. When the double pole, double throw switch was closed, both the vibrator and the resistor were connected across one of the strain gages. The vibrator very rapidly opened and closed the resistor connection so that two dashed lines were seen on the oscilloscope; one being the zero calibration and the other the voltage change caused by the resistor. Thus, the difference in the two could be very easily read. Two resistors were found necessary so that a maximum voltage change, corresponding to one of the resistors, could be read for a given voltage sensitivity. In this manner resistor A was calibrated to be 26.63 pounds and resistor B, 266.3 pounds. To further minimize the electrical noise that entered the system, all leads exposed to the atmosphere were shielded, as well as the vibrator which ran on A.C. current.

With the oscilloscope set for a fast sweep speed, 2 milliseconds per cm., the rate of loading could be observed (Plate 2). When the

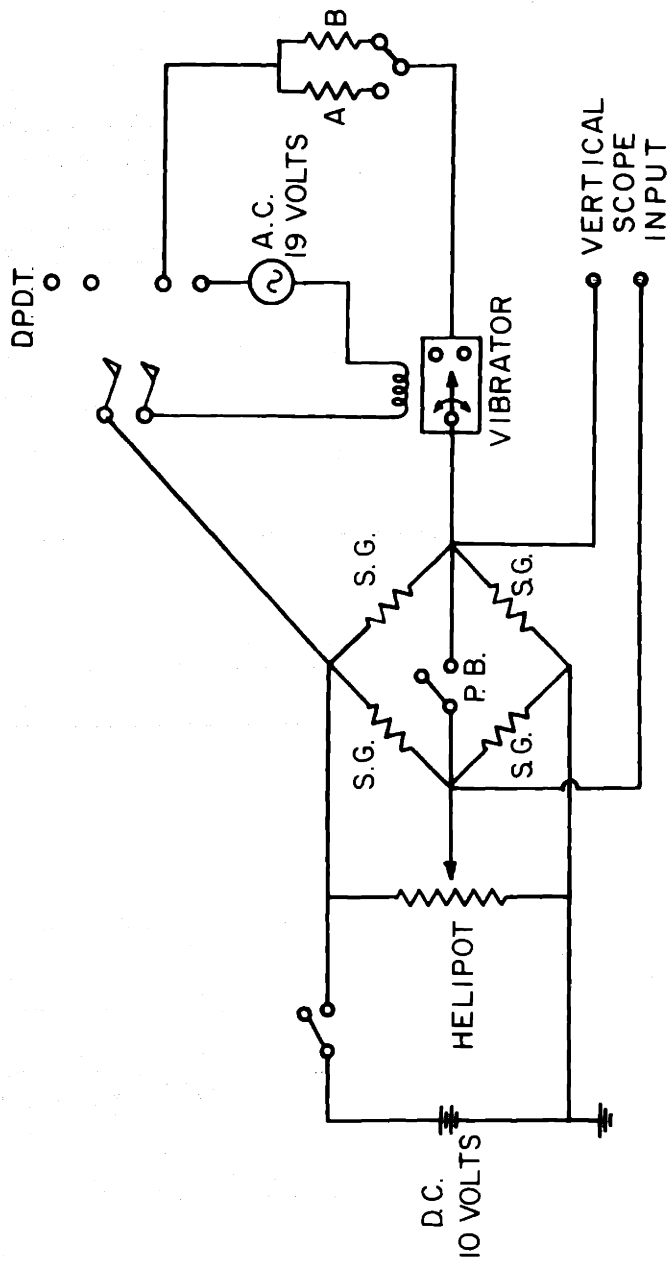


FIGURE 4 LOAD CELL CIRCUITRY

S.G. STRAIN GAGES ON LOAD CELL

P.B. PUSH BUTTON SHORTENING SWITCH

A CALIBRATING RESISTOR, 2000 OHMS

B CALIBRATING RESISTOR, 22,500 OHMS

DPDT DOUBLE POLE, DOUBLE THROW SWITCH

D.C. POWER SUPPLY WAS A QUAN-TECH LABORATORIES MODEL 170-B

OSCILLOSCOPE WAS A HEWLETT PACKARD MODEL 130 A

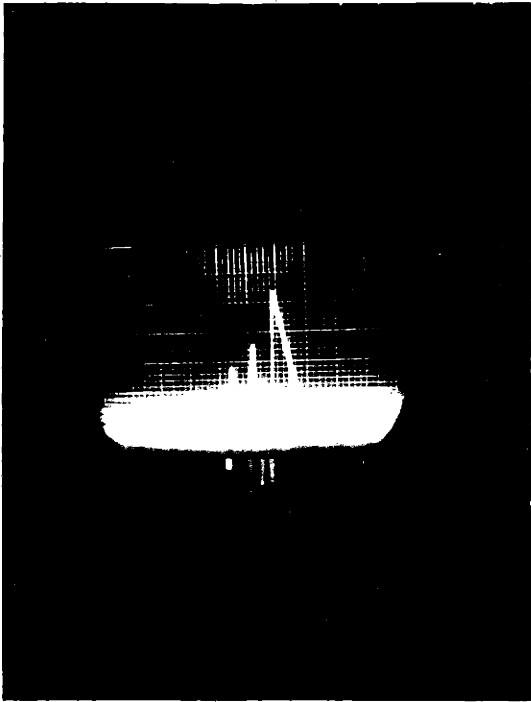
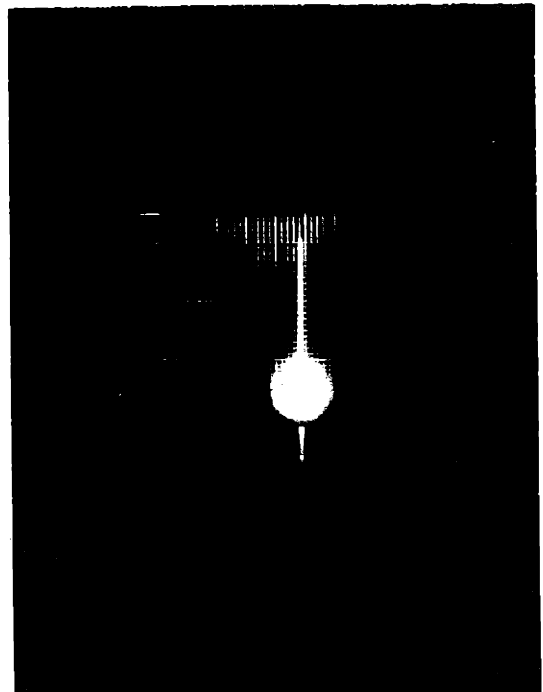


Plate 2

Loading Trace of the Oscilloscope  
Trace Speed 2 millise/c

Plate 3

Loading Trace of the Oscilloscope  
Trace Speed 5 sec/cm





sample broke, a sharp drop off followed by a rapidly damped oscillation is observed. The damped oscillation is due to a transient vibration of the load cell caused by the impact upon the sudden release of load. It was found, however, that some of the samples broke when the trace was not on the oscilloscope. To insure recording the load each time, the oscilloscope was run at a very slow sweep speed, 5 seconds per cm. Since the time of fracture was so rapid, this caused the loading rate and the sharp drop off to appear as a straight line (Plate 3).

