Web Course
Physical Properties of Glass

1. Properties of Glass Melts
2. Thermal Properties of Glasses

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Melt and Glass Properties

- Viscosity- chapter 9
- Surface Tension- chapter 9
- Thermal Expansion- chapter 10
- Heat Capacity- chapter 11
- Thermal Conductivity- chapter 12

Supplementary References on Viscosity

- Structure, Dynamics and Properties of Silicate Melts, *Reviews in Mineralogy*, Vol. 32 (1995), ed. JF Stebbins, PF McMillan and DB Dingwell (Mineralogical Society of America)- *several outstanding reviews of viscosity, relaxation, etc*.
- CA Angell, *Science*, **267**, (1995), 1924- *concepts of melt fragility, configurational entropy, etc.*
- JH Simmons and C Simmons, *Cer Bull* 68[11] 1949 (1989)- *Non-Newtonian behavior*
- HE Hagy in Introduction to Glass Science, ed. LD Pye, et al Plenum Press (1972)- *nice review of viscosity measurements*

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Why should we care about melt viscosity?

1. Glass Forming Tendency
    a. Nucleation, crystallization, phase separation kinetics

$$I_V^{HO} = N_V^0\left(\frac{k\cdot T}{3\pi\cdot a_0{}^3\cdot\eta}\right)\exp\left[\frac{-K\cdot\sigma^3}{T\cdot\Delta G_v{}^2}\right]$$

2. Melt Fining

$$\text{Stoke's Law:}\quad V=\frac{d^2 g(\rho_b-\rho_l)}{12\eta}$$

3. Manufacturing Process Control

4. Annealing Schedules/Permanent Stress

5. What else??

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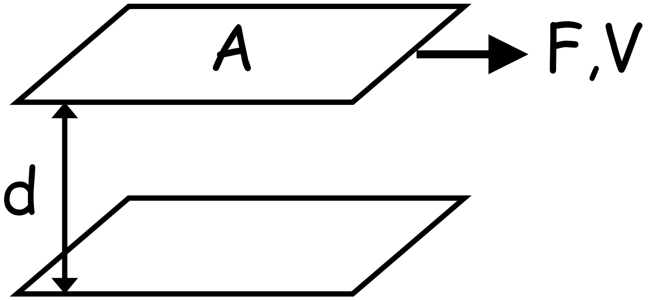
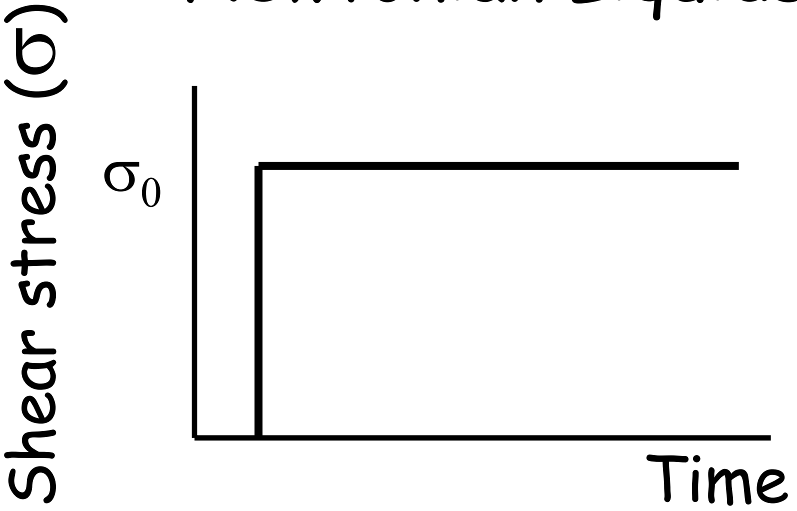
Viscosity Definitions

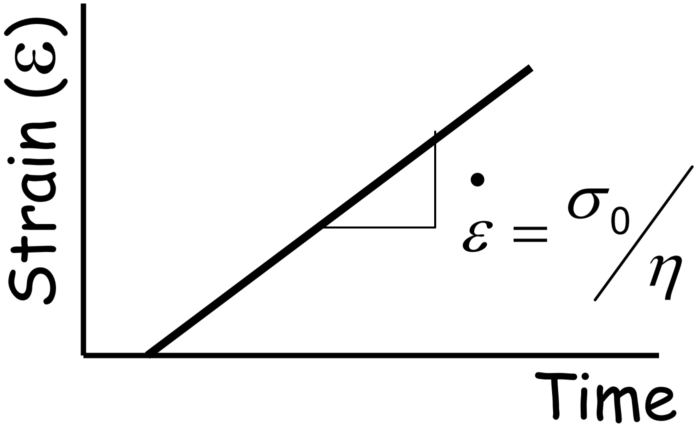


$$\text{Viscosity} \equiv \eta = {Fd}\big/{AV} = {\sigma_0}\big/{\dot{\varepsilon}}$$

Units: (dynes·cm)/(cm^2·(cm/s))
= dyne·s/cm^2 = *Poise* or
N·s/m^2 = Pa·s
1 Pa·s = 10 P
1 P = 1 dPa·s

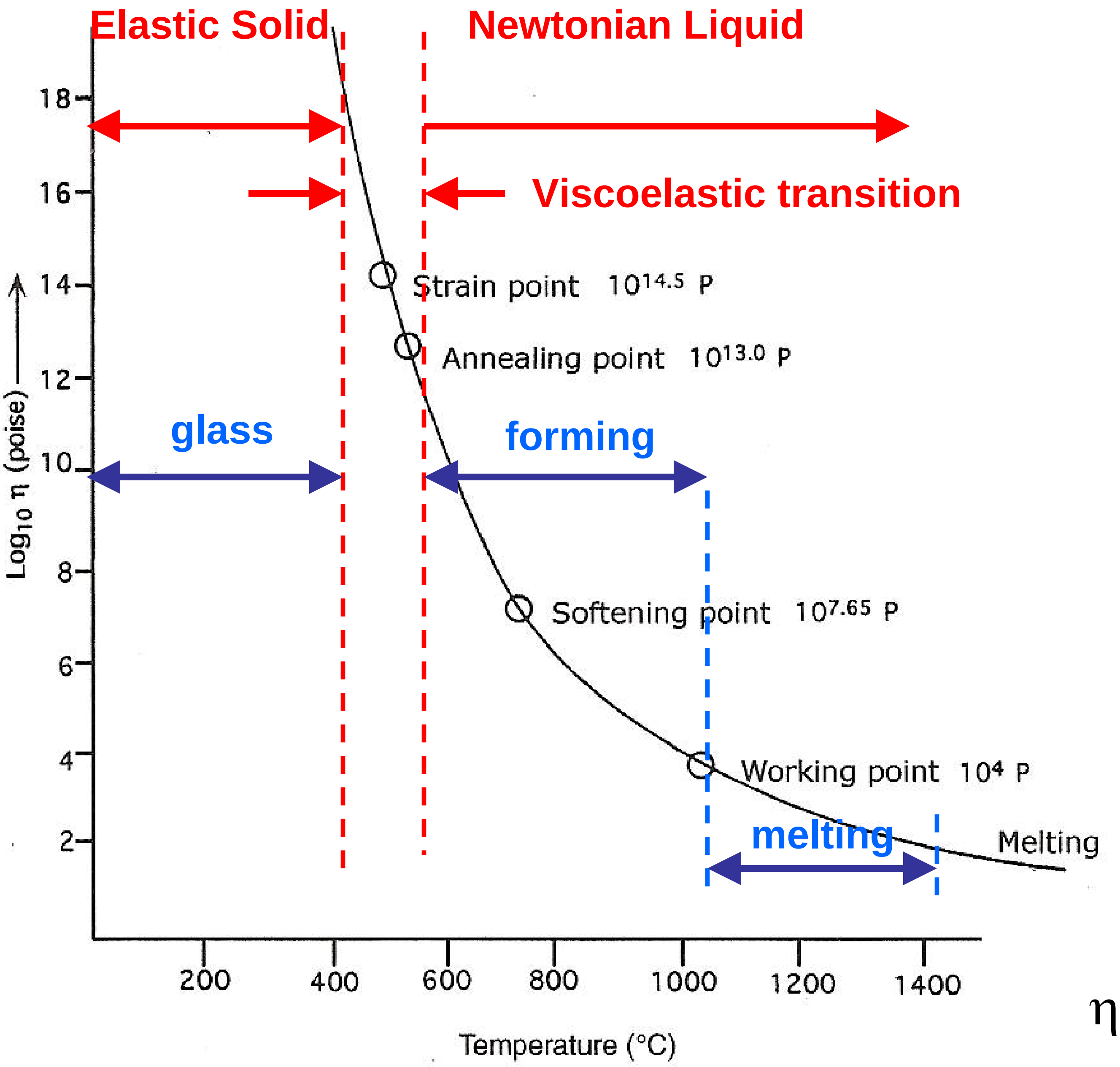
Newtonian Liquids:



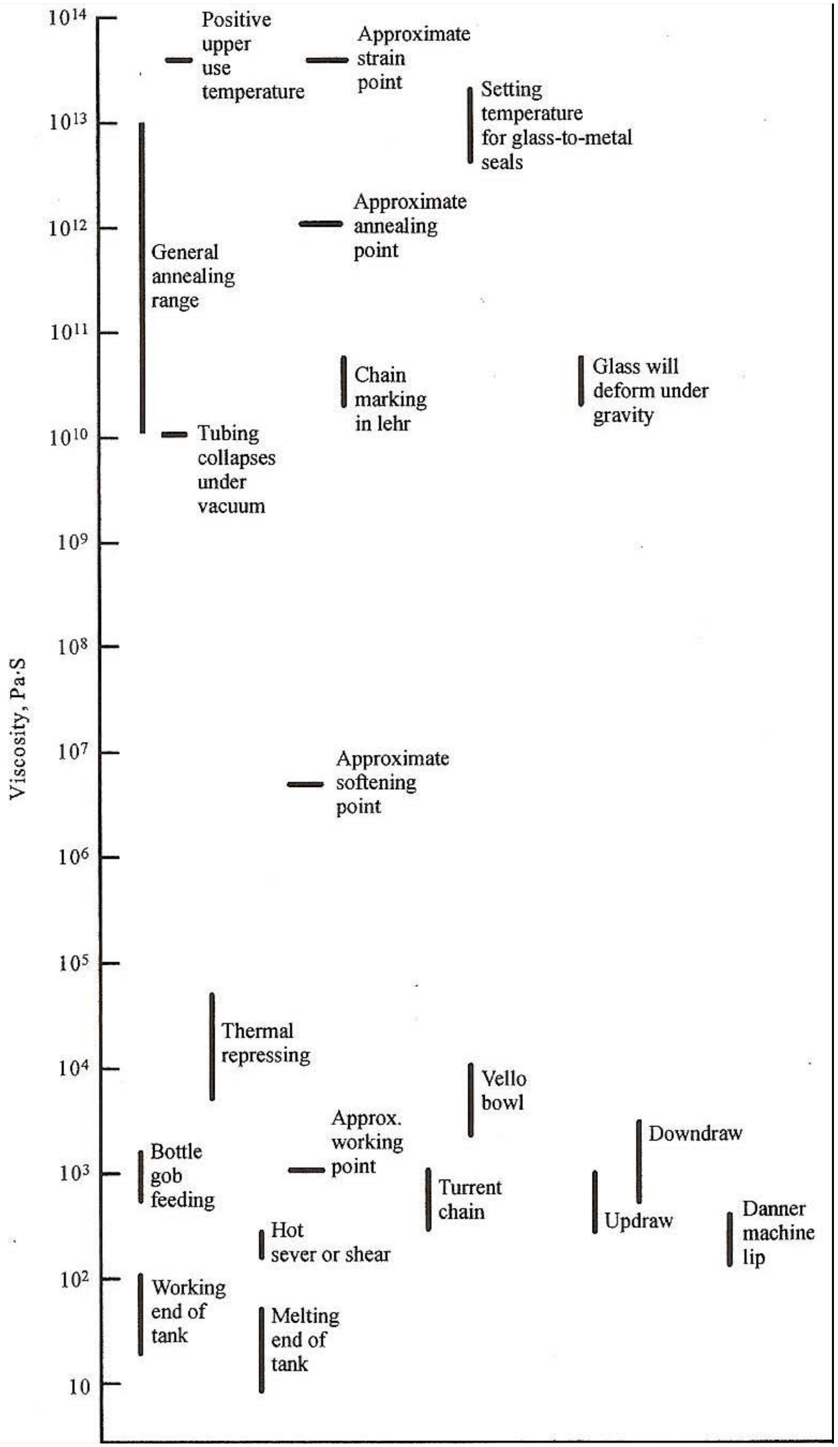


$$\dot{\varepsilon} = {\sigma_0}\big/{\eta}$$

Practical Consequences



$\eta(T)$ for SLS melt



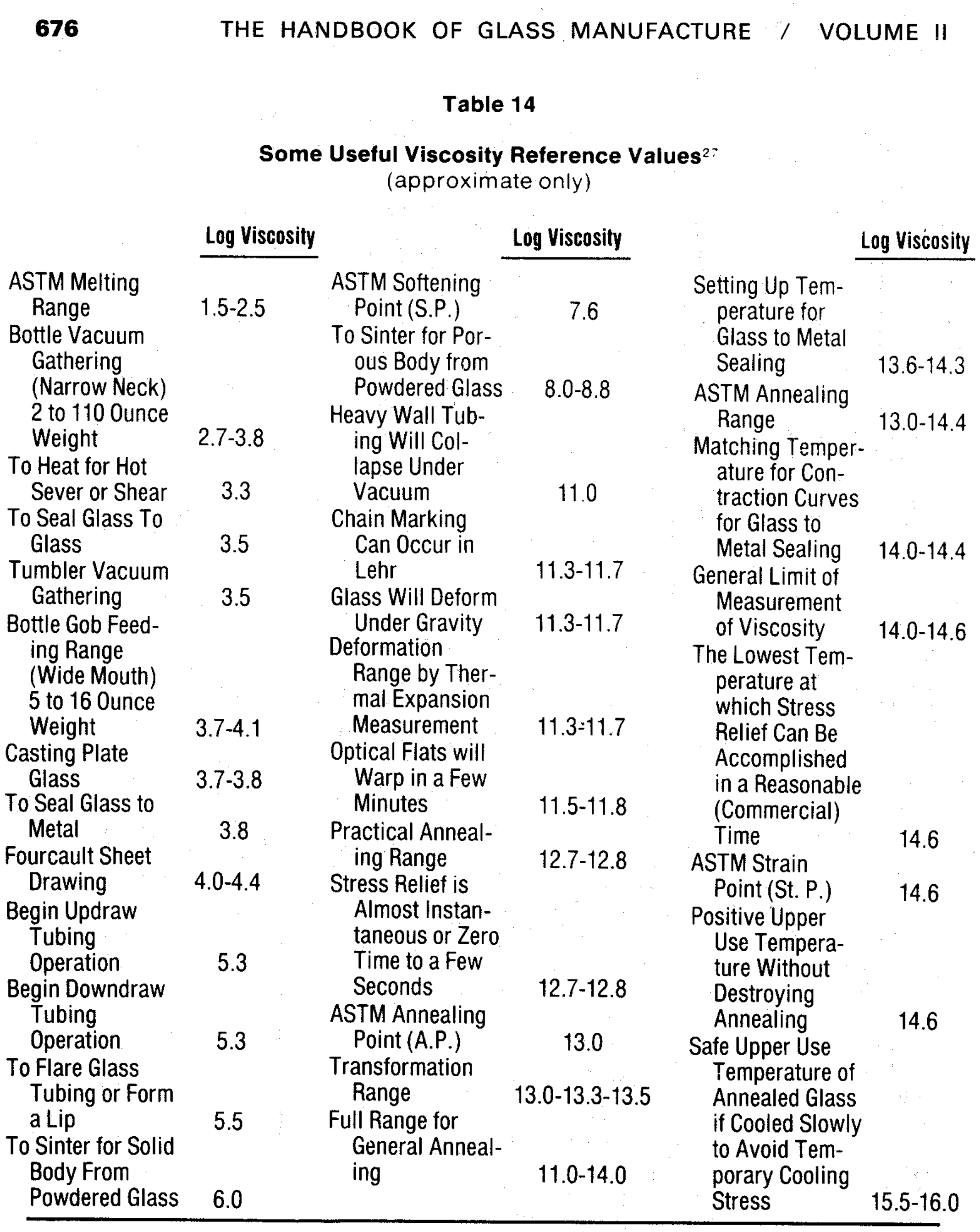

676 THE HANDBOOK OF GLASS MANUFACTURE / VOLUME II

Table 14

Some Useful Viscosity Reference Values[27]
(approximate only)

	Log Viscosity
ASTM Melting Range	1.5-2.5
Bottle Vacuum Gathering (Narrow Neck) 2 to 110 Ounce Weight	2.7-3.8
To Heat for Hot Sever or Shear	3.3
To Seal Glass To Glass	3.5
Tumbler Vacuum Gathering	3.5
Bottle Gob Feeding Range (Wide Mouth) 5 to 16 Ounce Weight	3.7-4.1
Casting Plate Glass	3.7-3.8
To Seal Glass to Metal	3.8
Fourcault Sheet Drawing	4.0-4.4
Begin Updraw Tubing Operation	5.3
Begin Downdraw Tubing Operation	5.3
To Flare Glass Tubing or Form a Lip	5.5
To Sinter for Solid Body From Powdered Glass	6.0

	Log Viscosity
ASTM Softening Point (S.P.)	7.6
To Sinter for Porous Body from Powdered Glass	8.0-8.8
Heavy Wall Tubing Will Collapse Under Vacuum	11.0
Chain Marking Can Occur in Lehr	11.3-11.7
Glass Will Deform Under Gravity	11.3-11.7
Deformation Range by Thermal Expansion Measurement	11.3-11.7
Optical Flats will Warp in a Few Minutes	11.5-11.8
Practical Annealing Range	12.7-12.8
Stress Relief is Almost Instantaneous or Zero Time to a Few Seconds	12.7-12.8
ASTM Annealing Point (A.P.)	13.0
Transformation Range	13.0-13.3-13.5
Full Range for General Annealing	11.0-14.0

	Log Viscosity
Setting Up Temperature for Glass to Metal Sealing	13.6-14.3
ASTM Annealing Range	13.0-14.4
Matching Temperature for Contraction Curves for Glass to Metal Sealing	14.0-14.4
General Limit of Measurement of Viscosity	14.0-14.6
The Lowest Temperature at which Stress Relief Can Be Accomplished in a Reasonable (Commercial) Time	14.6
ASTM Strain Point (St. P.)	14.6
Positive Upper Use Temperature Without Destroying Annealing	14.6
Safe Upper Use Temperature of Annealed Glass if Cooled Slowly to Avoid Temporary Cooling Stress	15.5-16.0

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Important Manufacturing Viscosities

Name	η (Pa·s)	Remarks
Melting pt (T_m)	10^{1}	
Melting range	$10^{0.5}$-$10^{1.5}$	Melting, fining
Working pt (T_w)	10^{3}	
Working range	10^{2}-10^{6}	Forming
Liquidus temp (T_l)	~10^{4}	No crystallization for $T>T_l$
Flow point	10^{4}	
Softening point (T_{Lit})	$10^{6.6}$	Littleton, flow under own weight
Crystallization temp (T_x)	~10^{7}	No crystallization for $T<T_x$
Deformation temp (T_d)	10^{10}-10^{11}	Dilatometric: expansion compensated by viscous flow
Glass transition (T_g)	10^{11}-10^{12}	
Annealing pt (T_{ap})	10^{12}	Internal stresses relieved <15 min
Strain pt (T_{sp})	$10^{13.5}$	Internal stresses relieved <15 hrs

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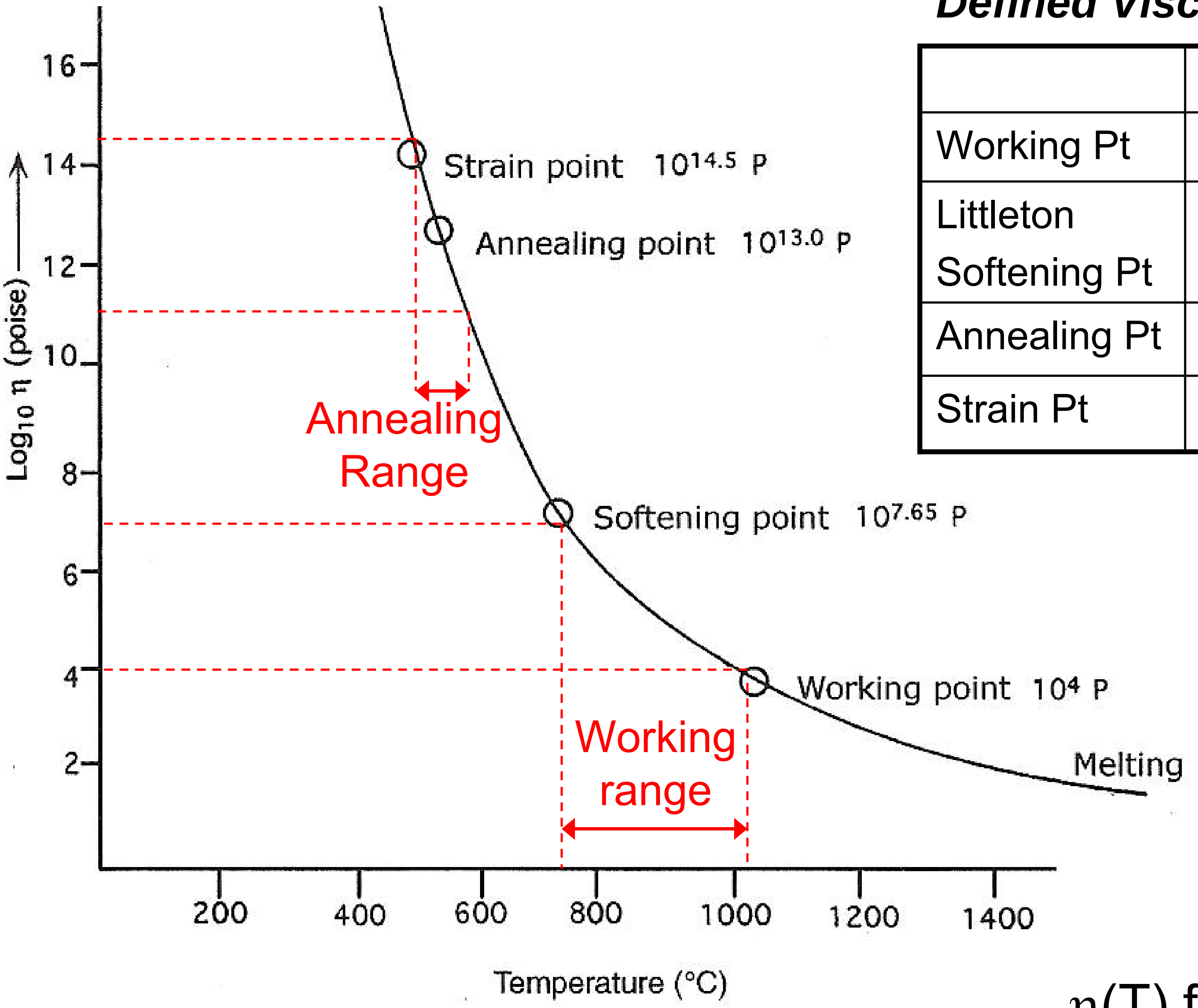

FIGURE 5.21 Viscosity η versus temperature for a typical soda-lime-silicate glass.

