NBS SPECIAL PUBLICATION **260-23**

Standard Reference Materials:

VISCOSITY OF A STANDARD
BOROSILICATE GLASS

Standard Reference Materials:

Viscosity of a Standard Borosilicate Glass

(Certification of Standard Reference Material 717)

A. Napolitano and E. G. Hawkins

Institute for Materials Research
National Bureau of Standards
Washington, D.C.   20234

Viscosity of a Standard Borosilicate Glass

A. Napolitano and E. G. Hawkins

The viscosity of a borosilicate glass has been measured at the National Bureau of Standards and four other laboratories. Determinations were made in the range 10^2 to 10^{14} poises (1525 to 470 °C). Measurements were made by the rotating cylinder, fiber elongation, beam bending, and parallel-plate methods. The results have been evaluated and the glass has been issued as Standard Reference Material No. 717.

Key words: Beam-bending; borosilicate glass; glass viscosity; parallel-plate; rotating cylinder; standard reference material; viscosity; viscosity standard.

1. Introduction

In a continuing program of establishing well-characterized glasses as standard reference materials, a borosilicate glass has been selected and promoted as a third viscosity standard. This glass is also a type of glass that is usually produced commercially in large quantities, can be manufactured in homogenous lots, and is stable in storage. In addition to its good optical quality, (i.e., free from severe cord, gas bubbles, stones, etc.) it has a low expansion and seals to Kovar[1] metal. Its transformation point is rather low and its expansion closely matches that of the Kovar metal from its strain point to room temperature.

This report gives the results of the viscosity measurements made at NBS and four laboratories[2] that participated in a "round robin" series of measurements. The data have been analyzed and tabulated in a "Certificate of Viscosity Values" and the glass has been issued as Standard Reference Material No. 717.

2. Glass Sample

Following the procedure used with the two previous standard reference glasses, No. 710 (soda-lime-silica) [1][3] and No. 711 (lead-silica) [2], a large quantity of borosilicate glass with the highest possible homogeneity was purchased. The lot consisted of about 545 kgs of glass in the form of strips having a cross section of 4.2 cm by 4.2 cm and 60 cm long with a few strips 45 cm long. All strips were numbered consecutively to show the sequence of production and also marked with the hour of delivery from the glass tank. There were several breaks in the continuous process where glass was discarded by the manufacturer, figure 1, because of striae, deviations from the target index, die marks, surface imperfections, or breakage.

Before delivery of the glass the manufactuer used 136 kg of the strip glass to form rods 0.6 cm by 0.6 cm and about 100 cm long by a reheating and drawing process. The weight lost in this drawing process was 86 kg. The remaining 50 kg of glass in rod shape was equivalent to approximately 650 lengths of 91.4 cm.

The homogeneity of the glass was checked by measuring the index of refraction (N_D-line) [1] on small samples of glass taken from each strip or every 2.5 kg of glass. Sampling of the rod shaped glass was about

[3] Figures in brackets indicate the literature references at the end of this publication.
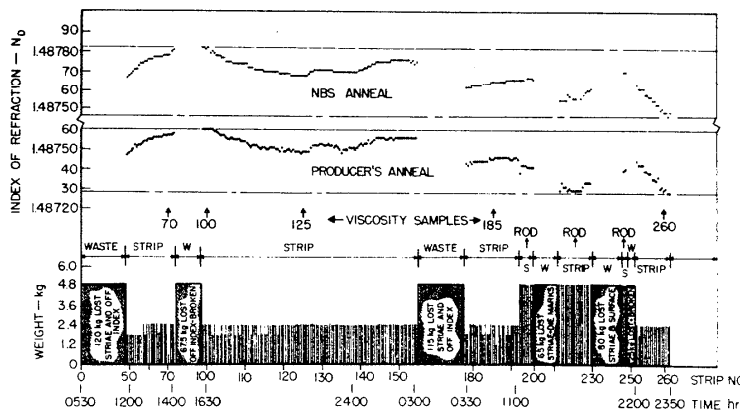

FIGURE 1. *Index variation and production history of Standard Glass No. 717.*

1

Table 1. *Viscosities of five samples of glass selected from the total lot of glass No. 717 (see fig. 1)*

