mental points from the linear curve are as follows:

t°C	$1/T \times 10^{3}$	Spec. Cond.	
565	11.9	2.74×10^{-12}	
846	. 9.0	2.06×10^{-9}	
1155	7.0	1.02×10^{-7}	
1234	6.6	1.96×10^{-6}	

DISCUSSION

The measurements which are described in this paper indicate that the equatorial conductivity of quartz at very low potentials is considerably less than the published values obtained at high potentials, and that the difference manifests itself as a greater slope of the temperatureconductivity curve. This suggests the existence of an exponential relation between conductivity and field strength. For the fields used in this work, the slope of the temperature characteristic corresponds to an activation energy of 41.2 Kcal. ^(C)The temperature-conductivity curve for periclase indicates an activation energy of 30 Kcal. Because of the different slopes of the quartz and periclase curves, they cross at a point corresponding to 650°C. Below this temperature the quartz is a better insulator than the periclase; above this temperature the periclase is superior.

While the potentials used in this study varied by only a few tenths of a volt, in no case was there a sudden increase in conductivity within this range, indicating no discharge of ions. Within these narrow limits, the conduction appeared to be ohmic. It seems probable that the mechanism in these oxides is electronic in nature, and resembles that in semiconductors.

The curves for both quartz and periclase show no discontinuities, and therefore conform to a simple conductivity relation

 $\kappa = a e^{-E/RT}$,

where E has the values previously given. There is no evidence of an ionic component entering in the conduction at the higher temperatures.

The author wishes to thank Drs. Louis Navias and Frederick Seitz for many helpful suggestions.

The Effect of Pressure on the Viscosity of Boric Anhydride Glass*

ERNEST B. DANE, JR., AND FRANCIS BIRCH Harvard University, Cambridge, Massachusetts (Received June 6, 1938)

The effect of pressure on the viscosity of B₂O₃ glass has been determined by a high pressure capillary flow method up to about 2000 kg/cm², at two temperatures, 516° and 359°C. The results are satisfactorily represented by the expression $\eta = \eta_0 e^{\alpha p}$, with $\alpha = 4.6 \cdot 10^{-4}$ cm²/kg at 516°, $\alpha = 15 \cdot 10^{-4}$ cm²/kg at 359°. The ratio of the viscosity at 1000 kg/cm² to the viscosity at 1 atmosphere is therefore 1.58 at 516°, 4.48 at 359°. The results are briefly compared with those for organic liquids.

1. INTRODUCTION

N UMEROUS studies have been made of the viscosity of glass as a function of temperature and composition, which is evidently a subject of fundamental importance for the

glass manufacturer. Other factors influencing the viscosity of glass, which are of interest primarily to the geological sciences, are the pressure and the presence of volatile components in solution. The effect of these factors does not appear to have been investigated for glass-forming materials. The magnitude of the effect of pressure

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upon the viscosity of a large number of liquids of initially low viscosity has, however, been measured by Bridgman,¹ and correlated with the complexity of the molecular structure. Similarly, the effect of temperature upon viscosity has been related by Sheppard² to the effective molecular weight in the liquid state. Wolarowitsch and Leontjewa³ have used Sheppard's theory to calculate the number of associated molecules in glasses of SiO_2 and B_2O_3 ; they find that the effective molecular weight corresponds, in B2O3 glass, to 53 molecules at 500°C, to 73 at 350°. These considerations lead us to anticipate an important effect of pressure upon the viscosity of glasses of even the simplest chemical composition.