Defined Viscosities

	log Pa·s	log P
Working Pt	10^{3}	10^{4}
Littleton Softening Pt	$10^{6.6}$	$10^{7.6}$
Annealing Pt	10^{12}	10^{13}
Strain Pt	$10^{13.5}$	$10^{14.5}$

$\eta(T)$ for SLS melt

Viscosity Classifications

- Working Range: Temperatures (ΔT) between ‘working point’ and ‘softening point’
  - **_Long glasses_**: large ΔT (shallow η(T) curves)
  - **_Short glasses_**: small ΔT (steep η(T) curves)
  - **_Hard glasses_**: Working range at greater temperatures than for S-L-S glass
    - Borosilicates, aluminosilicates, oxynitrides, silica, etc.
    - Sometimes defined as CTE$<6\times10^{-6}$/°C
  - **_Soft glasses_**: Working range at lower temperatures than for S-L-S glass
    - Soda-lime silicate, Pb-silicates
    - Sometimes defined as CTE$>6\times10^{-6}$/°C

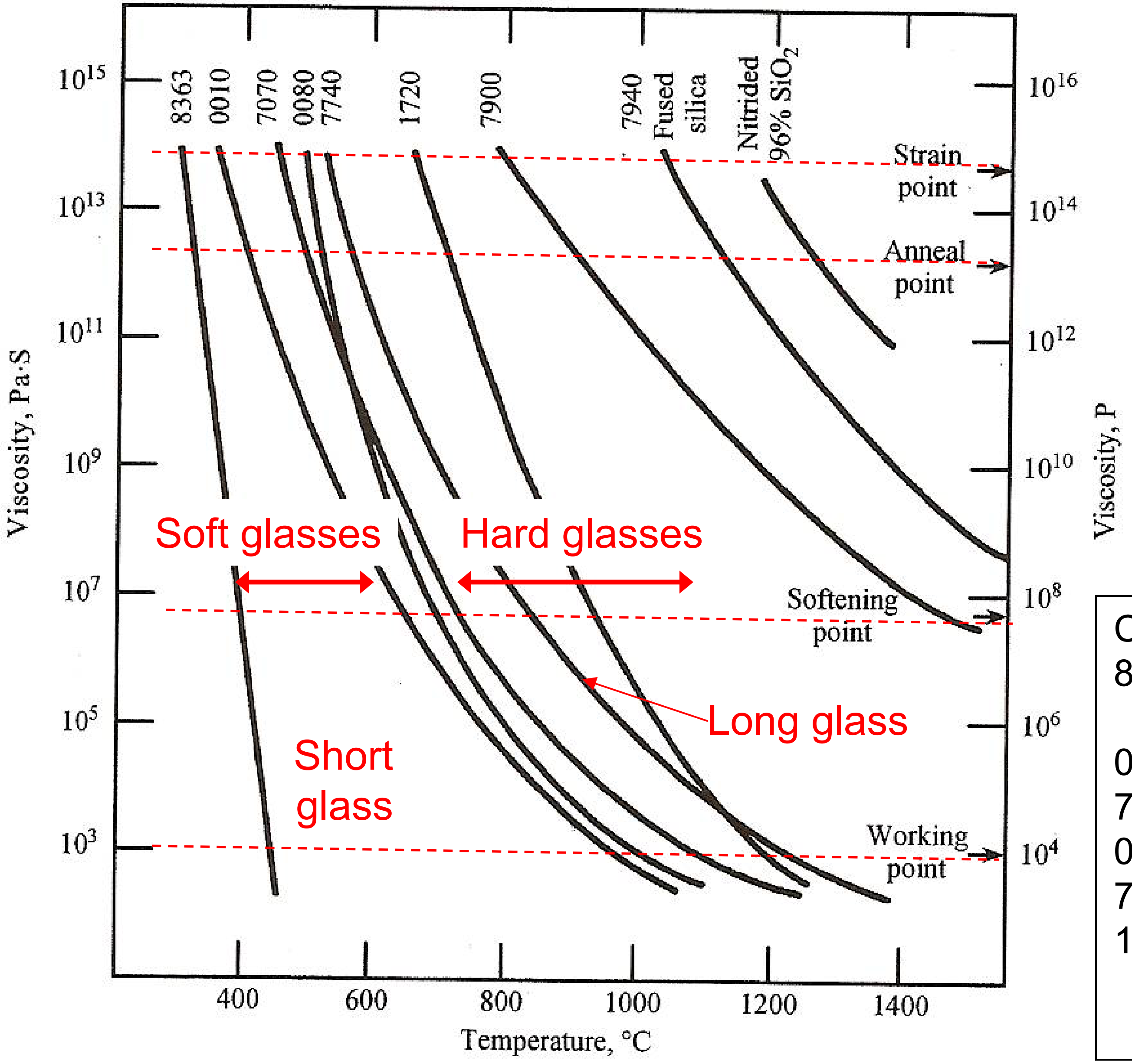

FIGURE 6.2 Viscosity versus temperature for some commercial glasses designated by glass codes (see Tables 6.1 and 6.2). (*Courtesy of Corning Incorporated.*)

From Seward and Varshneya (2001)

Corning Codes:
8363: High PbO radiation shield
0010: Pb-silicate tube
7070: Borosilicate
0080: SLS lamp glass
7740: Pyrex
1720: Alkaline-earth boro-aluminosilicate

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Measurement of Viscosity

Range	Method	Viscosity Values
Melting	Falling Sphere/Bubble Rise	$\eta<10^4$ Pa-s
	Margules Rotating Cylinder	$\eta<10^6$ Pa-s
Softening and Annealing	Parallel Plate	10^5 Pa-s$<\eta<$ 10^9 Pa-s
	Penetration Viscometer	10^5 Pa-s$<\eta<$ 10^9 Pa-s
	Fiber Elongation	10^5 Pa-s$<\eta<$ $10^{15.5}$ Pa-s
	Beam Bending	10^7 Pa-s$<\eta<$ 10^{12} Pa-s
	Disappearance of Stress	10^{11} Pa-s$<\eta<$ 10^{14} Pa-s

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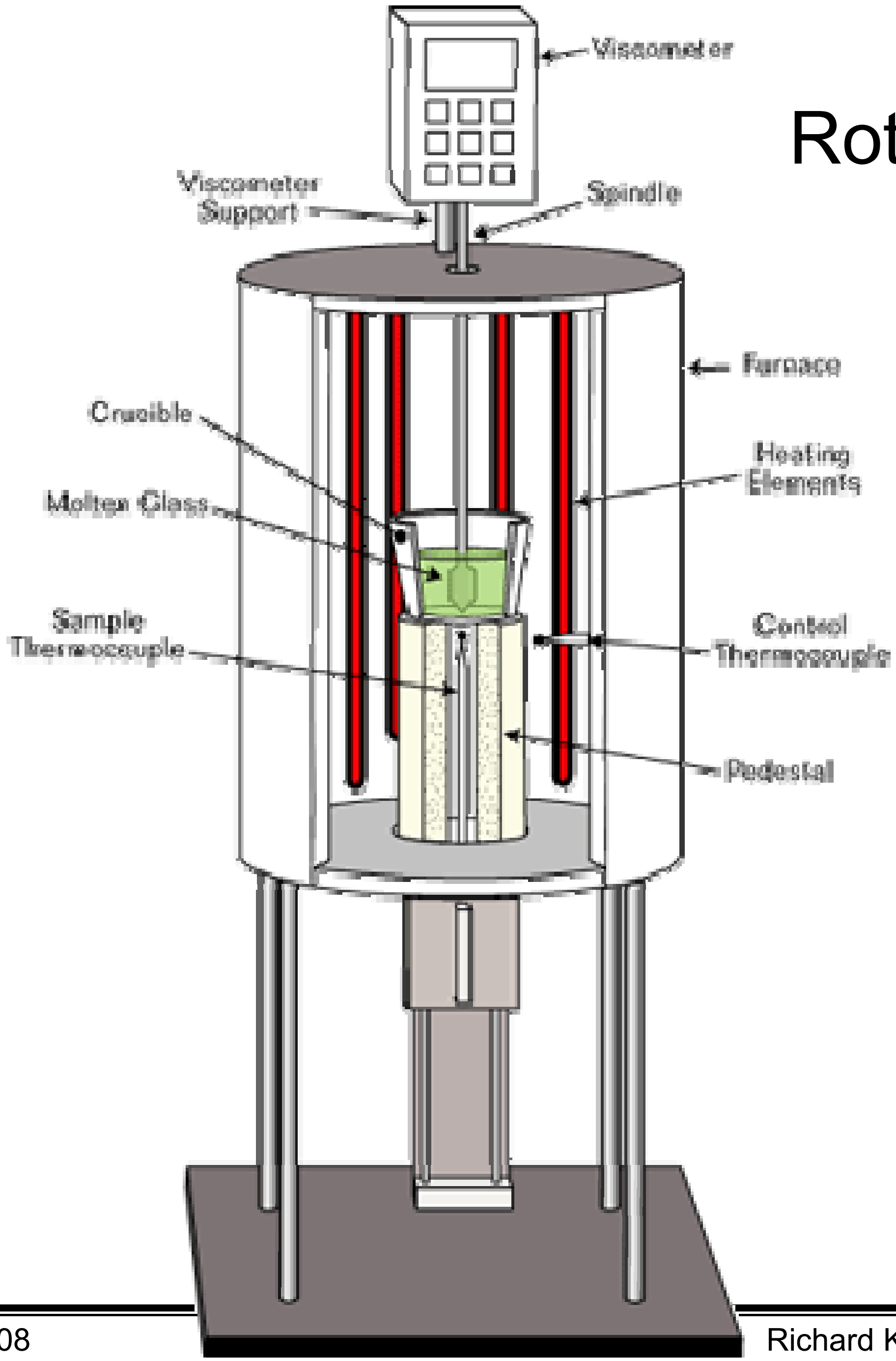
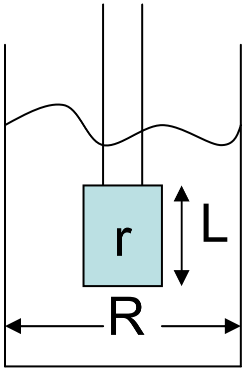


Rotating Spindle: 10-10^6 Pa·s

(ASTM C965-96)

$$\eta = \frac{1}{4\pi \cdot L}\left(\frac{1}{r^2}-\frac{1}{R^2}\right)\left(\frac{T}{\omega}\right)$$



T = torque
ω = rotational velocity

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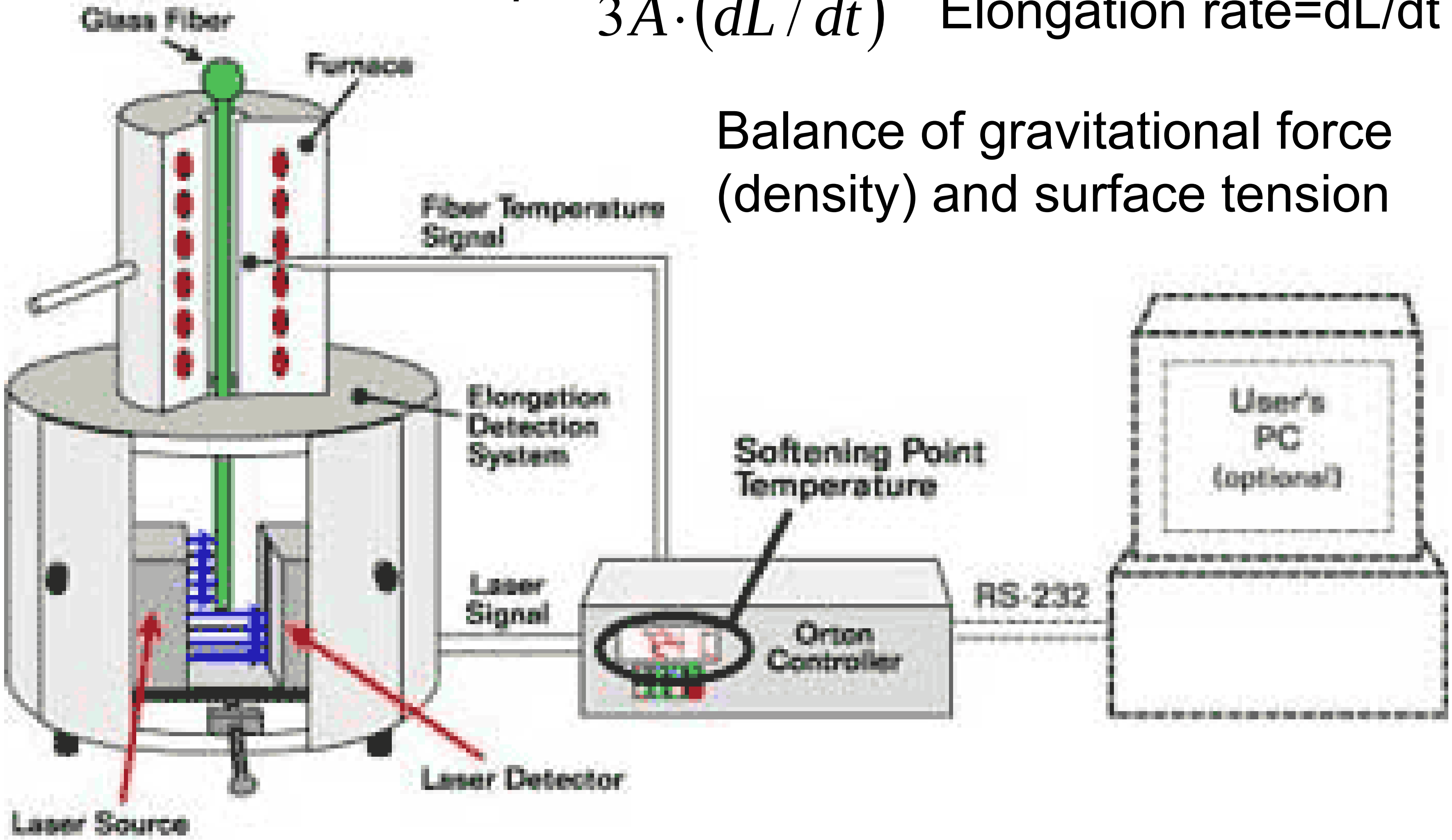
Littleton Softening Point: $10^{6.6}$ Pa·s

(fiber elongation- ASTM C338-93)

$$\eta = \frac{L \cdot F}{3A \cdot \left(dL / dt \right)}$$

Applied Stress= F/A
Elongation rate=dL/dt

Balance of gravitational force (density) and surface tension



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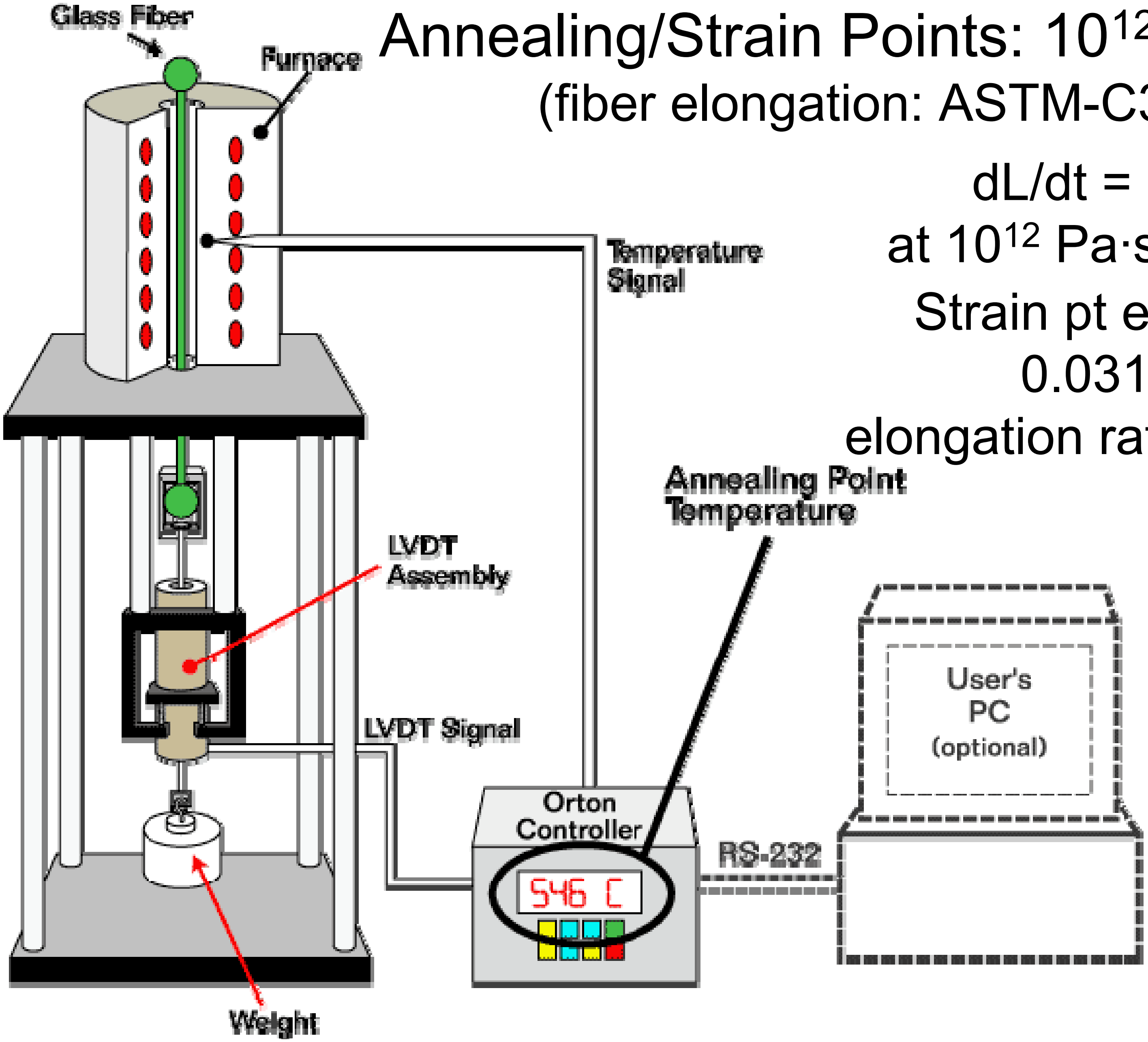
Annealing/Strain Points: 10^{12}, $10^{13.5}$ Pa·s