Strip No. 70		Strip No. 100		Strip No. 125		Strip No. 85		Strip No. 260	
Temp, °C	$\log_{10}\eta_{obs}$	Temp, °C	$\log_{10}\eta_{obs}$	Temp, °C	$\log_{10}\eta_{obs}$	Temp, °C	$\log_{10}\eta_{obs}$	Temp, °C	$\log_{10}\eta_{obs}$
Test Method: Fiber Elongation									
485.5*	14.603	515.0*	13.375	470.9*	15.236	539.5*	12.360	528.7*	12.788
568.6	11.404	549.0	12.024	501.1*	13.917	556.0	11.796	555.2	11.756
580.9	10.970	564.4	11.517	560.0	11.636	574.4	11.168	564.0	11.523
600.4	10.318	577.6	11.075	580.8	10.982	590.4	10.660	585.5	10.795
614.9	9.932	610.8	10.028	600.2	10.309	596.0	10.440	605.0	10.209
						620.7	9.792		
Test Method: Rotating Cylinder									
636.6	9.380	599.3	10.414	607.0	10.148	613.4	9.995	628.7	9.573
643.2	9.193	600.8	10.261	619.5	9.798	710.9	7.812	709.0	7.847
681.0	8.333	652.0	9.015	709.3	7.820	798.6	6.442	806.4	6.342
749.8	7.091	704.3	7.925	781.7	6.665	901.8	5.254	904.7	5.223
835.8	5.937	725.9	7.534	810.9	6.272	1010.7	4.332	1003.2	4.393
893.4	5.317	763.7	6.932	908.2	5.183	1104.3	3.736	1103.5	3.739
914.4	5.138	804.5	6.354	929.9	4.991	1196.0	3.250	1220.7	3.132
1078.9	3.846	858.8	5.690	996.2	4.446	1302.6	2.795	1320.3	2.732
1177.5	3.314	909.8	5.155	1027.0	4.214	1400.1	2.460	1393.3	2.487
1283.5	2.850	935.0	4.949	1095.0	3.773				
1359.6	2.569	983.2	4.534	1129.6	3.590				
		1051.0	4.032	1195.3	3.243				
		1144.2	3.513	1227.7	3.102				
		1250.4	2.975	1294.7	2.818				
		1300.3	2.813	1320.7	2.727				
		1333.7	2.690	1377.0	2.529				
		1401.2	2.455	1408.9	2.428				

* Times held at indicated temperature before viscosity measurements were made are as follows:
485.5, 47 hr; 515.0, 19 hr; 470.9, 71 hr; 501.1, 70 hr; 539.5, 1 hr; and 528.7, 2 hr.

every 1 kg of glass. The index of refraction was measured before (as received) and after they had all been given the same heat-treatment (annealing). The results of these measurements are shown in figure 1.

With the producer's anneal the index of refraction for the total lot ranged from 1.48728 to 1.48760, a change of 0.00032. Closer examination reveals that about 80 percent of the glass in the lot ranges from 1.48740 to 1.48760, a change of 0.00020. The NBS anneal gave comparable results: the index of refraction for the lot ranging from 1.48748 to 1.48782, a change of 0.00034; and 80 percent of the lot ranging from 1.48762 to 1.48782, a change of 0.00020.

It has been shown that such a variation in index for glass in this quantity [1, 2] denotes minimum composition changes and is within acceptable tolerances for the proposed physical property standard of viscosity. It is well known that the uniformity of index is not necessarily a unique indicator of uniformity of composition. In a continuous production of a quantity of glass in strip form such as this, where no deliberate changes are made in the batch composition, it is unlikely that a significant change in composition would not be reflected by a concurrent change in index. In this case, figure 1, the index of refraction does decrease slightly at the end of the

production run showing possible composition changes. It will be shown later that these changes had no measurable effects on the viscosity of the glass selected from this area.

The nominal chemical composition[4] for this glass is as follows:

SiO_2 —70 percent
B_2O_3—17
K_2O —8
Na_2O —1
Al_2O_3 —3
Li_2O —1

3. Apparatus and Method of Measurement

3.1. Laboratory A

The measurement of viscosity at the National Bureau of Standards was made by the rotating concentric cylinder and fiber elongation methods. The equipment for these measurements has been described in detail in previous papers [1, 3].

[4] This glass is not intended as a standard for chemical analysis. The above composition is offered only for information purposes.