In order to reduce the viscosity of most glasses, especially of silicate glasses, to an order of magnitude such that many of the more reliable methods of measuring viscosity can be applied, the temperature must be raised to from 400° to 1000°; there are evident difficulties in combining these temperatures with enough pressure to give measurable effects. There is the further serious difficulty that the dependence of viscosity upon temperature is so great that extremely close control of the temperature is essential. With these two factors in mind, we have chosen for an initial study a material of no geological importance, but one which is characterized by a low viscosity and also by an unusually low temperature coefficient of viscosity. This material is anhydrous boric trioxide, B2O3; an additional advantage in using this glass is that it has recently been the subject of a number of studies of its density, viscosity and other properties, as functions of temperature at ordinary pressure.4 The reasonably good agreement between the results of different investigators for the viscosity-temperature curve indicates the reliability

of B₂O₃ for the present purpose. Studies with the rotating-cylinder viscometer have demonstrated. moreover, the absence of a "yield point," or of any departure from purely viscous behavior, for temperatures above approximately 300°.

The method which we have adopted was originally used by Barus;5 with refinements of technique and of theory, it has been employed by Hersey and Snyder⁶ for a study of the effect of pressure on the viscosity of oils. The material under investigation is forced from a high pressure cylinder in which a constant pressure is maintained, through a capillary tube into the open air, where it is collected and weighed after a measured time interval. The rate of flow is found as a function of the pressure at the inner end of the capillary and from this relation may be derived the dependence of the viscosity upon pressure.

2. Apparatus and Procedure

With this method, the parts in which the high pressure is established, including the capillary, must all be maintained at the required high temperature. We have used one variety of stainless steel (Allegheny 44), for the pressure cylinder, and another (Allegheny metal), for the capillary and connecting pipe. The arrangement of the principal parts is shown in Fig. 1. The cylinder (A) is surrounded by a heavy copper cylinder (B), which in turn is placed centrally in a much longer tubular, wire-wound resistance furnace. Pressure is generated in a hydraulic press, of the type used by Bridgman, and measured by the change of resistance of a 200-ohm manganin coil, mounted in a cylinder at room temperature. The pipe (F) leads from the high temperature cylinder (A) to a block with two values outside the furnace; from this block runs another pipe to the hydraulic press. The two valves are arranged to permit the sudden application or release of the pressure in the cylinder (A). The glass is extruded from the capillary (E) at the bottom, where it is collected by appropriate methods.

The pressure medium was nitrogen; originally the gas was allowed to act directly upon the glass

⁶ M. D. Hersey and G. H. S. Snyder, J. Rheology 3, 298 (1932).

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¹ P. W. Bridgman, The Physics of High Pressure (Macmillan, New York).

⁽Macmillan, New York).
² S. E. Sheppard, Nature 125, 489 (1930). S. E. Sheppard and R. C. Houk, J. Rheology 1, 349 (1930).
⁸ M. P. Wolarowitsch and A. A. Leontjewa, Acta Phys. U. S. S. R. 7, 357 (1937).
⁴ G. S. Parks and M. E. Spaght, Physics 6, 67 (1935).
M. P. Volarovich and D. M. Tolstoi, Trans. Soc. Glass Tech. 18, 209 (1934). K. Arndt, Zeits. f. Elektrochem. 13, 578 (1907). M. P. Wolarowitsch, Acta. Phys. U. S. S. R. 2, 695 (1935). S. B. Thomas and G. S. Parks, J. Phys. Chem. 35, 2091 (1931). 35, 2091 (1931).

⁵ C. Barus, Am. J. Sci. 45, 87 (1893).



FIG. 1. Arrangement of high temperature cylinder and capillary.

in cylinder (A), but-it was soon found that enough gas dissolved in the glass to produce frothing when the pressure was released, and to carry glass into the cool part of tube (F), which became plugged after a few runs. A seal of

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molten tin used in an effort to separate the glass from the nitrogen apparently contaminated the glass. The final arrangement, which proved convenient as well as satisfactory, was to draw the molten glass by gentle suction into a thin-walled drawn copper tube (C), silver-soldered to the plug (G) which connects the capillary to the cylinder (A). When filled, the copper tube was closed and soldered at the top, and mounted as indicated in Fig. 1. Under pressure, this tube readily collapsed upon the glass, forcing it out through the capillary, with no direct contact between glass and nitrogen. A pressure difference of less than one atmosphere was required to flatten the copper tubing.