(fiber elongation: ASTM-C336-69)



$dL/dt = 2.5 \times 10^{-6}\ l/d^2$

at 10^{12} Pa·s (anneal pt)

Strain pt elongation rate is 0.0316 x annealing pt elongation rate (1.5 log units)

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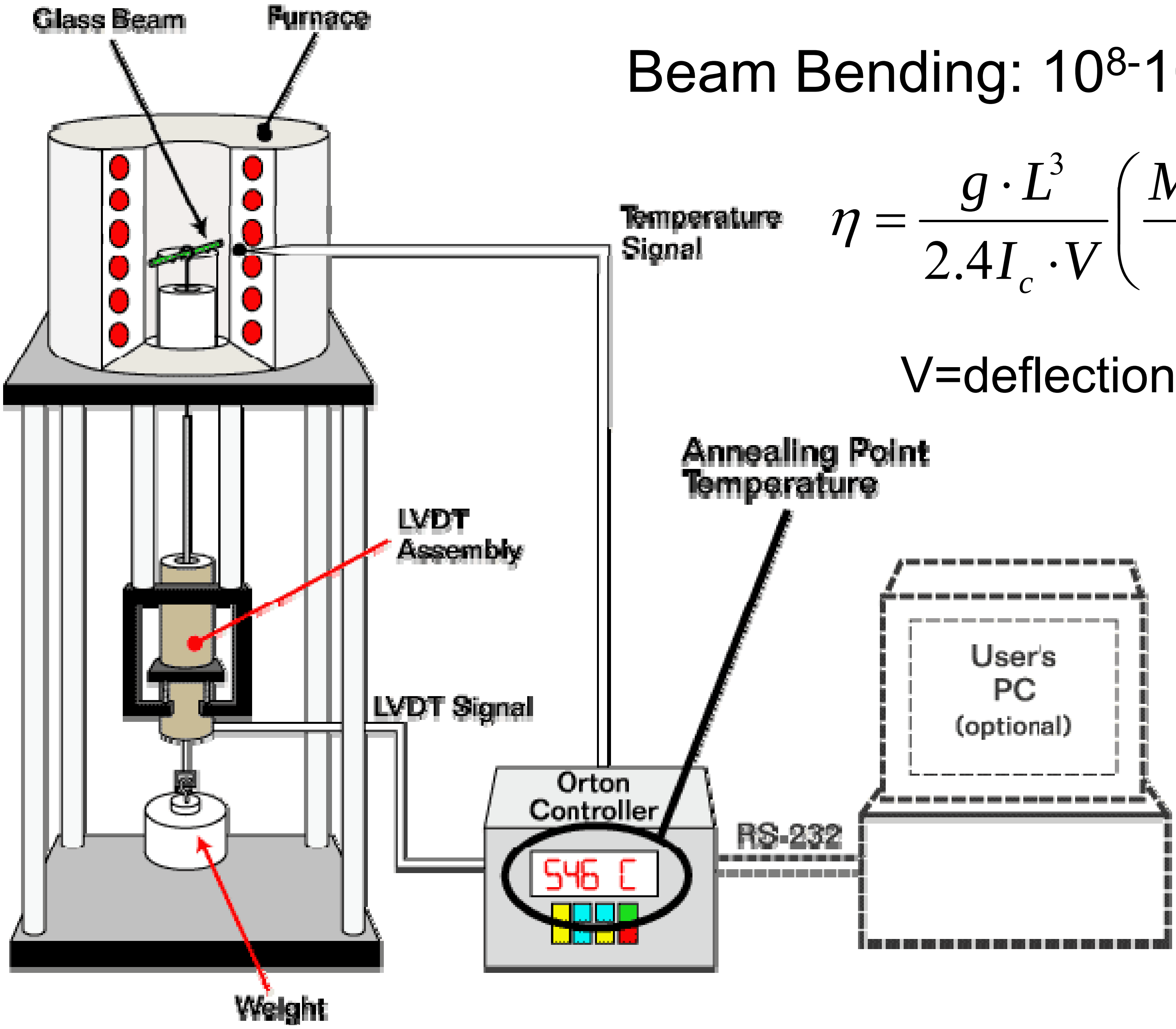
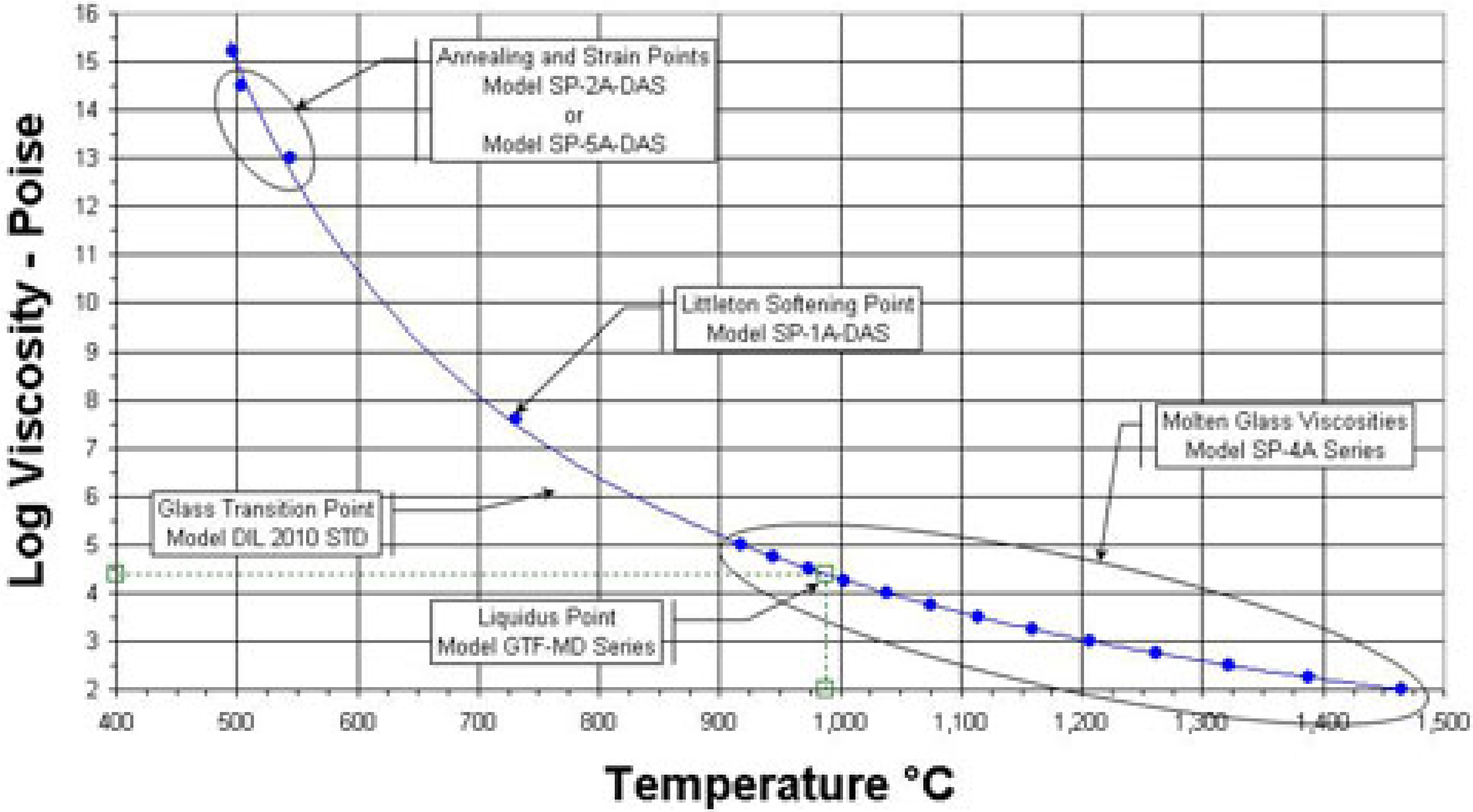
Beam Bending: 10^{8}-10^{13} Pa-s



$$\eta = \frac{g \cdot L^3}{2.4 I_c \cdot V}\left(\frac{M + A \cdot L \cdot \rho}{1.6}\right)$$

V=deflection rate

Orton Instruments to Determine the Viscosity as a Function of Temperature



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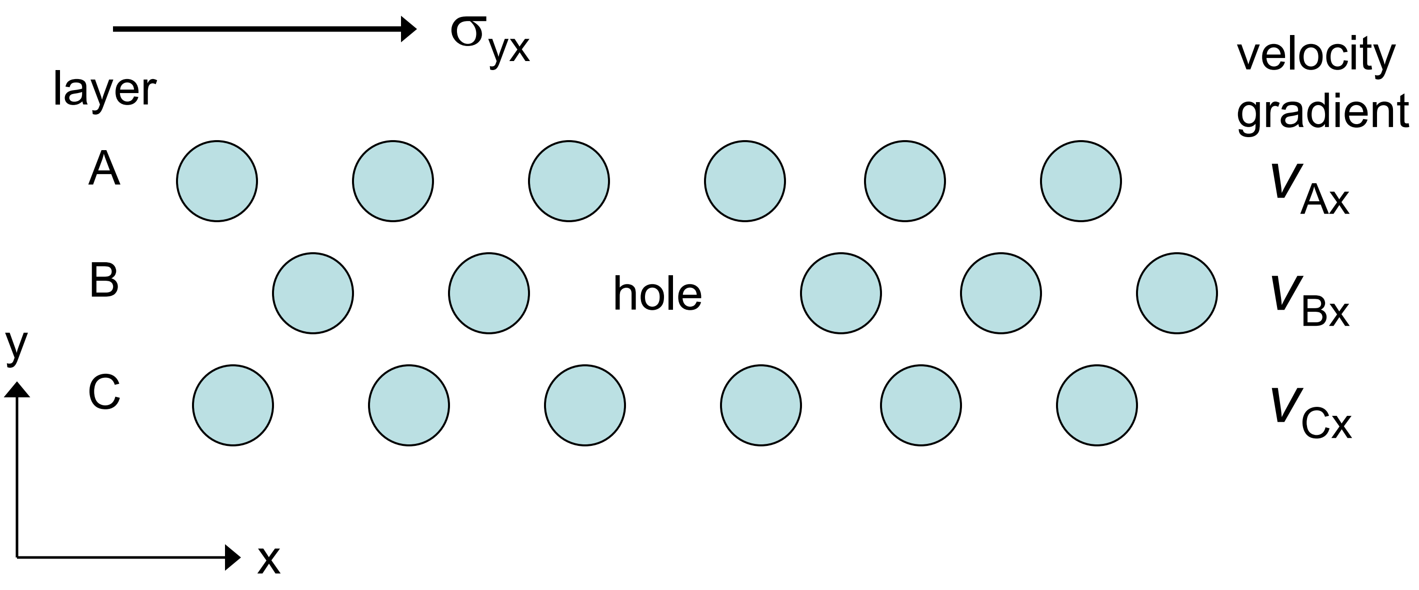
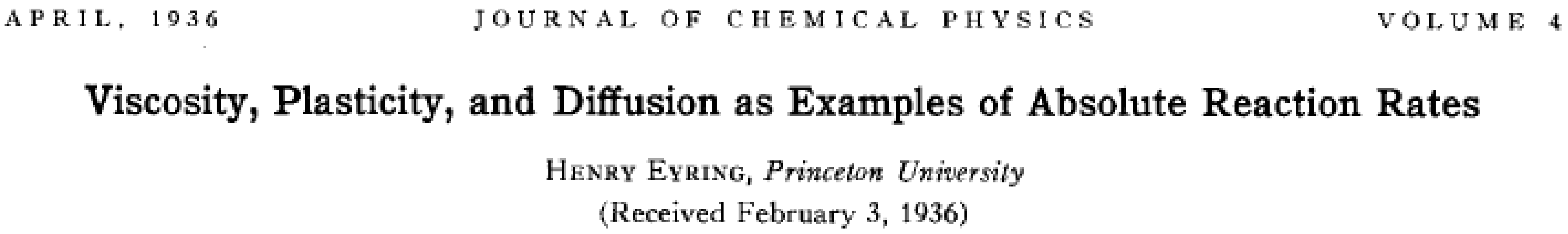
The temperature dependence of viscosity



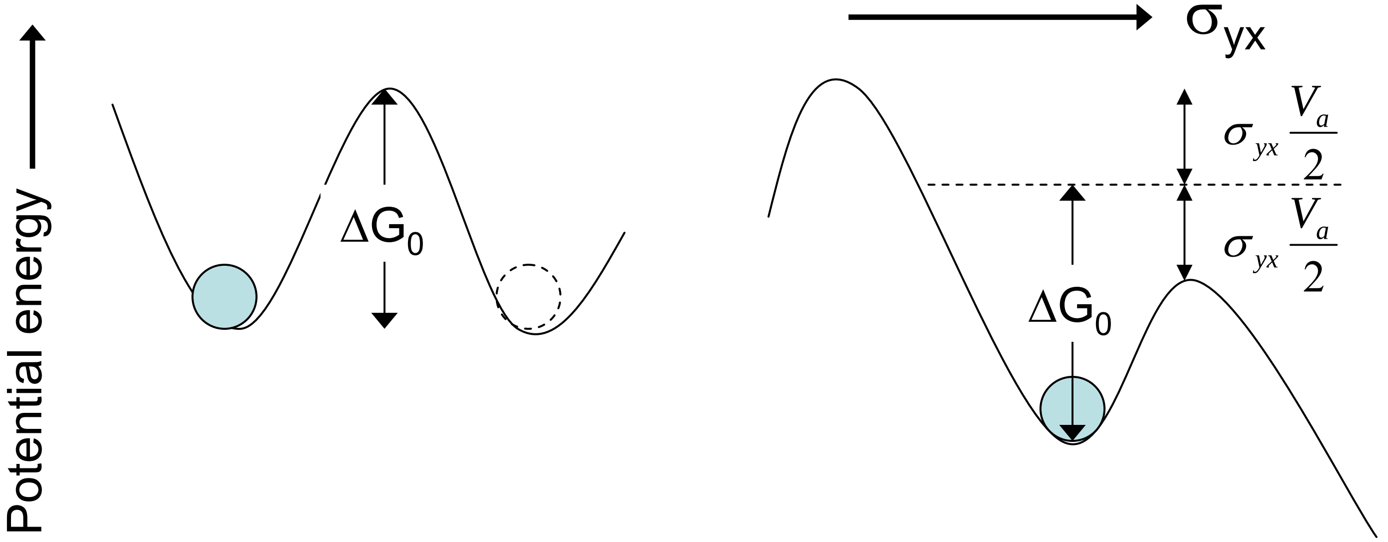
Consider the ‘activated’ motion of a hole under the action of a shearing stress


APRIL, 1936 JOURNAL OF CHEMICAL PHYSICS VOLUME 4

Viscosity, Plasticity, and Diffusion as Examples of Absolute Reaction Rates

HENRY EYRING, *Princeton University*

(Received February 3, 1936)



Jump frequency (υ_0), no shear:

- Same l-r as r-l
- Depends on barrier energy and probability of finding suitable hole as neighbor (P_h)

$$\upsilon_0 = [k_B T / h]\exp[-\Delta G_0 / k_B T] \cdot P_h$$

Applied shear biases potential energy function

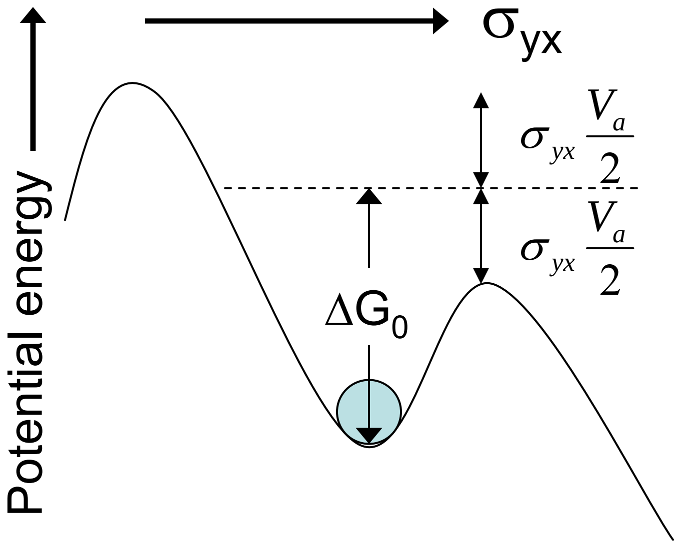
- V_a is atom volume
- Forward jump frequency (υ_+) exceeds reverse (υ_-)

$$\upsilon_+ = [k_B T / h]\exp[-(\Delta G_0 - \frac{\sigma_{yx} V_a}{2}) / k_B T] \cdot P_h$$

$$\upsilon_+ = \upsilon_0 \exp[\sigma_{yx} V_a / 2 k_B T]$$

$$\upsilon_- = [k_B T / h]\exp[-(\Delta G_0 + \frac{\sigma_{yx} V_a}{2}) / k_B T] \cdot P_h$$

$$\upsilon_- = \upsilon_0 \exp[-\sigma_{yx} V_a / 2 k_B T]$$



The net ‘forward velocity’ is

$$(v_{Bx} - v_{Ax}) = (\upsilon_+ - \upsilon_-)\delta x$$
$$\partial v / \partial y = (\upsilon_+ - \upsilon_-)\delta x / \delta y \approx (\upsilon_+ - \upsilon_-)$$
$$\partial v / \partial y = 2\upsilon_0 \sinh(\sigma_{yx} V_a / 2k_B T) \cong \upsilon_0 \sigma_{yx} V_a / k_B T$$
$$\textit{shear strain rate is } \dot{e}_{xy} = \partial v / \partial y,$$
$$\eta = \sigma_{yx} / \left[\upsilon_0 \sigma_{yx} V_a / k_B T\right] = \left[h / V_a\right]\left[\exp(\Delta G_0 / k_B T\right]\left(P_h\right)^{-1}$$

Consider the energy required to create a hole (ΔE_h), then P_h can be described by

$$P_h = \exp\left[-\Delta E_h / k_B T\right]$$

substituting P_h into the viscosity equation,

$$\eta = \left[h / V_a\right]\left[\exp\left(\Delta G_0 + \Delta E_h\right) / k_B T\right]$$