The loading traces were photographed with a Polaroid camera which was fitted on the oscilloscope. The camera was operated by hand through a cable release, and was turned on and off just before and after the load was applied. It was found necessary to cover the trace in the zero calibration position with drafting tape so that the film was not over-exposed.

The grips on the glass rods were made out of aluminum rods. The aluminum rods were machined into small cylinders with the dimensions:

length	2 inches
outside diameter	0.451 inches
inside diameter	0.323 inches

These holders fitted over steel rods that were connected respectively to the load cell and the lower, movable plate. The grips were attached by inserting a 1/8 inch steel pin through the grip and steel rod. It was found necessary to place a slot one inch long in the bottom steel rod to allow for elongation of the specimen when heated.

The load cell could be raised or lowered by a simple keyed screw mechanism. The sample was first attached to the load cell, then brought down over the bottom steel rod and the steel pin inserted. The sample

was then raised until the bottom steel pin just touched the top of the slot. The sample was now in position to be tested.

The furnace was built with a "clam shell" design for the convenience of inserting samples (Plate 4). A simple varigrip clamp and hinge connected the two halves together. Ordinary fire brick, 5 5/8 inches by 2 1/2 inches, was used for the two halves and a 1/2 inch mullite tube for the core. The mullite tube was wound in the axial direction with chromel A resistance wiring, .020 inches diameter. The wiring was done so that the heating unit consisted of two portions, a central zone and a buffer zone, each of which was run off a different variac. The central zone was 3 inches long and the buffer zone 1 1/4 inches long. It was found that the central zone represented a constant temperature region,  $\pm 5^{\circ}\text{C}$ . A chromel-alumel thermocouple was inserted through the middle of the central zone and its output was read by a Leeds and Northrup portable potentiometer. The furnace was mounted on a trucite platform that could be positioned before each run so that the thermocouple rested in the proximity of the necked down region of the glass rod. In order to eliminate heat losses out of the top of the furnace, fiber glass wool was placed around the top of the furnace after the sample was in position to be tested.

The icebox consisted of two concentric copper cylinders, 3/4 and 4 inches inside diameter and 5 5/8 inches high, soldered together by a copper plate on the top and bottom (See Plate 4). One-fourth inch glass insulation was wrapped around the outside. Liquid nitrogen was poured into the bottom via a funnel and a gas outlet was at the top of the icebox. A copper-constantan thermocouple was inserted through the middle of the icebox. The same potentiometer-platform arrangement

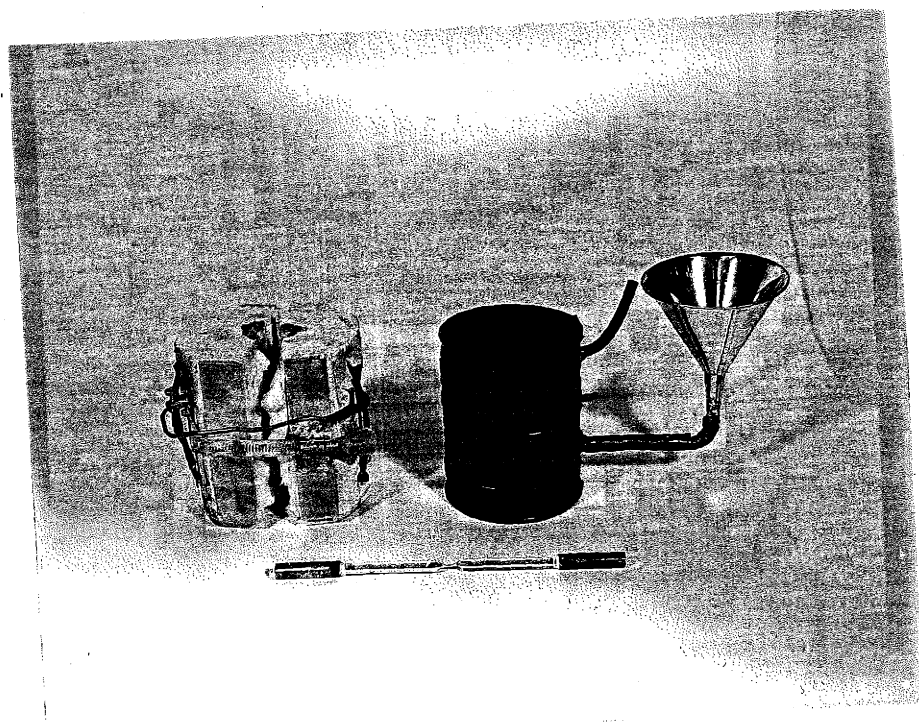


Plate 4: View of Furnace, Icebox, and Sample



Plate 5: Etching Apparatus

previously described for the furnace was used.

The etching apparatus (Plate 5) was built of lucite with polystyrene rollers. A 30 r.p.m. motor rotated one of the rollers which connected to the other via a rubber pulley. The siphon setup (as shown in Plate 5) was made of polyethylene and allowed the hydrofluoric acid to be dropped down onto the sample, while rotating on the rollers.

The diameters of the necked region were measured with a Spencer microscope, model number 419065, fitted with a Bausch and Lomb micrometer eyepiece. It was found that on the 6X objective one division of the micrometer was equal to 144 microns; the 3X objective was 276.5 microns.

The vacuum system used for the vacuum heat treatments was that built by J. Turnbaugh<sup>(43)</sup> for his internal friction measurements.

#### B. Sample Preparation

The glass chosen for these tests was commercial soda-lime-silica glass rods, 8 mm diameter, with the properties as given in Table II. From this base stock six inch specimens were cut. They were locally necked down by the use of a gas-air torch while the sample was being rotated in a glass lathe. The chuck of the lathe was moved out until the diameter of the necked region became approximately 1.0 to 1.5 mm. The final length of the glass rods was approximately 6 1/2 inches with the central portion resembling a hyperboloid of one sheet.

The cylindrical, aluminum grips were then attached to the glass rods with epoxy resin from a Hysol Epoxi-Patch Kit. It was found necessary to etch the ends of the glass rods before the holders were attached because:

TABLE II

R-G Kimble Standard Flint Glass Rod, 8 mm.

Strain Point	490°C
Annealing Point	520°C
Softening Point	770°C
Expansion (0-300°C)	$93 \times 10^{-7}/^{\circ}\text{C}$
Density	2.53 g/cc
Refractive Index	1.52
Transmission (2mm)	92 per cent
Specific Heat (average for range 25°C to 175°C)	0.200 cal/g°C
Thermal Conductivity (20°C)	0.0022 cal/sec.cm.°C
Young's Modulus	$10.3 \times 10^6$ p.s.i.