Constancy of temperature, essential for the success of this work, was assured by a thyratron control circuit and a resistance thermometer, described by Benedict,⁷ with certain improvements for which we are indebted to Mr. Dennison Bancroft. The temperature remained constant to within about 0.1°C, as measured by a chromel-alumel thermocouple inserted in the wall of the copper block near the capillary; runs were not started until the thermocouple had indicated the desired temperature for several hours.

Measurements were made successfully at two temperatures, around 500° and around 350°. The viscosity of the glass is so different at these two temperatures that very different methods of collecting samples were necessary. Near 500°, where the viscosity is about 10⁴ poises, the glass issuing from the end of the capillary spread over the end of the tube until enough accumulated to form a drop; when this drop fell, it carried with it a thread, which continued to spin out from the mass on the end of the capillary until the pressure was released. After a time the thread would part somewhere in the middle. At this temperature, the glass was caught in a small platinum $\sup(D)$, placed near the end of (E), which could be removed for weighing after the flow had stopped. The amount of glass remaining on the end of the tube was somewhat variable and could not be measured; a large part of the irregularity of the results at this temperature is probably to be ascribed to this cause. All attempts to wipe or cut off the last drop were defeated by the

⁷ Manson Benedict, Rev. Sci. Inst. 8, 252 (1937).

tendency of the glass to stick to everything it touches at this temperature. The effect of the last drop could be decreased by taking larger samples but this procedure, involving longer runs, increased the danger of temperature drift. At 500°, the viscosity changes by more than 2 percent per degree temperature change; the maximum change due to pressure was about 150 percent.

At 359°, where the viscosity is nearly 10⁸, the glass was extruded as a straight rod slightly larger in diameter than the bore of the capillary. with no tendency to spread over the end of the tube. As this rod showed no inclination to drop off even if left overnight, it was easy to get accurate samples by cutting off the rod at the end of the tube with a special pair of nippers. As a result, more regular results were obtained at this temperature in spite of the fact that the viscosity changes here by 8 percent per degree.

Several sizes of capillary were used, with inside diameters of 0.041 and 0.063 cm at 500°, and of 0.159 cm at 359°, with lengths varying from 7 to 40 cm. The outside diameters were, respectively, 0.15, 0.23 and 0.80 cm. The shorter ones were almost entirely enclosed in the end of the pressure cylinder; the longer ones were coiled between this cylinder and the bottom of the copper block. Although the latter arrangement left the capillary somewhat more exposed to temperature fluctuations, with care equally smooth results could be secured in either case. The diameters of the capillaries were not measured accurately, since only relative values were needed, No great precision can be expected for the absolute viscosity, which agrees roughly, however, with the values of other observers.

The glass was prepared from Merck's "reagent" grade anhydrous B_2O_3 by fusing at 1100° in a platinum crucible, holding at this temperature overnight, with about an equal time at 900° under a water-aspirator vacuum. At the end of this time, the glass had been quiet and free from bubbles for several hours. The viscosity at 900° is of the order of 100 poises.

A total of about 3.5 g of glass could be extruded from the collapsible tubes. The times for the individual runs were regulated to yield about 0.2 g in each sample, so that 15 or more points, at different inlet pressures, could be obtained

from a single charge. Since the duration of the runs was from 20 minutes to 10 hours, errors in the measurement of the time were negligible. The required pressure was built up in the press before the valve leading to the cylinder (A) was opened; the run was begun by suddenly opening this valve, and terminated by closing this valve and opening the release valve. Variation of inlet pressure during a run could be held within narrow limits by occasional pumping. At very low pressures, small changes of the zero of the manganin pressure gauge occasionally introduced uncertainties of as much as several percent. The chief sources of irregularity were temperature changes and variable retention of glass at the outside end of the capillary.