Simplifying as an Arrhenius equation:

$$\boxed{\eta = \eta_0 \exp\left(\Delta H_\eta / RT\right)}$$

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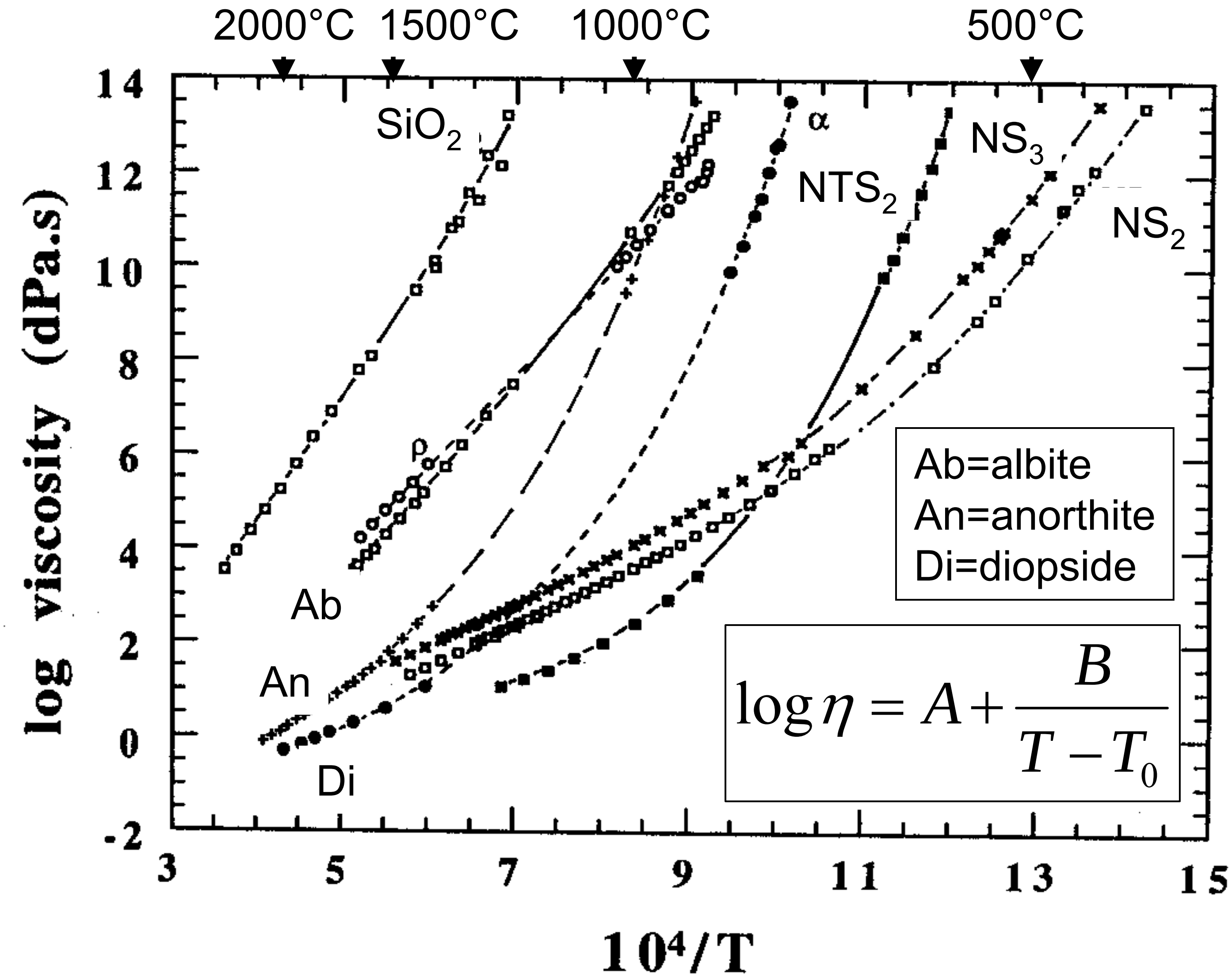
Most glass-forming liquids are non-Arrhenius

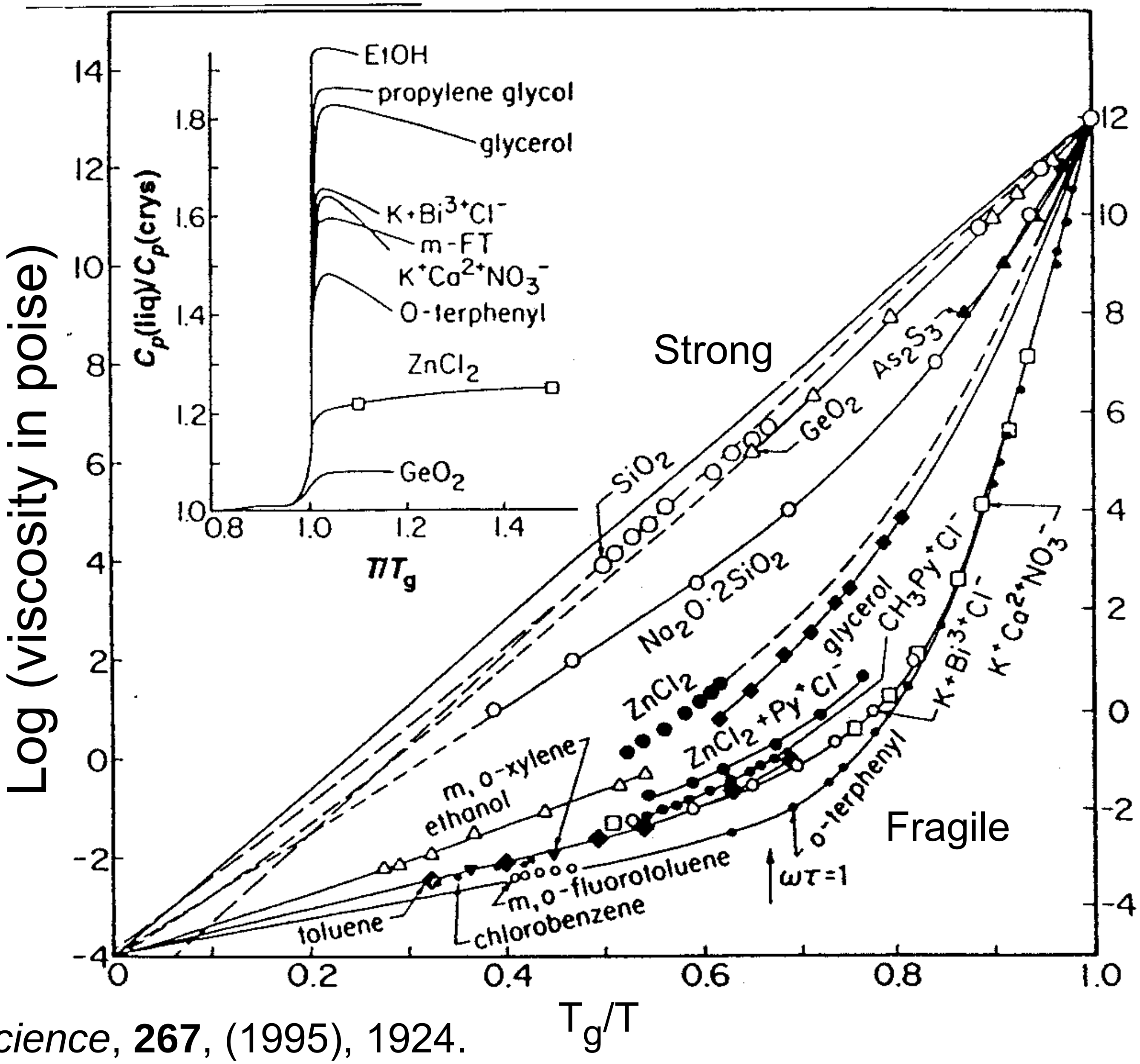


Ab=albite
An=anorthite
Di=diopside

$$\log\eta = A + \frac{B}{T - T_0}$$

From P. Richet and Y. Bottinga, in *Reviews in Mineralogy*, Vol. 32, (1995), p. 67-93

Melt Fragility



From C. A. Angell, *Science*, **267**, (1995), 1924.

Why the non-Arrhenius temperature-dependence?

1. Energy for hole formation (ΔE_h) is low at high temperatures
   - ΔH_η is greater at lower temperatures
2. Free-volume increases with temperature
3. Configurational entropy increases with temperature (Adam-Gibbs description)

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What accounts for viscous flow in a silicate melt?

What has to happen for flow to occur?

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What happens at the molecular-level that affects viscosity?

288 McMillan & Wolf: *Spectroscopy of Silicate Liquids*

At the short timescales, ‘melt structures’ are similar to ‘glass structures’….

- **Raman spectroscopy-** probing structure on timescales 10^{-12}-10^{-14} s
- Si-O stretching/bending modes remain dominate from room temperature into the melt
- Some evidence for some melt speciation reactions: $2Q^3 \leftrightarrow Q^2 + Q^4$

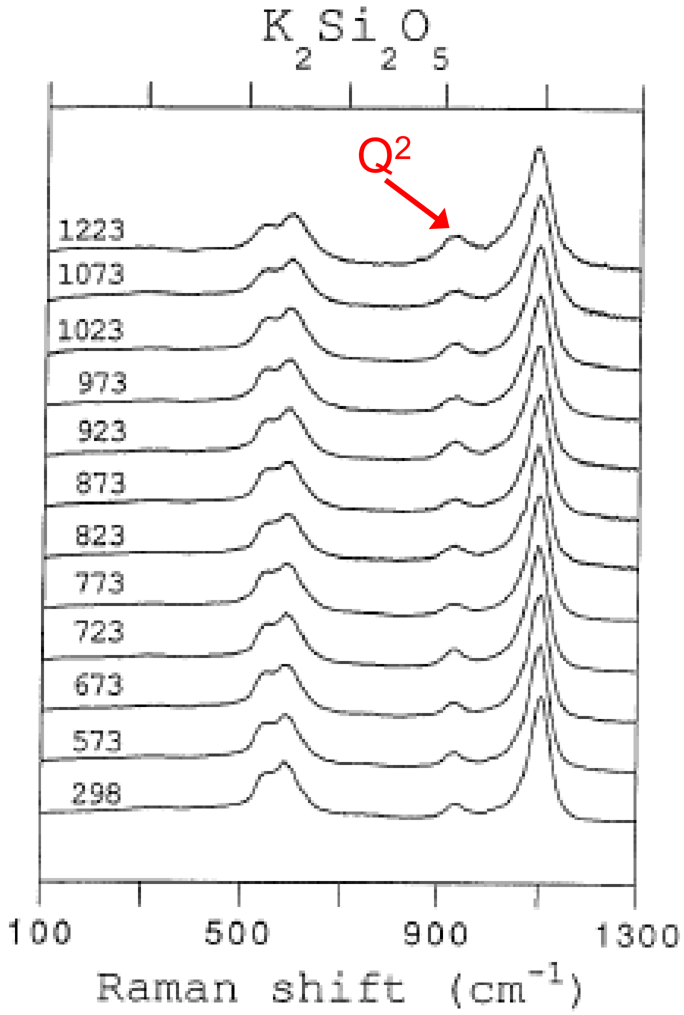
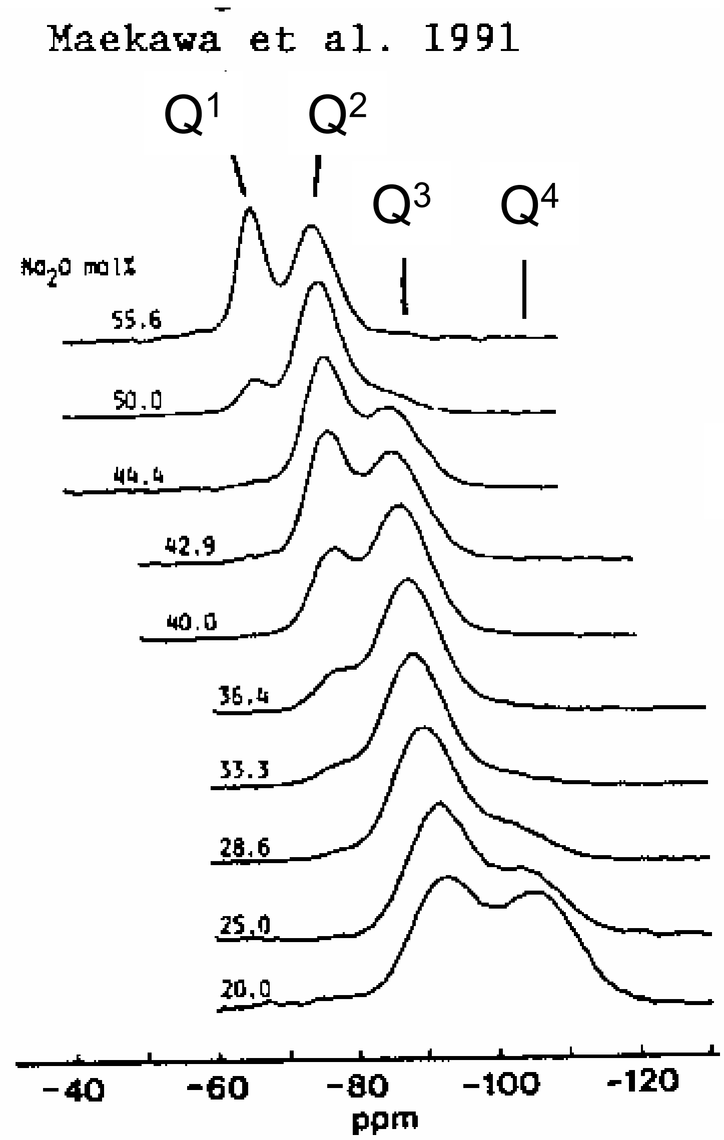


Figure 14. High temperature Raman spectra for $K_2Si_2O_5$ glass and supercooled liquid (McMillan et al., 1992). Temperatures are given in Kelvins. Spectra have been corrected for first-order Raman effects. The melting temperature for this composition is 1320 K, and the glass transition is at 765 K. The Q^2 peak is seen to increase in relative intensity with temperature, above T_g.

NMR provides structural information about glasses



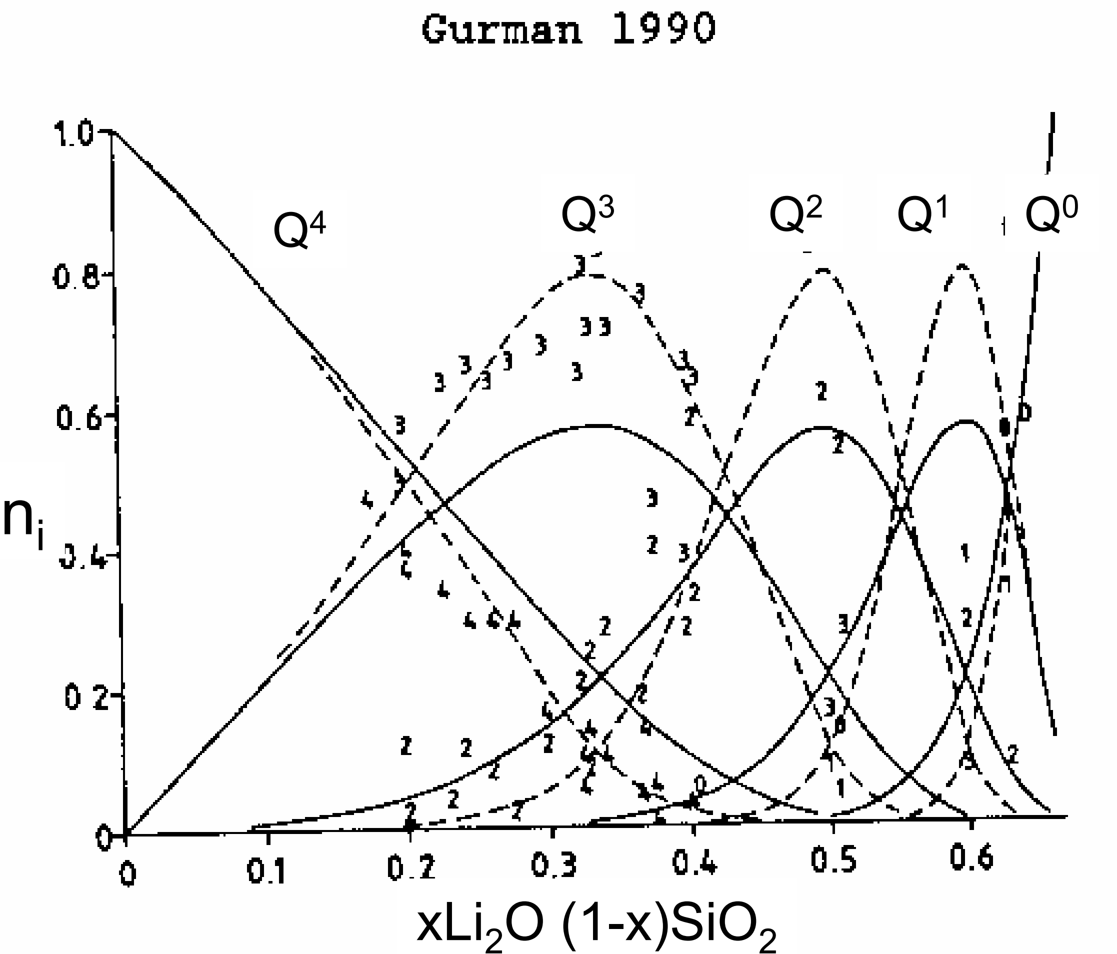


Fig. 2. Proportions of Q species in lithium silicate glasses. ———, $\Delta E/kT = 1$; - - - - - -, $\Delta E/kT = 2$. The numbers indicate experimental values of n_i, $i = 0$–4. Data from Raman and NMR studies.

Chemical exchange in melts: silicate species and viscous flow

- NMR exchange frequencies (kHz range) are comparable to the timescales for viscous flow in silicate melts
- The ‘lifetimes’ for Si-O bonds in a melt can be determined and compared with timescales associated with viscous flow
- At high temperatures, the Q^3-Q^4 exchange (Si-O bond rupture) is fast compared to the experimental time frame.

Stebbins: *Dynamics and Structure of Melts: NMR Studies* 223

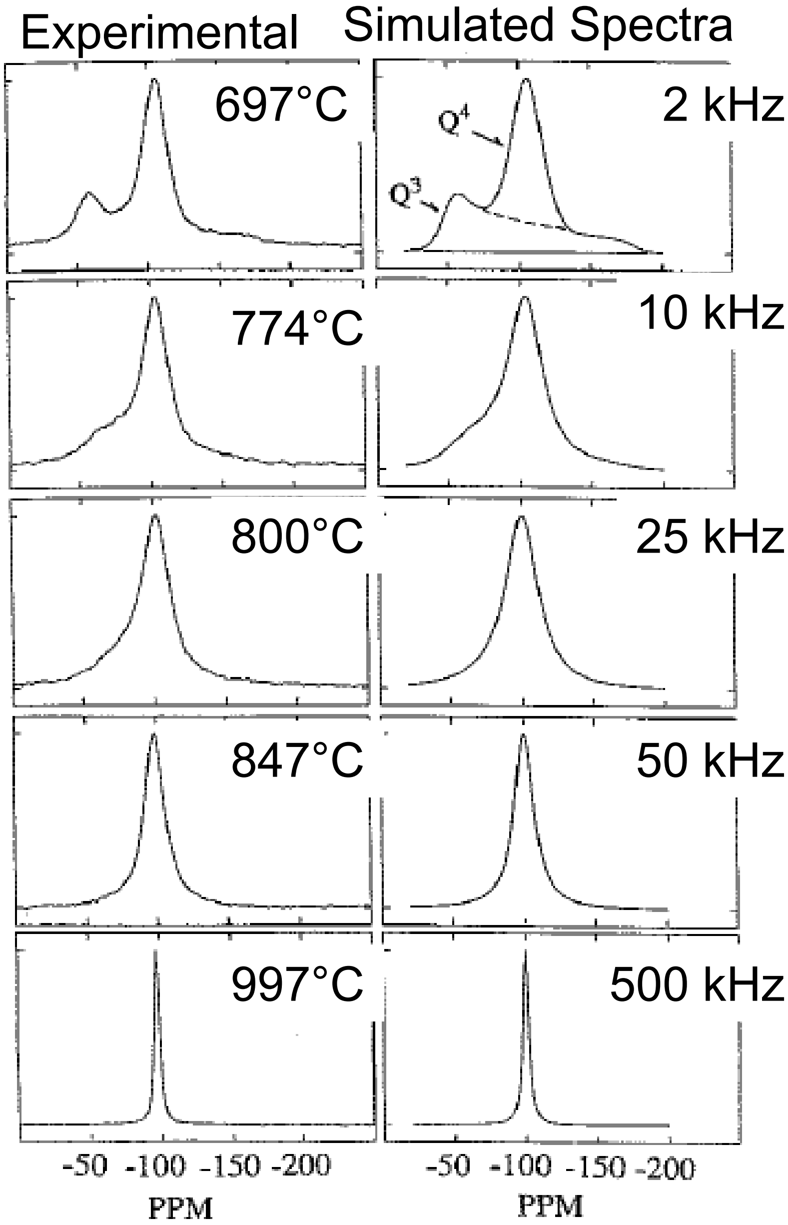


Figure 18. Static (i.e. non-MAS) ^{29}Si spectra of $K_2Si_4O_9$ glass and liquid (left) and multi-site exchange simulations (right). Temperatures: (a) 697°C; (b) 774°C; (c) 800°C; (d) 847°C; (e) 997°C. Exchange frequencies, in kHz: (f) 2; (g) 10; (h) 25; (i) 50; (j) 500. Q^4 and Q^3 static CSA patterns are labeled in the lowest temperature spectrum. [Used by permission of the editor of *Journal of the American Chemical Society*, from Farnan and Stebbins (1990a), Fig. 5, p. 36.]

