Viscosities of Phase-separated Glasses

by

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A Thesis submitted in partial fulfilment of
the requirements for the degree of
Master of Applied Science

in the Department
of
METALLURGY

We accept this thesis as conforming to the
standards required from candidates for the
degree of Master of Applied Science

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The University of British Columbia

February, 1968

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ABSTRACT

The effects of heat treatments on viscosity were analysed for three types of glasses. "Pyrex" glass could be approximated to a Newtonian liquid in the range of temperature 470 to 590°C. The activation energy for viscous flow varied from 65 to 85 kcal/mole according to the previous thermal history.

All glasses exhibited phase separation to different degrees according to the heat treatments to which they had been submitted. Phase separation and different degrees of devitrification could account for the variation in viscosity which have been encountered.

Several mathematical expressions were tested in an attempt to correlate viscosity change with time. The best fit was obtained with a relationship of the type

$$\eta = (a + bt)^c$$
 where c varied in the range 0.2 to 0.5. In the case of a ternary borosilicate glass, the value was found to be 0.5. This may suggest that phase separation is a diffusion controlled process.

ACKNOWLEDGEMENT

The author wishes to express his sincere gratitude to Dr. A.C.D. Chaklader for his advice and assistance throughout this work. He also wishes to express his thanks to all the members of the staff who helped in the realization of the creep testing equipment, and all those who assisted in any way in this investigation.

Financial assistance provided by the National Research Council under grant No. A - 2461 and by the Canada Council as a research scholarship to the author is gratefully acknowledged.

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1. INTRODUCTION

1.1 Definition and Importance of Viscosity for glass Fabrication

Glasses as a group of non-metallic materials occupy a very large section of all inorganic materials being used for industrial, technical and scientific purposes.

Glass manufacture is a large scale industry which has long been dependent on the skill and dexterity of individual craftsmen working under crude conditions with a little understood material. It is now dominated by continuous machine production which requires a precise control of the flow characteristics of glass, i.e. viscosity of the melt.

Since glass is a supercooled liquid, it does not have a specific melting point but softens gradually. This is due to the continuous decrease of the viscosity with increasing temperature. The knowledge of the viscosity, η , of a glass is of practical importance at all stages of the manufacturing process since it varies considerably. At room temperature it is in the range of 10^{20} poises or more. Then the glass is considered as "solid" because it is in a rigid state. As the temperature increases the viscosity reaches the strain point (S.P.). This temperature is defined as the temperature at which $\eta = 10^{14.6}$ poises and corresponds to the lower limit of the annealing range. The annealing treatment used in commercial practices is completed in sixteen hours at the S.P.

A viscosity of $10^{13.4}$ defines the annealing point A.P., and a value of 10^{11} to 10^{12} poises is the common range for the dilatometric softening point, where the viscous flow exactly counteracts the thermal expansion during measurements under given standard conditions. When the viscosity drops to $10^{7.6}$ poises the fiber softening point (F.S.P.) is attained. Then a fiber of 0.5 to 1 mm in diameter and 22.0 mm in length

elongates under its own weight at a rate of 1 mm per minute, when heated at a rate of 5°C per minute under standardized conditions. A continuous decrease of the viscosity leads to the glass working range. The upper end of this range corresponds to manual work and blowing; the lower end is used for the mechanical casting of the glass. The automatic machinery in use in industrial processes requires supplies of glass having a more or less constant viscosity and also a given viscosity-temperature relationship which corresponds to the rate of work for which the machine has been designed.

The degassing and the homogenization of the glass batches are performed at viscosities in the order of 10^2 poises or less. Then the fluidity of the glass is that of a normal liquid.

1.2 Measurement of the Viscosity of Glass

The coefficient of viscosity of a fluid is a measure of the internal friction in the liquid. Thus the measurement techniques require a knowledge of the forces or torques between the liquid and some solid surface, or some variable related to these, such as the energy loss or the damping time.

Since, as mentioned previously, the viscosity varies by more than twenty orders of magnitude, one cannot expect to cover the whole range of viscosities with a single instrument.

For values in the range below 10^8 poises standard methods of viscosity measurement can be used; the glass is then very corrosive and the temperature very high so that special equipment made of platinum or carbon is required. Many authors have used apparatus based on Stoke's law, in which the motion of a ball of heavy material such as platinum, is

followed in the glassy medium. Nevertheless, the rotating cylinder viscometer is considered to be the most accurate³, especially for the viscosity range of 10^3 to 10^8 poises. It is used either as a rotating device by motion of the outer cylinder or as an oscillating pendulum.

In the upper range of the viscosity measurement (above 10^8 poises), glass samples can be subjected to creep deformation. Fibres are twisted under torsion or stretched under a given load. More complicated methods, such as the elongation of rings, have also been used to calculate the viscosity. Bending of specimens by 3 or 4 point loading can be utilized for the same purpose. Finally the parallel plate viscometer, as it has been used recently by other workers⁴ was employed in the present work. This involves the study of compressive creep of glass cylinders between two parallel plates.

For most of these methods, the deformation involved in the experiment required difficult mathematical formulations of the viscous flow. Either a calibration of the apparatus, or restriction on the extent of the deformation allowing simplifying assumptions was used to overcome this difficulty. This limitation, however, is not applicable to the plate viscometer.

1.3 Accuracy of the Techniques

Measurements of the viscosity of a glass with reasonable accuracy are difficult. The problem encountered is the calibration of the measuring device. Many controversies exist as to the possible variation of the calibration factor of different types of rotating viscometers. When deformation curves are used, the knowledge of the actual applied stress is critical. Furthermore the material on which the experiment is performed may vary. It is well known that during

viscosity measurements at a temperature above the liquidus of the glass, devitrification often occurs in the glass-mix. Then the measurement gives the values of the viscosity for a mixture of a liquid (of unknown composition) and of solid crystalline particles. The only way to avoid this problem is by rapid measurements. Since the liquidus temperature may be fairly low and therefore corresponds to a high value of the viscosity, this source of error may not have been easily recognized or taken into account in the calculation of the viscosity.

In the determination of high viscosities where creep curves are used, the "calculus hypotheses" restrict the validity of the method to very small deformations which are difficult to measure accurately, and which can also be affected by parasitic phenomena.

As it is explained later, the thermal history, the degree of stabilization, relaxation phenomena and the phase-separation all occur in the range of temperature of the measurement and can modify the glass structure and therefore its viscosity.

Protracted experiments which allow low strain rates and may partly eliminate relaxation phenomena are nevertheless subject to some of the sources of errors mentioned above.

1.4 Composition Dependence of the Viscosity

Industrial requirements have led to extensive work on the viscosity-composition relationship in glasses over a wide range of temperatures.

Simpler systems, such as binary systems with SiO_2 as the main component and one of Na_2O^5 , or Li_2O or K_2O^6 as the second component, have been investigated. As expected, at a given temperature the

viscosity of the melts increases with the SiO_2 content. The change can be very important since a slight variation of composition can produce a several-fold change in the value of the viscosity. The results of different authors are in conflict because of the use of different experimental techniques and possibly due to the introduction of impurities during the measurement of the viscosity.

In addition, viscosity has been determined on systems where one component is replaced by another in a binary glass without changing the concentration of the second component; e.g. in the system $\text{Na}_2\text{O}-\text{SiO}_2$, an equivalent amount of oxide such as CaO ⁷, MgO or Al_2O_3 usually replaces some of the Na_2O . Sometimes B_2O_3 has been used to replace SiO_2 in a similar way. In the first three cases an increase in the viscosity, and in the last case a decrease, is observed. Thus lines of equal viscosity can be drawn on ternary diagrams.

A similar type of study on quaternary systems has been carried out by varying the ratio of two components keeping the other two constant.

In commercial glasses, systematic replacement of SiO_2 in small amounts by other components had been effected in order to obtain correction charts of the temperature-viscosity relationship. These charts are useful for practical manufacturing processes.

No conclusion can be drawn from these results, since additional work is necessary to understand the deformation of the oxide-ion-network during the flow of the glassy material and therefore to correlate the influence of each constituent on the viscosity of the glass. The impurities (other oxides or different ions) can act as a catalyst for crystallisation of the glass. Thus the viscous properties of the glass may be affected by the introduction of these impurities. Either

crystallization or phase separation, can change the viscosity of two apparently identical specimens by several orders of magnitude.

1.5 Thermal History Dependence of the Viscosity

The different heat treatments undergone by a glass from the molten stage until the viscosity measurement is taken, can modify significantly (up to several orders of magnitude) the value of the measured viscosity. Experiments conducted with the same specimen provide results which change continuously. The variation of some glass properties such as extension, index of refraction, or electrical conductivity as a function of the temperature of the heat treatment, substantiates this change. When subjected to an identical variation of the conditions of heat treatment the values of all these parameters do not vary identically. The lack of reproducibility between experiments is especially noticeable in the transformation range of temperature. Considerations of the stabilization of the glass have been made in an attempt to account for these effects. The high viscosity encountered at temperatures below the transition point would not allow the motion of the glass "particles" toward new sites where an equilibrium state could be achieved within a reasonable time. The technique of standard stabilization for glass consists of a heat treatment for various lengths of time at the temperature at which the experiment is to be performed. The time necessary to achieve some degree of stabilization varies with the temperature in the same manner as the viscosity. Therefore, at a low temperature the stabilization time exceed any reasonable period and is often such that stabilization becomes impossible.

1.6 Time Dependence of the Viscosity

Even on well stabilized glasses, a constant value of the

viscosity could not be obtained over a long period. The variation of the viscosity with time, which has been previously noticed by many researchers, was attributed to poor stabilization of the samples. This is particularly true in the transformation range⁸. Plots of viscosity-time curves on a double logarithmic scale exhibit approximately linear shape in the case of the borosilicate glasses⁹⁻¹⁰.

More recent works discovered new features on these curves¹¹. For lead or borosilicate glasses in the high temperature region of the transition temperature range, the viscosity-time plot is S-shaped. In the beginning, the rate of increase of the viscosity grows faster with time. For a given period of time a constant rate is then observed. Eventually the rate drops slowly to zero. The borosilicate glass in the lower temperature range exhibits a different behaviour, in that no asymptotic value of the viscosity is attained. A survey of the literature leads to the conclusion that time is an important parameter of the viscosity. However, in the annealing range sufficient consideration has not always been given to the delayed elastic effect and other relaxation phenomena, such as the change of density, which may give rise to small deformations. These parasitical deformations of the specimen may completely obscure the deformation due only to the viscous flow and may lead to erroneous conclusions about the actual viscous behaviour of the material.

1.7 Phase Separation in Glasses

Often on cooling the components of a glass melt separate into two or more distinct intermixed liquids of different chemical composition. The nucleation and growth of one liquid out of the other results from a very similar process to the one by which crystals nucleate and grow from a

solution.

In many glass systems, phase separation into two liquid phases occurs metastably below the liquidus temperature. Attempts to understand the opacification behaviour of $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ ternary glasses which had undergone heat treatment in the range of 550°C to 880°C ¹² led to the discovery of liquid immiscibility in glasses. The electron microscopy of fresh-fractured surface of such glasses showed clearly immiscible regions where droplets of one phase were surrounded by a matrix of another phase. The size and density of these droplets were correlated with the temperature and the time of the heat treatment.

Recently the possibility of metastable liquid immiscibility was discovered for different shapes of the liquidus line on the phase diagram¹³. On the schematic phase diagram of a binary system as shown in Figure 1a, a mixture of the composition represented by arrow (1) might undergo spontaneous phase decomposition even during a quench. For a composition corresponding to that represented by arrow (2) on Figure 1a or 1b, subliquidus heat treatment is required for the development of the phase separation.

Liquid-in-liquid colloidal immiscibility was found in quaternary systems, such as $\text{Li}_2\text{O}-\text{CaO}-\text{TiO}_2-\text{SiO}_2$ ¹⁴. A systematic study of the possible region of phase separation in various systems has been carried out by several workers. The phase separation phenomenon has also been observed for $\text{SiO}_2-\text{LiO}_2$ ¹⁵, and for SiO_2 with either CaO , SrO , BaO or Al_2O_3 ¹⁶. Ternary systems such as $\text{SiO}_2-\text{Al}_2\text{O}_3-\text{Y}_2\text{O}_3$ or $\text{SiO}_2-\text{Nb}_2\text{O}_5-\text{Y}_2\text{O}_3$ ¹⁷ and more complex glasses e.g. commercial products such as "Pyrex" or "Vycor"¹⁸ have also exhibited the same phenomenon. An imprecise knowledge of the exact liquidus position has hindered the investigation of phase separation in glasses.

a)

b)

Figure 1 : Theoretical phase diagrams of binary constituents leading to phase separation.

Composition 1 : Spontaneous phase separation ,even during quench .
 2 : Phase separation requires a subliquidus heat treatment .

The mechanism for the initial development of the phase separation has also been investigated. Charles¹⁸ proposed two initial mechanisms to account for the fact that the phase separation occurs below or above the spinodal. Each mechanism leads to different resultant characteristic structures through different kinetics of the transformation. Below the spinodal, spinodal-composition-modulations form and increase in amplitude to give a highly irregular two phase structure. The kinetics of this process, which are very fast, render unlikely the possibility of retaining a single phase by quenching unless the viscosity of the glass at the spinodal is very high.

1.8 Property Changes of Glass due to the Phase Separation

After phase separation, glass is no longer, indeed if it ever was, a homogeneous body, and the presence of the distributed heterogeneities modifies its properties.

Optically the glass is altered by the small droplets of the second phase. It becomes opalescent or opaque or its index of refraction changes.

Variations of the breaking strength of "Pyrex" rod according to heat treatment in the annealing range were observed^{14b}. The fine structure revealed by electron microscopy of fresh-fractured surface of glass¹⁴ displayed a tail-like wake left by the fracture front behind each droplet. The dispersed phase has a cohesive strength lower than the adhesive strength between the matrix and the droplets if the wake is single-tailed. A double-tailed wake indicated the opposite conclusion.

