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Studies on Glass

XV. The Viscosity and Rigidity of Glucose Glass

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By an electromagnetic torsion method, in which glucose glass threads were substituted for the phosphor-bronze suspension in a d'Arsonval galvanometer, the rigidity and viscosity of glucose glass have been measured between 12° and 37.5°C. The rigidity values were fairly constant around 2.5 (10^{10}) dynes per cm² between 12° and 30° but decreased rapidly above the latter temperature. The viscosity values ranged between 10^{15} and 10^{10} poises. These values decreased rapidly with rising temperatures but also depended greatly on the previous history of the glass threads, i.e., the extent to which the threads had been annealed and the amount of previous working to which they had been subjected. This finding suggests the existence of a series of glassy states for a substance such as amorphous glucose.

IF a cylindrical body is subjected at one end to a torsional couple while the other end is held stationary, there may result within the body (a) an elastic displacement or (b) viscous flow or (c) a combination of these two phenomena. For the elastic displacement we have the relation

$$R=2Cl/\pi r^4\theta, \qquad (1)$$

where R is the modulus of rigidity of the material of which the cylindrical body is composed, l and r are, respectively, the length and radius of the cylinder, θ is the angular displacement of the movable end, and C is the torsional couple. Correspondingly for viscous flow, the coefficient of viscosity is given by the equation

$$\eta=2Cl/\pi r^4\omega, \qquad (2)$$

where ω is the angular velocity of flow with the couple C. With some materials, under suitable conditions, both elastic displacement and viscous flow take place to a very appreciable extent. We have found that such is the case with glucose glass within the temperature range 12°–35°C.

PREPARATION OF THE GLASS SAMPLES

In the present study the glucose glass was used in the form of cylindrical threads, 10 to 14 cm long and 0.05 to 0.12 cm in diameter. Liquid glucose was first prepared by melting crystals of either Pfanstiehl C. P. α glucose or a special National Bureau of Standards material ("Sample 41") in accordance with the procedure of Parks, Huffman and Cattoir.[1] Then by dipping a small glass rod into a sample of this liquid, undercooled to about 100°, and withdrawing it slowly, threads of glassy glucose, 20 to 40 cm long, could be readily obtained. Perhaps a quarter of these were almost perfectly cylindrical with a cross section uniform to ±4 percent, a fact which was fairly clear from a careful inspection and which always was subsequently verified by weighing small sections taken from different portions of the thread.

The radius of these glass threads was readily calculated from the mass of a given length and the density value of 1.523 g per cc at 20°, given by Parks, Huffman and Cattoir. Before use the threads were kept in a vacuum desiccator over phosphorous pentoxide. The glass products of the two different samples of glucose crystals were apparently the same and the values of their properties depended only on the extent of their annealing and on their previous mechanical treatment.

THE TORSION APPARATUS

In the measurements these glucose threads were subjected to an electromagnetic torsional couple by substituting them for the phosphor-bronze suspension in a Leeds-Northrup type P d'Arsonval galvanometer of 116 ohms internal resistance. To complete the electric circuit

[1] G. S. Parks, H. M. Huffman and F. R. Cattoir, J. Phys. Chem. **32**, 1366 (1928).

through the movable galvanometer coil, a short spiral of very fine phosphor-bronze wire was then connected to the coil from below to function in place of the usual metallic suspension. The galvanometer was next connected in series with a two-volt battery, an adjustable resistance box and a milliammeter. The deflections of the galvanometer were read with a telescope and curved millimeter scale, placed at a distance of 49 cm from the movable coil.