There is, however, a possibility of systematic error due to the heating effect of forcing the glass through the capillary. The mechanical energy lost in transporting a given quantity of glass from the upper pressure to the lower pressure is transformed into heat; if this heat were not dissipated, the rise of temperature of the glass in passage might be as great as 70° for a pressure difference of 1000 kg/cm². We wish to realize as nearly as possible an isothermal flow. This may be approached by diminishing the velocity for a given pressure drop, that is, by using longer or finer capillaries. The effect of the heating is evidently to reduce the viscosity, whereas the effect of pressure alone, for isothermal flow, is to increase the viscosity. If the flow were too rapid, the heating effects might completely mask the true pressure effect.

The temperature difference which can exist between the axis and the wall of the capillary even when equilibrium conditions are reached has been calculated by Hersey⁸ and is negligibly small. The computation is more difficult when neither equilibrium nor adiabatic conditions exist; this case, which embraces all real experimental conditions, has been attacked by Hersey and Zimmer⁹ with some success. Experimentally, the natural approach appears to be to decrease the velocity of flow for a given pressure drop, by using successively longer or finer capillaries. As the velocity is decreased, equilibrium is ap-

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 ⁸ M. D. Hersey, Physics 7, 406 (1936).
 ⁹ M. D. Hersey and J. C. Zimmer, J. App. Phys. 8, 359 (1937).

proached and the apparent effect of pressure in increasing the viscosity increases toward a limiting value. Thus, when at 500° the mean velocity was reduced from 0.5 cm/sec. to 0.1 cm/sec., the apparent pressure coefficient was raised about 25 percent. A further reduction of the velocity to 0.06 cm/sec. gave no perceptible change in the pressure coefficient, within the rather large probable error, amounting to several percent. It seems unlikely that the value of the pressure coefficient for infinitely slow flow will be very much greater than is found with our finest capillary (40 cm long, 0.041 cm diameter). At 360°, the heating effect is certainly negligible.

No corrections have been applied for the compressibility of the glass, which is not known, nor for the elastic stretch of the capillary. These corrections are much smaller than the probable error due to the other causes which have been discussed. The absence of any appreciable creep or permanent stretch of the capillary was verified by taking measurements alternately at high and at low pressures. It is hardly necessary to add that these velocities of flow are far below the Reynolds critical velocity, by a factor of about 10⁹ at 500°. The shearing stress in the glass, at the wall of the capillary where it is greatest, is about 250 g/cm² for the longest capillary, and about 3100 g/cm^2 for the shortest and widest, with an inlet pressure of 1000 kg/cm².

3. Results

With this type of viscometer, the pressure to which the glass is subjected decreases from a high value P at the inner end of the capillary to one atmosphere, which we take as zero, at the outer end. If the viscosity varies with the pressure, and is given by $\eta(p)$, the rate of flow Q, in cm³/sec., will be given by the integral

 $Q = C \int_{p=0}^{p=P} dp / \eta(p),$

where C is a constant for a given capillary. The viscosity as a function of pressure may be obtained by taking the slope of a plot of Q as function of the inner pressure P, as shown by Hersey and Snyder. Another way of treating the results has been adopted here. If the viscosity were independent of the pressure, a plot of the

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quantity Q/P against P would be a straight horizontal line. On the other hand, if η increases with pressure, the values of Q/P will decrease as P increases, and the form of variation of η with the pressure may be derived from such a curve.

In Fig. 2 is shown a representative set of



FIG. 2. Experimental results at 516° C. Q/P in arbitrary units. The smooth curve is calculated from the expression, $\eta = \eta_0 e^{0.00046p}$.

points at 516°. This set in which the greatest inlet pressure, about 2000 kg/cm², was attained, is typical of a number of runs at this temperature, with regard to the average slope and to the consistency of the results. The average deviation of the points from any one of several smooth curves is about 2 percent of the ordinate. On the basis of these measurements alone, it is not possible to distinguish among the several simple analytical expressions for the variation of viscosity with pressure which suggest themselves. In the case of the results for 359°, shown in Fig. 3, the measured effect is much greater, the scattering is less, and the choice of expressions is consequently more restricted.

