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Analysis of Low Temperature Viscosity Data for Three NBS Standard Glasses

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The low temperature viscosities of three glasses established as viscosity standards at the National Bureau of Standards are reported. The data overlap results which appear on the published certificates between 10^9 and 10^{12} poise and present extensive measurements up to 10^{16} poise. The measurements were made using both the fiber-elongation and beam-bending methods. No evidence of an Arrhenius behavior was found for any of the three glasses, even though the measurements covered a narrow range of temperatures. An analysis of the inherent measurement uncertainty associated with each method indicates that the fiber-elongation measurements are more precise than the beam-bending measurements. Analysis of the data and its uncertainty by the Fulcher Equation supports the conclusions of the error analysis.

Key words: Beam-bending; fiber-elongation; Fulcher equation; glass viscosity; standard reference material; viscosity; viscosity standard.

1. Introduction

In the past few years three types of glasses [1–4][1] have been established as viscosity standards in a standard reference material program at the National Bureau of Standards. The characterization of these glasses has involved extensive measurements of viscosities for each of these glasses at high and low temperatures. The low temperature viscosity data obtained on these glasses has not been completely analyzed and is considered in more detail along with newer data.

These glasses:[2] No. 710, a soda-lime-silica; No. 711, a lead silica; and No. 717, a borosilicate have been certified for viscosity form 10^2 to 10^{12}P (poise). The viscosity determinations were made by the rotating cylinder method [1–4] at high temperatures, and by the fiber elongation [1] and beam-bending methods [5] at the lower temperatures. Recently, a parallel-plate method [6] was used to measure viscosities in the intermediate temperature range by one of the laboratories involved in the round-robin measurements on these glasses.

Even though viscosity values for each of the three glasses have been certified only up to 10^{12} poise, many determinations were made above this value. We present here viscosity data taken at this laboratory on the three standard reference glasses by the fiber elongation and beam-bending methods. The apparatus for the former has been well described previously [1]. The apparatus for the latter is a greatly modified version of that described by Hagy [5].

In the range of viscosities from 10^{11} to 10^{16} P, roughly the transformation region of a glass, the measured viscosity at each temperature is time dependent; i.e., the lower the temperature the longer it takes to reach the equilibrium viscosity value. Therefore, to reach equilibrium values within reasonable times, measurements are usually limited to an upper value of 10^{15} P. In a few cases in the work presented here, stabilization times at 10^{15} P and above lasted between 200 to 300 h. Viscosities obtained at these long times were very close to the expected equilibrium values at each of the temperatures measured.

2. Apparatus and Method of Measurement

2.1. Fiber Elongation Method

The apparatus used to measure viscosity by the fiber elongation method has been described in a previous paper [1]. Briefly, a fiber 10-cm long and of uniform diameter is placed under tension at a constant temperature. Its rate of elongation is recorded. The viscosity is calculated from the following equation:

$$\eta = \frac{Fl}{3A\dfrac{dl}{dt}} \tag{1}$$

[1] Figures in brackets indicate the literature references at the end of this paper.

[2] The nominal composition by weight percent for the soda-lime-silica glass is: SiO_2—70.5 percent, Na_2O—8.7, K_2O—7.7, CaO—11.6, Sb_2O_3—1.1, SO_3—0.2, and R_2O_3—0.2 (Fe_2O_3—0.02 percent). The nominal composition by weight percent for the lead silica is: SiO_2—46.0 percent, PbO—45.3, K_2O—5.6, Na_2O—2.5, and R_2O_3—0.6. The nominal composition by weight percent for the borosilicate glass is: SiO_2—70 percent, B_2O_3—17.0, K_2O—8.0, Na_2O—1.0, Al_2O_3—3.0, and Li_2O—1.0. These glasses are not intended as standards for chemical analysis. The compositions are given only for information purposes.

where

η = viscosity (poises; $1P = 10^{-1}$ Pa·s)
F = extending force (dyn) (1 dyn = 10^{-5} N)
l = fiber length (cm)
A = fiber cross-section area (cm^2); instantaneous value
$\frac{dl}{dt}$ = elongation rate (cm/s).