A thorough study of the electrical properties of the phase-

separated glass has also been carried out recently¹⁸⁻²⁰.

Dielectric measurements, explained in terms of Maxwell's theory of inhomogeneous dielectrics, give values for the loss factor and dielectric constant when the spatial distribution is known. The latter is determined through electron microscopic observations. When the values of these constants are known, the evolution and distribution of the new phase can be followed.

The electrical conductivity (d.c.) is a structure sensitive property which gives more information of the distribution of the most highly conducting phase. The activation energy for the conduction process is an intrinsic property of the most highly conducting continuous phase. Considerable changes in all these parameters after different heat treatments were observed. The recorded variation was in satisfactory agreement with the values deduced from electron-microscopic observations in the case of some commercial glasses.

1.9 Objectives of this Investigation

The purpose of the present work is to study the viscosity of different commercial glasses in order to obtain a better knowledge of their behaviour under variable conditions of temperature, strain rate, composition and thermal history. Only the transformation range, with viscosities varying from 10^{12} to 10^{15} poises, (when the phase separation may be most significant) was considered. This range is particularly important as it is believed that heat treatments above the transition point could erase the previous thermal history of the glass and thus produce the standardized material required in commercial practices¹⁻². This is not true for glasses where devitrification occurs in the same range of temperature.

2. EXPERIMENTAL

2.1 Material Selection

Three types of glass were used in this investigation and since they were available in different forms the procedures for making the specimens varied.

2.11 The Borosilicate Glasses

A borosilicate glass of the "Pyrex" type was used for samples numbered 3.112-10 to 3.122-05. Its composition is given in Table I. Batches of specimens were made from 9 mm rods available for glassware making. The rod was embedded in plaster of Paris to form a slab of cross section 2 inches by 2 inches along the length of the rod. The glass rod and plaster of Paris slab was cut into slices with a diamond impregnated alloy wheel. This procedure produced negligible chipping of the rod. Furthermore, it provided good flat specimen holders for a final polishing of the ends of the specimens on a grinding wheel. The resulting specimens were as perfectly cylindrical as possible, with both faces perpendicular to the axis of the cylinder. Their parallelism was controlled by measuring the height of the specimen on the three apices and the center of gravity of an equilateral triangle inscribable on the flat faces. The variation which could be observed was generally less than 10^{-4} inches which corresponded to the accuracy of the micrometer used for the control.

The heat treatment of these specimens was carried out in an argon atmosphere inside horizontal tube furnaces which were controlled by "Wheelco" thermistors. For heat treatment in the upper temperature range, the specimens were separated by molybdenum disks to prevent them from sticking to one another, and also placed inside a close fitting graphite mold in order to prevent the deformation due to viscous flow under their own weight.

TABLE I

THE CHEMICAL ANALYSIS OF DIFFERENT GLASSES

Type of Glass	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	Li ₂ O	B ₂ O ₅
"Pyrex"	80.5		2.2				3.8	0.4		12.9
"Corning"	67.4						6.9			25.7
Ahali Glass	72.84	.09	.65	.02	11.88	.58	.2,95	.40	trace	trace
Concentration of this element in % by weight										

For the lower range of temperatures, no special care was taken and the specimens were heat treated in air.

Another ternary borosilicate glass, the chemical analysis of which is given in Table I, was supplied by the "Corning Glass Works." The phase-separation of this glass has been studied in detail at Corning and other laboratories. Only ten cylindrical specimens, 9 mm in diameter were received from this company.

2.12 The Binary Glass

A binary glass of composition 70% SiO_2 - 30% Na_2O was made from a mixture of finely ground Brazilian quartz (particle size 55 microns) and Na_2CO_3 anhydrous powder supplied by the Nichols Chemical Company Limited (Montreal), the nominal purity of which was 99.0% Na_2CO_3 . The mixture was initially melted in a pure high density sintered alumina crucible which was subsequently replaced by a platinum crucible to avoid contamination. Each batch was melted at about 1200°C and held for several days at this temperature. Then it was poured into water, finely ground and remelted at the same temperature. The cycle was repeated at least three times in order to homogenize the glass and degas it. The specimens were prepared from the ground powder by a hot pressing technique to yield cylinders of 3/4 inches diameter and about 3/4 inches in height.

The hot pressing was carried out in a graphite die with a tungsten or molybdenum liner and with molybdenum plungers. The heating was provided by induction with a "Philips" induction unit. All the steps of the hot pressing were conducted in vacuo. When they were completed, the specimen was quenched by flushing the vacuum chamber with argon.

The compaction during the hot pressing was indicated by a dial

gauge attached to the end of the moving plunger. At first a fairly fast motion of this plunger, which lasted about the same time as that needed to raise the pressure on the specimen, was noticed. In order to insure the completion of the compaction, the specimen was left under pressure for a period of time, referred to as the "hot pressing time" taken from the instant when no motion of the dial was perceptible. The assembly used for the hot pressing procedure can be seen in Figure 2. A trial and error method was used in order to determine the range of values of the different parameters of the hot pressing, that is, temperature, pressure and duration, which provided good specimens. Then, maintaining the temperature as low as possible, a systematic scanning of the ranges for the two other parameters defined the best conditions for the process. Specimens free of gas bubbles of all sizes could not be obtained at temperatures lower than the softening point temperature.

In order to overcome this difficulty, a three step method was then used. The powder was first melted and degassed inside the die at the highest temperature achievable in a reasonable period of time, without any stress applied. Then it was cooled down to the temperature at which the heat treatment, if any, was carried out. The last step consisted in the actual hot pressing at a much lower temperature in order to shape the specimen.

Table 2 gives the details of the fabrication conditions used for the preparation of the specimens. In Figure 3 the binary phase diagram of the glass is shown. This was used to interpret the significance of the different temperatures of heat treatment in terms of the phases to be expected.

The specimens obtained through this procedure had a smooth shape

Figure 2 : Schematic drawing of the hot pressing assembly

1 Specimen	4 Graphite sleeve
2 Molybdenum ram	5 Graphite die
3 Molybdenum liner	6 Control thermocouple
7 Graphite ram	8 Insulating glass tube
9 Induction coil	10 Vacuum chamber

TABLE 2

PARAMETERS OF THE FABRICATION OF THE BINARY GLASS SPECIMENS

Number	Degassing treatment		Heat Treatment		Hot Pressing		
	Temperature °C	Duration minutes	Temperature °C	Duration minutes	Temperature °C	Duration minutes	Pressure psi
3.13			No heat treatment				
-000	1150	80			690	8	
1	1200	15			660	10	
2	1150	15			660	10	
3	1200	15			660	10	2000
4	1020	28			600	10	
5	1100	20			650	12	
6	1100	32			670	12	
3.13							
-100	1100	40	840	4	650	8	
1	1100	28	850	10	670	10	
2	1050	28	840	10	660	12	
3	1005	30	840	10	700	20	2000
4	1050	32	840	10	660	12	
5	900	200	840	10	600	10

Figure 3 : Partial phase-diagram of $\text{Na}_2\text{O}-\text{SiO}_2$

and were transparent. A brownish colour could be noticed in areas which had been in contact with molybdenum, although no similar coloration was observed with the tungsten. This may be explained by the diffusion of some molybdenum ions into the glass.

2.13 The Alkali Glasses

Glass beads of average diameter 400 microns were obtained from the "3M Company" St. Paul, Minnesota. Their chemical analysis is given in Table 1.

Two types of specimens were fabricated from the beads by the hot pressing technique, but due to the difference in the viscosity-temperature relationship between the two glasses, the method had to be adapted to avoid the extrusion of the specimen between the sleeve and the die. The same systematic variation of the parameters of the fabrication resulted in a simpler method of producing bubble free specimens. This was achieved at a temperature of 650°C, i.e., around the softening point, by applying a pressure of 2,000 psi over a period of 5 minutes. Optical microscopy could barely detect the boundaries of the beads in the specimens. A thinner liner which eliminated the scaling of the specimen during the removal from the hot pressing die could be used because the temperature was lower than for the binary glass. This resulted in less corrosive action and reduced interaction between the metal of the sleeve and the glass.

All specimens numbered from 3.141-000 to 3.142-220 were prepared according to this procedure.

Specimens numbered from 3.141-000 to 3.141-303 were made of glass beads only. Specimens numbered from 3.142-000 to 3.142-220 contained fine Brazilian quartz powder (55 microns) 5% by weight. The mixture of quartz powder and glass beads was wet-mixed with 5% by weight

of water in order to obtain an homogeneous mixture and to prevent separation from each other during the handling.

In spite of the numerous precautions taken during the preparation, many specimens had to be discarded as their shape was distorted and no longer cylindrical. This was due to the bonding of the tips of the plungers to the specimens which frequently broke during the removal of the specimen. The reshaping of the specimens was a very delicate operation, as dimensionally, a close tolerance was essential for the accurate measurement of the viscosity.

2.2 Experimental Procedure

2.21 Study of the Creep Behaviour

Since the viscosities to be determined were in the range of 10^{12} to 10^{15} poises a parallel plate viscometer was used. The principle of the measurements is as follows. The cylindrical specimen is compressed between two parallel plates under a constant load. The distance between the two plates of the viscometer is recorded as a function of time. Because of the critical dependence of the viscosity on the temperature, the whole operation is carried out at a precisely controlled temperature. For this purpose a special equipment was built. A schematic diagram of the apparatus is shown in Figure 4 and a photograph of it can be seen in Figure 5.

The two parallel plates were the tips of two 3/4 inch diameter molybdenum rods which were attached on stainless steel water cooled rams. Only the upper ram was movable. A given load was applied to the specimen by a piston installed directly on the upper ram which was activated by nitrogen under pressure. Special care was taken to reduce friction on the upper ram and to ensure uniaxial alignment. The frame was water-cooled to avoid

Figure 4 : Schematic diagram of the creep-testing apparatus .

Figure 5 : The creep-testing apparatus.

deformations which might result from temperature changes during the experiments.

The measurement of the displacement of the upper ram was obtained by the signal output from an electromagnetic transducer attached to the top of the ram. The calibration and resetting were accomplished by a micrometer screw mounted between the transducer and the ram. The transducer output was analysed by a "Philips PR 19300" direct reading measuring bridge. The output of the bridge was fed into a "Heathkit" servo recorder through a filtering device and a potential bias.

The temperature was measured at six points equally spaced around the specimen by Pt-Pt 10% Rh thermocouples. These thermocouples were held against the specimen elastically. Three of them were used to check the temperature of the furnace with a potentiometer. The added emf of the other three was fed into a "Honeywell" deviation multiplier used as a monitoring system for the control of the furnace temperature. By this arrangement the temperature could be held within $\pm .01^{\circ}\text{C}$.

The heating was provided by a three-independent-element resistance furnace. Preliminary experiments showed that in spite of the length of the heating zone with respect to its diameter, it was not possible to achieve a uniform temperature in the specimen with a single element furnace due to the heat sink effect of the water cooled rams. To know and control the temperature distribution inside the specimen, a special specimen was used in which three small holes in the center and close to its extremities had been drilled with an ultrasonic-driller. Three very thin chromel-alumel thermocouples were inserted in these holes and, by this means, temperatures were recorded along the vertical axis of the specimen. It was observed that in the case of the single-element furnace, gradients of temperature

up to 50°C could exist inside the specimen under steady state conditions. By the proper adjustment of the "Variac" autotransformers which were attached to each of the three elements, a close control of the vertical gradient of temperature could be maintained. Finally by trial and error a temperature gradient of less than 1°C (the sensitivity of the potentiometer used for the measurement) was achieved.

The whole of the hot zone was enclosed in an air-tight container constantly flushed with argon to prevent the oxidation of the molybdenum parts. In spite of this, considerable oxidation of the molybdenum components occurred especially during the introduction to and withdrawal from the hot furnace of the specimen. To insure the uniform quality of the surface between which the specimen were compressed, the tips of the rams were replaced by pure high density sintered alumina which broke frequently.

The operating procedure was as follows. The furnace was maintained at the desired temperature. The specimen was introduced through a removable door and loaded immediately under light pressure to ensure a uniform heating by the conduction heat transfer through the extremities. The time required to reach the equilibrium temperature in the specimen was found to be between ten and twenty minutes. This had been observed with the control-specimen. During this heating-up period calibration of the creep-recording equipment was carried out. A dial-gauge with an accuracy of 10^{-4} inches was used for this purpose. The desired pressure was then applied and the deformation of the specimen was recorded.

2.22 Electron Microscopy

Direct carbon replicas of preshadowed freshly fractured

specimens were observed with a "Hitachi" HU11A electron microscope.

Chromium, gold or platinum was used for the shadowing. Different etching techniques were also used. The specimen was broken by explosive fracture by squeezing it in a vise.

The principal etching agents were either 2% HF dilute solution used for different periods of time (one to forty seconds), or one of 2N HCl, 2N H₂SO₄, and 2% HF for two hours for "Pyrex" glass, or distilled water for one second in the case of the "Corning" glass.

For each specimen at least two different freshly fractured glass surfaces were replicated. From each replica at least two distinct pieces were mounted on copper grids for observation. The replicas were lifted from the sample by flotation in distilled water or in some difficult cases using 2% HF solution. A systematic scanning of each grid was done to give statistical results of the observed features. The magnification range varied from 5,000 to 80,000 times.

3. RESULTS

3.1 Measurement of the Viscosity

3.11 Calculation of the Viscosity from the Creep Curves

3.111 The Formula

The theory of the parallel plate viscometer allows one to correlate, at any moment, the rate of creep of a cylindrical specimen compressed under a constant load to the viscosity of the material as follows:

$$\eta = \frac{F}{3V} - \frac{1}{\frac{dh}{dt} \left(\frac{1}{h^2} + \frac{V}{2h^5} \right)} \quad (1)$$

η is the viscosity coefficient in poises, F the total applied load, h the height of the specimen at any time, t , V the volume of the specimen, and $-\frac{dh}{dt}$ the rate of creep, that is, the slope of the creep curve.

This result has been established for Newtonian liquids, i.e. liquids for which the viscosity is independent of the rate of shear²³.