TABLE 2. *Fulcher equation constants for five samples of glass measured by Laboratory A (NBS)*

Strip No.	A	B	T_0	σ
70	−1.491	4680.33	205.2	0.017
100	−1.576	4831.33	194.9	.029
125	−1.542	4787.73	197.3	.017
185	−1.583	4849.19	194.0	.018
260	−1.618	4907.03	189.9	.025
Combined	−1.562	4811.83	196.1	.023

TABLE 3. *Comparison of temperatures corresponding to nominal viscosities calculated from Fulcher equation parameters for each of the five samples*

	Temperature, °C					
$Log_{10}\eta$	S-70	S-100	S-125	S-185	S-260	Comb.
2.25	1456.4	1457.8	1459.9	1459.2	1458.4	1458.4
2.50	1378.0	1380.3	1381.8	1381.7	1381.4	1380.7
2.75	1308.9	1311.8	1312.8	1313.2	1313.2	1312.0
3.00	1247.4	1250.8	1251.4	1252.1	1252.4	1250.9
3.50	1143.0	1146.8	1146.9	1148.0	1148.6	1146.7
4.00	1057.6	1061.4	1061.2	1062.6	1063.3	1061.3
4.50	986.5	990.1	989.7	991.2	991.9	989.9
5.00	926.3	929.6	929.2	930.6	931.3	929.4
5.50	874.7	877.7	877.2	878.6	879.2	877.5
6.00	830.0	832.7	832.1	833.5	834.0	832.5
6.50	790.9	793.2	792.7	793.9	794.3	793.0
7.00	756.4	758.3	757.8	759.0	759.3	758.1
7.50	725.7	727.3	726.8	727.9	728.0	727.1
8.00	698.3	699.5	699.1	700.0	700.1	699.4
8.50	673.6	674.4	674.1	674.9	674.8	674.4
9.00	651.3	651.8	651.5	652.2	652.0	651.7
9.50	631.0	631.1	630.9	631.5	631.2	631.1
10.00	612.5	612.3	612.1	612.6	612.2	612.3
10.50	595.5	595.0	594.9	595.3	594.8	595.1
11.00	579.9	579.1	579.1	579.4	578.8	579.2
11.50	565.5	564.4	564.4	564.6	563.9	564.5
12.00	552.1	550.8	550.9	551.0	550.2	550.9

3.2. Other Participating Laboratories

The four other participating laboratories also made viscosity determinations at high temperatures (725–1525 °C) by the rotating concentric cylinder method. The techniques and modifications used by each laboratory have been described previously [1, 2].

In the low-temperature region (495–850 °C) Laboratory C made extensive viscosity measurements by the beam-bending [4] and parallel-plate methods [5]. The beam-bending data were determined at equilibrium temperatures and also at heating and cooling rates of 5°/min. The parallel-plate data were determined only for 5°/min. heating rate (630–850 °C).

All laboratories made the softening, annealing, and strain point determinations using the ASTM Methods of Test [6, 7].

4. Results

4.1. Viscosity Measurements Made at NBS (Laboratory A)

In assuming that the index changes throughout the lot are due to slight unintentional changes in composition, five samples of glass were selected from the lot for viscosity measurements by laboratory A, figure 1. Two samples were selected from the region of the highest index, strips No. 70 and No. 100; one from the region of the lowest index, strip No. 260; and, two in the intermediate range, strips No. 125 and No. 185. The results of the viscosity measurements on the five samples selected from the lot are given in table 1.

The data from both the low-temperature fiber elongation method and the high-temperature rotating concentric cylinder method for each of the five glasses were combined and fitted to the Fulcher equation [8] by the method of least squares combined with the Gauss-Newton iterative method. [9]

The Fulcher equation has the form:

$$Log_{10}\eta = A + B/(T - T_0) \qquad (1)$$

where

T = temperature in °C
η = viscosity in poises

and A, B, and T_0 = constants.

The constants A, B and T_0 for each of the five glasses and also for the five samples combined are given in table 2. Only data up to $\log_{10}$ 12 and under equilibrium conditions were used to determine these parameters.

Using the constants derived for each glass, temperatures for nominal values of $\log_{10}$ viscosity were calculated, and are given in table 3. The results of these calculations show that the temperatures for strip No. 70 are slightly lower for the same $\log_{10}$ viscosity values at the higher temperatures when compared to the remaining four glasses. The last column of table 3 gives the temperatures calculated from the combined equation derived from the data of all five glasses.