2.2. Beam-Bending Method

The measurement of viscosity by the beam-bending technique has been developed and described by Hagy [5] and has now been accepted as a method for determining low temperature viscosity by many laboratories. It is particularly useful for glasses that cannot be flame-drawn into fibers.

Unusual glass compositions may devitrify or phase-separate in the flame-working process so that fibers cannot be made. At the same time with some glasses, surface volatilization may occur and the fibers may be of different chemical composition. All of these problems are eliminated by grinding bulk samples of the glass into regular rods (square, round or rectangular cross-section) [5]. The beam-bending method has also been adopted as a standard to determine the annealing point and strain point of glass by the ASTM [7].

A schematic drawing of the assembly of the apparatus for the beam-bending technique is shown in figure 1.

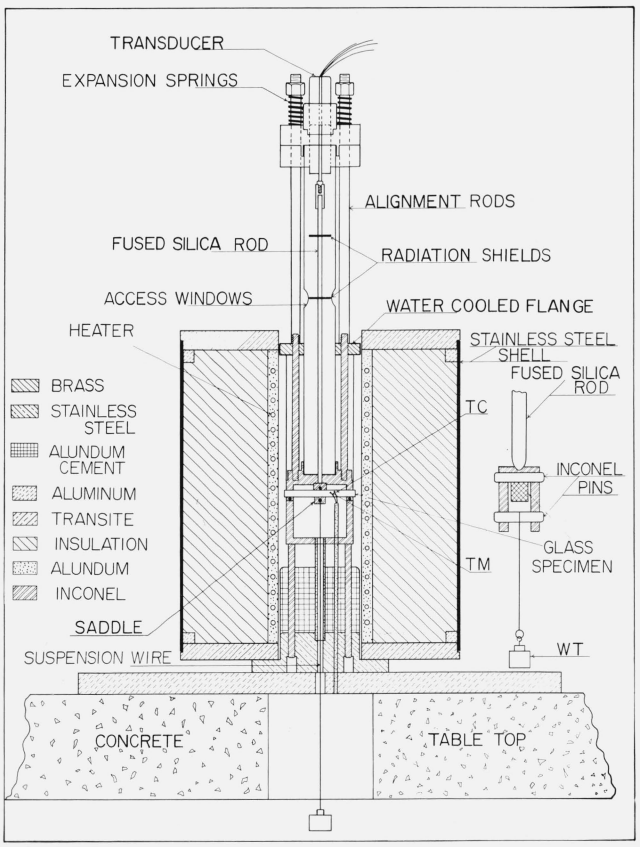

FIGURE 1. *Beam-bending apparatus showing furnace and table.*

This modified version of the beam-bending apparatus [5] was built at the National Bureau of Standards and is especially suitable for equilibrium viscosity measurements. The assembly consists of two sections. The first or bottom section is the sample holder and the second or top section is the transducer and sensor holder. The furnace and its apparatus have good temperature stability so that thermal equilibrium conditions are established in the glass sample before measurements are begun. The equilibrium conditions are especially helpful for long time measurements. The rate of bending can be continually monitored while the load is applied intermittently or continuously. All metal parts within the furnace are made of inconel.

The bottom half, figure 2, is the sample holder, which has two holes in the bottom. One of these, in the center, is for the suspension wire for the weight and is attached to the saddle. The other hole is for the thermocouples, one (Chromel-Alumel) for control and the other (Pt–Pt 10 percent Rh) to measure the test temperature. The sample holder is notched across one diameter, figure 2, to accommodate two inconel pins 0.3 cm in diameter that act as supports for the glass beam. The distance between supports is 5.715 cm and the glass beam about 6.5 cm long. The beams are square, rectangular, or circular in cross-section. Most of the beams used had square cross-sections with 0.318 cm and 0.635 cm sides. Samples with a rectangular cross-section (0.635 × 0.953 cm) were also used at high temperatures near the low-viscosity limit of the apparatus.