1. Some of the rods would not fit into the holders due to variations in the original diameter.
2. Some of the earlier samples broke at the holder; therefore, etching strengthened the ends.

In order to insure correct alignment of the holders after they were placed on the sample, the holders were pressed between two flat rulers. The epoxy was allowed to harden for one hour, then cured at 65°C for another hour.

The specimens were etched with 40 per cent hydrofluoric acid with the etching apparatus in Plate 5. During etching it was necessary to wash away the white deposit formed with tap water from a wash bottle. After etching, which lasted 8 to 10 minutes, the samples were dried with acetone and measured under the microscope. The smallest diameter of the necked region was measured since failure was assumed to occur at that point. The final diameter was approximately 0.7 to 0.8 mm which resulted in approximately  $3.5 \times 10^{-2}$  inches of the surface being removed. Plate 4 shows a view of the sample.

## V. DISCUSSION OF WORK DONE

### A. Results

#### 1. Preliminary Experiments

On fracturing the glass specimens it was found that the central portion of the necked region was often lost. Hence, it was decided to measure the diameter of the samples before testing. To insure that the diameter of the necked region remained constant while being heated to the testing temperature, diameters of samples were measured before and after heat treatment in the testing equipment. It was found that samples heated to temperatures up to 600°C had the same diameter before and after heat treatment. This compared very favorably with the elongation results given in Table III. These results were obtained by measuring; with a cathotometer, the elongation of a sample being heated in the testing apparatus. It can be seen that there was very little elongation up to 630°C; at approximately 650°C the sample began to flow at a noticeable rate. Thus, it was thought that the elongation up to 600°C was probably due mainly to thermal elongation; and hence, no observed change in the diameter of the necked region. By comparing under the microscope the two halves of a sample broken at 650 and 700°C, the center of the necked region was observed to attenuate into a cylindrical shape. Thus, it was decided that at 650 and 700°C the diameter at the point of fracture could be obtained by simply measuring the diameter of the cylindrical portion after fracture. At temperatures above 700°C, the sample was deforming too rapidly to be tested.

## 2. Loading Rate

Since it was decided to run the oscilloscope at a slow trace speed, the loading rate curve at various temperatures was obtained to insure that the strain gage was responding properly at all testing temperatures. Table IV presents these findings. At all temperatures and load levels, the curves had the characteristic rise and sudden drop off as that in Plate 2. From these curves the time of fracture was found to be dependent only on the load level.

## 3. Strength versus Temperature of Etched Glass

In Figure 5 the average of three separate runs of strength versus temperature is shown. In each run three samples were tested at each testing temperature. All the samples for a given run were prepared at the same time except for the etching process. The three samples that were to be tested were then etched and tested together. All samples up to 650°C were held at the testing temperature for approximately 2 minutes before they were fractured. The 650 and 700°C samples were tested immediately since they were viscously deforming at these temperatures. It is significant to note that all three runs showed a similar shaped curve, a maximum at 100°C followed by a continual decrease in strength to 700°C (See Table XIV). When comparing the average strengths of the runs at a given temperature, there seemed to be close agreement between the three runs at temperatures above 100°C. To confirm this, the coefficient of variation between the individual runs was found and is shown in Table V. \* It can

\* The reader is referred to Appendix B for the details of the statistics used in this report.



immediately be seen that the coefficient of variation of the individual runs decreased significantly above 100°C. To check the room temperature strength, all of the preliminary samples tested at room temperature were compiled and are shown in Figure 6. The average for these 71 samples was 289,000 p.s.i. with a coefficient of variation of 28 per cent. This compares favorably to the average obtained from the three temperature runs, which was 266,300 p.s.i. This also agrees with the results of Proctor<sup>(34)</sup> and Symmers, et al<sup>(38)</sup>. Proctor found that the tensile strength of etched soda glass was 320,000 p.s.i. with about a 30 per cent coefficient of variation. Symmers, et al found that the mean tensile strength of etched glass rods were of the order of 250,000 to 300,000 p.s.i. It was first thought that this decrease in strength with temperature was exponential; but on plotting the logarithm of strength versus the inverse of absolute temperature, no meaningful curve or curves could be drawn (Figure 7).

#### 4. Strength Below Room Temperature of Etched Glass

As in the above experiment, three separate runs were made testing three samples at room temperature and three at a lower temperature in each run. It was found that there is no apparent effect on strength upon lowering the temperature to a -100°C. These results are shown in Table VI.

#### 5. Strength versus Temperature of Unetched Glass

Two runs consisting of three samples at each testing temperature were made with the unetched glass samples and the average is shown in Figure 8. The samples were prepared and tested in the same manner as the etched samples except omitting the etching process. From these results it was concluded that temperature has no effect

on the strength of unetched glass up to 700°C.

#### 6. Special Tests

In order to investigate the damage done by heating etched glass, a series of controlled experiments were made at 400°C. To check the average strength recorded previously for 400°C, six samples were tested in the same manner as before (i.e. held at 400°C for 2 minutes before fracturing). The average of these six samples was found to be 158,783 p.s.i. which compares with the 172,300 p.s.i. recorded previously (Table VII). The time dependence of the damage was found by holding a sample at 400°C for 30 minutes before testing. These results are tabulated in Table VIII. On comparing this average strength of 91,266 p.s.i. to that obtained previously at 400°C, it can be concluded that the strength decreased with time.

By heating a sample to 400°C for two minutes, cooling to 100°C, and then testing it at 100°C, it was found that the damage is permanent (See Table IX). It is important to note that the strength value obtained in this manner was intermediate to that recorded at 400°C for the time intervals of 2 and 30 minutes. This would be expected since further damage is done while the sample cools to 100°C, but this damage is not as severe as that done at 400°C because of the lower temperatures involved. It should be pointed out that by coincidence the sample took 30 minutes to cool from 400°C to 100°C.

Etched samples that were heat treated at 400°C for 2 minutes were reetched, removing  $3 \times 10^{-2}$  cm from the surface, and tested at 100°C. From Table X it can be seen that reetching causes a significant increase in strength. This indicates that the damage is related only to the surface.

Since the strength obtained on reetching was slightly greater than that obtained previously at 100°C, it was thought that compaction of the sample might have occurred. To investigate this, it was decided to reetch samples that were not heat treated. While one etched sample was given a similar heat treatment to that above, three samples were etched and stored away. After the heat treatment of the one sample, all four samples were then reetched and tested together. Table XI presents these results. To investigate the compaction effect further, samples were heat treated at 400°C for 30 minutes before reetching and testing at 100°C (See Table XII). By holding the sample at 400°C for 30 minutes, it was thought that more compaction would occur, and hence, a higher strength on reetching. These results show that the strength of etched glass is not a sensitive enough property to detect compaction of glass at 400°C.

Samples were heated in a vacuum, .026 to .049  $\mu$ , at 400°C for 2 minutes, allowed to cool in the vacuum, and then tested at room temperature under atmospheric conditions. For comparison, samples were similarly heated and tested in air. These results show that the damage occurs in a vacuum as well as in air (Table XIII).