4.2. Viscosity Measurements Made at Participating Laboratories

The results received from each laboratory are given in tables 4, 5A, 5B, 5C, and 6. Since the four participating laboratories all used the rotating cylinder method at the higher temperatures these results are given in table 4. Only Laboratory C besides NBS made measurements at the lower temperatures, i.e., below the softening temperature. These data are given in tables 5A, 5B, 5C and 6. The data from each laboratory was treated in the

3

TABLE 4. *High-temperature viscosities of Glass No. 717 from participating laboratories*

Rotating Cylinder

Laboratory B		Laboratory C		Laboratory D		Laboratory E	
Temp, °C	Log$_{10}\eta_{obs}$	Temp, °C	Log$_{10}\eta_{obs}$	Temp, °C	Log$_{10}\eta_{obs}$	Temp, °C	Log$_{10}\eta_{obs}$
1475.5	2.241	1375.0	2.535	1521	2.10	1332	2.674
1447.2	2.337	1319.9	2.710	1499	2.15	1250	3.038
1411.1	2.455	1293.5	2.820	1479	2.20	1180	3.314
1376.7	2.563	1259.4	2.944	1441	2.30	1107	3.724
1344.4	2.623	1221.4	3.133	1406	2.40	1071	3.934
1308.9	2.750	1183.5	3.288	1377	2.50	997	4.458
1281.7	2.854	1144.4	3.491	1343	2.60	934	4.950
1248.3	2.981	1104.6	3.704	1318	2.70	876	5.509
1219.4	3.107	1068.6	3.928	1291	2.80		
1176.1	3.314	1021.5	4.238	1267	2.90		
1143.9	3.476	988.2	4.484	1243	3.00		
1115.5	3.630	956.2	4.745	1221	3.10		
1080.0	3.834	918.5	5.069	1197	3.20		
1035.0	4.073	889.8	5.344	1176	3.30		
1008.3	4.317	847.6	5.766	1154	3.40		
978.9	4.536	817.9	6.145	1135	3.50		
945.5	4.823	790.1	6.522	1117	3.60		
909.4	5.143	724.7	7.501	1102	3.70		
879.4	5.435			1088	3.80		
				1074	3.90		
				1060	4.00		

TABLE 5A. *Log viscosities of SRM 717 by the beam-bending method (5 °C/min heating rate)*

Temp, °C	← Log$_{10}\eta_{obs}$ →		Temp, °C	← Log$_{10}\eta_{obs}$ →	
	Run 1	Run 2		Run 3	Run 4
493	13.805		553	11.604	
503	13.580	13.677	558	11.316	
508	13.410	13.500	563	11.207	
513	13.220	13.220	568	11.104	
518	13.033	13.045	573	10.962	
523	12.828	12.892	578	10.847	
528	12.631	12.702	583	10.723	10.688
533	12.452	12.491	588	10.545	10.587
538	12.238	12.283	593	10.394	10.431
543	12.033		598	10.301	10.316
548	11.812		603	10.217	10.162
553	11.742		608	10.124	10.068
			613	10.021	9.932
			618	9.870	9.836
			623	9.765	9.723
			628	9.641	9.610
			633	9.524	9.522
			638	9.336	9.442
			643		9.356
			648		9.243
			653		9.149
			658		9.037
			663		8.883
			668		8.775
			673		8.657

TABLE 5B. *Log viscosities of SRM 717 by the beam-bending method (5 °C/min cooling rate)*

Temp, °C	← Log$_{10}\eta_{obs}$ →			
	Run 1	Run 2	Run 3	Run 4
557		11.669		
552	11.874	11.852		
547	12.107	12.079		11.939
542	12.312	12.253		12.164
537	12.509	12.471		12.401
532	12.693	12.632	12.547	12.583
527	12.870	12.848	12.754	12.769
522	13.045	13.025	12.931	12.926
517	13.220	13.161	13.114	13.114
512	13.389	13.334	13.294	13.290
507	13.496	13.490	13.430	13.455
502	13.634	13.606	13.628	13.623
497	13.841	13.782	13.846	13.788

TABLE 5C. *Log viscosities of SRM 717 by the beam-bending method (equilibrium conditions)*

Temp, °C	Log$_{10}\eta_{obs}$
546.5	12.037
533.5	12.500
525.5	12.840
514.0	13.248
504.5	13.621
495.0	14.134

TABLE 6. *Log viscosities of SRM 717 by the parallel plate method (5 °C/min heating rate)*

Temp, °C	Log$_{10}\eta_{obs}$
630	9.447
640	9.241
650	9.013
660	8.764
670	8.545
680	9.310
690	8.064
700	7.847
710	7.652
720	7.483
730	7.356
740	7.204
750	7.068
760	6.916
770	6.814
780	6.703
790	6.594
800	6.446
810	6.299
820	6.233
830	6.146
840	5.961
850	5.859

TABLE 8. *Comparison of log$_{10}$ viscosity versus temperatures data from each participating laboratory*