In Table I are given several simple expressions

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T °C	η/η_0	Q/P	VALUE OF COEFFICIENT IN CM ² /KG	η_{1000}/η_0
516° { 1,	$(1-\beta p)$ (1+ap)	$\frac{A(1-\beta P/2)}{A\ln(1+aP)/aP}$	$\beta = 0.00035$ a = 0.00053 a = 0.00046	1.54
359°	$e^{\alpha p}$ $e^{\alpha p}$	$\frac{A(1-e^{-\alpha T})}{2}$	$\alpha = 0.00046$	4.48

with numerical values for the coefficients to fit the data for 516°, and one expression for the data at 359°. In addition to the formula for $\eta(p)$ we give the integrated expression for Q/P, and the ratio η_{1000}/η_0 of the viscosity at 1000



FIG. 3. Experimental results at 359 C. Q/P in arbitrary units. The smooth curve is calculated from the expression, $\eta = \eta_0 e^{0.0015p}$.

kg/cm² to that at 1 kg/cm², at the same temperature. The most suitable expression appears to be $\eta = \eta_0 e^{\alpha p}$; this is consistent with the results at both temperatures and has received a certain amount of theoretical justification in Andrade's theory of viscosity.¹⁰ Of the other expressions which are consistent with the high temperature results, the straight line interpretation of Q/Pversus P, leads to an infinite viscosity at 2860 kg/cm²; this is certainly incorrect. The linear increase of viscosity with pressure gives a satisfactory fit at 516°, but not at 359°.

It is of some interest to compare these results with those of Bridgman and others for organic liquids. At 516°, the initial rate of increase of viscosity of B_2O_3 is about the same as that of methyl alcohol at 30°; at 359°, the initial rate

¹⁰ E. N. da C. Andrade, Nature, Mar. 1 and Apr. 12 (1930); Phil. Mag. 17, 497 and 698 (1934).

of increase of viscosity of the glass is greater than that of eugenol or of oleic acid, the pure liquids which showed the greatest effects among Bridgman's materials, and even greater than that of castor oil, studied by Hersey and Snyder. The viscosity of castor oil could also be represented approximately by an exponential expression up to 3000 kg/cm². Several lubricating oils studied by Dow11 showed increases of viscosity by factors of ten or more in the first thousand kg/cm². In Bridgman's work, the rate of increase with pressure of the *logarithm* of the viscosity generally fell off appreciably in the first few thousands of kg/cm², remaining relatively constant thereafter to 12,000 kg/cm². Caution is therefore recommended in applying the present results to pressures higher than 2000 kg/cm².

No general law for the effect of temperature upon the pressure coefficient can be derived from Bridgman's measurements at 30° and 75°; in some cases the increase of viscosity with pressure was greater at 30°, in others, at 75°. Dow's results for lubricating oils showed marked decreases of the pressure effect as the temperature increased, from about 40° to 100°. For B₂O₃ glass, the pressure coefficient α is about three times as great at 359° as at 516°. This is very much greater than might be anticipated on the basis of Andrade's theory, which gives a pressure coefficient roughly inversely proportional to the absolute temperature. The "reaction rate" theory of viscosity, recently reviewed by Ewell,12 which gives a very satisfactory account of the initial effect of pressure on the viscosity of pure liquids, may prove adequate to deal also with the more complicated case of vitreous materials, although, for the moment, data for a quantitative application to glasses are lacking.

¹¹ R. B. Dow, J. App. Phys. 8, 367 (1937). ¹² R. H. Ewell, J. App. Phys. 9, 252 (1938).

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