Table III

## Viscous Flow Measurements

	Temperature (°C)	Elongation (mm)
A.	250	-----
	528	0.079
	598	0.289
	619	0.446
	640	0.810
	659	2.073
	671	5.159
	692	15.509
B.	283	-----
	448	0.228
	516	0.360
	579	0.634
	614	0.898
	638	1.148
	654	1.853
	668	3.030
	688	11.282

Table IV

## Loading Rate

Load (lbs.)	Stress (p.s.i.)	Testing Temperature (°C)	Time of Fracture (milliseconds)
240	363,000	26	2.8
118	216,000	300	1.2
128	154,000	500	1.2
77.4	108,000	670	0.7
32.0	54,200	680	0.5

**Figure 5**  
**Strength versus Temperature of Etched Glass**

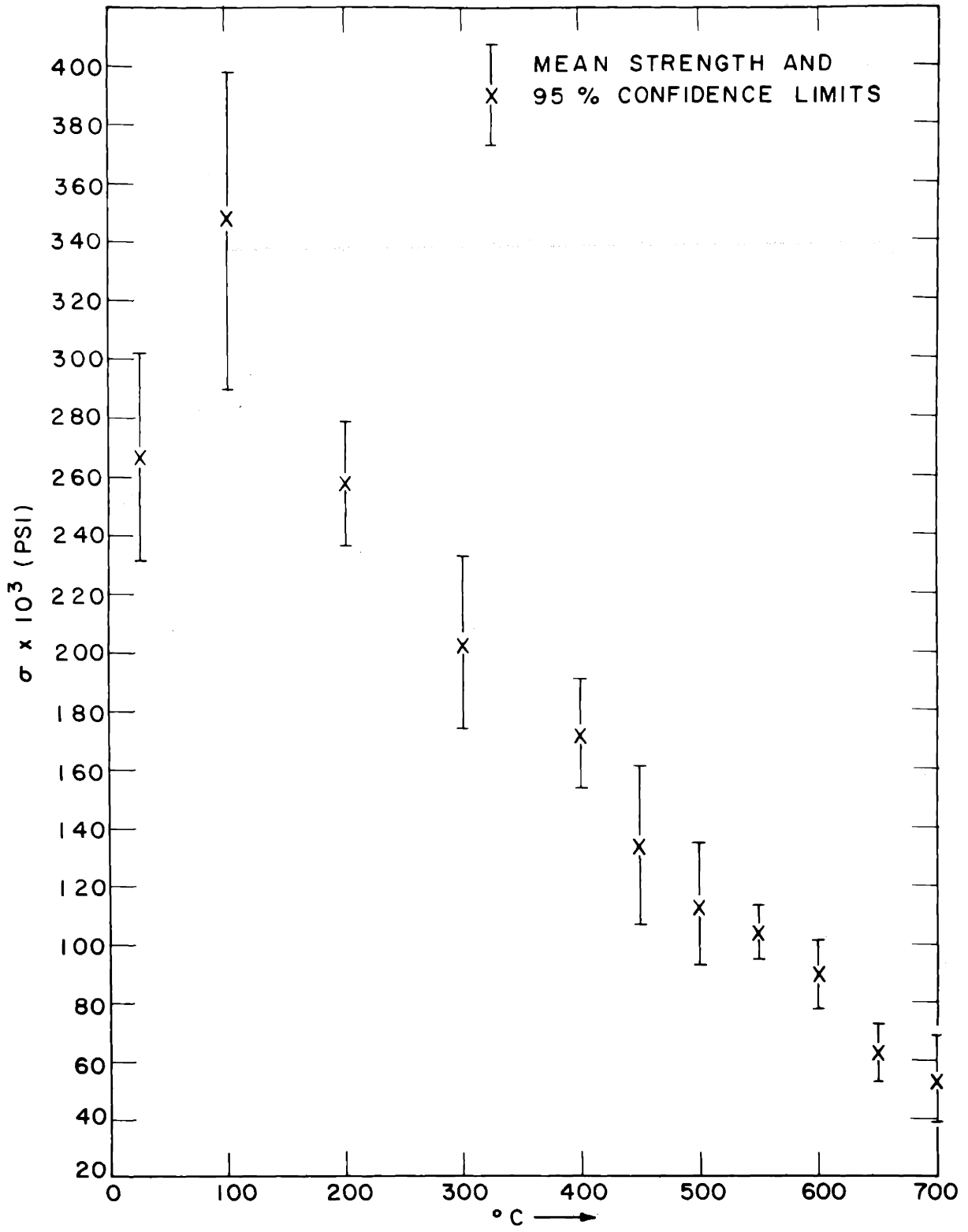


Table V

## Variation of the Averages

Testing Temp. °C	$\sigma \times 10^3$ p.s.i.	$\bar{\sigma} \times 10^3$ p.s.i.	$S \times 10^3$ p.s.i.	Coefficient of Variation %
26	257 156.3 385.6	266.3	114.8	44
100	342.3 264.6 442.3	349.7	97.0	28.3
200	251.2 246.5 275.0	257.56	15.3	5.94
300	187.6 206.6 215.0	203.06	14.02	6.9
400	177.6 179.0 160.3	172.3	10.42	6.05
450	- 154 113.6	133.8	29.0	20.9
500	106.6 117.95 117.3	113.95	6.41	5.64
550	- 106.5 102.2	104.35	3.04	2.92
600	107.6 93.33 69.9	90.28	15.08	16.7
650	- 68.53 56.13	62.33	8.78	14.1
700	60.7 47.6 53.1	53.8	6.6	12.5