Log$_{10}$ Viscosity, Poise*	Temperature, °C					Value from combined equation
	Laboratories					
	A	B	C	D	E	
2.00						1545.1
2.10				1519.9		1508.2
2.25	1458.4	1476.5		1461.1		1456.4
2.50	1380.7	1388.5	1378.2	1375.7	1384.0	1378.7
2.75	1312.0	1312.8	1309.4	1303.1	1314.7	1310.0
3.00	1250.9	1247.0	1248.2	1240.4	1252.9	1248.8
3.50	1146.7	1138.3	1143.9	1138.0	1147.9	1144.7
4.00	1061.3	1052.0	1058.4	1057.8	1061.9	1059.4
4.50	989.9	981.9	986.9		990.1	988.2
5.00	929.4	923.9	926.4		929.4	927.9
5.50	877.5	875.0	874.4		877.3	876.1
6.00	832.5		829.4			831.2
6.50	793.0		789.9			791.8
7.00	758.1		755.0			757.1
7.50	727.1		723.9			726.2
8.00	699.4		696.1			698.6
8.50	674.4		671.1			673.7
9.00	651.7		648.5			651.1
9.50	631.1		627.9			630.7
10.00	612.3		609.0			611.9
10.50	595.1		591.8			594.8
11.00	579.2		575.9			579.0
11.50	564.5		561.2			564.4
12.00	550.9		547.6			550.9

* One poise is 1 g/cm s, which is equal to 0.1 kg/m s.

TABLE 7. *Fulcher equation constants from the data submitted by each laboratory*

Laboratory	Range, °C	A	B	T$_0$	σ
A	550–1410	−1.562	4811.83	196.1	0.023
B	880–1475	−0.827	3603.35	305.6	.018
C	550–1375	−1.561	4814.88	192.6	.013
D	1060–1520	−0.612	3042.68	398.1	.011
E	875–1330	−1.528	4781.47	196.9	.017
Combined A–E	550–1520	−1.546	4775.14	198.3	.029

same manner as that for Laboratory A. In the case of Laboratory C only equilibrium data were used to solve for the best equation for that laboratory.

Using the constants derived from each laboratory's data, table 7, a comparison of temperatures for nominal values of log$_{10}$ viscosities are given in table 8. Calculations were made for each laboratory only in the temperature range in which the actual measurements were made. The data from all the laboratories was then combined and fitted to the Fulcher equation. This gave:
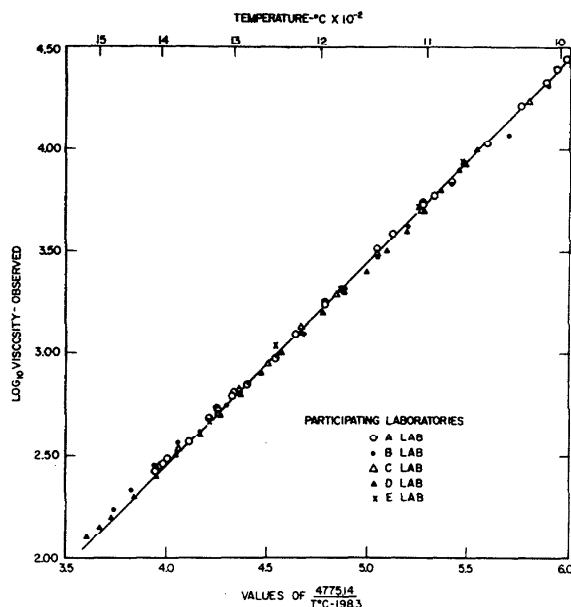
$$\log_{10}\eta = -1.546 + 4775.14/(T\ °C - 198.3) \qquad (2)$$

with a standard error in log$_{10}\eta$ = 0.029. Using eq (2), temperatures in the last column of table 8 were calculated for the specific log$_{10}$ viscosities.

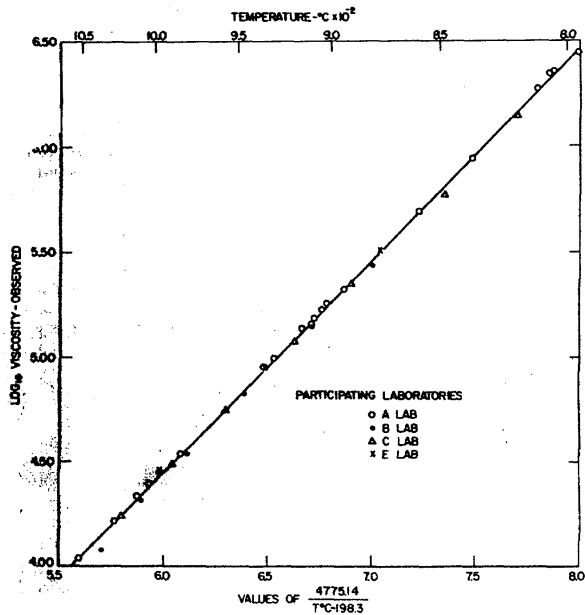FIGURE 2. *Observed values of log$_{10}$ viscosity plotted against the function of temperature $4775.14/T°C-198.3$ (1000–1520 °C).*