The torsional couples corresponding to the use of various current strengths were readily evaluated, by Eq. (1), in a calibration of the galvanometer in which suspensions of B. and S. No. 28 copper wire and No. 30 Chromel wire were employed and the current and corresponding deflections were measured. For this purpose the moduli of rigidity of these copper and Chromel wires were previously determined by measurement of the periods of angular oscillation when a brass rod of known moment of inertia was suspended from definite lengths of the wires in question.[2]

In the actual experiments with glucose thread suspensions the scale deflections of the galvanometer were read with the telescope to 0.5 mm at intervals over a period of twenty to forty minutes while the electric current was on; then the current was cut off and the elastic return of the galvanometer was noted, sometimes over a period of several hours. The character of the deflections in a typical case (a determination at 19.6°C) is shown in Fig. 1, where the scale deflection in cm has been plotted against the time in minutes. With the imposition of the electromagnetic couple there was an immediate elastic deflection θ_1, which was usually measured within an interval of 15 to 20 seconds. This was followed by a flow which was partly simple viscous and partly elastico-viscous in character and which is represented by the deflection θ_2. At the end of 31 minutes in this case the current was cut off and there followed an immediate elastic return and an elastico-viscous return in the course of 80 minutes, which together were equal to the quantity $\theta_1+\theta_2-\theta_3$. The permanent viscous flow due to the imposition of the electromagnetic couple for 31 minutes was represented by θ_3.

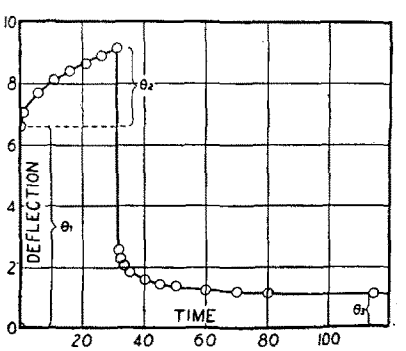

FIG. 1. The deflections (in cm on the galvanometer scale) plotted against the time (in minutes) in a typical torsion experiment with a glucose glass thread. The couple was applied here at 0 time and removed at 31 minutes.

[2] For this mode of evaluation of the modulus of rigidity see L. Page, *Introduction to Theoretical Physics* (Van Nostrand Co., New York, 1928), pp. 142, 143 and 109.

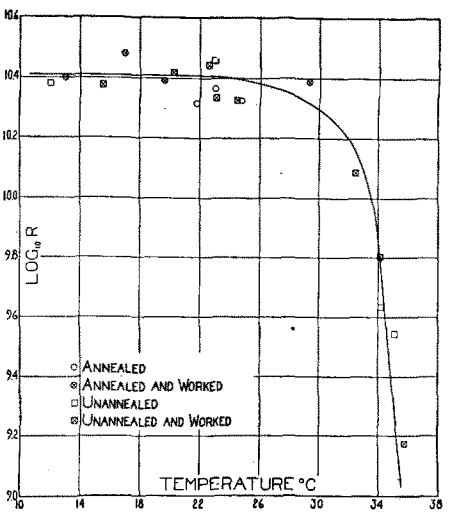

FIG. 2. The logarithm of the modulus of rigidity of some glucose glass threads plotted against the temperature.

The modulus of rigidity of the glucose glass was then calculated from these θ_1 values (converted to radians) by Eq. (1). The θ_3 values divided by the time of flow in seconds likewise yielded ω for the calculation of the corresponding viscosities by Eq. (2). The elastico-viscous effect (equivalent to $\theta_2-\theta_3$), involving as it does a decreasing elastic flow over an appreciable time interval, was thus left out of the calculations. It is an effect which has been recognized for many years in materials that possess some of the properties of both solids and liquids; but the various attempts to treat it in a theoretical way have not appeared very satisfactory.[3] If it had

[3] See for example: A. A. Michelson, J. Geol. 25, 405 (1917); L. N. G. Filon and H. T. Jessop, Phil. Trans. Roy. Soc. A223, 89 (1922); V. H. Stott in W. S. Turner, *The Constitution of Glass* (Society of Glass Technology,

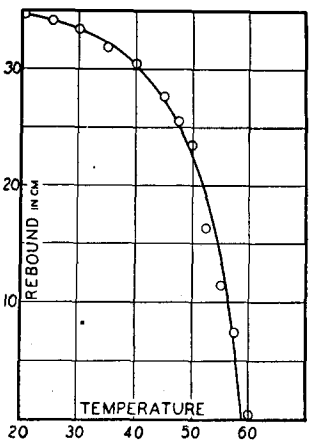

FIG. 3. The rebound distance of steel spheres, dropped from a height of 56 cm on a layer of glucose glass, plotted against the temperature.

been combined with the immediate elastic deflection in the calculations by Eq. (1), the corresponding values of R would be decreased by 35 percent on the average.