Figure 6  
Strength of Etched Glass at Room Temperature

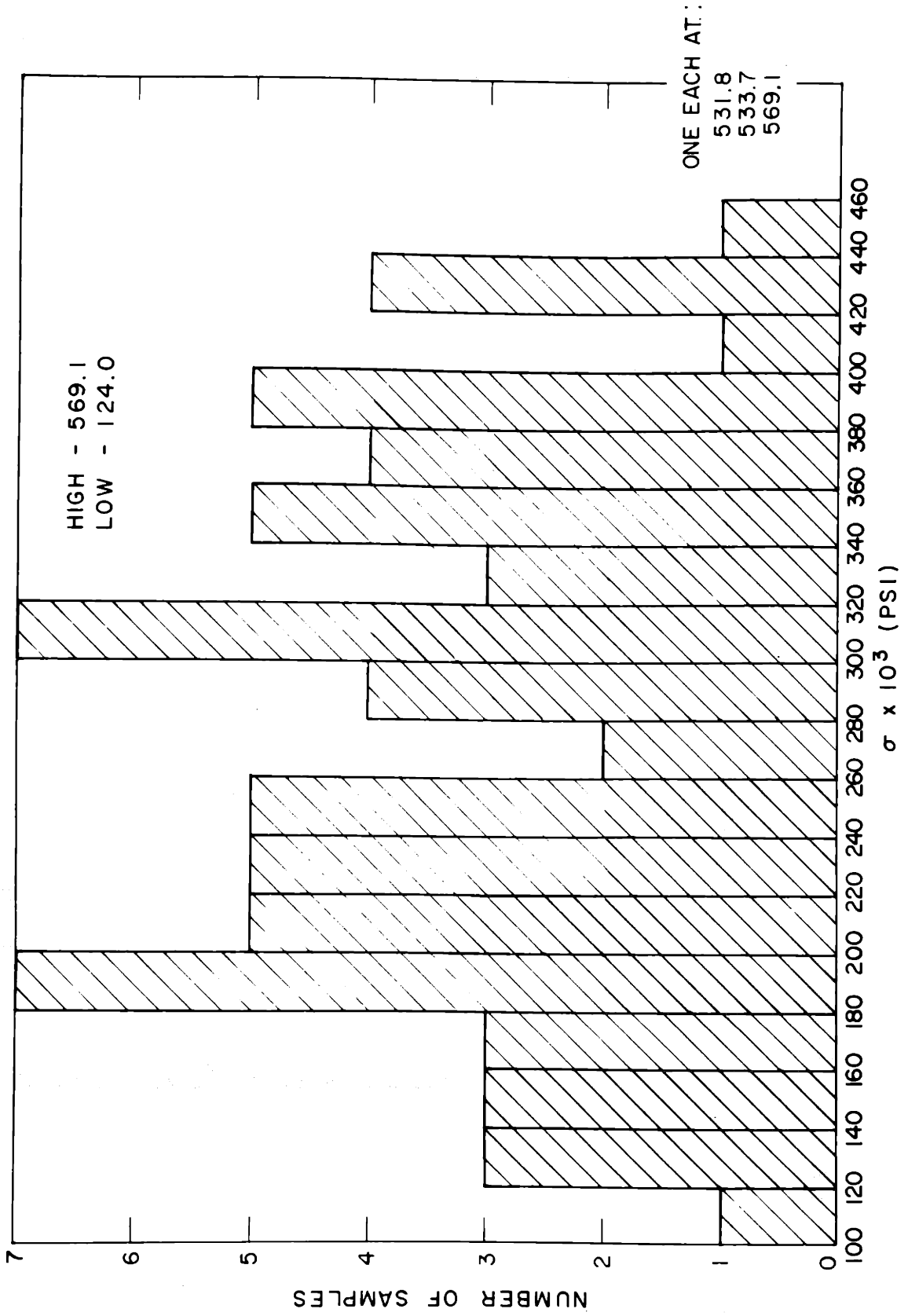


Figure 7

Logarithm of Strength versus Inverse of Absolute Temperature for Etched Glass

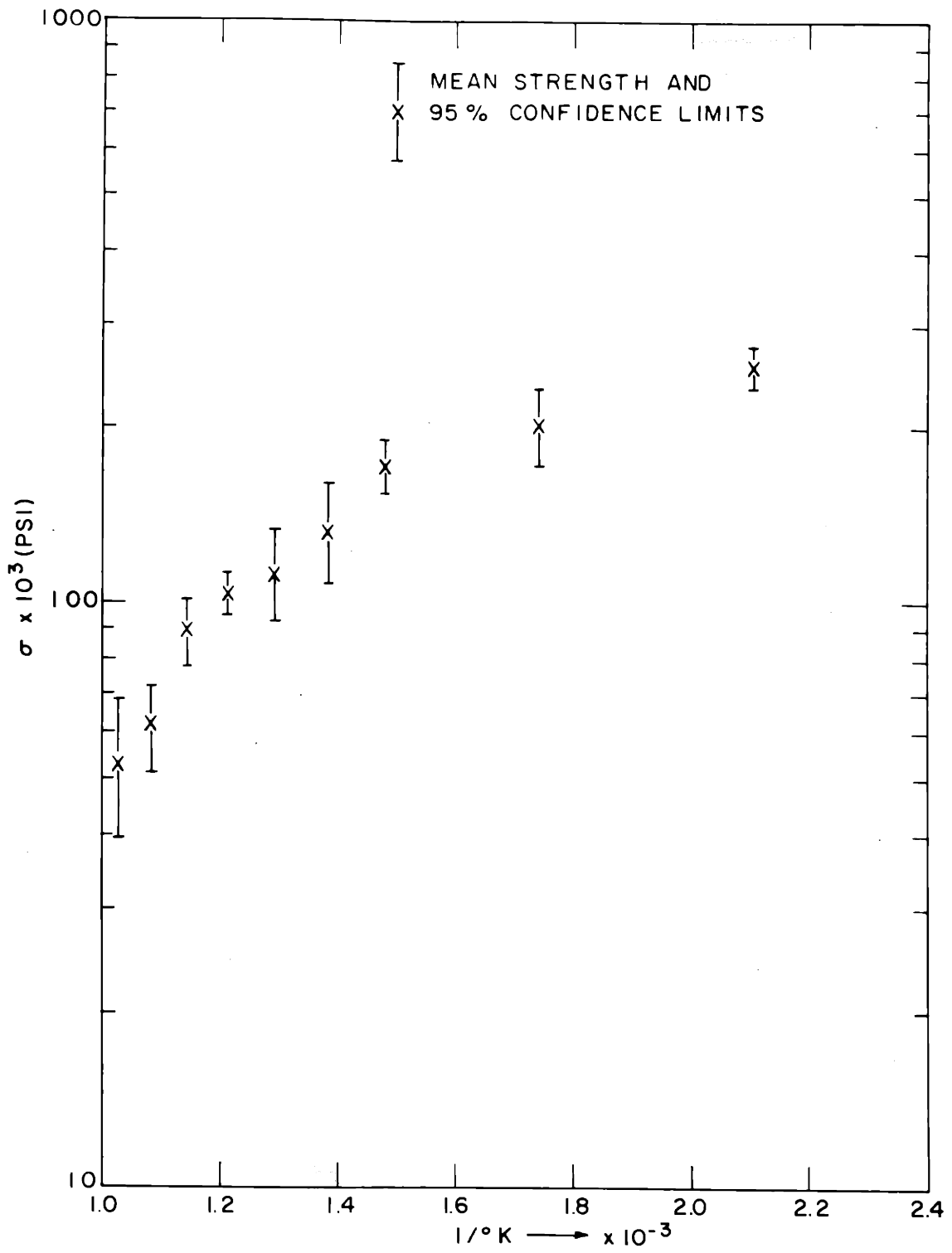


Table VI

## Below Room Temperature Tests

	Testing Temp. °C	$\bar{U} \times 10^3$ p.s.i.	$\bar{V} \times 10^3$ p.s.i.	$S \times 10^3$ p.s.i.	Coefficient of Variation %
I.	26	319.5	353.33	37.1	10.49
	26	393.0			
	26	347.5			
	-60	301.5	320.83	22.15	8.9
	-60	345.0			
	-60	316.0			
II.	26	412.0	450.0	51.9	11.52
	26	423.0			
	26	515.0			
	-100	414.0	496.66	109.4	22.1
	-100	621.0			
	-100	455.0			
III.	R.T.	428.0	457.0	40.9	8.95
	R.T.	486.0			
	-100	480.0	436.0	62.3	14.27
	-100	392.0			