3.112 Precision of the Measurements

The continuous recording of the creep curve could not be used directly for the measurement of the slope, primarily because of the non-linear response of the transducer used for recording the change of height as a function of time. Therefore the plot from the chart recorder were transformed by the use of calibration curves. This was a discontinuous process which introduced some error in the actual creep curve. This error was found to be less than 5%. The measurements of the creep rate were carried out on these replotted curves. Since this measurement involved drawing a tangent to the curve, a new systematic error was introduced. However, it was estimated to be in the same order as the previous error.

Therefore, the calculated values of the viscosity obtained from these measurements inherit an error in the range of 5% to 10%. Thus all the results given in the table can be considered as accurate within about 8%.

3.113 Flow Characteristics of the Glasses

The flow characteristics of the glasses used in this investigation were first determined in order to ensure that this flow behaviour was Newtonian. This was done by studying the creep curves of the "Pyrex" glass as a function of the stress applied at 568°C which is in the temperature range at which the subsequent measurements were made.

The applied load was varied from 3,900 psi to 31,200 psi. This allowed an 8-fold change in the shear rate. In Table 3 (Appendix I) the values of the viscosities at different elapsed times and at the applied pressure used in the experiments are given. A plot of the values of the viscosities obtained from the creep curves is shown in Figure 6. Some representative creep curves are also plotted in Figure 7.

The equation of the straight line which gives the best least square fit of the values of the viscosity as a function of the pressure can be written as follows

$$\eta = 10^{14} \times (A + B.P)$$

if η and P are measured in poises and psi respectively. The values of A and B are given in Table 4. For the maximum variation of the pressure P , the contribution to the value of the viscosity due to the term B varying with P is 16% and 7% respectively of the value of the constant term A , at 50 minutes and at 100 minutes. Therefore it can be assumed that since the variation is approximately within the precision of the determination of A , the value of B can be set to zero.

Figure 6 : Viscosity as a function of the pressure .

Figure 7 : Creep curves for different pressures.

TABLE 4

COEFFICIENTS OF THE LINE OR RELATIONSHIP BETWEEN VISCOSITY AND PRESSURE

at 50 mn			at 100 mn		
Coefficient	Error	Precision	Coefficient	Error	Precision
A = .150	± .006	4.0%	A = .168	± .007	4.2%
B = (.856	± .291)10 ⁻⁶	34.0%	B = (.548	± .337)10 ⁻⁶	61.5%

TABLE 7

PARAMETERS OF THE EQUATION $\log \eta = A + B \frac{1}{T}$

at 50 mn				at 100 mn			
Parameter	Value	Error	Precision	Parameter	Value	Error	Precision
			%				%

Glass as received

A	-3.58	.51	14.4	A	-3.45	.47	13.2
B x 10 ⁻⁴	1.418	.042	2.9	B x 10 ⁻⁴	1.421	.038	2.7
Q kcal/mole	65.4	1.9	2.9	Q kcal/mole	65.5	1.8	2.7

Glass after annealing

A	-9.27	.45	4.9	A	-8.40	.60	7.2
B x 10 ⁻⁴	1.904	.038	2.0	B x 10 ⁻⁴	1.838	.050	2.7
Q kcal/mole	87.6	1.7	2.0	Q kcal/mole	84.4	2.3	2.7

The scatter in the data is a reflection of the dependence of the viscosity on the thermal history of the specimens and will be discussed later on. However, the overall relationship as shown in Figure 6 suggests that the glass behaves as a Newtonian liquid. Equation 1 for the parallel plate viscometer can be used in this temperature range for the determination of the viscosity.

All subsequent experiments were carried out under a pressure of 16,500 psi.

3.12 Borosilicate Glasses

3.121 "Pyrex" Glass

3.1211 Variation of the Temperature

The temperature dependence of the viscosity of the "Pyrex" glass was investigated in two sets of specimens. In the first set, specimens were used as received and without subjecting them to any heat treatment. In Table 5 (Appendix I) data for the values of the viscosity versus temperature at a constant load are shown. In the same table, results from other experiments which were conducted in the same conditions of temperature and load have been included for comparison. These experiments, namely alignment of the ram after exchange of the tips and calibration of different parts of the equipment, were necessary to insure the uniformity of the experimental conditions. (Incidentally, other results obtained from the study of the glass densification during the test, were also included). A wider scatter is noticeable for these values which correspond to the temperature of 568°C. It can be accounted for by the variation of the glass batches which were used for the fabrication of the specimens.

The second set of specimens was "annealed" at 500°C for 44 hours in a furnace with an atmosphere of air. The results are given in Table 6 (Appendix I) and are plotted in Figure 9.

In both Figures 8 and 9, the logarithm of the viscosities is plotted versus the inverse of the absolute temperature. The curves appear to be linear. The equation of the straight lines is as follows:

$$\log \eta = A + \frac{B}{T}$$

In order to determine an activation energy Q for the flow process the previous equation can be rewritten:

$$Q = B \frac{R}{\log e}$$

where R is the gas constant. The values of the parameters A , B , and Q are given in Table 7.

The precision of the data given in this table is identical to the accuracy of the determination of the parameters by the least square fit method, assuming that the values of the viscosities are exact. One notices that this precision is better than the accuracy of the measurements of the viscosities. Therefore, this error could be neglected and Q could be given with the same precision as η , that is 8%. Nevertheless two different values of Q were found for the two sets of experiments:

$$Q_1 = 65 \pm 5 \text{ kcal/mole for the "as received" glass}$$

$$Q_2 = 87 \pm 7 \text{ kcal/mole for the "annealed" glass}$$

Some characteristics of the creep curves are shown in Figure 10.

3.1212 Effects of Different Heat Treatments

In order to study the effect of phase-separation on the viscosity of the "Pyrex" glass, heat treatments over the temperature range

Figure 8 : Variation of the viscosity with the temperature . Glass as received .

Figure 9 : Variation of the viscosity with the temperature . "Annealed " glass .

Figure 10 : Creep curves at different temperatures.

500 to 900°C, were carried out. Below 500°C no change could be noticed. Above 700°C, problems of reduction of the oxides, or crystallisation of the glass in contact with the graphite mold have been encountered. Such problems limited drastically the period of time during which the specimen could be held at the high temperatures without too many parasitic transformations.

Table 8 (Appendix I) summarizes the values of the viscosities of the specimens subjected to different heat treatments. In Figures 11 to 17 the viscosity values are plotted against the time of heat treatment in a log-log plot.

These plots suggest a linear variation of the logarithm of the viscosity versus logarithm of the time. The equations of the straight lines giving the best least-squares fit are found in Table 9, as $\log \eta = A + B \log t$, where η is in poises and t , the time of heat-treatments in hours.

In Figure, 18 B is plotted as a function of the heat-treatment temperature. There appears to be a maximum for the rate at which the viscosity changes with the time. This maximum is attained at about the temperature at which the measurements of the viscosity had been carried out.

A better account of the differences in the variations of the viscosity is shown in Figure 19 where, for a given time of heat treatment, the viscosity is plotted against the temperature of the heat treatment.

3.122 "Corning" Glass

Only a few specimens were obtained from the "Corning" research laboratories.

Figure 11 : 500° C

Figure 12 : 565 °C

Figure 13 : 575° C

Figure 14 : 600°C

Δ viscosity value _____ least square fit and precision at 50 minutes
○ -----
100

Viscosity as a function of the time of heat treatment at different temperatures.

TABLE 9

PARAMETERS OF THE EQUATION $\text{LOG } \eta = A + B \text{ LOG } t$
 FOR DIFFERENT HEAT TREATMENTS

Temperature °C	At 50 mn				At 100 mn			
	A	ΔA	B	ΔB	A	ΔA	B	ΔB
500	13.535	.111	-.059	.061	13.552	.103	-.056	.056
565	11.927	.094	1.32	.07	12.106	.161	1.19	.13
575	13.187	.087	.448	.048	13.229	.093	.519	.110
600	13.440	.036	.411	.022	13.512	.037	.450	.025
650	13.424	.028	.107	.025	13.509	.093	.122	.083
750	13.195	.363	.0228	.0325	13.265	.040	.0095	.0365
800	13.321	.018	-.0097	.018	13.378	.018	.021	.018

Figure 18 : Variation of the rate of change of the viscosity with the temperature of heat treatment .

Figure 19 : Viscosity as a function of the temperature of heat treatment after different times of heat treatment .

The viscosity of these specimens was determined after they had been subjected to different heat-treatments. The unusual shape of the creep curves is shown in Figure 20. Table 10 (Appendix I) gives the detail of the conditions of the experiments and the viscosities obtained from them.

3.13 The Binary Glass

Two sets of experiments were carried out with the binary glass. In the first case, no special heat treatment was applied. The glass was degassed at about $1,200^{\circ}\text{C}$, cooled down to 660°C , and hot pressed for five minutes at this temperature.

On the second set of specimens, an additional heat treatment at 850°C was used. The locations of the different temperatures with respect to the expected physical structure of the binary system are shown in the phase diagram of $\text{Na}_2\text{O-SiO}_2$ ²³ as given in Figure 3. The values of the viscosity for both sets of data are plotted against the reciprocal of the absolute temperature in Figure 21 and are given in Table II (Appendix I). The larger scatter of the results could be explained from some variation of the composition of the glass, lack of constancy of the heat treatments and presence of minute gas bubbles which appeared during the fabrication of the specimen. A difference in color has also been noticed from one specimen to the other. Because of the difficulties encountered with this type of glass, investigations were discontinued.

Figure 20 : Creep curves of "Corning" glass specimens.

a) No heat treatment

Δ viscosity value at 30 minutes
 $\circ$ viscosity value at 60 minutes
 $\square$ viscosity value at 90 minutes

b) Heat treated

Figure 21.: Viscosity of the binary glass as a function of the temperature .

3.14 Alkali Glasses

3.141 Alkali Glass without additives

Specimens made of hot pressed glass beads were tested at different temperatures. Before any test was performed the batches of the specimens were subjected to various heat treatments. The details about these heat treatments and the corresponding values of the viscosity are recorded in Table 12 (Appendix I). In Figures 22 and 23, a plot of the logarithm of the viscosity versus the reciprocal of the absolute temperature can be found.

A very large scatter of the results is noticeable. It could be accounted for by the lack of homogeneity of the material and the irregular devitrification of the glasses.

To control the devitrification of the specimens and ensure homogenization, experiments were conducted with an addition of quartz crystals to the bead mixture.

3.142 Alkali Glass + Quartz Powder

Two batches of specimens were made with a mixture of glass beads and quartz powder. The first series was tested straight after fabrication. The second series was "annealed" for 20 minutes at 500°C. In Table 13 (Appendix I), experimental details of the tests are given. In Figure 24 the logarithm of the viscosity versus the reciprocal of the absolute temperature curves are plotted. A large scatter still exists on the plots.

No heat treatment

Figure 22 Alkali glass

Figure 23 Alkali glass

Figure 24 Alkali glass + quartz powder

Viscosity value : Δ $\circ$ $\square$ $\diamond$ at 30
 Δ $\circ$ $\square$ $\diamond$ at 60 mn
 Δ $\circ$ $\square$ $\diamond$ at 90

Alkali glass : viscosity as a function of the temperature for different heat treatments and additions .

3.2 Structural Study

3.21 "Pyrex" Glass

In an attempt to correlate the variation of the measured viscosities with some internal change of structure of the specimen, an electron microscopic study on a set of specimens was carried out. The final viscosities of this set had values in the range 0.2 to 6.0 (10^4 poises).

Different shadowing and etching techniques were used. The most striking feature which is noticeable, is a constant grainy appearance of the microstructures. To determine whether this grainy structure was due to some spurious effect originating in the method of preparation of the specimen, different techniques were used on the same specimen. In Figures 25 a, b, c and d, microstructures of the specimen which had been etched for 1, 5, 10 and 30 seconds respectively, in diluted 2% hydrofluoric acid are represented. The different fragments were shadowed, after etching with platinum at an angle of 30 degrees and carbon replicas were made. In the background of all the microstructures, particles of about 100 Ångström in size are discernable. A few larger particles in the range of 1,000 to 2,000 Å are also seen in these Figures.

The specimen had been heat treated at 600°C for 19 hours and then creep tested for 100 minutes.

In Figures 26 a and b, gold was used for shadowing because of its peculiar growth properties on glass substrate. Figure 26a represents an unetched specimen while Figure 26b shows the same specimen after an etch of 1 second in distilled water.

a) 1 second

b) 5 seconds

c) 10 seconds

d) 30 seconds

Figure 25 : Microstructures of the same specimen etched for different times in diluted 2% HF solution .

a) No etching .

b) 1 second in water .

Figure 26 : Variation of appearance of the microstructure due to the etching technique .

On both photographs particles of about 200 to 400 Ångströms can be seen on a background of very fine particles (about 50 Å). The corresponding specimen was heat treated for 24 hours at 600°C and subjected to creep deformation for 70 minutes.

With different heat treatments of the glasses, various shapes, sizes and densities of particles have been encountered.

In some cases the particles were approximately spherical in shape; their size increased with the increasing period of heat treatment, and at the same time, a corresponding decrease of their density was observed. In Figure 27a, a uniform background of particles of about 120 Å in diameter is evident. This microstructure is exhibited by a specimen which had undergone a creep test of only 150 minutes. In Figure 27b, the microstructure of a specimen heat treated for 4 hours at 600°C and then creep tested for 100 minutes is represented. The size of the particles varied from 500 to 1,000 Å while their densities decreased with the corresponding increase in size. A heat treatment of 19 hours at the same temperature followed by a 100 minutes viscosity measurement test, revealed a structure of larger particles which had coalesced. Their diameter ranged from 800 to 1,500 Å as shown in Figure 27c. Eventually, after 24 hours at 600°C and a test of 110 minutes, particles between 2,000 and 3,000 Å covered the whole specimen, Figure 27d.

