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(Continued)

Viscosity of silica

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Experimental measurements of the viscosity of silica (SiO_2) are critically examined; the best measurements show an activation energy of 515 kJ/mole above 1400 °C and 720 kJ/mole below this temperature. The diffusion of silicon and oxygen in silica have temperature dependencies close to that of the high temperature viscosity. Mechanisms of viscous flow and diffusion of silicon and oxygen in silica are proposed that involve motion of SiO molecules. Viscous flow is proposed to result from the motion of line defects composed of SiO molecules At temperatures below 1400 °C the fraction of SiO molecules in line defects changes with temperature. The relaxation of this fraction to an equilibrium value depends on the time. These proposed mechanisms are consistent with experimental measurements of silica viscosity. © *2002 American Institute of Physics.*
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I. INTRODUCTION

The viscosities of liquids and melts are among their most important properties. In glasses, viscosities determine melting conditions, temperatures of working and annealing, rate of removal of bubbles, maximum temperature of use, and crystallization rate. In geology magma behavior, volcanic eruptions, and lava flow rate depend directly on silicate viscosity.

Recently, there has been much interest in mass transport in glass-forming liquids near the glass transition temperature.[1–6] In these discussions the viscosity of silica (SiO_2) is usually considered as an example of a "strong" liquid in which the activation energy for viscous flow is constant. One purpose of this article is to provide a critical assessment of experimental data on the viscosity of silica. The conclusion is that there are two separate temperature regimes in the viscosity of silica in which the activation energy for flow is quite different. Another purpose of this article is to examine theories for the viscosities of network liquids like silica, and to present some new suggestions for models of flow of silica in the two different regimes of different activation energy.

This discussion contains the following sections: experimental measurements of the viscosity of silica; temperature dependence of viscosity; theories of viscosity; viscosity of silica; flow and a line defect; defect concentration; diffusion and viscosity; and conclusions.

II. EXPERIMENTAL MEASUREMENTS OF SILICA VISCOSITY

Experimental measurements of the viscosity of silica are given in Table I and Fig. 1. The measurements of Urbain *et al.*[7] were made over a wide temperature range (1192 −2482 °C) and are the values usually quoted. Their measurements for viscosities below 10^6 poise (10^5 Pa s) were made with a rotating cup; for higher viscosities they used a penetration method (isothermal deformation). All the measurements described in this article were on type I silica, which is made by melting highly pure crystalline quartz. The main impurity is aluminum, at about 10–50 ppm, which does not influence the viscosity much. Water (OH) is also present in small quantity (<10 ppm). The activation energy for viscous flow was constant throughout the measurement range at 515 kJ/mole in Urbain's results; the data given in Table II of Ref. 7 when plotted as log viscosity vs 1/T give a straight line with a correlation coefficient from linear regression of 0.999 78. The data in the table were apparently selected from more measurements, which are plotted in Fig. 1 of Ref. 7.

The measurements of Bowen and Taylor[8] at temperatures from 2085 to 2310 °C had about the same activation energy as those of Urbain *et al.* but were about an order of magnitude smaller. The measurements of Bruckner[9] from 1686 to 2006° also had about the same activation energy as those of Urbain *et al.*, but were about a factor of three higher. The measurements of Bacon *et al.*[10] from 1935 to 2322 °C agree reasonably well with those of Urbain *et al.*, but are quite scattered. Earlier measurements of Bockris *et al.*[11] from about 1920 to 2060 °C have about the same activation energy as those of Urbain *et al.* but are a factor of about ten smaller; the data of Solomon[12] from 1720 to 2000 °C showed a lower activation energy (about 373 kJ/mole) and are about a factor of ten smaller than those of Urbain *et al.* The author concludes that from 1400 to 2500 °C the viscosities of Urbain *et al.* are the most reliable, with an activation energy of 515 kJ/mole.

At temperatures from 1400 to 1000 °C Hetherington *et al.*[13] measured the viscosity of silica by a fiber elongation technique. These authors took special care to stabilize the silica in an "equilibrium" condition. They found that silica with different fictive temperatures had quite different measured viscosities at temperatures below 1400 °C; from their measurements the glass transition temperature (the temperature at which the viscosity is 10^{13} poise) was about 1185 °C

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TABLE I. Viscosity values for amorphous silica considered to be the most reliable.