5

FIGURE 3. *Observed values of log_{10} viscosity plotted against the function of temperature $4775.14/T°C-198.3$ (800-1050 °C).*
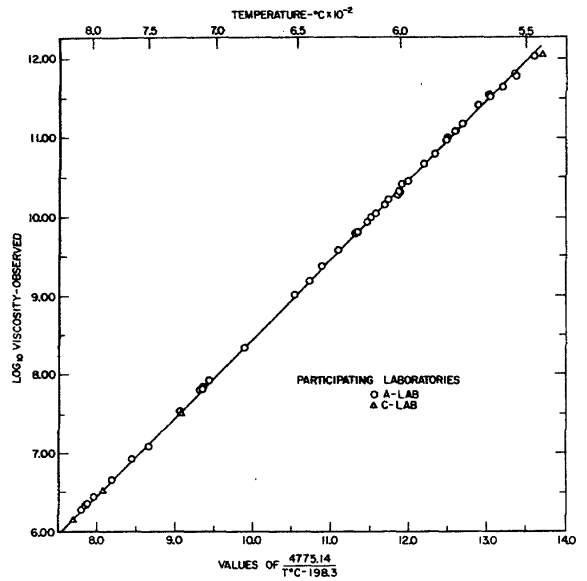
FIGURE 4. *Observed values of log_{10} viscosity plotted against the function of temperature $4775.14/T°C-198.3$ (550-800 °C).*
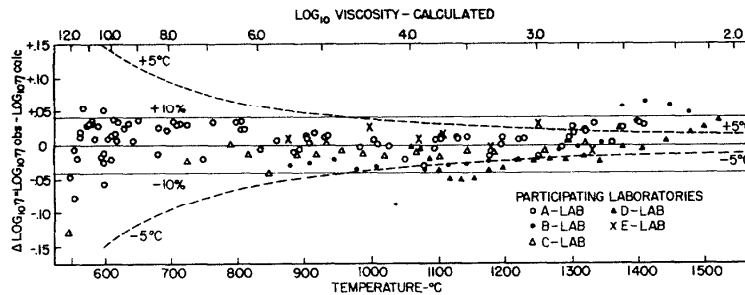

FIGURE 5. *Differences in observed and calculated log_{10} viscosities.*

0 line represents the final equation, eq (2).

The data from each laboratory has been plotted against the temperature function of the final equation in figures 2, 3, and 4 between the values log_{10} 2 and log_{10} 12 viscosity. The differences between the observed and calculated log_{10} viscosities frôm eq (2) have been plotted in figure 5 to indicate the magnitude of scatter. Most of the differences are within the arbitrary limits of ±5 °C and ±10 percent viscosity except those at the very high temperatures, 1400 to 1525 °C. This departure of the observed log_{10} viscosities at the high temperatures from the calculated values is partly due to the failure of the Fulcher equation in fitting low-temperature (high-viscosity) data [10].

The beam-bending data submitted by Laboratory C has been compared to the final equation (curve) in figures 6 and 7. In these plots the dashed part of the curve is an extrapolation of the calculated curve (log_{10} 2 to log_{10} 12 viscosity). A comparison of the fiber elongation and beam bending data under equilibrium conditions are shown in figure 8. Laboratory C also submitted viscosity data obtained by a new method, the parallel-plate viscometer, and this data is compared to the final curve in figure 9. The agreement is very good especially in view of the fact that none of this data was used to calculate the curve.
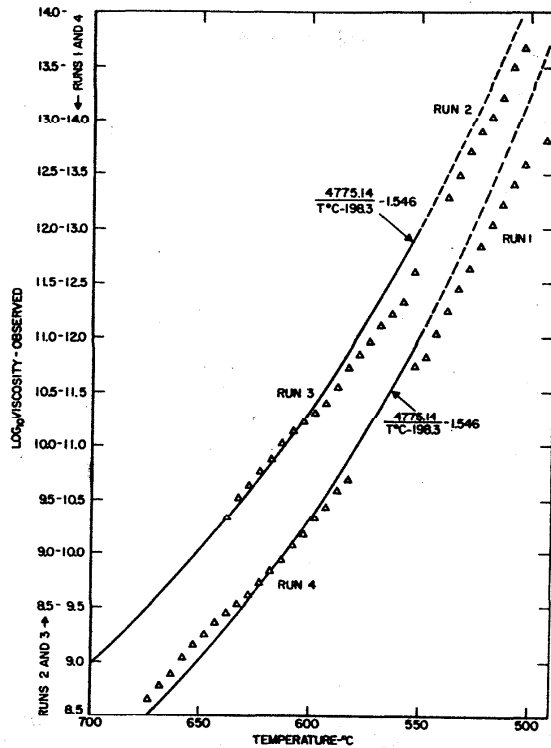
6