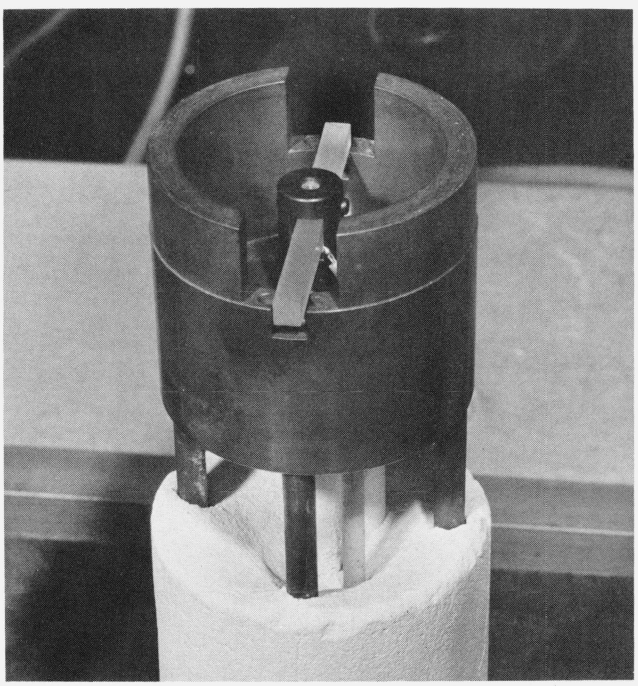

FIGURE 2. *The inconel sample holder showing glass bar and saddle.*
Note thermocouple next to glass bar.

An inconel saddle sitting on the glass specimen was used to apply the load and measure the deflection of the sample. The saddle has an inconel pin, 0.3 cm in diameter, which contacts the top surface of the sample and it reaches below the sample where a wire is attached. The wire extends below the furnace and provides a convenient means for applying the load. An indentation at the top of the saddle assembly provides a seat for a silica rod attached to the transducer element from the top section which measures the deflection of the sample. The separation of loading and deflection measuring devices in this instrument allows for a continuous measurement of the deflection rate during loadings and unloadings of the sample, thus yielding modulus and delayed elastic effect data.

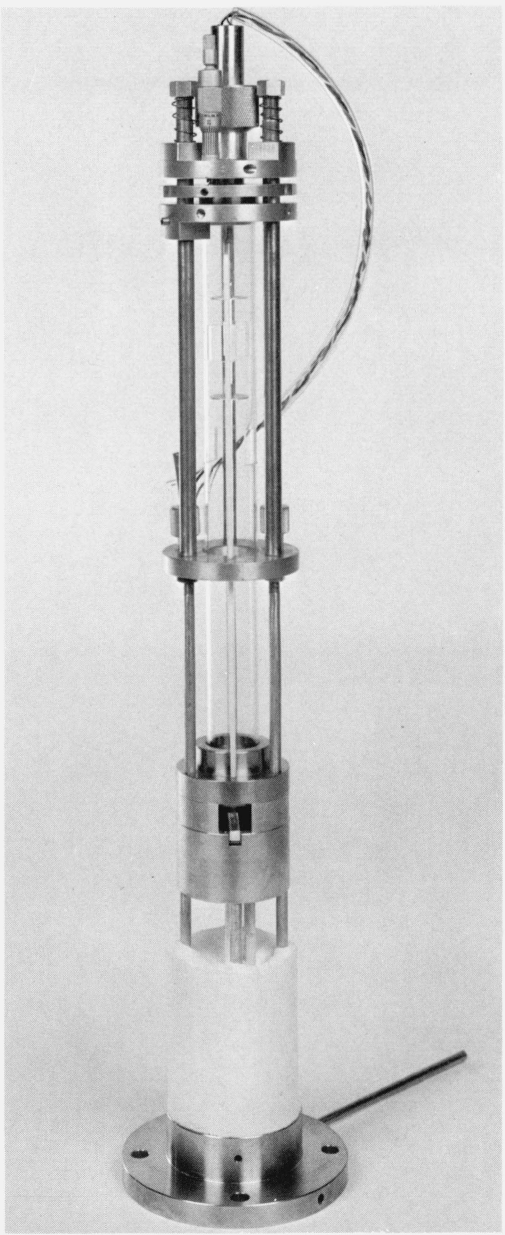

FIGURE 3. *Complete beam-bending apparatus without furnace.*

The top half of the instrument consists of two sections (e.g., the cover and measuring sections), figures 1 and 3. The lower part consists of an inconel cover which fits over the sample holder and sits close to the bar. Insulation above it reaches up to a water-cooled flange just above the furnace which prevents heating of the transducer element. Three brass rods serve to align the transducer support, but its vertical position is solely determined by the outer fused silica cyclinder. The transducer element is attached to a fused silica rod situated inside the cylinder and resting on the glass specimen by means of the saddle described above. This configuration reduces the thermal expansion correction to a negligible value during nonisothermal measurements. Springs at the top of the brass rods help seat the transducer holder firmly on the outer silica cyclinder.