**Figure 8**  
**Strength versus Temperature of Unetched Glass**

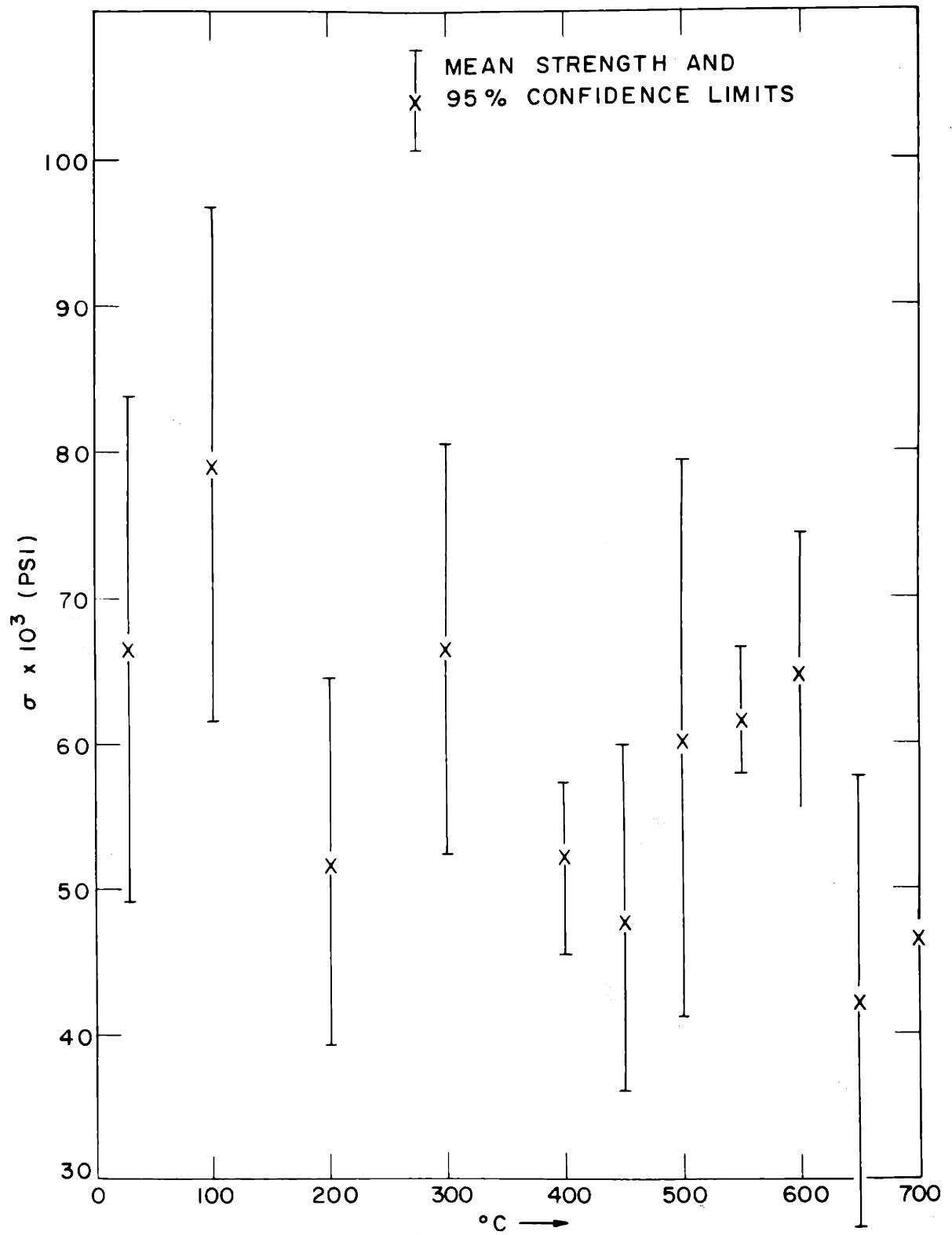


Table VII

Testing Temperature 400°C - 2 minutes

$\sigma \times 10^3$ p.s.i.	$\bar{\sigma} \times 10^3$ p.s.i.	$S \times 10^3$ p.s.i.	Coefficient of Variation %
166.2			
166.8			
159.8	158.783	12.78	8.05
172.5			
149.2			
138.2			

Table VIII

Testing Temperature 400°C - 30 minutes

$\sigma \times 10^3$ p.s.i.	$\bar{\sigma} \times 10^3$ p.s.i.	$S \times 10^3$ p.s.i.	Coefficient of Variation %
96.7			
103.8			
134.0	91.266	20.45	22.45
82.4			
77.7			
53.0			



Table IX

Heated to 400°C (2 minutes), cooled to 100°C, and tested

$\bar{U} \times 10^3$ p.s.i.	$\bar{U} \times 10^3$ p.s.i.	$S \times 10^3$ p.s.i.	Coefficient of Variation %
110.0	109.583	4.43	4.04
118.2			
102.1			
107.2			
114.0			
106.0			

Table X

Heated to 400°C (2 minutes), cooled, reetched, heated to 100°C and tested

$\bar{U} \times 10^3$ p.s.i.	$\bar{U} \times 10^3$ p.s.i.	$S \times 10^3$ p.s.i.	Coefficient of Variation %
438	470.5	25.1	5.34
466			
448			
510			
471			
490			

Table XI

Testing Temperature 100°C

Heat treated, reetched	433.8 x 10 <sup>3</sup> p.s.i.
No heat treatment, reetched	449.0 x 10 <sup>3</sup> p.s.i.
	510.0 x 10 <sup>3</sup> p.s.i.
	548.0 x 10 <sup>3</sup> p.s.i.

Table XII

Heated to 400°C (30 minutes), cooled, reetched,  
heated to 100°C and tested

411 x 10<sup>3</sup> p.s.i.  
591 x 10<sup>3</sup> p.s.i.  
478 x 10<sup>3</sup> p.s.i.