FIGURE 6. *Beam-bending data (5 °C/min heating rate) compared to the final equation, eq (2).*
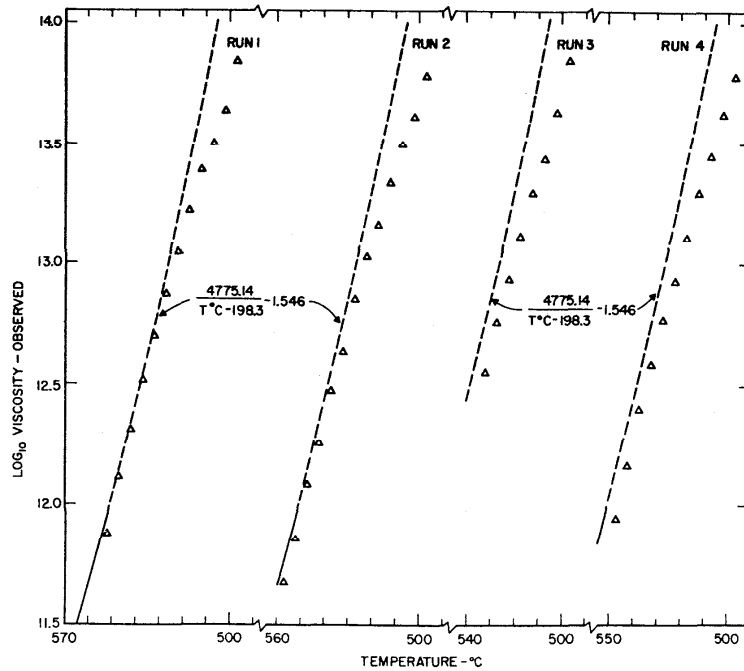
Dashed line is extrapolation of final equation.

TABLE 9. *Softening, annealing, and strain points of Standard Glass No. 717*

Temperature, °C

Laboratory	A	B	C	D	E	Average
Softening Point	723	722	717	721	716	720
Annealing point	517	516	516	515	515	516
Strain Point	469	472	466	466	473	471

4.3. Softening, Annealing, and Strain Points

The softening, annealing, and strain points were determined by all the participating laboratories and are given in table 9. The methods of test and definitions of these points are given in the ASTM Standards.

5. Summary

NBS has established a third Standard Reference Material for the viscosity of glass: No. 717 (Borosilicate).

Viscosity measurements have been made on this glass by five laboratories. The temperature range covered was 495 to 1525 °C. The rotating cylinder, fiber elongation, beam-bending, and parallel- late methods were used.
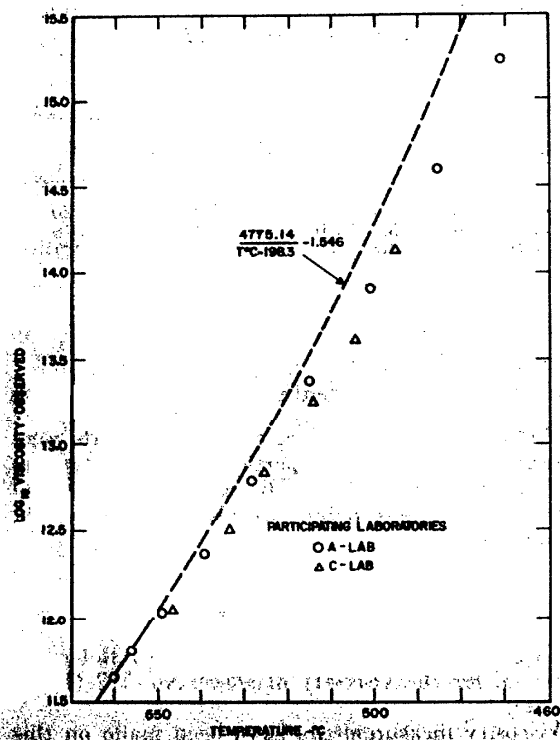

FIGURE 7. *Beam-bending data (5 °C/min cooling rate) compared to the final equation, eq (2).*

Dashed line is extrapolation of final equation.