The transducer is the linear deflection type with actual deflections of less than 0.6 cm measured in all of this work. The transducer element, as shown before, directly measures the bending of the center of the glass beam or specimen. The transducer output was 800 mv for each cm of travel and the rate of travel is calculated from a recorder trace. The temperature is controlled with a precision of $\pm$ 1/2 °C and is measured with a high sensitivity potentiometer (precision better than 0.1 °C).

The formula used for calculating viscosity by the beam-bending method is as follows:

$$\eta=\frac{gL^3}{2.4I_cV}\left(M+\frac{AL\rho}{1.6}\right) \tag{2}$$

where

η = viscosity (poises; $1P=10^{-1}$ Pa·s)
g = acceleration of gravity (cm/s^2)
L = support span (beam $= 5.715+[.92\times10^{-4}\times(T-20)]$; T = temp °C
I_c = cross-sectional moment of inertia (cm^4) generaly 1/12 b^4 for square cross-sections of side b. (See reference [7].)
V = rate of deflection (cm/min) of the midpoint of the beam
M = mass of applied load (g)
ρ = density of glass specimen (g/cm^3)
A = cross-sectional area of specimen (cm^2).

3. Measurement Uncertainties

In order to estimate the inherent uncertainties in the two methods for measuring viscosity, it is necessary to consider the equations relating the physical measurements to viscosity (eqs. (1) and (2)) and evaluate the accuracies of these measurements. In the fiber elongation measurement, we find the following relationship:

$$\frac{\Delta\eta}{\eta}=\frac{\Delta F}{F}+\frac{\Delta l}{l}-\frac{2\Delta r}{r}-\frac{\Delta\left(\frac{dl}{dt}\right)}{\left(\frac{dl}{dt}\right)} \tag{3}$$

where r represents the radius of the fiber. The beam-bending method yields:

$$\frac{\Delta\eta}{\eta} = \frac{\Delta F}{F} + \frac{3\Delta l}{l} - \frac{4\Delta b}{b} - \frac{\Delta v}{v} \qquad (4)$$

where the force $F = Mg$ and we ignore the small contribution from the second term in the bracket of eq (2).

Since the measurement uncertainties can be both positive and negative, all the terms are additive. The following estimates are used for each measurement:

$$\Delta F/F = 0.003$$
$$\Delta l/l = .02$$
$$\Delta b/b = .02$$
$$\Delta r/r = .02$$
$$\frac{\Delta(dl/dt)}{(dl/dt)} = \Delta v/v = \begin{cases} .05 \text{ per time interval} \\ .01 \text{ when averaged over several intervals.} \end{cases}$$

This yields an uncertainty of ± 4.5 percent in the fiber elongation measurement, and ± 10 percent in the beam-bending measurement. Therefore, because of limitations in the size and deflection rate measurements, the beam-bending method yields an appreciably larger uncertainty than the fiber elongation method. However, glasses which can easily lose alkali oxides or other components during the drawing process are best measured by the beam-bending method for which ground cast pieces provide suitable samples.

4. Results and Analysis

The viscosity results obtained by both the fiber elongation and beam-bending methods were fitted to the Fulcher equation. The merits of this equation have been discussed in previous papers [1–4].

Since the data only cover a small range of viscosities the Fulcher equation, due to its simplicity, provides the easiest interpolation formula. We will use it here to compare both methods of measurement. The Fulcher equation follows:

$$\log_{10}\eta = A + \frac{B}{T - T_0} \qquad (5)$$

where

η = viscosity (poises)
T = temperature °C
A, B, T_0 = constants.