NMR exchange and viscosity timescales coincide

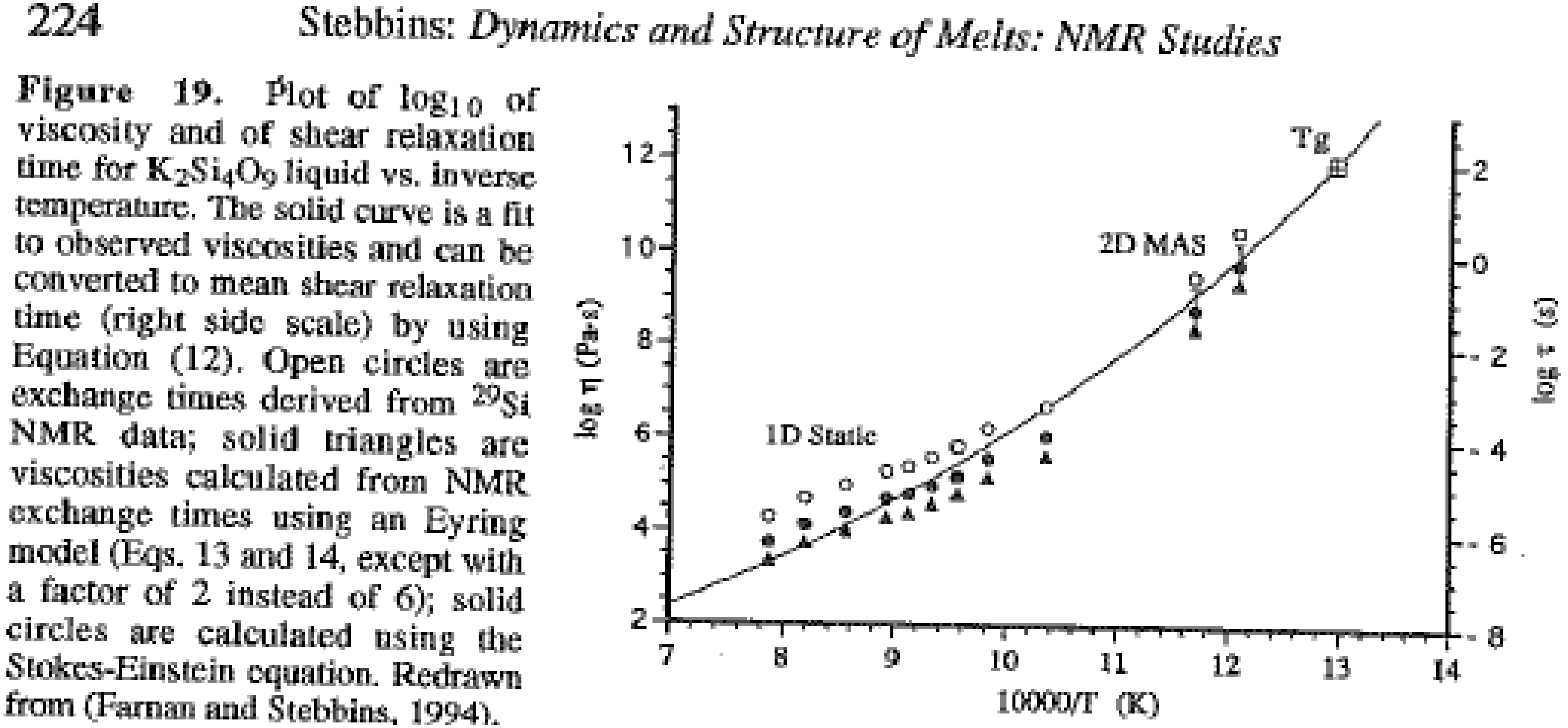


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Figure 19. Plot of $\log_{10}$ of viscosity and of shear relaxation time for $K_2Si_4O_9$ liquid vs. inverse temperature. The solid curve is a fit to observed viscosities and can be converted to mean shear relaxation time (right side scale) by using Equation (12). Open circles are exchange times derived from ^{29}Si NMR data; solid triangles are viscosities calculated from NMR exchange times using an Eyring model (Eqs. 13 and 14, except with a factor of 2 instead of 6); solid circles are calculated using the Stokes-Einstein equation. Redrawn from (Farnan and Stebbins, 1994).

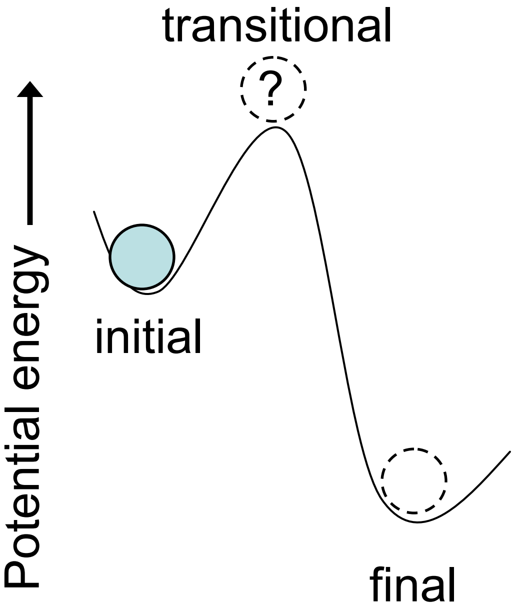
1. Maxwell relationship: $\eta = \tau_{shear} \cdot G_\infty$
2. Assume that $\tau_{shear} \approx \tau_{ex}$
3. Calculate diffusivity (D) from τ_{ex} : $D = d^2/6\tau$, d is ‘jump distance’
4. Calculate viscosity from $\eta = k_B T/(dD)$

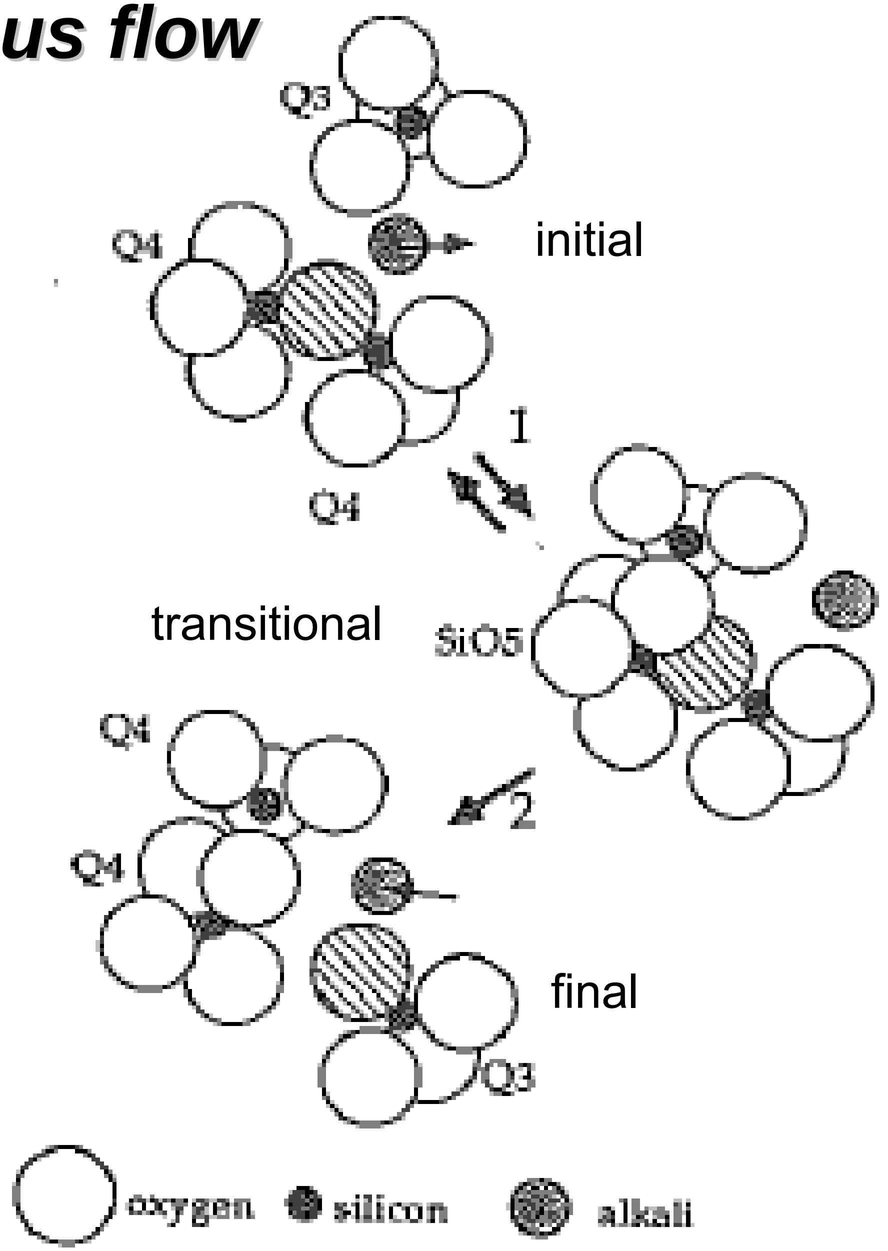
Stebbins model for viscous flow

Si-O bond-rupture through Q^3-Q^4 site exchange

- Conversion of one bridging oxygen to a nonbridging oxygen
- ‘Diffusion’ of modifying cation from one silicate unit to another

- Creation of an SiO_5 transitional site?





NMR evidence for transitional sites ‘frozen into’ quenched glass structures

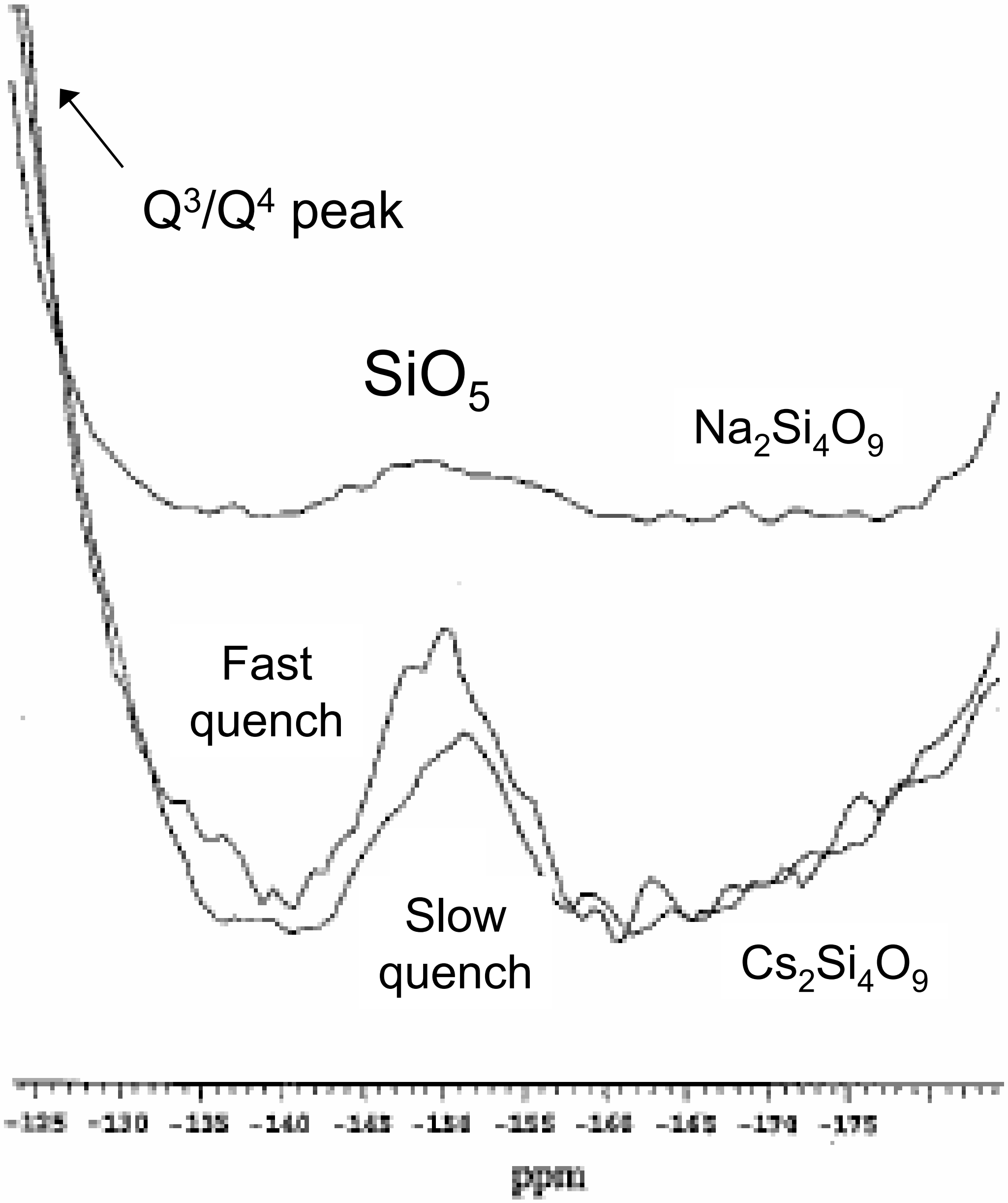


Figure 12. ^{29}Si MAS spectra for $Cs_2Si_4O_9$ and $Na_2Si_4O_9$ glasses, with vertical scale expanded greatly to show $^{[5]}$Si peak. Note that this feature is more intense in the fast-quenched sample (higher fictive temperature). The steep slope to the left is the side of the SiO_4 peak; that to the right is the side of the spinning sideband. [Used by permission of the editor of *Journal of Non-Crystalline Solids*, from Stebbins and McMillan (1993), Fig. 3, p. 120.]

Effects of composition on viscosity

Viscosity is determined by

- **Molecular attractive forces**, especially associated with glass-forming oxides
  - Si-O vs. Ge-O
- **Number of non-bridging oxygens** in structure
  - Alkali oxide additions reduce viscosity
  - Water (-OH) and fluorine reduce viscosity
- **Coordination number** of the cation
  - B[3] vs. B[4]

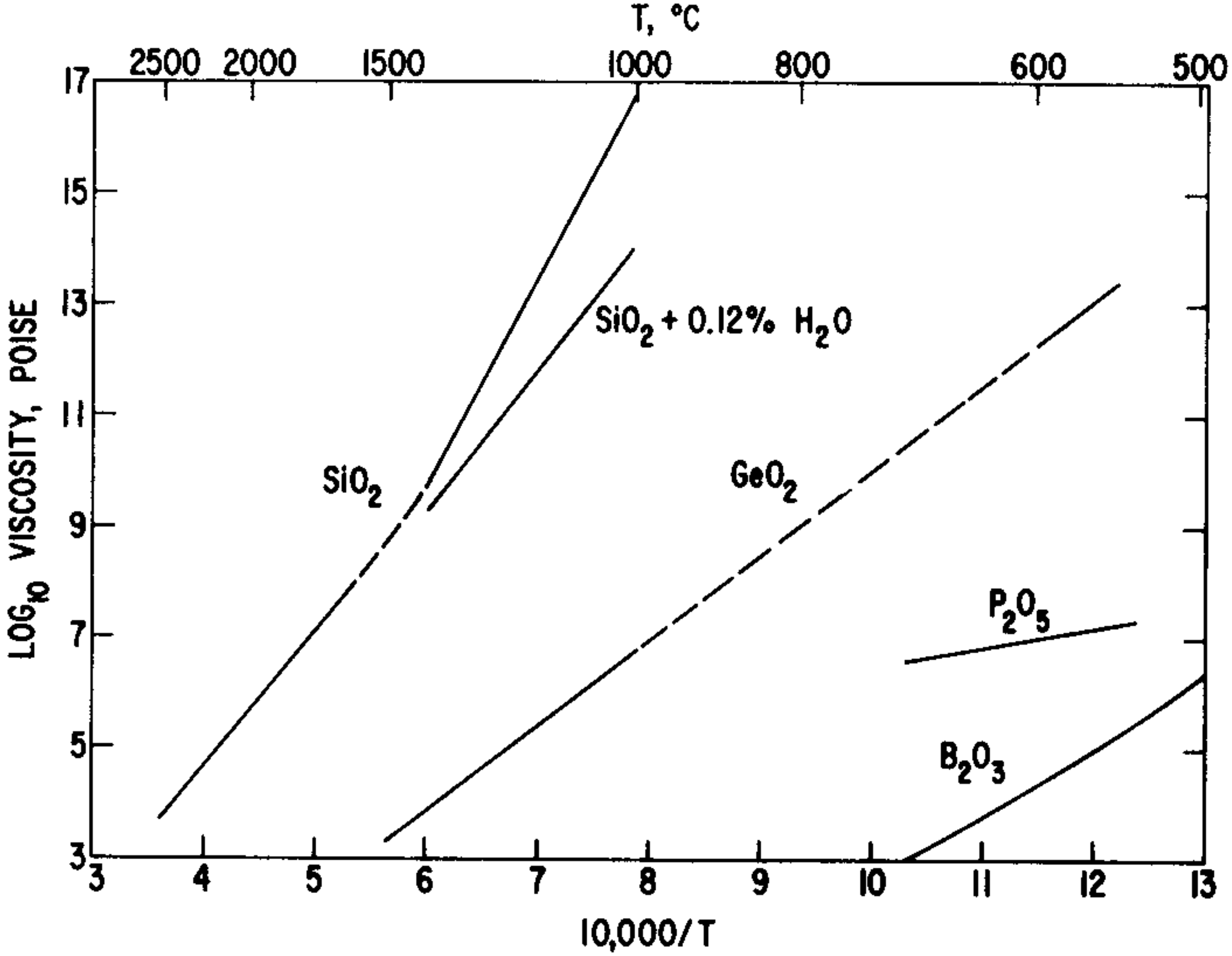
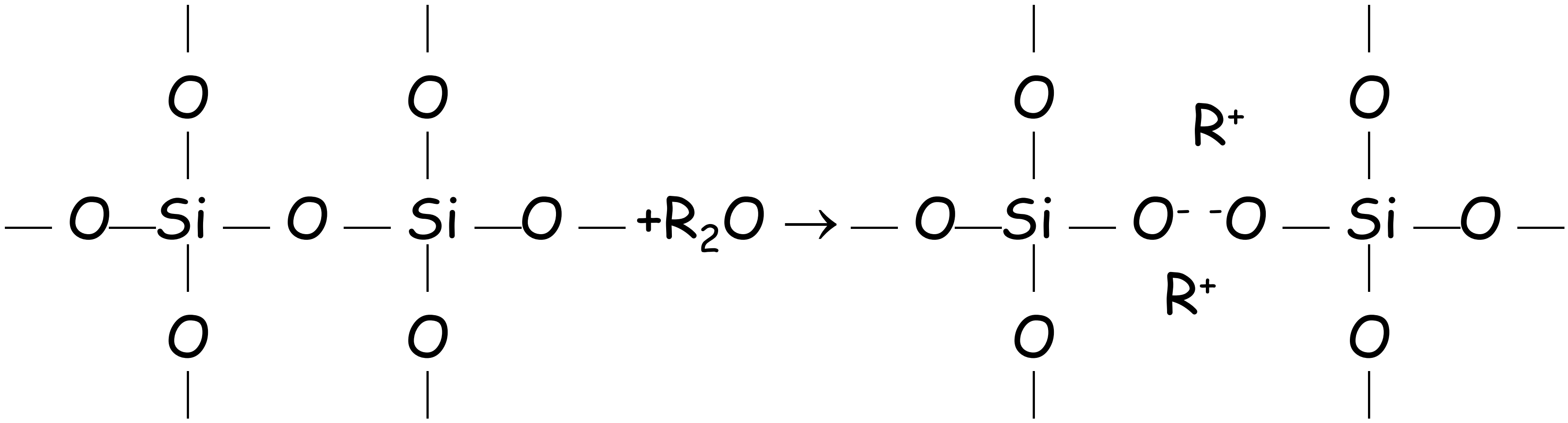
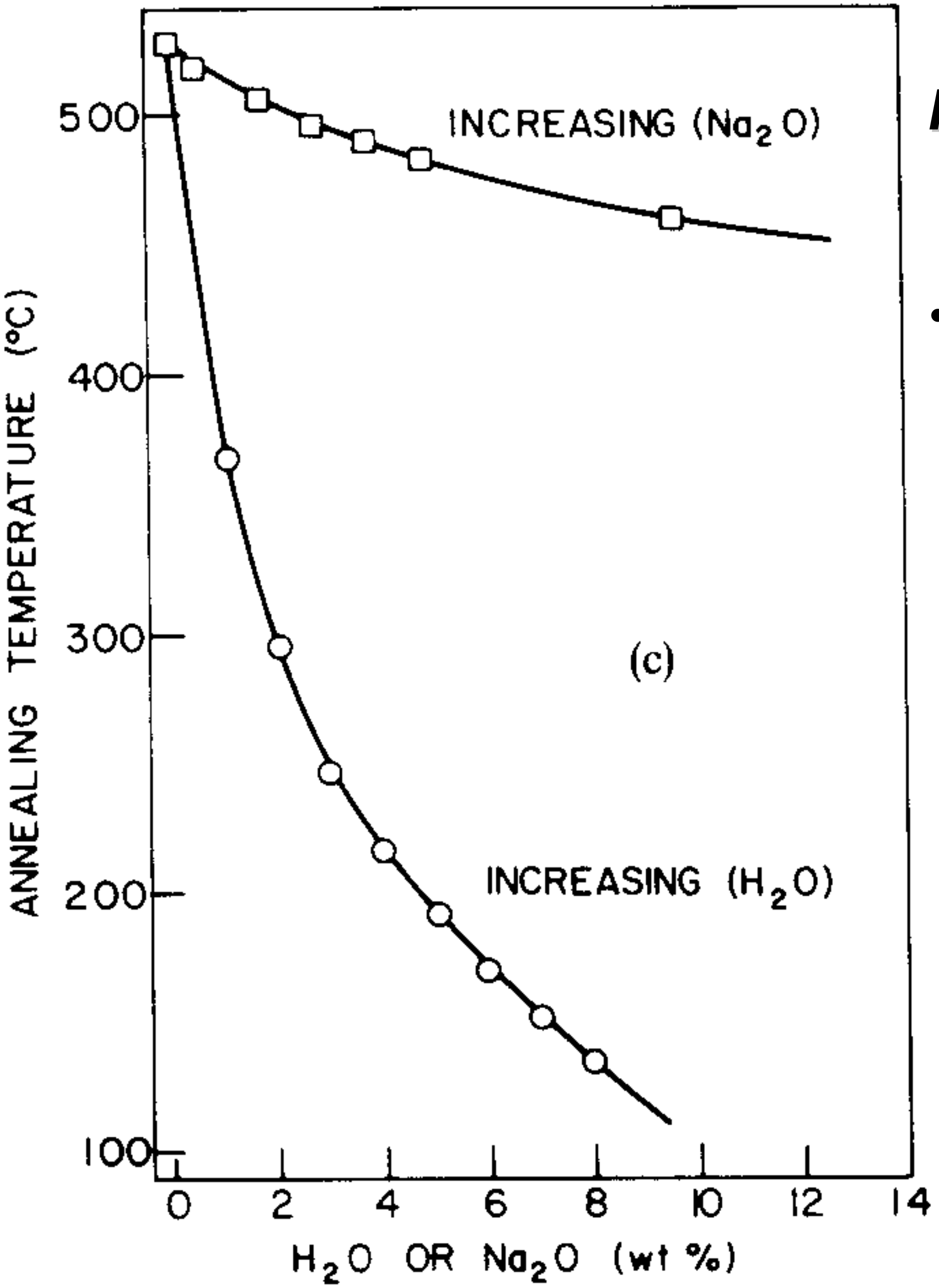