Table XIII

Heated to 400°C, cooled and tested at room temperature  
under atmospheric conditions

Heating Environment	$\sigma \times 10^3$ p.s.i.	$\bar{\sigma} \times 10^3$ p.s.i.	$S \times 10^3$ p.s.i.	Coefficient of Variation %
Vacuum (0.034 to 0.049 $\mu$ )	84.0			
Vacuum (0.034 to 0.045 $\mu$ )	82.9	73.43	17.38	23.5
Vacuum (0.026 to 0.034 $\mu$ )	53.4			
Atmosphere	53.8			
Atmosphere	47.3	55.28	8.82	15.95
Atmosphere	64.75			

## B. Discussion of Results

Before the results are discussed it would be beneficial to summarize the results obtained on the strength-temperature dependence of etched glass. On heating etched glass from room temperature, the strength rose to a maximum at 100°C; after which there was a significant decrease in strength as the temperature was increased. On conducting a series of controlled experiments at 400°C, the damage was found to:

1. increase with time
2. be permanent
3. relate only to the surface
4. occur in a vacuum as well as in air

In the following discussion three possible causes for the heat treatment damage of both glass fibers and etched glass, will be discussed:

1. surface devitrification
2. adsorbed surface water
3. bulk water

Ernsberger<sup>(11)</sup> has experimentally shown how surface devitrification leads to strength impairment; surface devitrification caused micro-cracks that could act as stress concentrators. However, this concept does not fully explain a few important questions.

Ernsberger<sup>(11)</sup>, using the technique of ion exchange, did not observe any surface devitrification below 400°C for plate glass. Damage to glass fibers has been observed at annealing temperatures as low as 100°C<sup>(40)</sup> and my results on etched glass showed that the damage may begin as low as 200°C. Also, it is hard to reconcile with the devitrification hypothesis that the strength of glass fibers has

been shown to decrease immediately and then reach a constant value on annealing for 2 hours at 300°C. At 600°C the total strength decay occurred immediately (6),(40). An induction period would seem necessary for devitrification to cause a measurable strength impairment; and hence, no immediate decrease in strength could be detected. Also, Ernsberger<sup>(11)</sup> showed that at 650°C, devitrification after 2 hours is more severe than after 1 hour which seems to be contradictory to the observed leveling off of strength as reported above. Finally, Otto's significant increase in strength on drawing a fiber at 649°C and testing at 538°C is inconsistent with the devitrification concept because it would seem that devitrification should have still occurred at 538°C.

All of the observed experimental results on the strength of both melt drawn glass fibers and etched glass may be related to the adsorbed water on glass in some complicated manner. The rise in strength of etched glass at 100°C can be attributed to an increase in the surface energy of the glass due to an expulsion of the physi-absorbed water. However, for fibers carefully drawn from a melt no increase in strength is reported upon heating the fiber to 100°C. This could be due to the surface condition of the fiber being better than that of etched glass; thus, the increase in surface energy of fibers may be offset by the slight damage caused by the expulsion of the physi-absorbed water.

The expulsion of the chemi-absorbed water was suggested by Otto<sup>(30)</sup> as the cause for the surface damage done to glass upon heat treating. However, one would expect that the bulk water in the glass would also be driven off along with the chemi-absorbed surface water. Thus, the

question arises as to the damage, if any, done by the diffusion and expulsion of bulk water. It can be shown that the diffusion of bulk water is only related to the surface by reviewing Todd's report<sup>(42)</sup>. By treating the diffusion problem as that of a semi-infinite body, he showed that only a thin layer of glass is involved in the diffusion process. By using Todd's diffusion constants of  $6.1 \times 10^{-13} \text{cm}^2/\text{sec}$  at  $430^\circ\text{C}$  and  $2.0 \times 10^{-11} \text{cm}^2/\text{sec}$  at  $505^\circ\text{C}$ , it is found that the depth at which the water concentration reaches the original concentration is  $41.4 \times 10^{-6} \text{cm}$  at  $430^\circ\text{C}$  for 2 minutes and  $234 \times 10^{-6} \text{cm}$  at  $505^\circ\text{C}$  for 2 minutes. Todd checked this experimentally by baking out a sample, polishing off about  $7.6 \times 10^{-3} \text{cm}$  from the surface, and observing that on baking out again, the diffusion of water followed the original diffusion curve. When I reetched my heat treated samples, I removed approximately  $3.0 \times 10^{-2} \text{cm}$  from the surface. Thus, any damage done by the diffusion of bulk water would be observed as a surface effect only.

However, on comparing the results of Thomas<sup>(40)</sup> and Cornlissen, et al<sup>(6)</sup> to those of Todd<sup>(42)</sup>, it may be concluded that the diffusion of the bulk water has a negligible effect on the strength of glass. At the bake-out temperature of  $300^\circ\text{C}$ , Todd found that the surface water was completely evolved at a time between 42 and 74 minutes. He concluded that at a temperature greater than  $300^\circ\text{C}$ , the surface water is completely removed within 42 minutes. Thomas's data showed that a constant value in strength is reached after annealing for less than 2 hours at  $300^\circ\text{C}$  and 30 minutes at  $450^\circ\text{C}$ . If it is assumed that the strength impairment is due only to the chemi-absorbed water leaving the surface, Thomas's results are consistent with Todd's. Furthermore,

at temperatures of 550°C or greater, both Thomas and Cornlissen observed an immediate decrease in strength to a constant value. This would correspond to an immediate repulsion of the absorbed surface water, followed by a slow diffusion of the bulk water out of the glass which causes no further strength impairment. Devitrification could now become of prime importance and cause a second decrease in strength as reported by Cornlissen, et al. The reason that Thomas did not observe this second decrease is probably due to his not holding the fiber for a longer time at the annealing temperature. Cornlissen, et al reported the second decrease in strength to occur after 8 hours at 550°C and 1 hour at 650°C; whereas, Thomas only held his fiber for 4 hours at 600°C.

The difficulty in either water concept is describing the exact mechanism as to why the expulsion of water results in a defective glass surface. If it is assumed that this expulsion of water causes micro-cracks, the depth of a critical flaw can be calculated from Griffith's criterion:

$$\sigma = \sqrt{\frac{2E \gamma}{\pi c}}$$

taking \*  $E = 10^7$  p.s.i.

$$\gamma = 3.1 \times 10^{-3} \text{ lb/in.}$$

Using the strength values of etched glass at 400 and 500°C, which are approximately 150,000 and 110,000 p.s.i., the critical depths are found to be  $2.2 \times 10^{-6}$  cm and  $4.1 \times 10^{-6}$  cm respectively. It is hard to believe that the expulsion of chemi-absorbed surface water resulted in a flaw of this magnitude. Even in considering the diffusion of the

\* These values are taken from Proctor's<sup>(34)</sup> report.

bulk water, it is difficult to conceive of a mechanism that explains how the flaw forms and grows since the depth of the "diffusing water layer" increases faster than the depth of the critical flaw. The reader is referred back to the previous calculations made on the diffusion of bulk water at 430 and 505°C (page 56).

The results of the strength versus temperature of unetched glass are in good agreement with these of Kingery and Pappis<sup>(25)</sup> and the inferences drawn by Shand<sup>(35)</sup> (See page 9 of Literature Survey). Thus, it can be seen that:

1. Surface flaws are of prime importance in the strength impairment of unetched glass up to 700°C.
2. For very short fracture times, 0.5 to 2.8 milliseconds, the effect of temperature upon the stress corrosion of surface flaws is negligible.