The log viscosity results of each method are given in tables 1–6 and are compared with the combined data for each glass in figures 4–6. The constants for each solution are given in table 7. The standard deviations listed in table 7 support the error analysis of the data which indicates that the fiber elongation method gives results with less scatter than the beam-bending method. In general, the values are larger than the measurement uncertainties calculated in section 3, and this is due to a detectable systematic deviation of the data from the Fulcher equation and to some probable random operator variations in preparing the test.

TABLE 1. *Low-temperature viscosities of SRM 710 Glass by the fiber elongation method*

Temp. °C	Log η_{obs}	Log η_{calc}	Deviation	10^4/K
519.2	15.048 (265)*	14.976	−0.072	12.62
529.4	14.190 (50)	14.352	.162	12.46
538.4	13.804 (100)	13.839	.035	12.32
548.9	13.385 (65)	13.282	−.103	12.17
556.6	12.968 (18)	12.899	−.070	12.05
558.3	12.854 (16)	12.817	−.038	12.03
560.2	12.751 (16)	12.726	−.025	12.00
564.7	12.486 (16)	12.516	.030	11.94
565.7	12.480 (16)	12.470	−.010	11.92
569.4	12.311 (8)	12.304	−.007	11.87
571.6	12.203 (2)	12.206	.003	11.84
574.6	12.064 (1)	12.076	.012	11.80
575.8	12.000 (1)	12.024	.024	11.78
580.4	11.804 (0.5)	11.831	.026	11.72
585.2	11.645	11.634	−.011	11.65
590.0	11.425	11.444	.019	11.59
600.1	11.066	11.060	−.006	11.45
603.2	10.904	10.947	.043	11.41
609.8	10.712	10.713	.001	11.33
618.7	10.436	10.411	−.025	11.21
626.5	10.144	10.159	.015	11.12
628.4	10.067	10.099	.032	11.09
633.9	9.918	9.929	.011	11.03
639.6	9.734	9.758	.024	10.96
648.0	9.586	9.515	−.071	10.86

*Numbers within parenthesis denote hours the fiber was held at indicated temperature before viscosity measurements were made.

TABLE 2. *Low-temperature viscosities of SRM 710 Glass by the beam-bending method*

Temp. °C	Log η_{obs}	Log η_{calc}	Deviation	10^4/K
510.8	15.341 (85)*	15.380	0.039	12.76
518.5	14.989 (15)	14.895	−.094	12.63
525.3	14.453 (63)	14.490	.037	12.53
536.1	13.830 (21)	13.885	.055	12.36
540.4	13.633 (15)	13.656	.023	12.29
548.0	13.298 (2.5)	12.268	−.030	12.18
554.9	12.954 (5)	12.933	−.021	12.08
562.8	12.576 (2)	12.566	−.010	11.96
563.0	12.573 (2)	12.557	−.016	11.96
569.5	12.252 (1)	12.270	.018	11.87
579.8	11.850	11.837	−.013	11.73
589.5	11.511	11.454	−.057	11.59
595.6	11.225	11.223	−.002	11.51
600.0	11.139	11.062	−.077	11.45
610.0	10.591	10.710	.119	11.33
619.9	10.261	10.380	.119	11.20
629.4	10.057	10.080	.023	11.08
640.0	9.871	9.762	−.109	10.95
660.0	9.211	9.206	−.005	10.72

*Numbers within parenthesis denote hours the beam was held at indicated temperature before viscosity measurements were made.

TABLE 3. *Low temperature viscosities of SRM 711 Glass by the fiber elongation method*