For a given period of heat treatment at different temperatures, various microstructures were observed. In Figure 28, the different structures which were encountered after a heat treatment lasting 24 hours at increasing temperatures are shown. There was a general tendency for the particles to increase in diameter with increasing temperature up to about 575°C. This was followed by a decrease in the size of the particles which composed the background, with an infrequent occurrence of larger particles.

a) No heat treatment .

b) 4 hours at 600°C .

c) 19 hours at 600°C .

d) 24 hours at 600°C .

Figure 27 : Variation of the size of the particles with the time of heat treatment .

a) At 500°C

b) At 565°C

c) At 575°C

d) At 650°C

e) At 750°C

f) At 800°C

Figure 28 : Variation of the size of the particles with the temperature of heat treatment for 24 hours .

The change of the particle shape was also noticeable in the high temperature range.

Under some conditions, a transformation from a spherical shape to a more irregular angular one has been observed. In Figures 29a, b, near perfect spheres and odd shaped particles coexist. The specimens which represent this microstructure were heat treated for 2 and 4 hours at 750°C respectively and then tested for 70 minutes. A longer heat treatment (22 hours at the same temperature) or a heat treatment for the same length of time but at higher temperature (4 hours at 800°C) led to the elimination of smooth spherical particles. These are replaced by rough-surfaced irregular ones with occasional square crystals. Some of these crystals have been found to achieve a size up to several microns across as shown in Figure 29d.

3.22 "Corning" Glass

An obvious change of the structure of these glasses could be observed, without any magnification, after the creep test or after any heat treatment. The glass which was almost transparent but whitish due to grinding, came out yellowish in transmitted light and blueish in reflected light.

Because of the high sensitivity of this material to any heat treatment, the different specimens were classified according to their final viscosity, rather than according to their heat treatments.

In Figure 30, the different structures observed for decreasing viscosity are shown. The highest value of the viscosity corresponds to a structure in which only very fine particles form the background. Their diameters varied from 70 to $120 \text{ \AA}$. When the viscosity dropped from 0.73

a) 2 hours at 750°C.

b) 4 hours at 750°C .

c) 22 hours at 750 C.

d) 4 hours at 800°C.

Figure 29 : Transformation of the shape of the particles .

to $0.58 (10^{14} \text{ poises})$, the dimensions of the particles grew and ranged from 100 to 200 Å as seen in Figure 30b. For a further decrease of the viscosity down to $0.42 (10^{14} \text{ poises})$, the range of the sizes of the particles was shifted towards higher values and lay between 150 and 300 Å as shown in the microstructure represented by Figure 30c. Eventually, for the smallest achieved measurement of the final viscosity, 0.28×10^{14} poises, a new type of structure appeared. Large smooth circular particles, in the range of 400 to 600 Å, emerged from a background of grainy small particles of 80 Å (Figure 30d). The larger particles seemed to have coalesced.

a) 0.73×10^{14} poises.

b) 0.58×10^{14} poises.

c) 0.42×10^{14} poises.

d) 0.28×10^{14} poises.

Figure 30 : Variation of the microstructure with the viscosity .

4. DISCUSSION

4.1 Theory of the Plate Viscometer

4.11 Theoretical Treatment

The purpose of a theory is to express the physical law which relates the measured variables with the properties of the tested material. In the case of the plate viscometer, it is desired to find an equation relating the plate separation at any time to the viscosity of the specimen.

It is well known that the behaviour of plastic materials under stress is very complex because both elastic and viscous deformations take place simultaneously. No single theory is able to take into account the actual viscous flow which is encountered in practice.

The first attempt²⁴ in this field used the following simplifying assumptions about the flow behaviour. If the central point of the cylinder undergoing viscous flow is considered as a fixed origin, the gradient of velocity with respect to this origin, is linear along each axis with respect to itself. In this case, the force, applied on the specimen, dissipates energy in the volume of the specimen according to the relationship:

$$E = \frac{3}{2} \eta V \alpha^2 \quad (2) \quad \text{where } E \text{ is the energy } (F \frac{dl}{dt}),$$

η the viscosity and α the coefficient of the gradient of velocities. This leads to the relationship:

$$\frac{F t}{6 \eta V} = \frac{1}{h} - \frac{1}{h_0} \quad (3)$$

where h_0 is the height of the specimen at time $t = 0$ and h the height at time t . This result is valid only for very small deformations.

A more elaborate theory²⁵ originated from the general equation of motion of a Newtonian fluid of viscosity η .

$$\rho \frac{\partial v}{\partial t} + \rho v \cdot \nabla v = -\nabla p + \eta \nabla^2 v + \frac{1}{3} \eta \nabla x \nabla \cdot v \quad (4)$$

Considerations of continuity and symmetry, along with the restriction to very slow motion of every point, permitted a reduction to equation (5).

$$\rho \frac{\partial v}{\partial t} = -\nabla p + \eta \nabla^2 v \quad (5)$$

Equation (5) was then solved in cylindrical co-ordinates introducing the boundary conditions. Assumptions were made that no slippage occurred at the plates and that the steady state flow condition was achieved. Therefore this relationship is not applicable for the initial stage of the creep deformation. A further simplification was subsequently introduced which is justified when the radius of the cylinder R is at least ten times larger than the height h . Then a parabolic variation of the velocity of the fluid is observed. It was also assumed that a given horizontal plane remained horizontal during the deformation. Under these conditions equation (5) can be integrated into equation (6).

$$\frac{F t}{3\eta V} = \left(\frac{1}{h^4} - \frac{1}{h_0^4} \right) \frac{V}{8\pi} \quad (6)$$

Finally, a theory²⁶ has been derived on the basis of the calculation of the apparent Young's modulus for rubber cylinders²⁷. This produced the relationship given in equation (1) where the restriction of $R > 10h$ and the limitation to a small amount of deformation can be eliminated. The details of this derivation are given in Appendix (III).

$$\frac{F t}{3\eta V} = \frac{1}{h} - \frac{1}{h_0} + \frac{V}{8\pi} \left(\frac{1}{h^4} - \frac{1}{h_0^4} \right) \quad (1)$$

This relationship is particularly applicable to a wide range of specimen thickness because, as the assumption became improbable, their consequences are relatively unimportant. The corresponding term becomes negligible with respect to the others.

4.12 Validity of the Assumptions

4.121 The specimen is deformed under uniaxial compression

Although, because of the design and the fairly tight fit of the sliding elements, no motion of the rams could occur perpendicularly to their axis, the axial symmetry of each specimen was checked after the test to ensure that no shear stress had been applied on them during the measurement.

4.122 Horizontal planes remain horizontal during the flow

Special care was taken to use specimens with parallel faces, and faces perpendicular to the axis of the specimen. The parallelism was controlled by measuring the thickness of the specimen on three equally spaced points around the perimeter. Specimens having a thickness difference of more than 10^{-4} inch (the accuracy of the micro-meter used for the control) were discarded.

Similar measurements were carried out to check the parallelism after the creep test. Due to the wear of the tips of the rams, variations of the thickness of the specimen up to 10^{-3} or more were sometimes observed. In such cases, the results were considered to be doubtful. The parallelism was especially critical in the case of high viscosity values, where the whole deformation of the specimen could be of the same order as the tilting deformation.

4.123 "A given horizontal plane remains a plane during the deformation."

As already mentioned, this leads to specimens, the axial section of which consists of two segments of a parabola. On the photographs of Figure 31, the axial section of some deformed specimens can be seen; they show the parabolic deformation.

a) Before deformation.

b) After deformation : the scaling of the edge
is due to the adhesion to the tip of the ram.

Figure 31 : Parabolic deformation of the specimen .

4.2 Variation of the Viscosity with Time

4.21 General Considerations

In Appendix III, it has been established that the time, the viscosity and the height of the specimen can be related together by a formula as:

$$\int_0^t \frac{F}{3\eta V} dt = \phi(h) \quad (i)$$

where F is the load applied on the specimen, η the viscosity at time t and V the volume of the specimen; the right hand side is a function of the height of the specimen. In the case where the viscosity is a constant with respect to the time, the expression can be reduced to: $\phi(h) = \frac{F}{3\eta V} t$ (j).

That is, a linear relationship exists between $\phi(h)$ and t .

To determine to what extent η was a function of the time, the variation of $\phi(h)$ with the time has been compared with a linear variation. To evaluate the deviation of $\phi(h)$ from a straight line, $\phi(h)$ has been developed into a polynomial of second degree with respect to t , as :

$\phi(h) = a + bt + ct^2$. The values of the unknown parameters a , b , and c were determined by the least square fit method which was programmed in a 7044 IBM computer. All calculations involved in this work were done by the same computer.

In Table 14, the values of the parameters a , b and c are given and in Figure 32, the corresponding curves are plotted. The ratio $r = c/b$ and the product $r t_f$ are calculated at the same time. t_f is the total time of each experiment. r gives an estimation of the relative importance of the parabolic term in $\phi(h)$ at the beginning of the experiment, while $r t_f$ gives the same information for the end of the experiment; thus, they give a measure of the departure of $\phi(h)$ from a linear expression. In this calculation,

TABLE 14

PARAMETERS OF THE PARABOLIC APPROXIMATION OF $\phi(h)$
FOR SOME EXPERIMENTS

Number	$A \times 10^x$		DA/A	$B \times 10^y$		DA/B	$C \times 10^z$		DC/C	C/B	T_f	$T_f * C/B$
	A	x		B	y		C	z				
3.1211												
-10	-0.501	-02	-3.955	0.139	00	0.049	-0.205	-02	-0.253	-0.0148	11.46	-0.170
11	0.601	-01	0.182	0.118	00	0.028	-0.257	-02	-0.087	-0.0219	13.10	-0.287
12	0.221	-01	0.369	0.769	-01	0.040	-0.219	-02	-0.117	-0.0284	10.38	-0.295
13	0.176	-01	0.196	0.341	-01	0.029	-0.437	-03	-0.141	-0.0128	14.12	-0.181
14	0.165	-01	0.241	0.226	-01	0.064	-0.581	-03	-0.201	-0.0257	10.46	-0.269
15	0.160	-01	0.206	0.121	-01	0.083	-0.293	-03	-0.232	-0.0242	12.94	-0.313
16	0.578	-02	0.444	0.813	-02	0.109	-0.292	-03	-0.233	-0.0358	12.50	-0.448

Figure 32 : $\phi(h)$ as a function of time for different tests.

an attempt was made to take into account the transient phenomena such as delayed elasticity which might interfere with the viscous flow. Different weights have been given to the different measurements of h so that the first thirty minutes of the experiment were not taken into account to the same extent as the later part of the experiment. The value of thirty minutes had been suggested³² by the relaxation time of this type of glass for this range of temperature.

In order to eliminate entirely the "transient phenomenon," the same calculation was carried out neglecting completely the first fifty minutes of the creep. Similar results were found where the importance of the parameter c is not negligible for long periods of time. Finally, because of the exponential variation of the relaxation time with the temperature, an identical procedure was used with creep curves of varying length of time to determine whether a transient effect would alter the results for even longer periods of testing than had been considered so far. In Table 15, the values of a , b and c for the different curves are reported. The plots of $\phi(h)$ versus time is given in Figure 33. Even after a long period of time, the plot of $\phi(h)$ is not a straight line, that is, the slope of the log-log plot is not equal to 1. Thus, it is reasonable to assume that a variation of the viscosity with the time has been detected. In addition, the variation of the viscosity with the duration of the heat treatment at 565 and 575°C as reported previously, showed a maximum in this range of temperature which is also the range at which most of the creep tests were carried out. Thus, a time dependence of the viscosity was expected.

4.22 Expressions for the Variation of the Viscosity with the Time

At any moment, the viscosity of the specimen can be obtained from the slope of the tangent to the curve $\phi(h)$ versus time by the relationship:

TABLE 15

PARAMETERS OF THE PARABOLIC APPROXIMATION
FOR TESTS OF VARIOUS DURATION

Number	$A \times 10^x$ A x		DA/A	$B \times 10^y$ B y		DA/B	$C \times 10^z$ C z		DC/C	C/B	T_f	T_f *C/B
3.1212												
303	0.895	-02	0.076	0.161	-02	0.028	-0.365	-05	-0.159	-0.0023	75.70	-0.171
414	0.298	-01	0.043	0.261	-02	0.050	-0.212	-04	-0.134	-0.0081	43.30	-0.352
309	0.174	-01	0.067	0.622	-02	0.023	-0.425	-04	-0.085	-0.0068	36.00	-0.246
404	0.463	-01	0.128	0.173	-01	0.054	-0.467	-04	-0.655	-0.0027	30.00	-0.081
308	0.236	-01	0.075	0.553	-02	0.047	-0.752	-04	-0.109	-0.0136	29.10	-0.395
310	0.612	-02	0.145	0.461	-02	0.029	-0.605	-05	-0.698	-0.0013	28.80	-0.038
311	0.652	-02	0.118	0.232	-02	0.052	-0.264	-04	-0.155	-0.0114	27.20	-0.310
601	-0.785	-02	-0.481	0.336	-01	0.020	-0.390	-03	-0.068	-0.0116	23.50	-0.273
204	0.203	-01	0.147	0.159	-01	0.055	-0.222	-03	-0.230	-0.0139	17.00	-0.237
412	0.661	-02	0.160	0.507	-02	0.062	-0.113	-03	-0.161	-0.0223	17.00	-0.379
413	0.123	-01	0.130	0.521	-02	0.074	-0.125	-03	-0.160	-0.0241	17.00	-0.409
305	0.903	-02	0.187	0.133	-01	0.040	-0.175	-03	-0.188	-0.0132	15.90	-0.209
411	0.952	-02	0.170	0.760	-02	0.055	-0.209	-03	-0.112	-0.0275	15.60	-0.430
3.1212												
-415	0.361	-02	0.456	0.507	-02	0.113	-0.198	-03	-0.226	-0.0390	11.20	-0.437
3.112												
41	-0.115	-00	-0.158	0.821	-01	0.090	-0.346	-02	-0.195	-0.0422	9.00	-0.380
3.1212												
307	0.543	-02	0.428	0.656	-02	0.164	-0.296	-03	-0.384	-0.0451	8.10	-0.366
409	0.521	-02	0.470	0.105	-01	0.123	-0.480	-03	-0.327	-0.0456	7.00	-0.319
408	-0.595	-02	-0.210	0.112	-01	0.056	-0.383	-03	-0.187	-0.0343	7.00	-0.240

Figure 33: Different appearance of the $\phi(h)$ plots for various durations of experiment.

$$\eta = \frac{1}{\frac{d\phi(h)}{dt}} \frac{F}{3V} \quad (7)$$

To get a reasonable variation of η , a fairly accurate knowledge of the shape of $\phi(h)$ is necessary. An approximation in the values of the required slopes gave a preliminary idea of the shape of $\eta = f(t)$. The following procedure was used. At a given point A of the plot of $\phi(h)$, the slope of the tangent is the angular coefficient of the secant which joins its two nearest neighbours. This procedure is inaccurate for small values of curvature of the plot. A damping effect of the errors could be obtained by the use of a secant joining points further apart from A. Plots of long lasting experiments were analysed by this improved method.