Urbain *et al* (Ref. 7)		Hetherington *et al.* (Ref. 13)	
Temperature °C	log η η in poise	Temperature °C	log η η in poise
2482	3.53	1400	9.81
2382	3.92	1300	11.22
2268	4.36	1200	12.83
2168	4.80	1100	14.65
2061	5.25	1000	16.82
1964	5.79		
1870	6.36		
1776	6.90		
1652	7.79		
1599	8.08		
1438	9.48		
1375	9.97		
1306	10.95		
1250	11.40		
1192	12.15		

The fictive temperature is the temperature at which the properties of glass are the same as those of the melt in metastable equilibrium. Thus the fictive temperature is related to the rate at which a glass is cooled from above the glass transition temperature; the more rapid the cooling rate the higher the fictive temperature. The measured viscosity below about 1400 °C in silica increases or decreases with time to the value for metastable equilibrium at long time. Hetherington

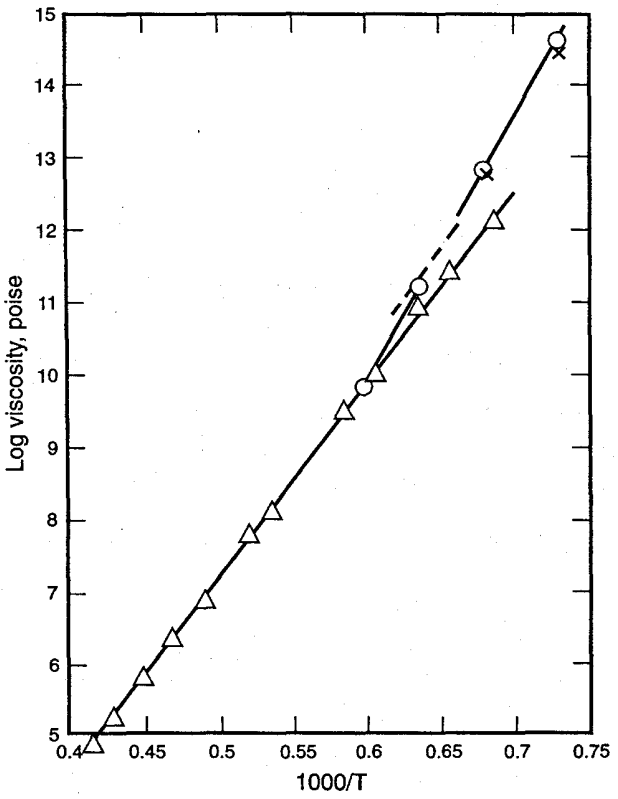

FIG. 1. Log viscosity of silica as a function of reciprocal temperature. (Δ) Urbain *et al.* (Ref. 7); (O) Hetherington *et al.* (Ref. 13); (---) Fontana and

TABLE II. Values of $\eta D/T$ for organic liquids data from Ref. 22

Benzene T °C	$D\eta/T\times10^9$	Pentane T °C	$D\eta/T\times10^9$	Cyclopentane T °C	$D/T\times10^9$
15	4.44	−60	4.58	0	4.19
25	4.44	−19.9	4.55	5	4.10
35	4.29	0	4.27	15	4.40
45	4.23	20	4.21	20	4.48
55	4.57	40	3.98	25	4.51
65	4.50	mean	4.32±0.25	30	4.57
mean	4.41±0.13			35	4.54
				45	4.18
				mean	4.37±19

et al. found an activation energy of about 712 kJ/mole for viscous flow of stabilized silica glass at temperatures between 1400 and 1100 °C, as shown in Fig. 1. At temperatures below about 1100 °C the time to stabilize the glass (reach metastable equilibrium) was longer than experimental times. Hetherington *et al.* found the same absolute value of viscosity as Urbain *et al.* at 1400 °C, but higher values than those of these authors at lower temperatures. The measurements of Fontana and Plummer[14] at temperatures from 1236 to 1335 °C by beam bending agree quite well with those of Hetherington *et al.* except below about 1280 °C, where the values of Fontana and Plummer become slightly higher (see Fig. 1). Viscosity measurements by beam bending at two temperatures by Kimura[15] agree closely with those of Hetherington *et al.* Measurements by Volarovich and Leontieva[16] from 1332 to 1436 °C showed an activation energy of 712 kJ/mole but were about a factor of three higher than those of Hetherington *et al.* Thus the measurements of four independent groups of investigators are consistent with an activation energy of about 712 kJ/mole at temperatures below 1400 °C. It is likely that the measurements of Urbain *et al.* in the temperature range from about 1187 to 1400 °C were made on glass with a fictive temperature higher than the measurement temperature, and were therefore not the viscosities of the glass at metastable equilibrium. Perhaps the penetration method used by these authors led to a rapid measurement, so that the glass was not at equilibrium; the details of the measurement methods are apparently only available in a thesis.

I conclude that the most reliable experimental measurements of the stable viscosity of silica are those of Urbain *et al.*[7] from 2500 to 1400 °C:

$$\eta = 5.8(10)^{-7}\exp(515\,400/RT), \tag{1}$$

and those of Hetherington *et al.*[13] from 1400 to 1000 °C:

$$\eta = 3.8(10)^{-13}\exp(712\,000/RT), \tag{2}$$

with viscosity in poise and activation energy in J/mole. Equation (1) extrapolates to $\log n = -6.24$ as T approaches infinity, somewhat lower than the values for some other liquids.[5]

The reasons for concluding that the measurements of Urbain *et al.* are the most reliable are: (1). The measured values of viscosity fit very well to the Arrhenius equation from 1400 to 2500 °C. (2). The measured values have the

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