Temp. °C	Log η_{obs}	Log η_{calc}	Deviation	10^4/K
396.3	15.321 (335)*	15.341	0.020	14.94
411.1	14.451 (90)	14.464	.013	14.62
414.5	14.299 (260)	14.275	−.024	14.55
420.7	13.927 (65)	13.940	.013	14.42
422.3	13.869 (210)	13.855	−.014	14.38
431.5	13.429 (20)	13.387	−.042	14.19
441.3	12.902 (4)	12.916	.014	14.00
441.9	12.911 (4)	12.889	−.022	13.99
451.4	12.441 (2)	12.460	.019	13.80
456.0	12.280 (1)	12.261	−.019	13.72
460.7	12.042 (1)	12.062	.020	13.63
466.2	11.856	11.837	−.019	13.53
470.1	11.631	11.681	.050	13.46
475.3	11.509	11.479	−.030	13.36
482.2	11.202	11.219	.017	13.24
488.2	10.987	11.001	.014	13.14
491.3	10.864	10.891	.027	13.08
492.8	10.840	10.839	−.001	13.06
495.4	10.720	10.748	.028	13.01
501.5	10.565	10.541	−.024	12.91
506.5	10.399	10.376	−.023	12.83
511.9	10.204	10.203	−.001	12.74
516.9	10.065	10.046	−.019	12.66
521.9	9.897	9.893	−.004	12.58
526.7	9.727	9.750	.023	12.50
535.7	9.506	9.490	−.016	12.37

*Numbers within parenthesis denote hours the fiber was held at indicated temperature before viscosity measurements were made.

TABLE 4. *Low temperature viscosities of SRM 711 Glass by the beam-bending method*

Temp. °C	Log η_{obs}	Log η_{calc}	Deviation	10^4/K
398.0	15.118 (110)*	15.161	0.043	14.90
408.3	14.612 (20)	14.582	−.030	14.68
420.8	13.951 (20)	13.923	−.028	14.41
430.2	13.462 (6)	13.456	−.006	14.22
434.3	13.244 (1)	13.260	.016	14.14
441.6	12.912 (1)	12.921	.009	13.99
448.8	12.607 (1)	12.598	−.009	13.85
452.9	12.510 (1)	12.420	−.090	13.78
458.1	12.144 (1)	12.199	.055	13.69
475.3	11.570	11.508	−.062	13.36
479.6	11.235	11.343	.108	13.29
494.9	10.781	10.785	.004	13.02
502.0	10.481	10.539	.058	12.90
502.0	10.588	10.539	−.049	12.90
503.0	10.425	10.505	.080	12.89
510.4	10.309	10.258	−.051	12.76
520.9	9.970	9.921	−.049	12.60

*Numbers within parenthesis denote hours the beam was held at indicated temperature before viscosity measurements were made.

TABLE 5. *Low temperature viscosities of SRM 717 Glass by the fiber elongation method*

Temp. °C	Log η_{obs}	Log η_{calc}	Deviation	10^4/K
470.9	15.236 (71)*	15.263	0.027	13.44
485.5	14.603 (47)	14.587	−.016	13.18
501.1	13.917 (70)	13.905	−.012	12.92
515.0	13.375 (19)	13.330	−.045	12.69
528.7	12.788 (2)	12.791	.003	12.47
539.5	12.360 (1)	12.384	.024	12.31
549.0	12.025	12.038	.013	12.17
555.2	11.756	11.818	.062	12.07
556.0	11.796	11.790	−.006	12.06
560.0	11.636	11.651	.015	12.00
564.0	11.523	11.514	−.009	11.95
564.4	11.517	11.500	−.017	11.94
568.6	11.404	11.359	−.045	11.88
574.4	11.168	11.166	−.002	11.80
577.6	11.075	11.061	−.014	11.76
580.8	10.982	10.958	−.024	11.71
580.9	10.970	10.954	−.016	11.71
585.5	10.795	10.807	.012	11.65
590.4	10.660	10.653	−.007	11.58
596.0	10.440	10.479	.039	11.51
600.2	10.309	10.351	.042	11.45
600.4	10.318	10.345	.027	11.45
605.0	10.209	10.207	−.002	11.39
610.8	10.028	10.035	.007	11.31
614.9	9.932	9.916	−.016	11.26
620.7	9.792	9.749	−.043	11.19

*Numbers within parenthesis denote hours the fiber was held at indicated temperature before viscosity measurements were made.