The other attempt consisted in the use of the first computed approximation of $\phi(h)$. By differentiation of the polynomial which approximates $\phi(h)$, η is given as follows:

$$\eta = \frac{F}{3V} \frac{1}{b + 2ct} \quad (8)$$

The shortcoming of this method is that it provides a plot of the viscosity with a curvature which has the opposite sign of the curvature of the plot obtained by the previous method.

Some other functions have been tried. The shape of some $\phi(h)$ curves and the expected difficulties brought about by a delayed elastic effect, led to the attempt of an exponential decay of $\phi(h)$ with the time which gives as follows:

$$\eta = \eta_{\infty} \left\{ 1 - a \exp \left(- \frac{t}{\tau} \right) \right\} \quad (9)$$

Because of the lack of precision of the first approximation, it was not possible to linearize the system of equations which gives the parameters η_{∞} , a and τ . Thus the recurrence calculation became divergent and could not provide the values of the parameters.

To account for the linear variation of the viscosity which had been found by earlier workers⁹⁻¹⁰, a logarithmic fit of $\phi(h)$ versus t was attempted, to calculate the values of A and B in the relationship:

$$\eta = A + Bt \quad (10)$$

The fitting function could not be determined with enough accuracy, suggesting that a closer fitting equation might be found.

Considerations of mechanisms such as diffusion, which might control the change of viscosity, led to a tentative parabolic variation of the viscosity with time:

$$\eta = (a + bt)^{\frac{1}{2}} \quad (11)$$

A much better fit of the data was obtained. This suggested that an improvement could be made by introducing a third parameter, the exponent of the function, obtaining the following relationship:

$$\eta = (a + bt)^c \quad (12)$$

A good fit for the data resulted from this new equation. In Table 16, the parameters in these four different mathematical models are compared using the data of the "Corning" glass experiments. The last model: $\eta = (a + bt)^c$ appears to give the most coherent accuracy for the determined parameters. In Figures 34 - 37, the plots of the different models are compared to the plot of the "measured" values of the viscosity. The former refers to the data obtained from the measurement of the slope of the tangent of the $\phi(h)$ -versus-time curve. In Table 17 and in Figures 38 to 40, a similar comparison was made with the longest lasting creep tests. In Table 18 (Appendix II), the values of a , b and c for most experiments are reported with their corresponding accuracies.

From these tables, it can be noticed that the exponent is not completely independent of the other variables, but no systematic correlation could be established between c and some other experimental parameters.

TABLE 16

COMPARISON OF THE DIFFERENT MATHEMATICAL MODELS FOR "CORNING" GLASS SPECIMENS

Function	A	$\Delta A/A$	B	$\Delta B/B$	C	$\Delta C/C$
<u>Specimen No. 3.122 - 00</u>						
$\eta = 10^{14} \times C / (A - Bt)$	1.00	.077	.0666	.159	.179	.000
$\eta = 10^{13} \times (A + Bt)$	.480	.118	.551	.010		
$\eta = 10^{14} \times C / \sqrt{A + Bt}$	-.0249	3.69	1.00	.011	.145	
$\eta = 10^{14} \times (a + Bt)^C$	-.00596	.146	.0226	.050	.514	.018
<u>Specimen No. 3.122 - 01</u>						
$\eta = C \times 10^{14} / (A - Bt)$	1.00	.072	.0728	.150	.259	.000
$\eta = (A + Bt) \cdot 10^{13}$	.717	.144	.894	.014		
$\eta = C \times 10^{14} \sqrt{A + Bt}$	-.448	.213	1.00	.012	.226	
$\eta = 10^{14} (A + Bt)^C$	-.0212	.037	.0479	.059	.4896	.015
<u>Specimen No. 3.122 - 02</u>						
$\eta = C \times 10^{14} / (A - Bt)$	1.00	.079	.0676	.157	.186	.000
$\eta = (A + Bt) 10^{13}$	.529	.079	.567	.007		
$\eta = C \times 10^{14} \sqrt{A + Bt}$	.271	.456	1.00	.014	.152	.000
$\eta = 10^{14} (A + Bt)^C$	.00685	.126	.0279	.043	.537	.014

TABLE 16 continued

Function	A	$\Delta A/A$	B	$\Delta B/B$	C	$\Delta C/C$
<u>Specimen No. 3.122 - 04</u>						
$\eta = 10^{14} \times C/(A - Bt)$	1.00	.046	.0460	.103	.335	.000
$\eta = 10^{13} \times (A + Bt)$	.626	.245	.849	.018		
$\eta = 10^{14} \times C/\sqrt{A + Bt}$	-.463	.144	1.00	.007	.221	
$\eta = 10^{14} \times (A + Bt)^C$	-.00242	.587	.0378	.033	.442	.011

Figure 34 : n° 3.122-00

Figure 35 : n° 3.122-01

Figure 37 : n° 3.122-04

Figure 36 : n° 3.122-02

Comparison between the different mathematical models for the viscosity-time relationship in the case of the "Corning" glass .

TABLE 17

COMPARISON OF THE DIFFERENT MATHEMATICAL MODELS OF THE VARIATION OF η WITH t
 FOR 3 LONG LASTING "PYREX" GLASS EXPERIMENTS

Function	A	$\Delta A/A$	B	$\Delta B/B$	C	$\Delta C/C$
<u>Specimen No. 3.1212 - 309</u>						
$\eta = 10^{14} C/(A - Bt)$	1.00	.023	.0137	.085	1.02	.000
$\eta = 10^{13} (A + Bt)^C$	.444	.931	1.46	.027		
$\eta = 10^{14} (A + Bt)^C$	.0693	.186	.181	.024	.293	.008
<u>Specimen No. 3.1212 - 310</u>						
$\eta = 10^{14} C/(A - Bt)$	1.00	.028	.00262	.702	1.32	.000
$\eta = 10^{13} (A + Bt)^C$	.773	.888	1.99	.041		
$\eta = 10^{14} (A + Bt)^C$	.840	.188	1.74	.029	.104	.012
<u>Specimen No. 3.1212 - 313</u>						
$\eta = 10^{14} C/(A - Bt)$	1.00	.025	.00452	.159	3.73	.000
$\eta = 10^{13} (A + Bt)^C$	.373	.425	3.11	.001		
$\eta = 10^{14} (A + Bt)^C$	115.	.226	120.	.051	.255	.014

Figure 38 : n° 3.1212-309

Figure 39 : n° 3.1212-310

Figure 40 : n° 3.1212-313

Comparison between the different mathematical models for the viscosity-time relationship in the case of long lasting experiments.

However, it appears that the scatter of the values of c decreases as the temperature of heat treatment of the specimen increases, and that it is less than that of the experiments where the specimens have not been subjected to any heat treatment before the test. This would suggest the existence of some homogenization process leading towards a more uniform structure, thus erasing the previous thermal history of the glass. The value of c , then would be in the vicinity of 0.3.

In the case of the "Corning" glass the values of c are very close to 0.5. This would confirm the findings of other workers¹³, namely, that the controlling mechanism of phase separation in the range of temperature of the transformation, is a diffusion process. But as no data are available to show the importance of the geometric distribution of the second phase and the relative viscosity of the two phases, which may modify the value of the overall viscosity of the glass, the experimentally determined values of c may be fortuitous.

With respect to the viscosity which is correlated to the phase-separation, the temperature of heat treatment was found to be important, as a maximum was observed on the plot of the viscosity versus heat treatment temperature, Figure 18 and 19. Simple thermodynamical considerations of the miscibility gap, added to the variation of the viscosity with the temperature, could explain this maximum.

The viscosity data of the specimens subjected to the heat treatment at 575°C were further analysed. In Figure 41, the viscosity of these specimens is plotted against the real time of heat treatment in a log-log plot. The real time refers to the time of heat treatment in the heat treatment furnace, plus the time involved in the creep testing. For a short period of heat treatment, it appears that the values of the viscosity are much closer to the approximate straight line than they were on the previous plot.

Figure 41 : Viscosity versus true time of heat treatment.

This reflects the relative importance of the time of creep on the overall heat treatment of the specimen. On the other hand, when the creep test was carried out after a much longer period of heat treatment and when the viscosity at the beginning of the creep test is much higher, the change in the values of the viscosity during the creep test was more rapid than for the same period of heat treatment when no stress was applied on the specimen. The explanation for this change in the flow behaviour of the glass may be either that the glass no longer acted as a Newtonian liquid when a certain degree of phase separation was achieved, or that the growth rate of the second phase under stress changed when a given size of the droplets of the second phase was reached.

4.23 Activation Energy of the Flow Process

In the case of the "Pyrex" glass the temperature coefficient of the viscosity can be represented by a relationship as follows:

$$\eta = a e^{\left(\frac{Q}{R.T}\right)}$$
 This relationship is commonly accepted by most authors to relate the temperature dependence of the viscosity. The narrow range of temperature which had been considered here, resulted in a constant value of the activation energy Q for the whole range. The value of 87 kcal/mole which was obtained for the "annealed" glass, was in good agreement with the value of 80 kcal/mole found for stabilized boric glasses in the transformation range³².

On the other hand, the glass which had been tested as received, had an activation energy of 65 kcal/mole, for the flow process. At the lower end of the temperature range the values of the viscosity of this glass were lower than those of the heat treated glass. The presence of residual stresses inside the glass could account for this effect. But the higher value of the activation energy of the flow process suggested a higher energy barrier which may be due to some ordering effect within the glass structure resulting from some initial stage of phase separation, although the latter was not detected.

4.3 Interpretation of the Electron Microscopy

4.31 "Corning" Glass

Different degrees of phase separation were easily detected with specimens made out of "Corning" glass. The formation and the growth of droplets of a new liquid phase were observed during different heat treatments. But a quantitative correlation between the variation of the viscosity and the development of the second phase was not possible without extensive investigations involving the quantitative determination of the amount of the new phase present at any time. Only the structure which corresponded to the end of a given test could be observed. No information whatsoever on the previous states of evolution of the phenomenon could be deduced from this observation in order to discuss the different shapes of plots of the variation of the viscosity with time. The previous data on phase separation of this glass could not be used as the phase separation in the present case was partially carried out while the specimen was undergoing the creep test; that is, while under stress. For, if the phase separation is assumed to be a diffusion controlled process, the effect of the applied load used during the test may be significant enough to change the nucleation and growth characteristics of the second phase as evidenced in Figure 30 .

4.32 The "Pyrex" Glass

Extensive evidence of phase separation can be seen in this glass. The formation, growth and the eventual dissolution of a second phase with different heat treatments are easily noticeable. This second phase has different mechanical properties from the bulk as suggested by the appearance of freshly-fractured surfaces which were etched before replication.

The viscosity of the second phase is expected to be different from the bulk. Therefore its spacial distribution and the sizes of the droplets are to be taken into consideration to account for the observed change of the overall viscosity. In addition, although the microstructures shown in Figures 25 to 29, are quite representative of a given specimen, other structural characteristics in isolated places have also been observed in the same specimen.

The distribution of the second phase was not always uniform in the bulk of the whole specimen. In Figure 42, different areas of the same specimen can be seen. The distribution of the droplets of the second phase varies widely from cases where almost no droplets are observed (Figure 42a) to cases where the droplets are quite dense (Figure 42d), with all possible intermediate states. Several islands of phase-separated glass exist amongst zones where no phase separation has occurred. From a theoretically computed model proposed for the early stage of phase separation, Charles¹⁸ considered the formation of this type of structure. In most cases, these islands are of a circular type as shown in Figure 43.

Different appearances of phase separation are shown in Figures 44 to 47 (Appendix IV). For the same specimen, wide variations of the overall structure were observed. The size, shape, distribution and density of the apparent features also varied greatly. In the section dealing with the results, a continuous transition in the shape of the particles from a pure spherical shape to angular crystals has been reported. The fact that many authors considered phase separation as an early stage of crystallisation concurs with this observation. This remark applies especially to the formation of glass-ceramics by converting the pure glassy state to the completely crystallised ones. An analogy between the shape of the two curves given in Figure 48 and Figure 19 favors this explanation.

a)

b)

c)

d)

Figure 42 : Different areas of the same specimen .

a)

b)

Figure 43 : Islands of phase-separation.

Figure 48 : Growth rate and relative nucleation rate of PbTiO_3 crystals from glass as a function of temperature.

The former represents the viscosity-temperature of heat treatment relationship at a given time. The latter is the plot of the nucleation and growth rate of lead titanate crystals from a glass²⁹. The growth rates of crystals from a glass and the corresponding viscosities have been empirically correlated. In the case of the crystallization of silicates this relationship can be written as follows³⁰.

$$V = \frac{k_1}{\eta} + k_2 \log \eta \quad (13)$$

where V is the growth rate, k_1 and k_2 are two empirical constants and η is the viscosity. Since phase separation can be considered as an early stage of crystallisation, a similar relationship may exist between the viscosity and the growth rate of the new phase. Unfortunately, the structural study did not reveal sufficient information on the growth of the second phase to allow an evaluation of these coefficients in the present case.