In order to maintain a constant temperature in the glucose sample during the measurements, the galvanometer was placed inside a large wooden box which was provided with a glass door in front and otherwise thermally insulated. By means of a fan, a thermoregulator and an electric heating coil within this box temperatures could then be maintained constant to $\pm 0.1°$.

After the development of the method measurements were made with about twenty-five different glucose threads within the temperature range 12°–38°C. Each specimen was used in the torsion apparatus for only one determination at a particular temperature, and then was cut into sections and weighed for proof of its uniformity. Some of these threads were used immediately after their preparation; others were first annealed at 30°–32° for several days; still others, after installation in the galvanometer, were subjected to a preliminary "working," i.e., a series of strong deflections before the actual measurements.

THE RIGIDITY RESULTS

The values of the modulus of rigidity, calculated from the immediate deflections of the galvanometer when the current was imposed, were very constant around 2.5 $(\pm 0.4)\times 10^{10}$ dynes per cm^2 over the temperature range 12°–30°C. Above 30° they fell off 94 percent within about 6° and it is clear that for this type of measurement the rigidity of glucose glass practically disappears above 36°. The experimental results are plotted in Fig. 2, from which it appears that previous annealing and working of a glucose thread produced no appreciable effect on its rigidity. Incidentally, it is of interest to note that our value of 2.5 (10^{10}) dynes per cm^2 at 20°C is only about 8 percent of the rigidity reported by Sosman[4] for vitreous silica fibers at the same temperature.

Several earlier studies[5] in this laboratory have shown that the values of some physical properties of a glass in the softening region depend greatly upon the time involved in the performance of the experiment. Thus a glass-forming substance at a given temperature may function as a solid for one type of measurement and as a very viscous liquid for another type involving a considerably greater interval of time. This point has been recently emphasized by Richards[6] in his

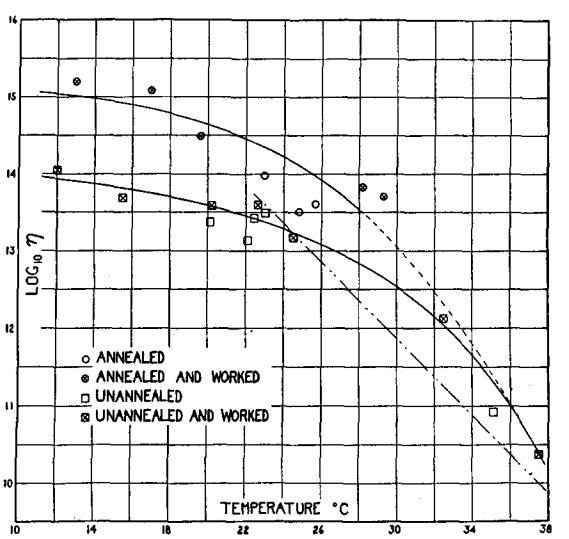

FIG. 4. The logarithm of the viscosity of some glucose glass threads plotted against the temperature. Annealed threads are represented by the upper and unannealed threads by the lower curved line. The dot-dash line represents the earlier results of Parks, Barton, Spaght and Richardson.

Sheffield, 1927), pp. 73, 155; H. Umstätter, Kolloid Zeits. **70**, 174 (1935); J. D. Ferry and G. S. Parks, Physics **6**, 356 (1935).

[4] R. B. Sosman, *The Properties of Silica* (Chemical Catalog Co., New York, 1927), p. 446.

[5] G. S. Parks, S. B. Thomas and W. A. Gilkey, J. Phys. Chem. **34**, 2028 (1930); S. B. Thomas, ibid. **35**, 2103 (1931); G. S. Parks and S. B. Thomas, J. Am. Chem. Soc. **56**, 1423 (1934).