TABLE 6. *Low temperature viscosities of SRM 717 Glass by the beam-bending method*

Temp. °C	Log η_{obs}	Log η_{calc}	Deviation	10^4/K
460.0	15.752 (138)*	15.799	.047	13.64
482.6	14.733 (38)	14.713	−.020	13.23
490.8	14.368 (15)	14.345	−.023	13.09
501.7	13.993 (15)	13.873	−.120	12.91
508.0	13.606 (3)	13.610	.004	12.80
517.7	13.162 (1)	13.218	.056	12.65
526.6	12.849 (0.5)	12.871	.022	12.51
542.0	12.308 (0.5)	12.297	−.011	12.27
544.3	12.221 (1.5)	12.214	−.007	12.24
550.7	11.941	11.987	.046	12.14
555.2	11.769	11.831	.062	12.07
563.1	11.528	11.563	.035	11.96
573.4	11.288	11.224	−.064	11.81
575.0	11.179	11.172	−.007	11.79
585.1	10.822	10.854	.032	11.65
591.0	10.682	10.673	−.009	11.57
594.3	10.605	10.573	−.032	11.53
613.3	10.105	10.020	−.085	11.28
615.3	9.943	9.964	.021	11.26
616.5	9.896	9.931	.035	11.24
618.1	9.868	9.886	.018	11.22

*Numbers within parenthesis denote hours the beam was held at indicated temperature before viscosity measurements were made.

TABLE 7. *Fulcher equation constants from the data obtained by each method*

	A	*B*	T_0	St'd. Dev. of Log η
SRM 710–F	−1.388	4208	262.0	0.051
SRM 710–B	−1.716	4513	246.8	.062
SRM 710–FB	−2.008	4669	242.9	.060
SRM 711–F	−2.588	5160	108.5	.023
SRM 711–B	−4.688	6801	55.3	.055
SRM 711–FB	−3.360	5740	88.8	.041
SRM 717–F	−9.049	12417	−39.8	.027
SRM 717–B	−7.112	10414	5.5	.047
SRM 717–FB	−7.936	11224	−12.9	.040

F—fiber elongation method.
B—beam-bending method.
FB—both methods combined.

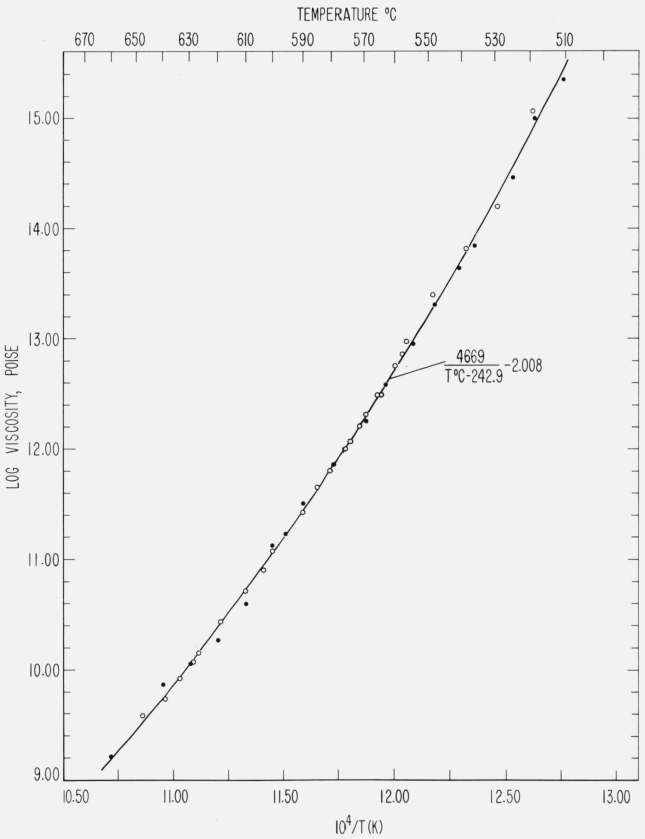

FIGURE 4. *The log viscosities obtained by each method for SRM 710 compared to the equation representing the combined data from both methods.*
○—fiber elongation method, and ●—beam-bending method.