4.33 The other Glasses

Electron micrographs of the binary glass and the alkali glasses showed the presence of phase separation in all the specimens. The degree of separation varied from one specimen to the other, and the size and density of the new phase similarly varied widely as shown in Figures 49 and 50. On the other hand a fairly high degree of crystallinity was encountered in the same specimens as it can be seen in Figures 51 and 52.

4.4 Changes of Viscosity due to Phase Separation

4.41 Theoretical Considerations

4.411 Effects of the Physical Structural Changes

As previously mentioned, a phase-separated glass consists of a heterogeneous system of at least one immiscible phase finely dispersed in the form

a)

b)

Figure 49: Phase separation in a binary glass heat treated for 10 mn at 850 °C .

a)

b)

c)

d)

Figure 50 : Phase separation in the alkali glass .
a and b Microstructure of a glass as fabricated,
c and d Microstructure of a glass heat treated for
10 mn at 500°C.

a)

b)

c)

d)

Figure 51 : Different degree of crystallinity in the binary glass.

a) No heat treatment .

b) No heat treatment .

c) Heat treated 20 mn at 550°C.

d) Heat treated 7 mn at 650°C.

Figure 52 : Different degrees of crystallinity in the alkali glass.

of droplets, the size of which may vary from one hundred to several thousand Ångströms in diameter. This classified the mixture at the lower limit of emulsions³¹ and in the field of colloids³².

Considerations on the Reynold's number R of the flow of a glass undergoing creep lead to the following remarks. In the present case R is of the order of 2×10^{-22} . $R = \frac{Ud}{\nu}$, the shear rate $U = 2 \times 10^{-5}$ cm/s, the distance between the particles $d = 10^{-4}$ cm and the dynamic coefficient of viscosity $\nu = 10^{13}$ cm²/s.) This value is very low and the type of flow should be similar to the flow of a fluid of lower viscosity at a very slow velocity between closely packed obstacles. The surface tension and the particle-particle interaction have not been taken into account in this comparison. Both of these however, should have a major effect on the actual flow. Although a pseudo-plastic behaviour should occur for this type of fluid, the flow can still be Newtonian because of the very low velocity involved in this study. The viscosity of emulsions³³ or colloids³⁴ is very sensitive to parameters of the suspended phase such as volume concentration, size, size distribution of the droplets and relative viscosity. Although in the case of colloids no single equation can completely represent the volume-concentration-viscosity relationship, exponential expressions of the type $\log \eta = \log \eta_0 + kc$ where k is approximately constant, are generally adequate to relate the experimental behaviour.

At higher concentrations of the second phase, coalescence and bridging of the droplets might occur and give a sudden change in the viscosity of the mixture. It would be similar to the inversion of emulsions. Then the plot of relative viscosity of the solution (viscosity of the mixture/viscosity of the solvent), as a function of the concentration, follows a curve as shown in Figure 53.

Figure 53 : Viscosity versus concentration of the suspended phase for an emulsion .

From the arguments above, it follows that viscosity values may vary by several orders of magnitude due only to physical structural changes with phase separation in glass.

4.412 Effects of the Chemical Change

When the second phase precipitates out from the glassy matrix, the concentration of the different components of the matrix should change accordingly. Although it is not possible to foresee the exact changes of composition of the phase separated glass, the importance of the variations of the viscosity due to the composition fluctuations can be estimated from available data in the literature.

For a borosilicate glass³⁵ having the formula, $\text{Na}_2\text{O} + x \cdot \text{B}_2\text{O}_3 + (4 - x) \text{SiO}_2$, the change of the viscosity with the concentration of B_2O_3 , at 575°C , is given in Figure 54. A rapid change of two orders of magnitude occurs in the viscosity values when the concentration of B_2O_3 increases from 0 to 10%.

For the binary glass $\text{Na}_2\text{O}-\text{SiO}_2$ ³⁶, at 575°C , the logarithm of the viscosity increases from 9.4 to 10.3 when the concentration of SiO_2 varies from 74.05 to 79.84%.

Figure 55 : Log isokoms in poises in the system $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ at 575°C .

Figure 54 : Variation of the viscosity with the composition in a glass of formula $\text{Na}_2\text{O} + x \text{B}_2\text{O}_3 + (4-x) \text{SiO}_2$ at 575°C .

For the alkali glass, some information is provided by the log-isokoms³⁷⁻³⁹ of the system $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ at 575°C given in Figure 55. Although the presence of other impurities are not being considered, small variations of the composition of the main constituents are followed by important changes of viscosity.

Compositional changes alone can modify the viscosity values by several orders of magnitude.

4.42 Other Experimental Observations

In support of the above considerations experimental evidence of similar phenomena are discussed below.

The great variation of the observed structures, as well as the great scatter of the viscosity measurements suggest a probable phase separation phenomenon which is followed by the crystallisation of the type observed by other workers. For glasses of the $\text{Na}_2\text{O}-\text{Nb}_2\text{O}_5-\text{SiO}_2$ ⁴⁰ system, drastic changes in the structure are detected for different rates of heat treatment as well as for slight variations of the final temperature of the heat treatment. A few degrees of temperature difference may lead to important changes in the structural characteristics. At the same time the viscosity - temperature relationship exhibits an unusual shape with a minimum after which the viscosity increases sharply with the temperature. The corresponding plots are shown in Figure 56 for the glass of the system $\text{Na}_2\text{O}-\text{Nb}_2\text{O}_5-\text{SiO}_2$ and in Figure 57 for a glass the composition of which is unknown⁴¹. The same author also found a curve showing a minimum for the plot of the viscosity as a function of the heat treatment. This minimum corresponds to a very short period of heat treatment which has not been investigated in the present case (Figure 58). One can suggest that a similar V-shaped curve exists for the plot of the viscosity versus temperature

Figure 5.6 : Viscosity measurements at a heating rate of 66°C/h for different glasses.

Figure 5.7 : Effect of the temperature on the viscosity of the original glass melt and of the crystallisation products .

○ induction period
 Δ 3000s after the start of crystallisation
 □ 7000s

Figure 5.8: Variations of viscosity with time during heat treatment of submicrocrystallizing glass .

○ 754°C
 Δ 784°C

in the glasses studied here. The scatter in the data would then result from the fact that in the course of the heat treatments or in the preparation of the specimen, some critical temperature corresponding to the sharp change of the viscosity-temperature of heat treatment relationship was locally exceeded. This is quite likely because of the difficulties that have been encountered in controlling the temperature of the high frequency furnace.

CONCLUSION

Variation of viscosity in the transformation temperature range with respect to thermal history, were investigated for different glasses.

A parallel-plate viscosimeter which allowed few restrictions on the conditions of the viscous flow, was used for the viscosity measurements.

"Pyrex" glass could be approximated to a Newtonian liquid in the range of temperature 470 to 590°C for the flow conditions of the experiments. Then, the activation energy of the viscous flow varied from 65 to 85 kcal/mole according to the previous thermal history.

All glasses exhibited a variation of viscosity with time. Several mathematical expressions were tested in an attempt to express this variation. The best fit of the experimental results, was obtained with a relationship of the type $\eta = (a + bt)^c$ where a , and b are parameters for which no physical interpretation was found. The exponent c varied in the range .2 to .5 and appeared to depend on the temperature of the heat treatment.

Microstructures of the different glasses revealed phase separation to different degrees according to the thermal history. In some cases different amounts of devitrification were noticed. Although no quantitative correlation could be noticed, phase separation could be an explanation for the variation of the viscosity with heat treatment. On the other hand, in the case of a ternary borosilicate glass, where phase separation was quite extensive, the value of $c = 0.5$ in the viscosity-time-relationship suggested that diffusion may be the rate controlling process of phase separation.

SUGGESTIONS FOR FURTHER WORK

A precise correlation between the viscosity and the structural changes can be obtained by extensive work with "Corning" type glasses which exhibit an important and easily controllable phase separation. Some complementary information can be obtained from electrical measurements carried out at the same time on the glass which undergoes phase separation.

For the other types of borosilicate glasses which have been used in the present work, measurements of the viscosity at various temperatures may determine the critical temperature where the viscosity and heat treatment relationship showed a minimum.

APPENDIX I

TABLE 3

PRESSURE VARIATION

No.	Pressure in psi	Duration in mn	Viscosity at 50 mn	10^{14} poises at 100 mn or at t_{max}
3.112-10	3900	70	.154	.196
1		71	.153	.173
20		>100	.143	.154
1	7800	>100	.156	.156
2		>100	.187	.205
3		73	.156	.156
30		74	.153	.167
1	11700	71	.157	.166
2		70	.143	.153
40		72	.251	.279
1		90	.224	.274
2		70	.215	.274
3		70	.177	.193
4		85	.228	.228
5	15600	>100	.228	.286
6		80	.147	.184
7		80	.148	.174
8		>100	.164	.168
9		77	.174	.192
9b		70	.173	.185
50		85	.146	.162
1		84	.170	.198
2	19500	73	.164	.168
3		70	.170	.170
4		80	.163	.171

TABLE 3. continued

No.	Pressure in psi	Duration in mn.	Viscosity at 50 mn	10^{14} poises at 100 mn or at $t_{\max}$
3.112-60	23400	100	.182	.205
1		84	.153	.158
2		100	.191	.196
3		76	.185	.185
4		100	.191	.191
5		0	.202	.202
70	27300	100	.156	.156
1		73	.164	.164
2		72	.185	.183
3		70	.170	.184
80	31200	50	.271	
1		74	.158	.170
2		77	.177	.189
3		90	.170	.208
4		75	.190	.197

VISCOSITY TEMPERATURE RELATIONSHIP

Pyrex glass "as received"			
No.	Temperature °C	Viscosities in 10^{14} poises	
		at 50 mn	at 100 mn
3.121			
-10	474	2.63	3.21
1	473	2.62	2.87
2	506	3.60	4.62
3	504	3.35	4.15
4	526	2.81	
5	524	1.92	2.26
6	543	.823	.898
7	544	.691	.840
8	585	0754	0942
Control tests:			
3.112			
-56	567	.148	.184
9	567	.174	.192
9B	567	.173	.185
0	568	.251	.279
1	568	.224	.274
2	568	.215	.274
3	568	.177	.228
4	569	.228	.193
5	568	.228	.284
7	568	.148	.174
8	568	.164	.169

TABLE 6

TEMPERATURE-VISCOSITY RELATIONSHIP OF
"PYREX" GLASS ANNEALED 44 HOURS AT 500°C

No.	Temperature °C	Viscosity in 10^{14} poises	
		at 50 mn	at 100 mn
3.121			
-20	591	.0541	.0770
1	588	.0778	.0991
2	578	.126	.150
3	568	.241	.255
4	558	.446	.469
5	548	.846	.955
6	538	1.45	2.12
7	528	3.44	

EFFECT OF THE HEAT TREATMENT ON THE VISCOSITY

No.	Heat treatment		Viscosity	
	Temperature °C	Time hours	at 50 mn 10 ¹⁴	at 100 mn poises
3.1212				
-101	500	3	.231	.247
2		4.71	.361	.361
3		24.21	.287	.318
4		62.41	.395	.395
5		109.3	.332	.358
6		133.3	.275	.275
7		289.	.195	.198
8		289.	.182	.205
201	565	11.	.190	.209
2		11.	.211	.249
3		23.8	.569	.578
4		23.8	.538	.555
301	575	2.16	.224	.250
2		4.33	.221	.298
3		14.9	.824	.736
4		15.7	.690	.970
5		19.	.537	.537
6		26.5	.630	.630
7		26.5	.547	.852
8		176.	1.95	1.95
9		176.	1.30	1.73
10		199	1.03	1.36
1		199.	1.36	1.36
3.1212				
-312	575	340	2.71	3.86
3	1	340	2.62	3.93
3.1212				
-401	600	.5	.178	.203
2		.5	.191	.217
3		1.	.282	.368
4		1.	.356	.381
5		3.89	.466	.773
6		3.89	.443	.582
7		19.	.819	.905
8		19.	.895	.959

TABLE 8 continued

No.	Heat treatment		Viscosity	
	Temperature °C	Time hours	at 50 mn 10 ¹⁴ poises	at 100 mn 10 ¹⁴ poises
9	650	24.4	1.34	1.63
10		24.4	1.03	1.197
1		71.5	1.37	2.01
2		75.5	2.23	2.92
3		212.	1.69	2.80
4		213.	1.79	3.66
5		236.	2.68	3.29
6		236.	3.11	4.58
-501		.5	.257	.300
2		.5	.219	.239
3		9.9	.352	.398
4		9.9	.397	.432
5		9.9	.350	.385
6		48.	.406	.446
7		48.	.393	.411
3.1212				
-601	750	2.05	.146	.152
2			.143	.153
3			.177	.227
4			.180	.215
5		4.15	.142	.184
6		4.15	.148	.173
7		21.7	.209	.214
8		21.7	.201	.210
9		21.7	.193	.231
10		47.8	.160	.202
1		47.8	.150	.162
2		47.8	.146	.158
-701	800	.033	.217	.217
2		.083	.191	.191
3		.083	.213	.221
4		.166	.207	.251
5		2.71	.217	.250
6		2.71	.234	.279
7		4.6	.160	.212
8		4.6	.184	.223
9		22.8	.179	.237
10		22.6	.246	.263
11		22.6	.233	.287
-801	900	1.	.178	.190
2		1.	.196	.216
3		1.	.209	.222

TABLE 10PARAMETERS OF THE "CORNING" GLASS TESTS

No.	Heat Treatment		Viscosity	
	temperature °C	time hours	at 50 mn 10 ¹⁴ poises	at 100 mn
3.122				
-00			.348	.442
1	560	3.	.484	.675
2	560	3.	.503	.687
3	600	3.		.174
4	690	3.	.493	.658
5	750	3.1	.109	.211

APPENDIX I (Continued)