Figure 9-7. Variation of log (viscosity) vs. 10,000/T for simple glass-forming oxides. (After R. H. Doremus, *Glass Science*, Fig. 2, p. 105. Wiley & Sons, New York, 1973. Reproduced with permission of the publishers.)

Reminder: Effect of Modifier Additions on Silicate Glass Networks



$$\boxed{\begin{array}{l} B0 + R_2O \rightarrow 2NBO \\ 2Q^4 + R_2O \rightarrow 2Q^3 \end{array}}$$

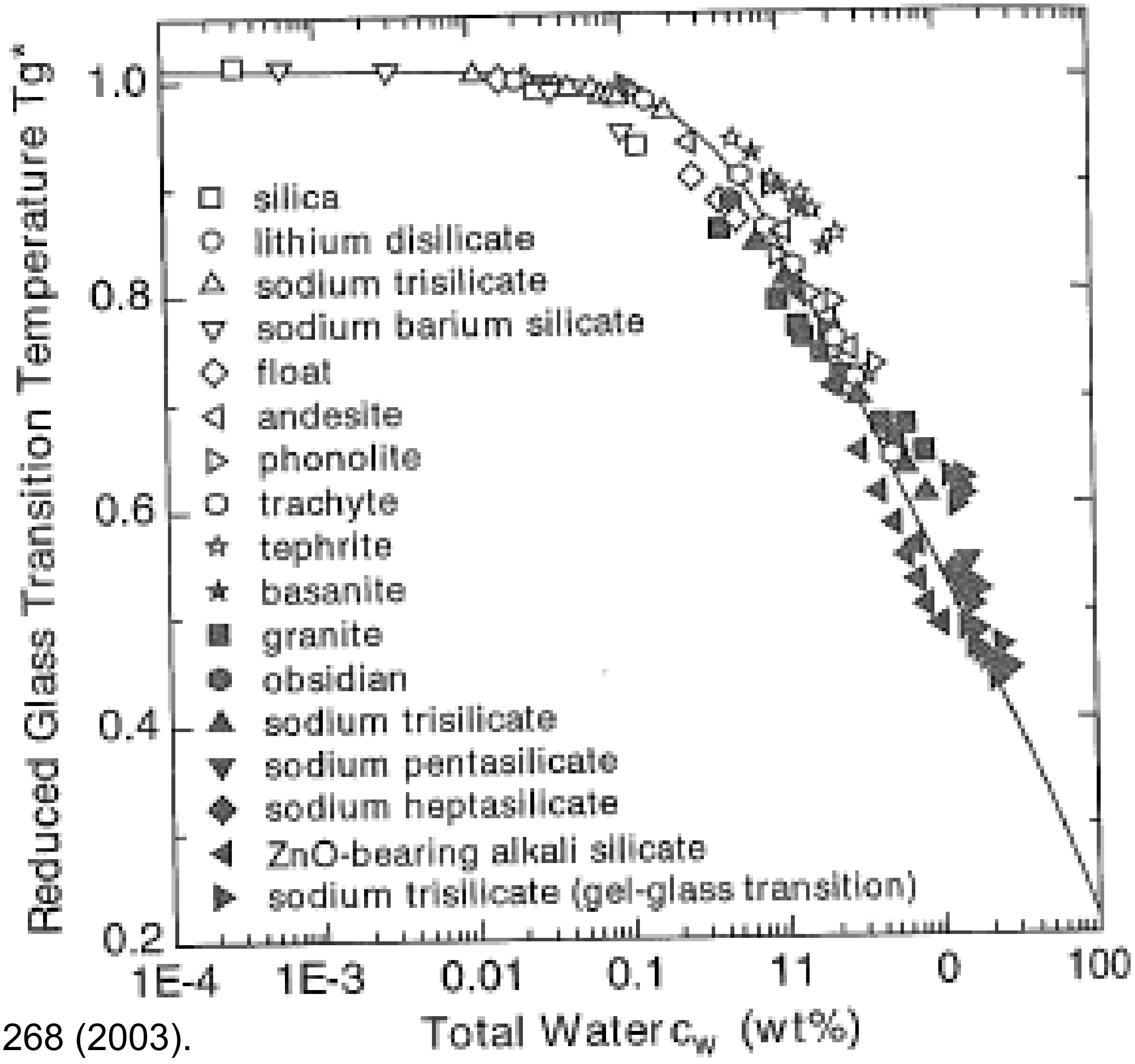


Increasing the modifier content reduces viscosity

- Water is a particularly effective flux

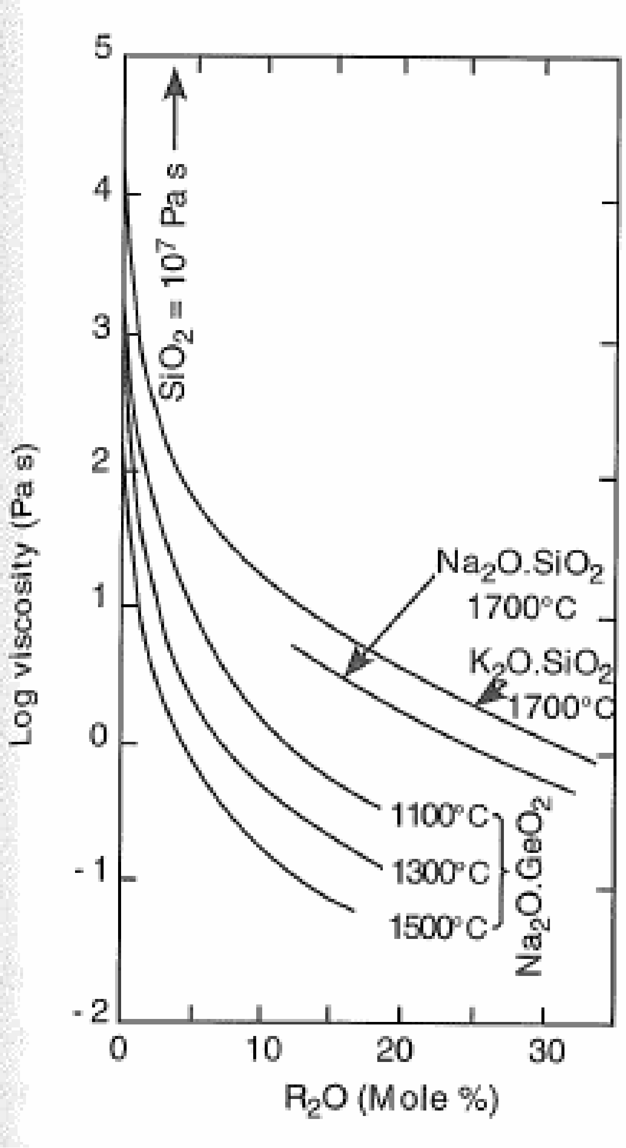
Na-K-Zn-Al-silicate
(Wu, JNCS, 41 381, 1980)

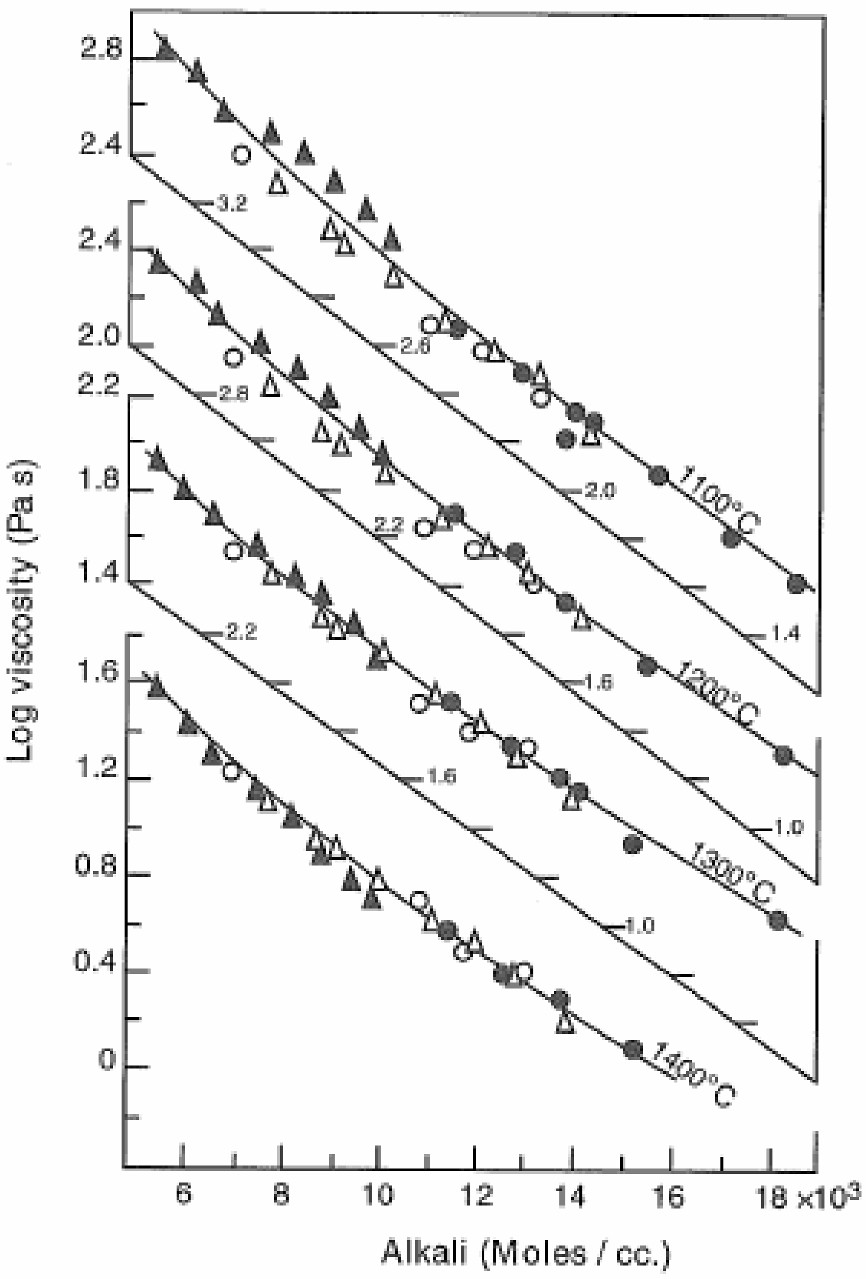
The effect of water on T_g ($\eta \approx 10^{12}$ Pa·s) of silicate glasses



Deubener, et al., JNCS 330, 268 (2003).

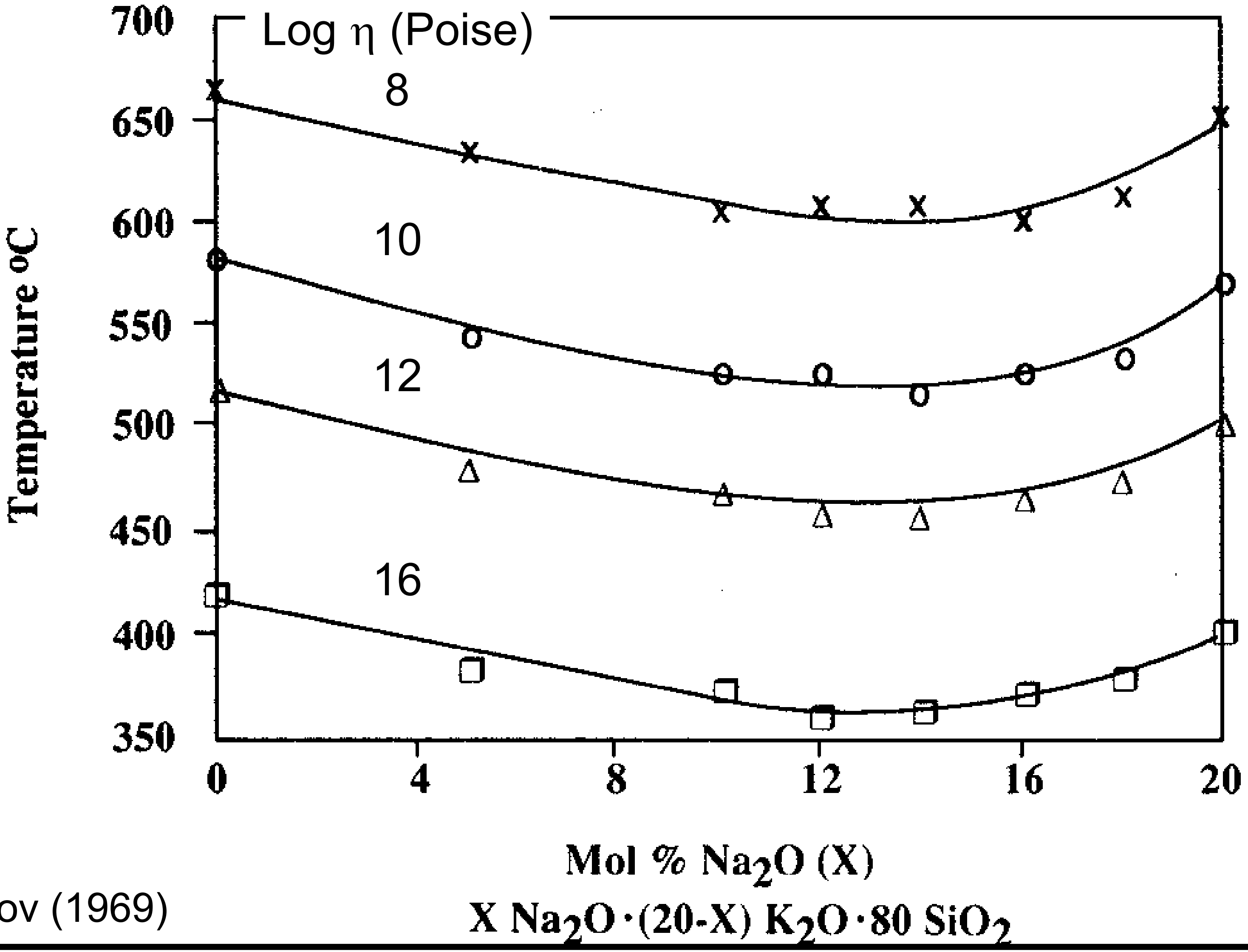
The effects of modifier content on melt viscosity





H. Rawson, *Properties and Applications of Glass*, Elsevier, 1980.

Isokom temperatures for mixed alkali melts



Nemilov (1969)