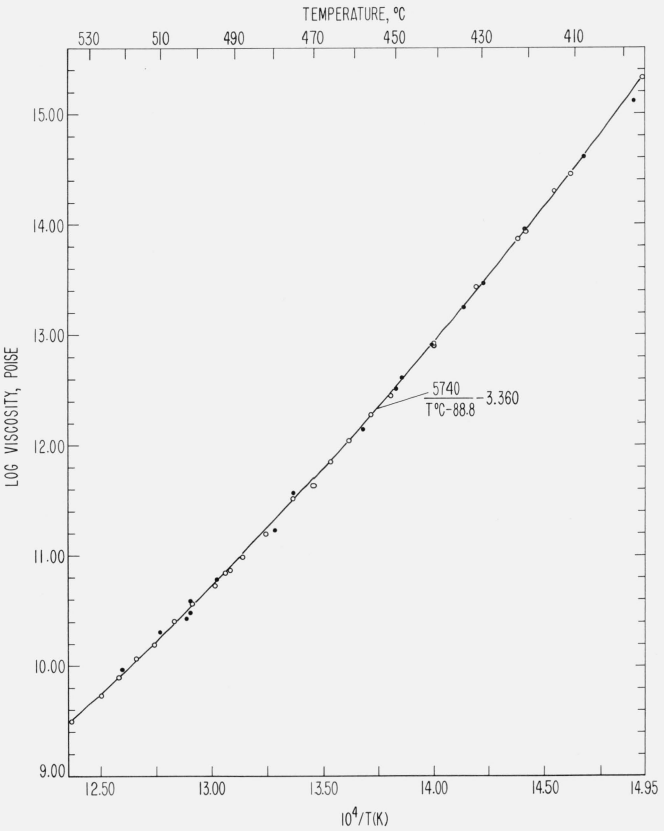

FIGURE 5. *The log viscosities obtained by each method for SRM 711 compared to the equation representing the combined data from both methods.*
○—fiber elongation method, and ●—beam-bending method.

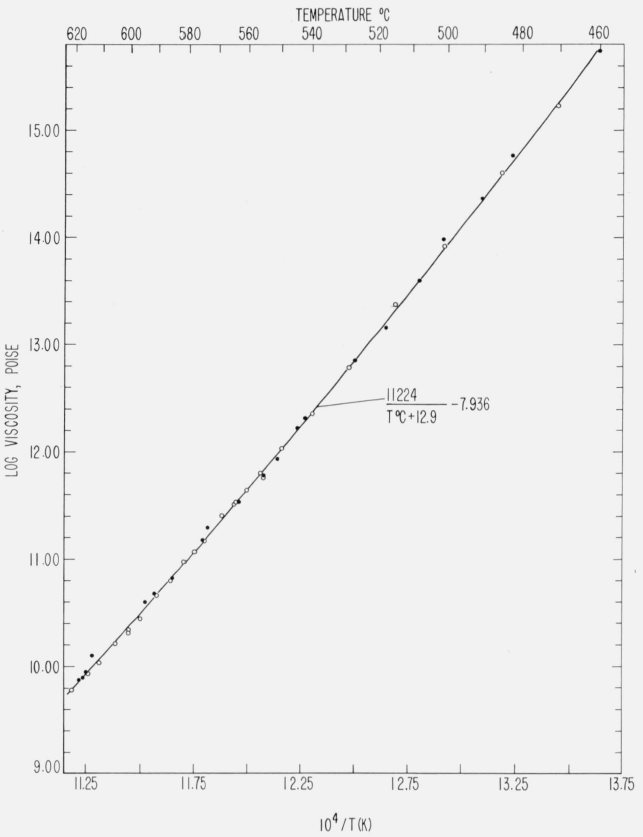

FIGURE 6. *The log viscosities obtained by each method for SRM 717 compared to the equation representing the combined data from both methods.*

○—fiber elongation method, and ●—beam-bending method.

5. Summary

The viscosity of three standard glasses were measured at the lower temperatures (corresponding to the range 10^9 to 10^{15} P) by the fiber elongation and beam-bending methods.

The beam-bending apparatus was built with major modifications to previously existing equipment and used for studies in the measurement of viscosity at low temperatures.

The results of each method were compared to each other and to the combined data of both methods. It was shown that the scatter in viscosity data was less with the fiber elongation method than with the beam-bending method.

Using the Fulcher equation to analyze the data, no Arrhenius behavior was found for each of the three glasses over a temperature range of 150 °C (see figs. 4–6). This corresponds to viscosities ranging from $10^{9.5}$ to about 10^{16} P.

6. References

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