TABLE 11

CONDITIONS OF THE TESTS WITH THE BINARY GLASS

No.	Fabrication	Test					
		Heat treatment		Temperature °C	Viscosity		
		time mn	temperature °C		at 30 mn 10 ¹⁴ poises	at 60 mn poises	at 90 mn mn
3.13							
000	15 minutes			510	.0551	.0375	80
1	at 1200°C			513	.0403	.0381	70
2	for degassing,			515	.0367	.0376	70
3	then heat			518	.144	.139	70
4	treatment, if			521	.0465	.0539	80
5	any, then 5			326	.0596	.0623	70
6	min at 660°C			527	.0397	.0412	100
	under 2000						
3.13	psi.						
-100		180	850	506	.0502	.0620	90
1		10	850	515	.0551	.0526	70
2		10	850	517	.0275	.0295	62
3		10	850	518	.108	.148	130
4		10	850	518	.0516	.0564	70
5		10	850	518	.0738	.0878	80

APPENDIX I (Continued)

TABLE 12

EXPERIMENTAL CONDITIONS OF THE TEST WITH THE ALKALI GLASS

No.	Heat treatment		Temperature °C	Test			Time mn
	temperature	time		Viscosity 10 ¹⁴ poises			
	°C	mn		at 30 mn	at 60 mn	at 90 mn	
3.141							
-000			558	.303	.582		70
1			568	.196	.258		70
2			571	.115	.132		80
3			572	.0513	.0596		80
4			575	.0583	.0703		80
5			575	.0753	.0930		70
6			576	.0802	.129		70
7			576	.137	.154	.185	100
8			576	.149	.156		70
9			578	.0765	.104		70
10			578	.0612	.0694		70
11			595	.1014	.101	.100	80
100	550	20	582	.0739	.0870		70
1			583	.201	.241		70
2			583	.200	.237		80
3			585	.105	.115		70
4			585	.0748	.0841		70
5			592	.0877	.0855		70
6			606	.0502	.0620	.739	90
7	550	20	610	.0550	.0375		

TABLE 12 continued

No.	Heat treatment		Test				Time mn
	temperature	time	Temperature °C	Viscosity 10 ¹⁴ poises			
	°C	mn		at 30 mn	at 60 mn	at 90 mn	
3.141							
-200	555°C	15	577	.161	.146		70
1			582	.0669	.638		70
2			588	.129	.127		70
3			592	.0551	.0555		70
4	555°C	15	602	.0820	.105		70
300	650°C	7	573	.128	.142		70
1			576	.355	.353		70
2			578	.151	.149		70
3	650°C	7	583	.125	.129		70
400	650°C	20	559	.119	.159	.322	90
1			586	.135	.132	.130	90
2			588	.236	.234		60
3			589	.135	.252		70
4			598	.138	.198	.212	150
5	650°C	20	599	.155	.152		80
500	670°C	27	576	.142	.194		70
1			577	.0904	.109		70
2	670°C	27	579	.650	.648		70

EXPERIMENTAL CONDITIONS OF THE ALKALI GLASS AND QUARTZ POWDER TESTS

No.	Temperature °C	Viscosity at 30 mn at 60 mn at 90 mn 10 ¹⁴ poises			Time mn
3.142					
-000	533	.262	.280	.389	110
1	545	.411	.408	.406	100
2	546	.148	.176	.274	140
3	550	.425	.424	.422	92
4	553	.133	.192	.227	100
5	554	.0429	.0525	.0683	120
6	558	.0329			50
7	559	.0213	.0227		60
8	559	.112	.252	.646	130
9	559	.115	.113		80
10	561	.109	.139		60
1	561	.092	.127	.130	120
2	561	.128	.152		80
3	576	.0932	.244	.333	120
4	576	.128	.258		80
5	578	.0709	.105		280
6	587	.0737	.105		80
7	590	.278	.316		21
8	591	.451	.447	.443	100
9	591	.197	.274	.293	100
20	591	.101	.0985		60
1	592	.0697	.0766		60
2	598	.123	.123		60
3	610	.0272	.0356	.0557	140
4	612	.228	.229	.306	100
3.142					
-100	589	.276	.273	.283	160
1	594	.0944	.155	.172	120
2	595	.129	.131		70
3	595	.153	.145	.142	180
4	596	.0841	.0990		70
5	598	.122	.149		60
6	598	.0958	.113		60

APPENDIX II

The tables which follow contain all the information about the parameters of the mathematical model of the viscosity-time relationship given by:

$$\eta = (a + bt)^c \cdot 10^{14} \quad \text{in poises}$$

The computed values of the coefficients a , b and c are given with their computed relative error $\Delta a/a$, $\Delta b/b$ and $\Delta c/c$ respectively.

The ratio a/b is provided as a measure of the relative importance of both terms.

t_f is the total time of the experiment in minutes/10.

σ is a measure of the quality of the fit and is defined as

follows:

$$\sigma = \sqrt{\sum_{i=1}^n \left| \frac{\phi_M(h) - \phi_C(h)}{\phi_M(h)} \right|^2} \cdot \frac{1}{n}$$

where ϕ_M and ϕ_C are respectively, the measured and the computed values of $\phi(h)$ at a given time t , and n is the number of values of t for which the calculation has been done.

TABLE 18

Number	$a \times 10^x$		$\Delta a/a$	$b \times 10^y$		$\Delta b/b$	$c \times 10^z$		$\Delta c/c$	a/b	t_f	σ
	a	x		b	y		c	z				
3.112												
-10	0.130	-02	1.243	0.148	-02	0.426	0.376	00	0.065	0.8810	7.00	0.006
1	0.318	-03	2.021	0.699	-03	0.593	0.320	00	0.080	0.4557	7.10	0.006
1	0.805	-23	3.127	0.115	-22	1.751	0.364	-01	0.040	0.7024	7.00	0.006
2	0.625	-03	0.707	0.129	-22	0.169	0.340	00	0.035	0.4851	16.10	0.013
3	0.798	-22	6.886	0.476	-22	3.431	0.374	-01	0.109	1.6818	7.30	0.007
30	-0.218	-10	2.885	0.849	-10	1.420	0.858	-01	0.077	-0.2568	7.30	0.026
1	0.344	-08	0.628	0.131	-07	0.227	0.111	00	0.018	0.2623	7.10	0.004
2	-0.125	-04	0.472	0.452	-04	0.186	0.232	00	0.027	-0.2770	7.00	0.007
40	-0.216	-06	1.115	0.370	-05	0.100	0.155	00	0.014	-0.0583	7.16	0.002
2	-0.197	-02	0.279	0.243	-02	0.126	0.328	00	0.026	-0.8099	8.00	0.004
3	-0.109	-04	0.277	0.377	-04	0.080	0.195	00	0.012	-0.2883	7.00	0.001
4	-0.319	-02	0.245	0.277	-02	0.122	0.229	00	0.025	-1.1528	8.50	0.007
5	-0.575	-03	0.107	0.108	-02	0.030	0.277	00	0.007	-0.5343	15.00	0.003
6	-0.143	-02	0.738	0.295	-02	0.297	0.420	00	0.085	-0.4856	8.00	0.024
7	0.651	-03	0.268	0.104	-02	0.058	0.371	00	0.023	0.6280	8.00	0.004
8	0.113	-24	3.425	0.597	-25	0.855	0.318	-01	0.074	1.8880	10.50	0.009
9	0.576	-06	3.283	0.307	-04	0.143	0.194	00	0.022	0.0188	7.170	0.005
9b	0.420	-24	5.614	0.657	-24	2.236	0.330	-01	0.089	0.6399	6.50	0.006
50	-0.165	-04	0.137	0.464	-04	0.048	0.218	00	0.009	-0.3558	8.50	0.003
1	-0.241	-03	0.424	-0.570	-03	0.142	0.296	00	0.036	-0.4233	15.10	0.021
2	0.324	-05	0.656	0.302	-04	0.101	0.193	00	0.017	0.1074	7.30	0.004
3	-0.635	-03	2.948	0.309	-02	0.675	0.388	00	0.193	-0.2053	7.00	0.038
4	0.269	18	6.354	0.615	18	3.380	0.441	-01	0.279	0.4372	7.10	0.028
60	-0.305	-03	0.200	0.107	-02	0.038	0.330	00	0.014	-0.2838	11.50	0.006
1	0.933	-08	0.825	0.379	-07	0.151	0.125	00	0.032	0.2460	8.40	0.010
2	0.140	-34	7.800	0.546	-34	2.484	0.236	-01	0.097	0.2570	9.00	0.031
3	0.178	-04	2.267	0.173	-03	0.252	0.238	00	0.064	0.1028	7.60	0.013
4	-0.173	-05	2.469	0.723	-04	0.057	0.220	00	0.017	-0.0239	12.80	0.009

TABLE 18 continued

Number	$a \times 10^x$		$\Delta a/a$	$b \times 10^y$		$\Delta b/b$	$c \times 10^z$		$\Delta c/c$	a/b	t_f	σ
	a	x		b	y		c	z				
5	0.180	02	0.322	0.274	01	0.509	0.448	00	0.190	6.5618	10.80	0.003
6	0.186	-04	0.928	0.106	-03	0.163	0.216	00	0.035	0.1747	7.10	0.008
70	0.733	-08	0.913	0.441	-07	0.118	0.122	00	0.029	0.1661	9.20	0.008
1	0.120	-16	1.178	0.311	-16	0.328	0.492	-01	0.030	0.3854	7.20	0.008
2	0.104	-11	0.999	0.148	-11	0.287	0.656	-01	0.035	0.7050	7.20	0.008
3	0.542	-07	1.460	0.111	-06	0.383	0.121	00	0.072	0.4891	7.00	0.014
80	-0.993	-04	2.578	0.326	-02	0.131	0.317	00	0.034	-0.0304	5.16	0.004
1	-0.522	-04	0.275	0.148	-03	0.073	0.249	00	0.024	-0.3526	7.30	0.008
2	0.103	-13	1.721	0.820	-13	0.339	0.600	-01	0.036	0.1252	7.65	0.008
3	0.120	-05	0.421	0.356	-05	0.067	0.156	00	0.022	0.3369	9.05	0.006
4	0.422	-37	4.738	0.358	-37	0.967	0.198	-01	0.070	1.1775	7.50	0.012
3.1211												
-10	0.000	-38	5.229	0.000	-38	1.491	0.200	-01	0.063	0.3255	11.46	0.027
1	0.311	-06	2.344	0.139	-04	0.031	0.266	00	0.015	0.0223	13.10	0.008
2	-0.129	-03	0.120	0.371	-03	0.032	0.323	00	0.000	-0.3487	10.38	0.008
3	-0.101	-05	2.844	0.118		0.042	0.197	00	0.007	-0.0086	14.12	0.004
4	0.241	-02	0.208	0.973	-02	0.049	0.289	00	0.007	0.2475	10.46	0.002
5	-0.433	-03		0.113	00	0.133	0.409	00	0.021	-0.0038	12.94	0.009
6	0.7431	00	1.742	0.615	00	0.615	0.380	00	0.078	1.2077	12.50	0.013
3.1211												
-00	0.324	-03	2.840	0.415	-02	3.610	0.196	00	0.178	0.0781	7.10	0.073
1	0.287	03	5.340	0.474	03	3.118	0.130	00	0.107	0.6061	7.20	0.017
6	0.673	-01	0.716	0.128	00	0.269	0.291	00	0.028	0.5254	7.30	0.005
7	0.153	-01	0.442	0.606	-01	0.118	0.305	00	0.014	0.2525	10.70	0.004
8	0.756	-07	0.287	0.195	-06	0.040	0.184	00	0.018	0.3883	9.30	0.005

TABLE 18 continued

Number	$a \times 10^x$		$\Delta a/a$	$b \times 10^y$		$\Delta b/b$	$C \times 10^z$		$\Delta c/c$	a/b	t_f	σ
	a	x		b	y		c	z				
3.1212												
-101	0.275	-03	0.339	0.303	-02	0.032	0.370	00	0.008	0.0908	9.20	0.002
2	0.321	-03	0.215	0.184	-02	0.067	0.259	00	0.009	0.1743	13.32	0.008
3	-0.266	-02	0.218	0.609	-02	0.088	0.370	00	0.019	-0.4371	11.00	0.009
4	0.847	-04	0.682	0.750	-03	0.092	0.220	00	0.014	0.1130	16.70	0.008
5	0.368	-04	6.319	0.286	-04	3.130	0.112	00	0.219	1.2882	11.40	0.067
6	0.225	-04	1.553	0.997	-03	0.106	0.256	00	0.015	0.0226	11.60	0.013
7	0.636	-05	3.809	0.685	-04	0.515	0.207	00	0.084	0.0929	10.48	0.023
8	-0.233	-05	0.569	0.381	-04	0.060	0.198	00	0.009	-0.0612	12.08	0.005
-201	0.345	-02	1.116	0.354	-01	0.150	0.338	00	0.023	0.0973	12.20	0.009
2	0.653	-02	0.510	0.831	-02	0.171	0.242	00	0.024	0.7852	17.00	0.010
3	0.761	-04	0.707	0.137	-03	0.212	0.229	00	0.041	0.5564	8.00	0.007
4	0.435	-04	0.298	0.258	-03	0.059	0.231	00	0.010	0.1686	9.00	0.008
-301	0.864	-05	0.646	0.385	-04	0.173	0.175	00	0.022	0.2244	9.44	0.006
2	0.426	-05	1.197	0.122	-03	0.102	0.174	00	0.011	0.0350	10.60	0.004
4	0.528	-01	1.990	0.505	-01	0.815	0.246	00	0.089	1.0459	12.10	0.026
9	-0.364	-01	0.595	0.277	00	0.074	0.515	00	0.014	-0.1312	29.10	0.009
5	0.890	-03	0.312	0.338	-02	0.099	0.171	00	0.009	0.2635	14.00	0.004
6	0.223	-02	0.405	0.139	-01	0.118	0.221	00	0.012	0.1608	15.90	0.013
7	0.219	-02	2.603	0.248	-01	0.428	0.277	00	0.050	0.0882	10.20	0.013
11	0.841	00	0.583	0.174	01	0.263	0.104	00	0.012	0.4831	28.80	0.013
10	0.693	-01	0.298	0.181	00	0.066	0.293	00	0.009	0.3823	36.00	0.010
13	0.116	02	0.485	0.120	02	0.164	0.255	00	0.015	0.9651	75.70	0.023
-401	-0.542	-03	0.096	0.545	-03	0.049	0.270	00	0.009	-0.9959	7.00	0.001
2	-0.166	-04	0.316	0.366	-04	0.096	0.190	00	0.017	-0.4552	11.00	0.004
3	-0.393	-02	0.223	0.390	-02	0.108	0.300	00	0.019	-1.0083	11.40	0.006
4	0.192	-03	0.343	0.920	-03	0.053	0.215	00	0.010	0.2086	30.00	0.013