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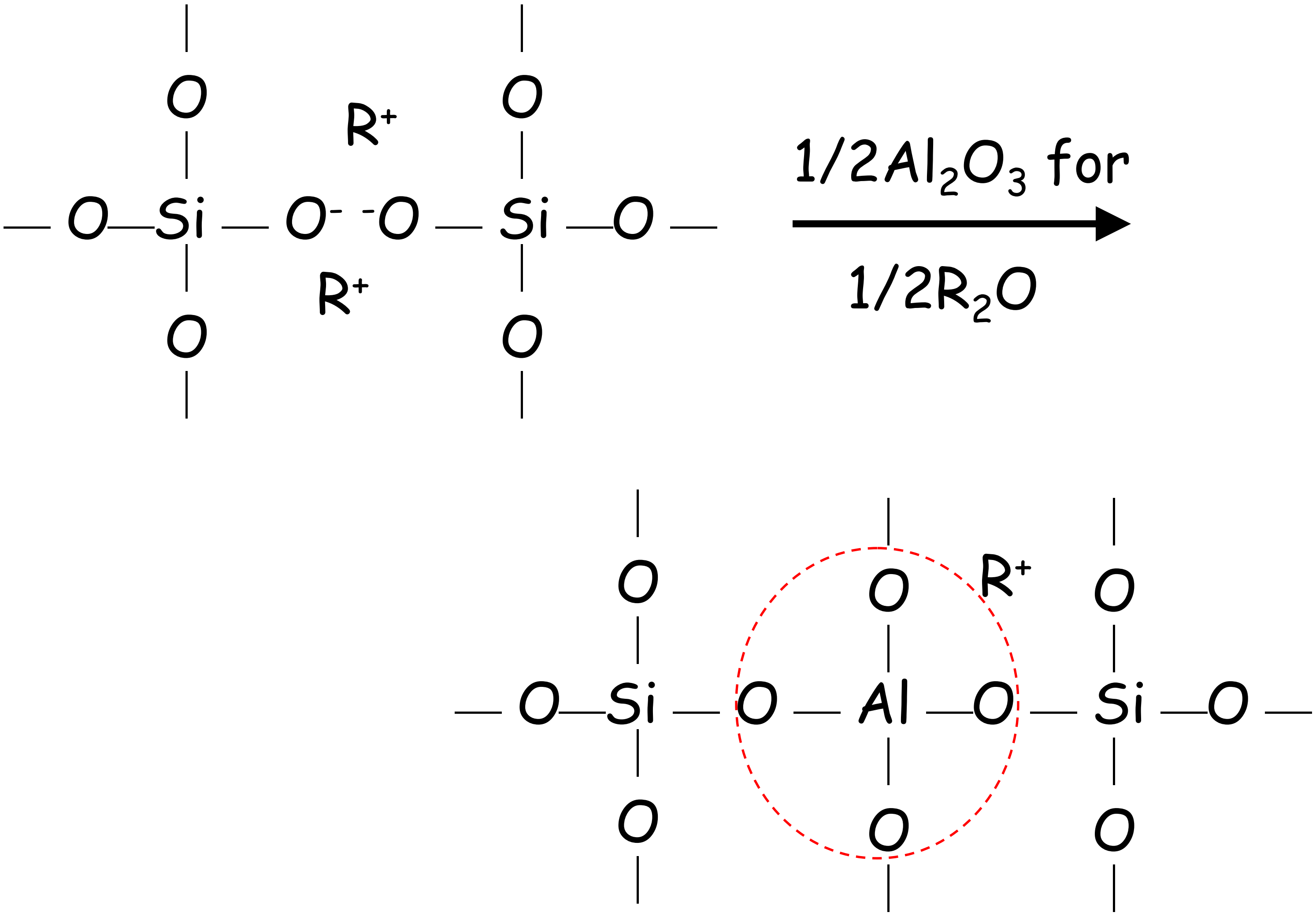
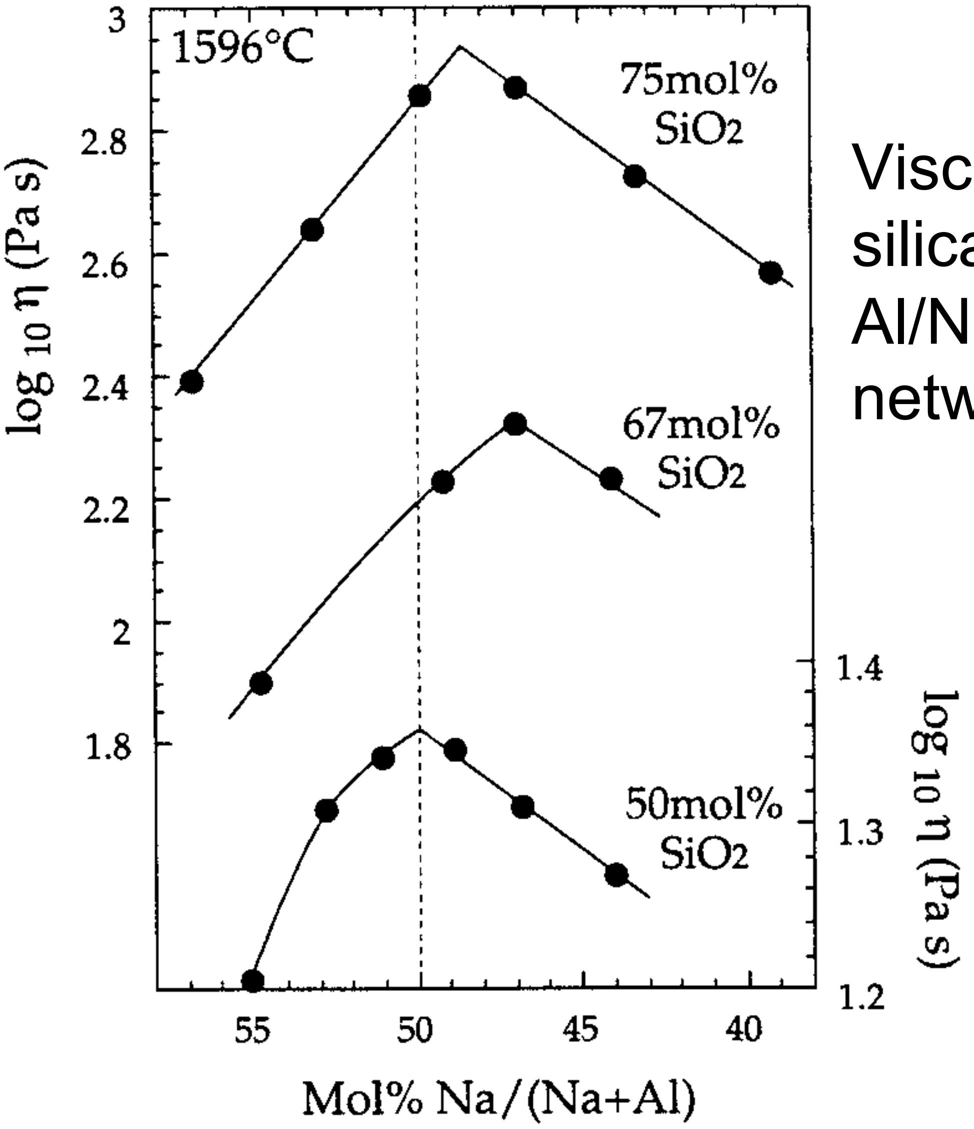
Reminder: Effect of Alumina Additions on Silicate Glass Networks



$1/2Al_2O_3$ for $1/2R_2O$

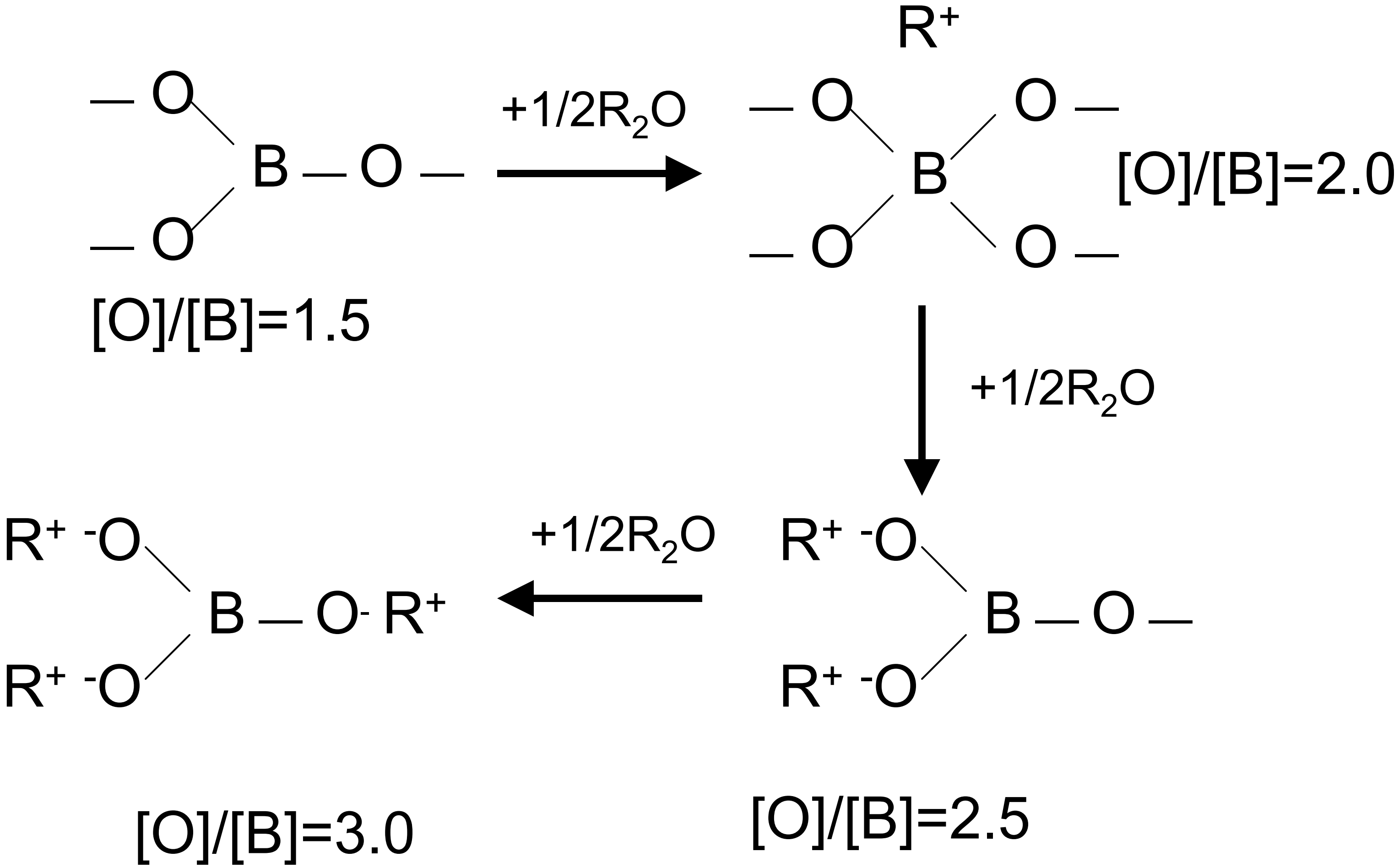


Viscosity of alkali alumino-silicate melts is greatest when Al/Na≈1- fully cross-linked networks….

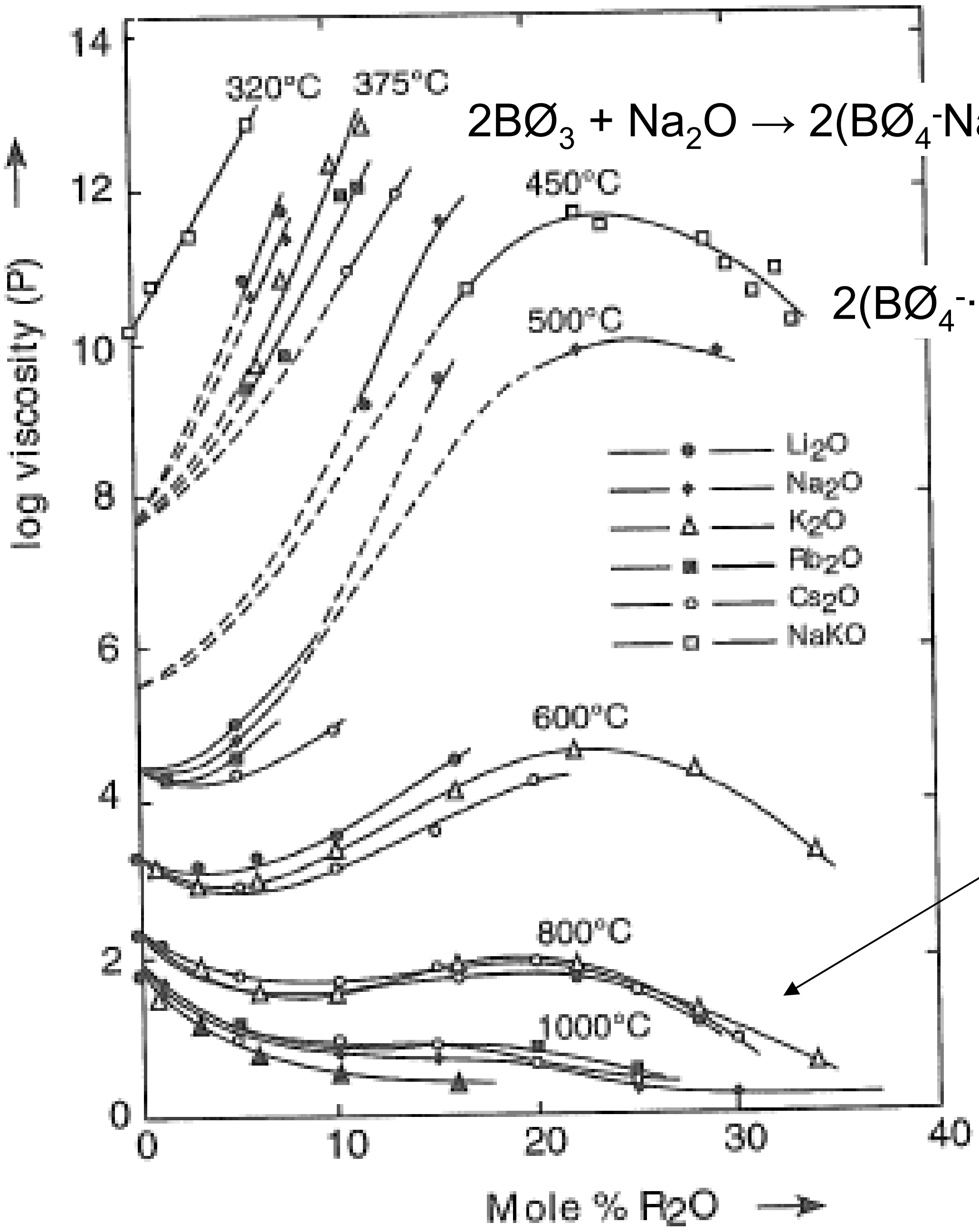
Toplis et al., Geochim. Cosmochim. Acta. **61**[13] 2605 (1995)

Fig. 2. Measured viscosities along the 50 mol%, 67 mol%, and 75 mol% SiO_2 isopleths at 1596°C. The accuracy of the compositional analyses and the precision of the viscosity measurements are both smaller than the size of the symbols.

Reminder: Effect of Alkali Addition on Borate Glass Networks



Alkali borate melt viscosity



$2B\O_3 + Na_2O \rightarrow 2(B\O_4^{-}Na^{+})$

$2(B\O_4^{-}\cdot Na^{+}) + Na_2O \rightarrow 2(B\O O_2^{2-}\cdot 2Na^{+})$

Note the loss of the 'borate anomaly' effect at high temperatures (low viscosity)

J. Am. Ceram. Soc., 89 [1] 13–19 (2006)
DOI: 10.1111/j.1551-2916.2005.00657.x

Temperature-Induced Structural Modifications Between Alkali Borate Glasses and Melts

L. Cormier,*,†,‡ O. Majérus,‡,§ D. R. Neuville,¶ and G. Calas*,‡

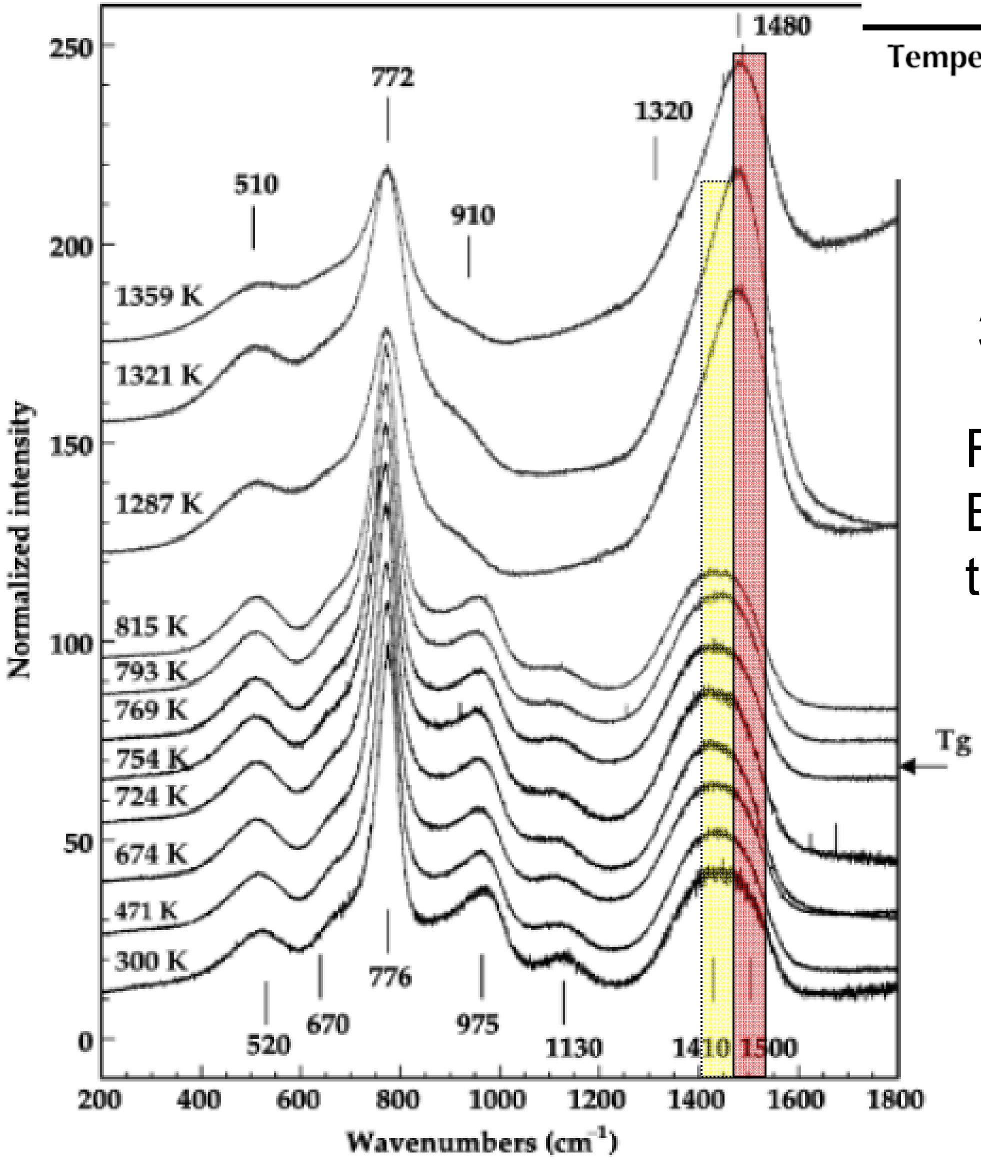


Fig. 3. Raman spectra for the 6LB2 glass from room temperature to 1359 K. The glass transition temperature (T_g) is indicated.

$38.6Li_2O{\cdot}61.4B_2O_3$ glass and melt

Raman spectra indicate that the $BØ_2O^-$ triangles replace $BØ_4^-$ tetrahedra in the melt

Cormier et al., JACerS, 89 13 (2006)

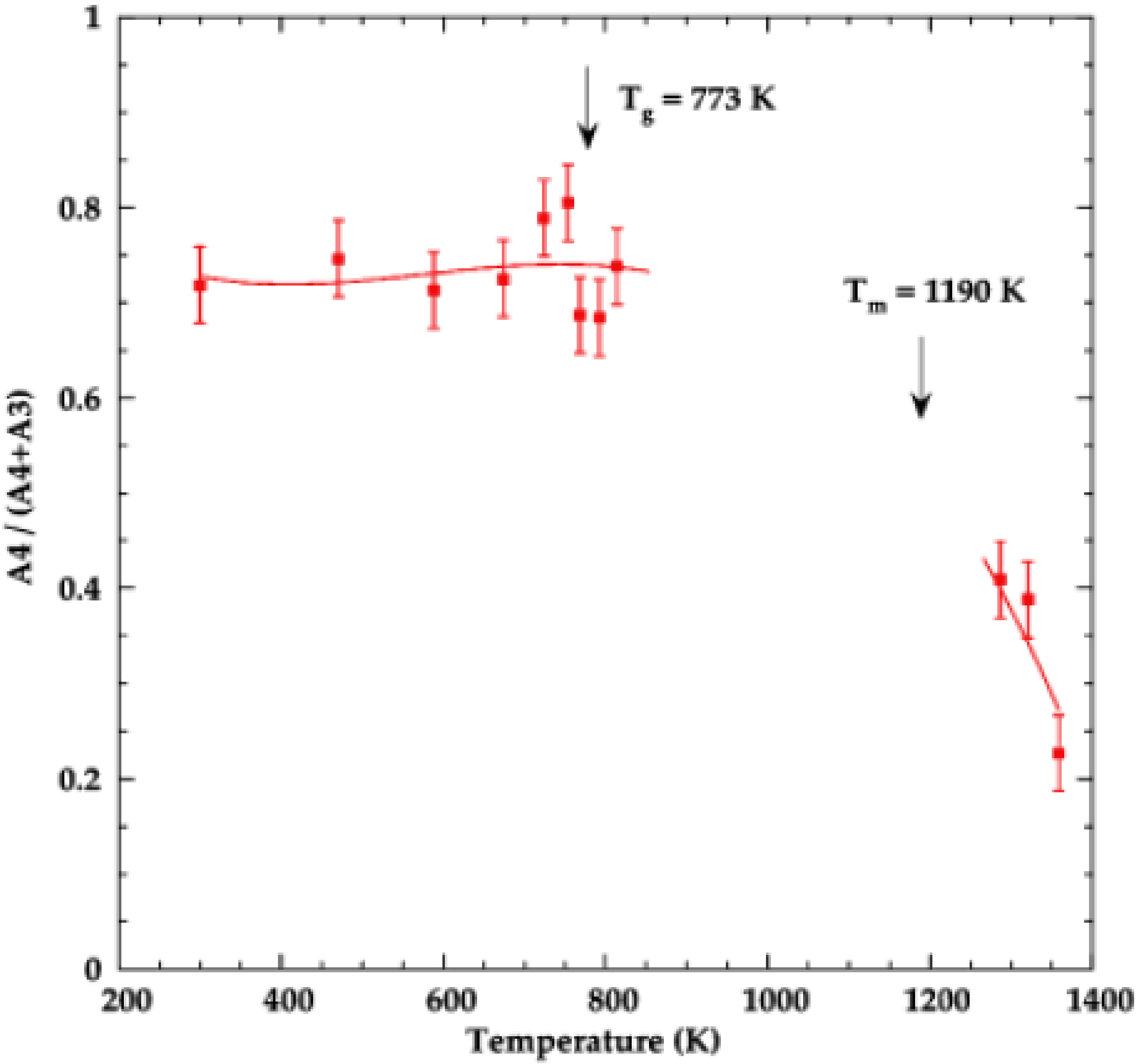


Fig. 4. Ratio of the relative area for the two high-frequency bands of the Raman spectra for the LB2 sample. The temperatures of glass transition and melting are indicated. The line is a guide for the eye.