Figure 8. *Comparison of equilibrium A-beam-bending and C-plate-rotation data to the final equation, eq (2).*
Dashed line is extrapolation of final equation.

Figure 9. *Data from parallel-plate method compared to final equation, eq (2).*

A viscosity temperature curve was determined from these measurements by fitting the data to the Fulcher equation by the method of least squares combined with the Gauss-Newton iterative method.

The softening, annealing, and strain points of this glass have been determined by five participating laboratories.

The authors wish to thank all the participating laboratories for their cooperation in making viscosity measurements on this glass. They also acknowledge the help received from Joseph H. Simmons for the computer calculations.

6. References

[1] Napolitano, A., and Hawkins, E. G., Viscosity of a standard soda-lime-silica glass, J. Res. Nat. Bur. Stand. (U.S.), 68A (Phys. & Chem.), No. 5, 439 (Sept.–Oct. 1964).
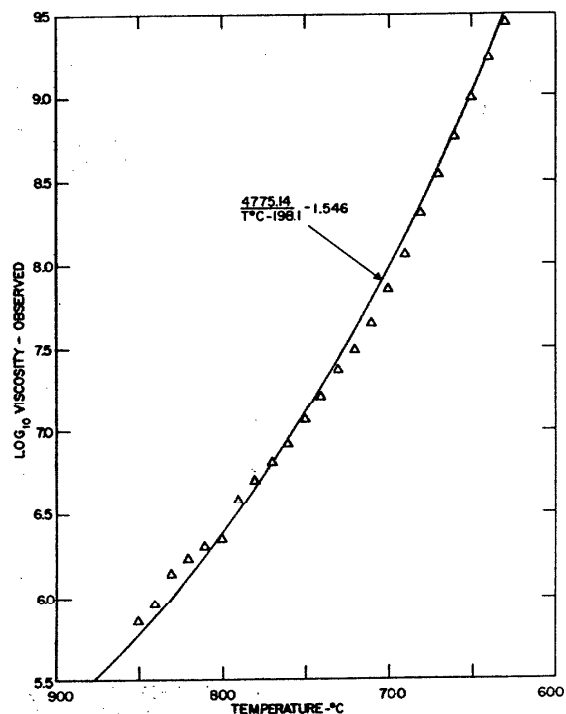
[2] Napolitano, A., and Hawkins, E. G., Viscosity of a standard lead-silica glass, Nat. Bur. Stand. (U.S.) Misc. Publ. 260–11, 1 (1966).

[3] Napolitano, A., Macedo, P. B., and Hawkins, E. G., A wide range (up to 10^{10} P) rotating cylinder viscometer, J. Res. Nat. Bur. Stand. (U.S.), 69A (Phys. & Chem.), No. 5, 449 (Sept.–Oct. 1965).

[4] Hagy, H. E., Experimental evaluation of beam-bending method of determining glass viscosities in the range 10^8 to 10^{15} poises, J. Am. Ceram. Soc. 46, No. 2, 93 (1963).

[5] Fontana, E. H., A versatile parallel-plate viscometer for glass viscosity measurements to 1000°C, Am. Ceram. Soc. Bull. 49, No. 6, 594 (1970).

[6] ASTM Standards, Softening Point of Glass ASTM Designation C338–57 (Reapproved 68) Part 13 (1970).

[7] ASTM Standards, Annealing Point and Strain Point of Glass, ASTM Designation C336–69 and ASTM Designation C598–67T, Part 13 (1970).

[8] Fulcher, G. S., Analysis of recent measurements of viscosity of glass, J. Am. Ceram. Soc. 8, No. 6, 339 (1925); 8, No. 12, 789 (1925).

[9] Macedo, P. B., Viscoelasticity of glasses, Mechanical and Thermal Properties of Ceramics, Nat. Bur. Stand. (U.S.), Spec. Publ. 303, 169 (1969).

[10] Macedo, P. B., and Napolitano, A., Inadequacies of viscosity theories for B_2O_3, J. Chem. Phys. 49, No. 4, 1887 (1968).

☆ U.S. GOVERNMENT PRINTING OFFICE: 1971 O—402-008