TABLE 18 continued

Number	$a \times 10^x$		$\Delta a/a$	$b \times 10^y$		$\Delta b/b$	$C \times 10^z$		$\Delta c/c$	a/b	t_f	σ
	a	x		b	y		c	z				
5	0.385	-02	1.700	0.269	-01	0.353	0.324	00	0.048	0.1428	8.00	0.008
6	0.382	-02	0.402	0.100	-01	0.116	0.268	00	0.016	0.3817	11.50	0.006
7	0.511	-01	0.457	0.955	-01	0.138	0.374	00	0.020	0.5354	10.00	0.004
8	-0.607	-01	1.583	0.108	00	0.957	0.186	00	0.062	-0.5641	7.00	0.008
9	0.142	00	2.366	0.210	00	1.008	0.261	00	0.090	0.6769	7.00	0.012
13	0.280	00	0.932	0.637	00	0.216	0.474	00	0.032	0.4389	17.00	0.010
3.1212												
-501	-0.375	-08	0.497	0.294	-07	0.089	0.233	00	0.015	-0.1274	13.40	0.007
2	-0.292	-03	0.699	0.179	-02	0.176	0.317	00	0.034	-0.1636	7.00	0.005
3	0.116	-02	0.412	0.446	-02	0.095	0.283	00	0.016	0.2598	11.40	0.004
4	0.556	-02	0.192	0.595	-02	0.055	0.294	00	0.011	0.9345	18.00	0.005
5	0.956	-04	2.740	0.441	-02	0.092	0.285	00	0.016	0.0217	13.80	0.009
6	0.169	-03	3.469	0.204	-02	0.527	0.231	00	0.066	0.0826	9.60	0.014
7	0.350	-03	1.039	0.226	-02	0.241	0.229	00	0.029	0.1548	9.20	0.008
-601	-0.144	-04	0.590	0.729	-04	0.214	0.238	00	0.057	-0.1981	9.60	0.009
2	-0.434	-05	3.059	0.359	-04	0.290	0.226	00	0.076	-0.1211	8.30	0.009
3	0.219	-04	3.751	0.545	-03	0.100	0.279	00	0.028	0.0401	12.50	0.006
4	-0.629	-03	0.159	0.428	-03	0.082	0.253	00	0.013	-1.4696	12.00	0.008
5	-0.162	-03	0.423	0.249	-03	0.101	0.288	00	0.035	-0.6521	14.90	0.013
6	0.107	-03	0.796	0.217	-03	0.144	0.294	00	0.053	0.4947	12.00	0.016
7	-0.120	-03	0.154	0.242	-03	0.067	0.279	00	0.014	-0.4973	8.10	0.006
8	-0.289	-03	0.672	0.977	-03	0.110	0.300	00	0.031	-0.2957	13.00	0.009
9	0.482	-05	0.903	0.275	-04	0.131	0.184	00	0.024	0.1754	9.00	0.004
10	-0.906	-03	0.298	0.126	-02	0.097	0.311	00	0.026	-0.7173	12.10	0.008
6	0.297	-04	8.463	0.994	-03	0.283	0.346	00	0.083	0.0299	9.00	0.018
2	-0.527	-04	0.803	0.116	-03	0.168	0.240	00	0.048	-0.4562	13.90	0.018

TABLE 18 continued

Number	$a \times 10^x$		$\Delta a/a$	$b \times 10^y$		$\Delta b/b$	$C \times 10^z$		$\Delta c/c$	a/b	t_f	σ
	a	x		b	y		c	z				
3.1212												
-701	0.107	-04	0.645	0.122	-03	0.067	0.219	00	0.012	0.0875	12.88	0.006
2	0.199	-05	1.023	0.386	-05	0.324	0.154	00	0.046	0.5149	11.86	0.014
3	0.112	-05	0.481	0.190	-05	0.143	0.138	00	0.021	0.5881	14.32	0.010
4	-0.126	-04	1.361	0.699	-05	0.720	0.165	00	0.076	-1.8065	23.50	0.226
5	-0.506	-03	0.359	0.154	-02	0.114	0.330	00	0.026	-0.3284	11.00	0.010
6	-0.196	-02	0.648	0.480	-02	0.253	0.394	00	0.059	-0.4082	9.00	0.019
10	-0.222	-02	0.166	0.236	-02	0.068	0.328	00	0.016	-0.9426	14.00	0.006
7	-0.346	-02	0.066	0.265	-02	0.030	0.393	00	0.009	-1.3059	10.30	0.003
8	-0.750	-03	0.220	0.210	-02	0.061	0.378	00	0.018	-0.3580	12.20	0.009
9	-0.765	-03	0.277	0.131	-02	0.078	0.329	00	0.022	-0.5839	11.80	0.005
-801	-0.127	-02	0.091	0.221	-02	0.032	0.370	00	0.008	-0.5717	7.00	0.001
2	-0.124	-03	0.345	0.255	-03	0.116	0.239	00	0.021	-0.4836	9.00	0.003
3	-0.801	-03	0.273	0.157	-02	0.083	0.332	00	0.021	-0.5096	9.00	0.004
3.122												
-00	-0.596	-02	0.279	0.227	-01	0.066	0.514	00	0.018	-0.2629	13.00	0.007
5	-0.806	-02	0.167	0.116	-01	0.049	0.713	00	0.038	-0.6931	15.30	0.016
4	-0.242	-02	0.687	0.378	-01	0.053	0.442	00	0.011	-0.0640	16.60	0.005
2	-0.685	-02	0.233	0.280	-01	0.051	0.537	00	0.014	-0.2449	13.40	0.005
1	-0.212	-01	0.189	0.479	-01	0.077	0.490	00	0.015	-0.4425	11.44	0.006

APPENDIX III

THEORY OF THE PLATE VISCOMETER

The initial calculations and hypotheses only apply for the deformation under load of rubber cylinders between two parallel plates. If it is assumed that the cylinder is bounded to the plates and thus there is no slippage at the plates, the total deformation is derived as follows:

The total displacement of any element of the cylinder can be considered to arise from the superposition of two simple displacements:

- 1 - a pure homogeneous deformation defined by the displacement of one plate towards the other.
- 2 - the subsequent displacements necessary to cause points in the planes of the bounded surfaces to be restored to their original position.

Since rubber is incompressive, the force F_1 which must be applied to maintain the first deformation, that is, a compressive strain e in the vertical direction, is given by equation (a).

$$F_1 = E \pi a^2 e \quad (a)$$

where a is the radius of the disc and E the Young's modulus of the material.

In order to calculate the corresponding system of forces which has to be applied to the bounded surface, in order to account for the second displacement, one may assume that horizontal planes remain planes during the deformation. Therefore vertical diametral sections of the cylinder take up parabolic forms²⁸, so that the volume contained within them is unchanged.

For a cylinder of diameter r , we have the following relationship:

$$\pi r^2 h = \pi r^2 (h - d) + k \cdot \frac{4}{3} \pi r h$$

When the compressive displacement d , is small and the radius r , much greater than the radial displacement k , then k is given by equation (b)

$$k = \frac{3}{4} r \frac{d}{h} \quad (b)$$

In an elementary crown of width dx , the displacement k may be maintained by an excessive hydrostatic pressure dP , acting on the curved face. Classical elasticity theory gives dP as in equation (c).

$$dP = - \frac{8 E k}{3 h^2} dr \quad (c)$$

Integrating (c) between $r = r$ and $r = a$ with $P = 0$ on the outside surface, one gets equation (d).

$$P = Ed (a^2 - r^2) \frac{1}{h^3} \quad (d)$$

This pressure acting on the plates creates a corresponding force F_2 obtained by integrating $P 2 \pi dr$ between $r = 0$ and $r = a$. That gives equation (e)

$$F_2 = Ed \frac{\pi}{2} \frac{a^4}{h^3} \quad (e)$$

To apply these results to a viscous liquid cylinder, it suffices to substitute the viscosity to the rigidity modulus and the rate of approach of the plates with respect to one another, to the displacement. One then obtains equations (f) and (g)

$$F_1 = - 3 \eta V \frac{1}{h^2} \frac{dh}{dt} \quad (f)$$

$$F_2 = -3 \eta V^2 \frac{1}{2h^5} \frac{dh}{dt} \quad (g)$$

Calling $F = F_1 + F_2$, the viscosity and the rate of creep can be related by equation (k)

$$\eta = \frac{F}{3V} \left(-\frac{dh}{dt} \frac{1}{h^2} + \frac{V}{2\pi h^5} \right) \quad (1)$$

On integrating between the limits $t = t$ and $t = 0$, one gets equation (i)

$$\int_0^t \frac{F}{3\eta V} dt = \phi(h) \quad (i)$$

$$\text{with } \phi(h) = \frac{1}{h} - \frac{1}{h_0} + \frac{V}{8\pi} \left(\frac{1}{h^4} - \frac{1}{h_0^4} \right) \quad (k)$$

When the viscosity does not depend upon the time the right hand side of

$$\text{the equation becomes: } \frac{Ft}{3\eta V} = \phi(h) \quad (j)$$

a)

b)

c)

d)

Figure 44 : Different structures on a same specimen .
n° : 3.112 - 80 , no heat treatment .

APPENDIX IV

a)

b)

c)

d)

e)

Figure 45 : Different structures on a same specimen .
n° 3.122 - 407 heat treated for 24 h at 600°C.

a)

b)

c)

d)

Figure 46 : Different microstructures encountered on a same specimen heat treated 24 h at 600°C.

APPENDIX IV (Continued)

a)

b)

c)

d)

e)

f)

Figure 47: Different microstructures encountered in the glasses.

LIST OF REFERENCES

1. Littleton J.T., Ind. Eng. Chem., 25, 748, (1933).
2. Obrey G.N., I. Am. Ceram. Cos., 17, 315, (1934).
3. Lillie H.R., Phys. Rev., 36, 347, (1930).
4. Gilard P. and de Bast, J. Advances in Glass Technology, VI International Congress on Glass, Washington, (1962).
5. Heidtkamp G. and Endell, K, Glass Tech. Ber., 14, 89, (1936).
6. Shartsis L., Spinner L., and Capps W., J. Am. Ceram. Soc. 35, 155, (1952).
7. English S., J. Soc. Glass Tech. 40, 1052, (1926).
8. Lillie H.R., J. Am. Ceram Soc. 16, 619, (1933).
9. Dale A.E. and Stanworth J.E., J. Soc. Glass Tech. 29, 414, (1945).
10. Prod'homme M., Verre et Refractaire, 14, 193, 261, (1960).
11. Zijlstra A.L., Phy. and Chem. of Glass., 4, 143, August (1963).
12. Sastry B.S. and Hummel F.A., J. Am. Ceram. Soc., 43, 81, (1959).
13. Ray R., J. Am. Ceram. Soc., 44, 670, (1960).
14. Stanley A. and others J. Am. Ceram. Soc. 45, 1, (1962).
- 14B. Brearley and others, Phy. and Chem. of Glass, 3 - 6, 69, December, (1962).
15. Averyanov and others, Structural Transformations in Glasses at High Temperature, Consultants' Bureau, 63, (1965).
16. Galakhov F., Structural Transformations in Glasses at High Temperature, Consultants' Bureau, 90, (1965).
17. Bandar A., Structural Transformations in Glasses at High Temperature, Consultants' Bureau, 99, (1965).
18. Charles R.J. and others, Phy. and Chem. of Glass, 6,5, 181, October, (1965).
19. Charles R.J., J. of Am. Ceram. Soc. 46, 4, 235, (1963).
20. Charles R.J., J. of Am. Ceram. Soc. 49, 2, 55, (1966).
21. Gent A.N., British J. of Applied Phy., 11, 85, February, (1960).
22. Kracek J.C., J. of Am. Chem. Soc. 61, 2869, (1939).
23. Frenkel J., Journal of Phy., IX, 5, 385, (1945).

- 25 Dienes G.J. and others, Journal of Applied Physics, 17, 458, (1946).
- 26 Gent A.N., and others, Proc. Inst. Mech. Engrs. (London), 173, 111, (1959).
- 27 Gent A.N., and others, British Jour. of App. Phys. 11, 85, (1960).
- 28 Adkins J.E., Proc. Comb. Phil. Soc., 50, 334, (1954).
- 29 Bergeron and others, Jour. of Am. Ceram. Soc. 48, 3, 115, (1965).
- 30 Petronskii and others, The Structure of Glass, Consultants' Bureau, 118, (1964).
- 31 Becker P., Emulsions: Theory and Practice; Reinhold N.Y., (1957).
- 32 Duclaux J., Eolloids et Gets; Gauthier Villars, Paris, (1958).
- 33 Therman P., Rheology of Emulsions; MacMillan, N.Y. (1963).
- 34 Mill C.C., Rheology of Dispersed Systems; Pergamon Press, (1959).
- 35 English I.J., J. Soc. Glass. Tech., 9, 83, (1925).
- 36 English I.J., J. Soc. Glass Tech., 7, 25, (1923).
- 37 Stott V.H. and others, J. Soc. Glass. Tech. 9, 207, (1925).
- 38 English I.J., J. Soc. Glass Tech., 7, 25, (1923).
- 39 Lillie H.R., Phy. Rev., 36, 347. (1930).
- 40 Layton and others, J. of Am. Ceram. Soc. 50, 7, 369, (1967).
- 41 Stanworth J.E., Physical Properties of Glass: Clarendon Press, Oxford, 190.