## VI. CONCLUSIONS

1. On heating etched soda-lime-silica glass, there is an increase in strength to 100°C, after which there is a significant decrease in strength to 700°C. The increase in strength is suggested to be due to an increase in the surface energy of the glass resulting from the expulsion of physi-absorbed surface water. Further work is necessary to determine the exact mechanism for the damage done by heating etched glass.

2. With short fracture times, 0.5 to 2.8 milliseconds, the strength of unetched soda-lime-silica glass remains more or less constant up to 700°C. This is due to the effect of temperature upon stress corrosion becoming negligible at the short fracture times.

3. There is no apparent effect on the strength of etched glass upon lowering the testing temperature to -100°C.

4. The strength of etched glass is not a sensitive enough property to detect compaction of glass at 400°C.

## VII. RECOMMENDATIONS

In order to determine conclusively the exact effect that surface devitrification has on the strength of glass, strength measurements should be made on glass that is completely void of water. This can be done by drawing and testing glass fibers in a vacuum. In all stages of the experiment, extreme care should be taken to exclude the presence of any water. Special emphasis should be placed upon studying the strength as a function of both time and temperature. These results can then be compared to those obtained from glass with known adsorbed water.

Concurrently, an investigation, using the ion exchange technique of Ernsberger<sup>(11)</sup>, should be made on devitrification as a function of time and temperature. If strength is dependent upon devitrification these results should correspond to those obtained in the above study on the strength of glass in the absence of adsorbed water.

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**IX. APPENDIX****A. Details of Experimental Data**

Table XIV

## Strength versus Temperature of Etched Glass

	Testing Temperature °C	$\sigma \times 10^3$ p.s.i.	$S \times 10^3$ p.s.i.
I.	26	257.0	21.3
	100	342.3	58.2
	200	251.2	32.8
	300	187.6	7.3
	400	177.6	9.8
	500	106.6	24.8
	600	107.6	10.4
	700	60.7	22.34
II.	26	156.3	38.0
	100	264.6	45.4
	200	246.5	10.6
	300	206.6	59.4
	400	179.0	38.4
	450	154.0	27.9
	500	117.95	27.62
	550	106.5	6.39
	600	93.33	23.2
	650	68.53	10.64
	700	47.6	3.815
III.	26	385.6	68.5
	100	442.3	84.5
	200	275.0	22.1
	300	215.0	26.2
	400	160.3	11.9
	450	113.6	22.7
	500	117.3	22.82
	550	102.2	7.44
	600	69.9	2.1
	650	56.13	9.54
700	53.1	2.975	

Table XIV Cont.

On compiling these results

Testing Temperature °C	$\bar{\sigma} \times 10^3$ p.s.i.	$\bar{s} \times 10^3$ p.s.i.	Coefficient of Variation %
26	266.3	46.5	17.4
100	349.7	64.7	18.9
200	257.56	25.45	9.9
300	203.06	37.75	18.55
400	172.3	23.85	13.87
450	133.8	25.5	18.5
500	113.95	24.65	21.65
550	104.35	7.12	6.83
600	90.28	14.7	16.3
650	62.33	10.2	16.35
700	53.8	15.95	29.6



Table XV

## Strength versus Temperature of Unetched Glass

	Testing Temperature °C	$\sigma \times 10^3$ p.s.i.	$S \times 10^3$ p.s.i.
I.	26	62.28	7.38
	100	74.93	22.7
	200	58.7	16.82
	300	59.12	14.12
	400	52.95	4.86
	450	37.22	6.96
	500	56.86	24.4
	550	63.5	4.93
	600	84.75	9.43
	650	43.33	13.4
	700	61.62	38.1
II.	26	70.65	22.15
	100	83.16	6.55
	200	44.76	2.93
	300	73.76	12.95
	400	51.70	7.96
	450	55.133	12.1
	500	63.5	8.35
	550	59.6	3.75
	600	44.73	8.55
	650	40.9	15.95
	700	31.14	0.79

Table XV Cont.

On compiling these results

Testing Temperature °C	$\bar{\sigma} \times 10^3$ p.s.i.	$\bar{S} \times 10^3$ p.s.i.	Coefficient of Variation %
26	66.46	16.50	24.9
100	79.05	16.69	21.1
200	51.73	12.10	23.4
300	66.44	13.55	20.4
400	52.33	6.59	12.61
450	47.97	11.20	23.4
500	60.18	18.33	30.5
550	61.55	4.37	7.1
600	64.74	8.98	13.85
650	42.12	14.68	34.9
700	46.38	26.95	58.3

## B. Statistics

If a physical effect is due to a large number of independent causes, the measurements of the over-all effect exhibit a nearly normal distribution. This distribution is characterized by the familiar bell-shaped curve whose dispersion is described by the standard deviation. Thus, the standard deviation is an indication of the non-uniformity or dispersion of breaking strengths. As given by Dixon and Massey -

$$S = \left[ \sum_{i=1}^N \frac{(x_i - \bar{x})^2}{N-1} \right]^{\frac{1}{2}}$$

Where  $x_i$  = individual points (p.s.i.)

$\bar{x}$  = average of set of points

$N$  = number points in set

Since repeated runs were made, independent estimates of the standard deviation,  $S$ , are made on each set of repeated runs, and these estimates are then pooled to give a final estimate using the formula,

$$S^2 = \frac{V_1 S_1^2 + V_2 S_2^2 + \dots + V_n S_n^2}{V_1 + V_2 + V_n}$$

where  $V_1$  = degrees of freedom of each variance =  $N - 1$

This pooled estimate of variance has  $(V_1 + \dots + V_n)$  degrees of freedom.

In order to allow meaningful comparison between each complete set of points, all the deviation indices should be divided by their respective means; and thus, a coefficient of variation can be gotten from each set:

$$\text{Coefficient of variation} = \frac{S}{\bar{x}} \times 100\%$$

The error limits for a parameter are estimated from statistics by calculating<sup>(45)</sup>:

$$\text{statistic} \pm t \sqrt{\text{estimated variance of the statistic}}$$

Where  $t$  = student's statistic

These error limits can be used to write the following probability statement which can be used as an interval estimate for the parameter -

$$\text{Probability } \left\{ \begin{array}{l} \left( \text{statistic} - t \sqrt{\text{estimated variance of the statistic}} \right) \\ \leq \text{parameter value} \\ \leq \left( \text{statistic} + t \sqrt{\text{estimated variance of the statistic}} \right) \\ = 1 - \alpha \text{ (confidence level)} \end{array} \right\}$$

Thus, the error limits about the average  $\bar{\sigma}$  are given by

$$\bar{\sigma} \pm t \sqrt{s^2/N}$$

The interval estimate for the parameter  $\sigma$  (i.e. the true strength for which the average  $\bar{\sigma}$  is only a point estimate) is given by,

$$\text{Probability } \left\{ \bar{\sigma} - t \sqrt{s^2/N} \leq \sigma \leq \bar{\sigma} + t \sqrt{s^2/N} \right\} = (1 - \alpha).$$