[6] W. T. Richards, J. Chem. Phys. **4**, 449 (1936).

consideration of the thermal relaxation time of glass. In the present case, while the glucose glass above 36° has lost practically all of its rigidity in these thread torsion tests, it still retains considerable elasticity for a briefer impact test. This point was recently proved by Mr. Charles O. Yoakum, Jr. in our laboratory when he repeated the rebound experiment of Tammann and Klein[7] with a 0.2 cm layer of glucose glass resting upon a steel floor. Steel spheres (0.88 cm in diameter), when dropped from a height of 56 cm upon this layer of glucose glass, rebounded to various distances depending upon the temperature, as shown in Fig. 3. For example, the average distance of rebound was 34.7 cm at 20.5°, 27.2 cm at 45.0°, 16.4 cm at 52.5° and 0.5 cm at 60.0°C. Thus the elastic rebound did not fall to one-half of the 20° value until the temperature of the glucose reached 52°; and the rapid loss of solidity in this briefer impact test comes about twenty degrees higher on the temperature scale than with the torsion experiments on the threads.

The Viscosity Results

The viscosity values, calculated from the permanent flow by Eq. (2), ranged from 1.6×10^{15} poises at 13° for a glucose thread which had been previously annealed and "worked" to 2.4×10^{10} poises for a thread at 37.5°C. Above 32° the effect of annealing and prior working should not be very noticeable, but below 20° the annealed samples displayed on the average over ten times the viscosity of the unannealed and a preliminary working of the thread was necessary to obtain reasonably consistent results. This preliminary working led to an increase in the viscosity value in all cases, and interfered somewhat with the reliability of tests which were made to determine whether or not the glucose displayed "true" (i.e., η independent of shearing rate) viscosity at the lowest temperatures. On the whole, however, these tests seemed to indicate that the requirements of true viscosity were met, at least approximately, at 19°C.

The various viscosity results are shown graphically in Fig. 4, with two curves—the upper for the annealed and the lower for the unannealed samples. From this plot of the data it is evident that the thermal and mechanical history of a thread was all-important in determining the magnitude of its viscosity below 30° and that in this region it is impossible to assign any one value for this property at a given temperature. This point is also emphasized by the divergent position in the figure of the straight dot-and-dash line, which represents the earlier viscosity values obtained by Parks, Barton, Spaght and Richardson.[8] Between 34° and 24° these investigators used a torsion method with glucose glass cylinders of 0.83 cm diameter and 2.5 cm length, which had been annealed but not subjected to preliminary working. Even though the diameter of the cylinders was next reduced to 0.53 cm, their method failed completely below 22° on account of the excessive brittleness of the glass in this form.

Discussion

In our judgment these viscosity results throw considerable light upon the glass problem. Apparently the properties of a glass are not functions of merely two variables, such as pressure and temperature, as is the case with ordinary liquids and crystals; rather they are functions of pressure, temperature and *time* (i.e., previous history). Hence, at a given temperature and pressure there are a whole series of glucose glasses which may coexist and show considerable variations in certain properties. For this reason it is more logical to refer to the *glassy states* of glucose or of any other substance rather than to the "glassy state," as has been done by some investigators who thus have hoped to emphasize the rather marked characteristics displayed by matter in an amorphous, practically solid condition.

This concept of a series of glassy states for a substance will be discussed further in a subsequent paper.

Acknowledgment

We wish to thank Mr. Charles O. Yoakum, Jr. for the measurements on the elasticity of glucose glass by the ball-rebound method.

[7] G. Tammann and R. Klein, Zeits. f. anorg. allgem. Chemie **192**, 161 (1930); see also G. Tammann, *Der Glaszustand* (Leopold Voss, Leipsig, 1933), pp. 48–51.

[8] G. S. Parks, L. E. Barton, M. E. Spaght and J. W. Richardson, Physics **5**, 193 (1934).