Raman spectra indicate that the $BØ_2O^-$ triangles replace $BØ_4^-$ tetrahedra in the melt

$$BØ_4^-Li^+ \leftrightarrow BØ_2O^-Li^+$$

Note that B-O bonds are broken, and that such configurational changes will contribute to changes in heat capacity….

Cormier et al., JACerS, 89 13 (2006)

Effects of composition on viscosity

Component	Effect on Viscosity		Glass
	High Temp	Low Temp	
Alkali oxide	-	-	Softer
Alkaline earths	-	+	Shorter
PbO	-	-	Softer
Al_2O_3	+	+	Harder
B_2O_3	-	+	Shorter
OH^-/F^-	-	-	Softer

Modifications to soda-lime silicate melt viscosity, after Beerkens, 1997.

Viscosity dependence on temperature and composition

- Vogel-Fulcher-Tamman (VFT) Equation

$$\log \eta = A + \frac{B}{T - T_0}$$

- Lakatos Method*: empirical additivity factors

$$A = -2.4550 + \sum a_i \cdot p_i$$

$$B = 5736.4 + \sum b_i \cdot p_i$$

$$T_0 = 198.1 + \sum t_i \cdot p_i$$

For S-L-S melts, T (°C) and η (Pa·s), p_i (mole fraction oxide per mole SiO_2)

*T. Lakatos, et al., *Glass Technology*, 13 88 (1972)

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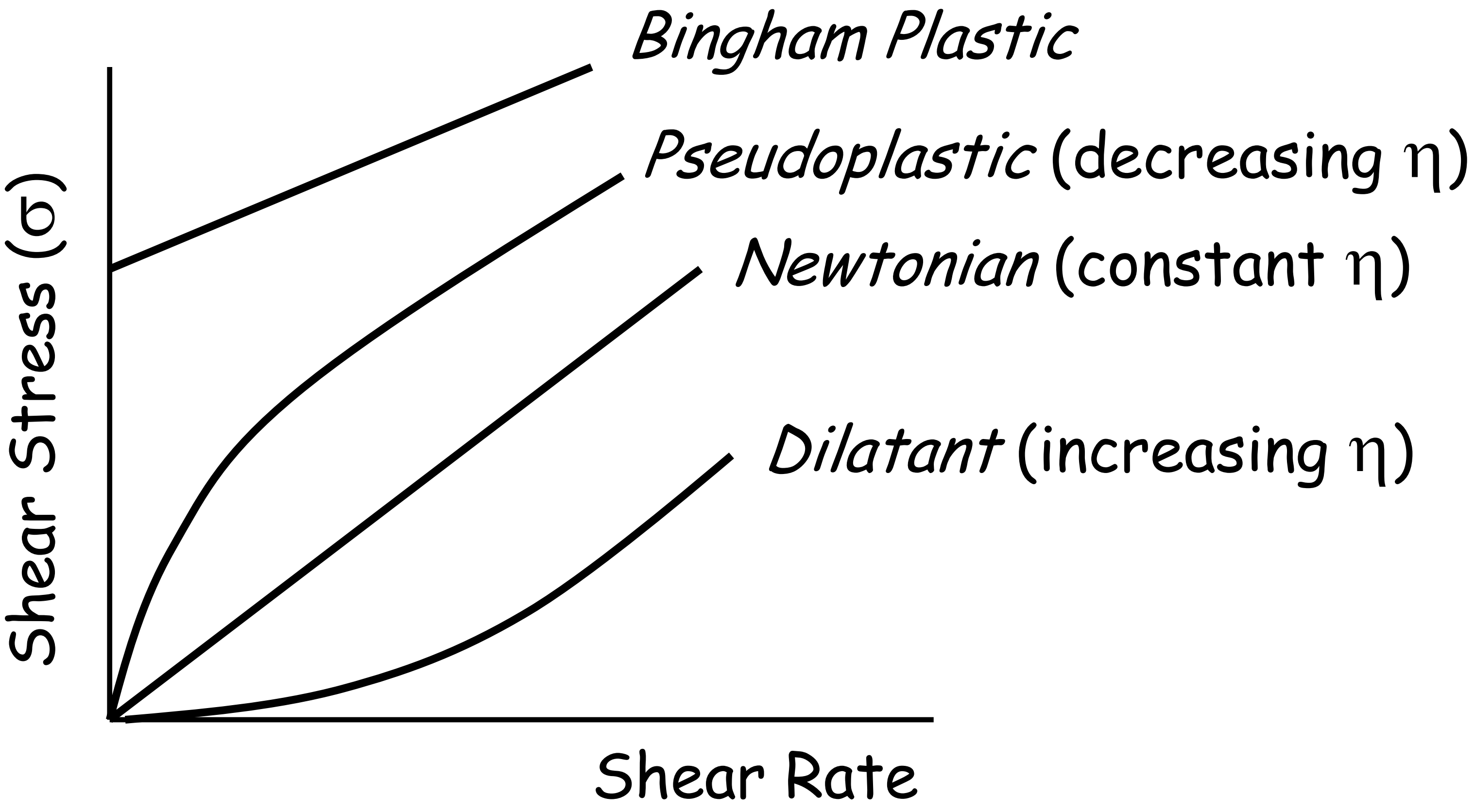
Lakatos additivity parameters (after Beerkens, 1997)

	a_i	b_i	t_i
Na_2O	+1.4788	-6039.7	-25.07
K_2O	-0.8350	-1439.6	-321.0
MgO	-5.4936	+6285.3	-384.0
CaO	-1.6030	-3919.3	+544.3
B_2O_3	-15.880	+7272.1	+521.4
Al_2O_3	+1.5183	+2253.4	+294.4
PbO	+1.3058	-5880.0	-275.5

Valid for the log(viscosity) range 1-12 Pa·s

Not all liquids exhibit Newtonian viscosity behavior



Non-Newtonian Viscosity

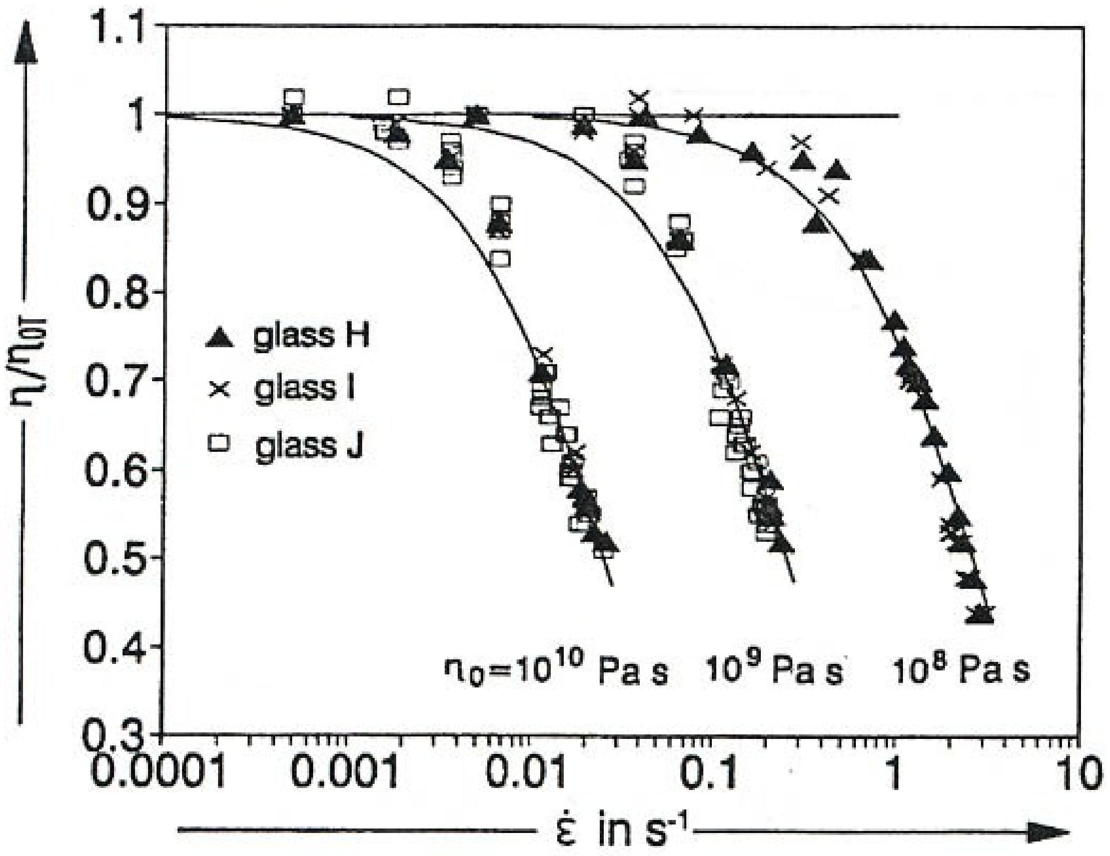


Figure 4. Normalized non-Newtonian viscosity as a function of normalized deformation rate for glass melts H, I and J at three Newtonian viscosities.

Shear thinning- decreasing *effective* viscosity with increasing deformation rates

- fiber drawing
- press-and-blow

Greater problem at higher temperatures

Yue & Brückner
Glastech. Ber (1996)

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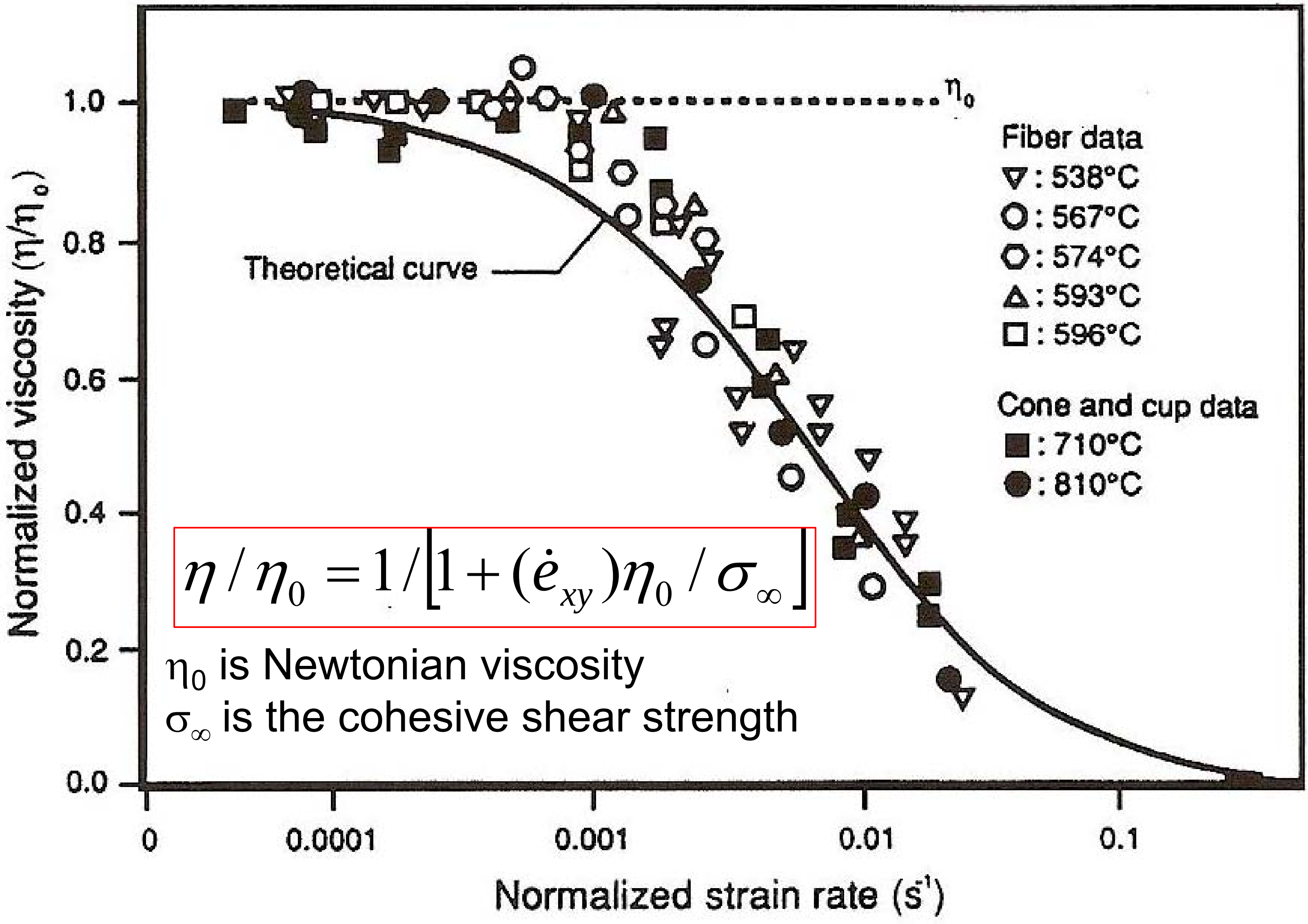
Non-Newtonian Viscosity

Simmons and Simmons, *Cer Bull* 68[11] 1949 (1989)

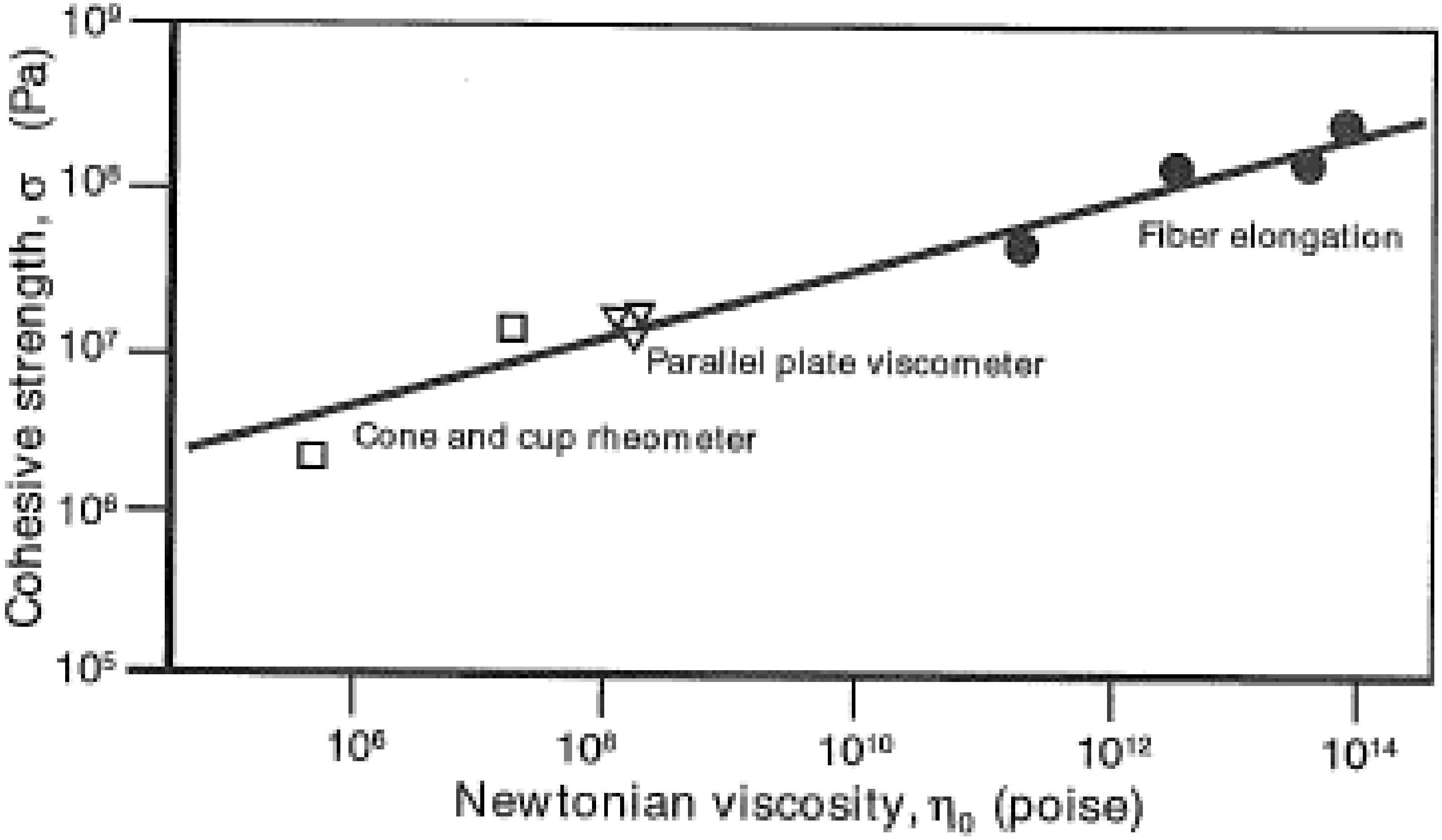


$$\eta/\eta_0 = 1/\left[1+(\dot{e}_{xy})\eta_0/\sigma_\infty\right]$$

η_0 is Newtonian viscosity

σ_∞ is the cohesive shear strength

Cohesive strength increases with viscosity



- Viscosity becomes nonlinear at high shearing rates
- Shear stress builds up if stress relaxation rate is sufficiently low
- If shear stress>σ_∞, then ‘liquid fracture’ can occur

Simmons and Simmons, *Cer Bull* 68[11] 1949 (1989)

Consequences of Non-Newtonian Viscosity

- High-speed glass processing
  - Fiber attenuation
  - Container processing
- Source for glass inhomogeneities
  - Induced phase separation or crystallization in high shear regions

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JOURNAL OF MATERIALS SCIENCE 39 (2004) 6539–6549

Deformation, stress relaxation, and crystallization of lithium silicate glass fibers below the glass transition temperature

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E-mail: reis@umr.edu

- Fibers heated below T_x
- Stress in ‘bent’ regions reduces ‘effective’ viscosity
- Examine differences in crystallization behavior

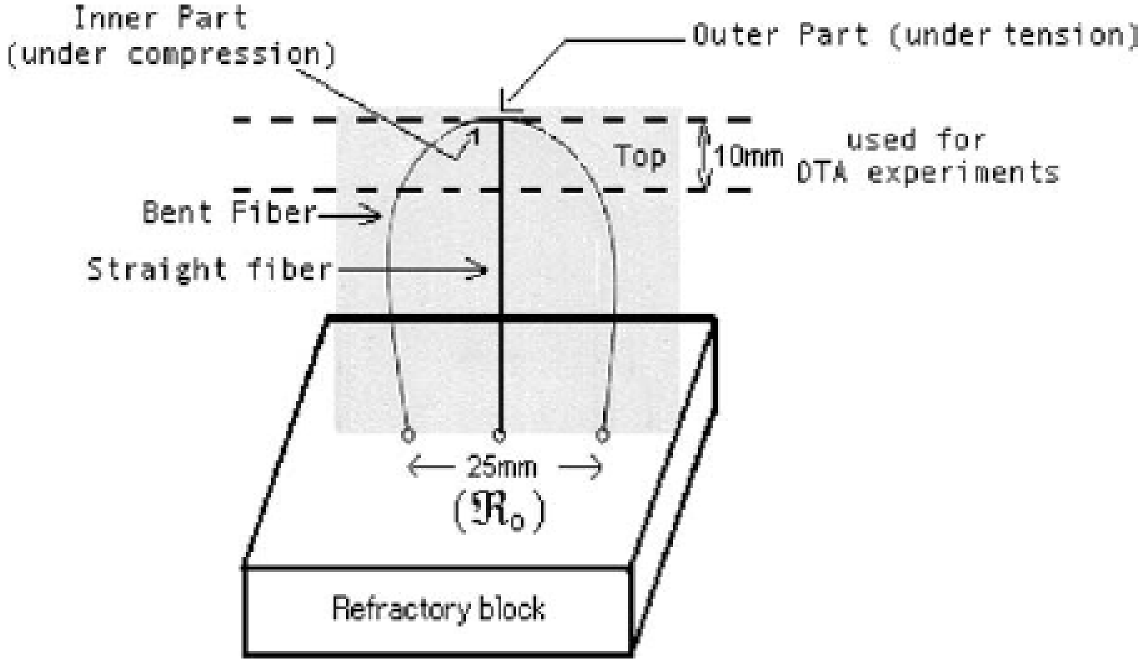

Figure 1 Schematic diagram of the glass fibers in a refractory block for heat treatment. Length of the glass fiber: 120 mm. Diameter of the glass fiber: 150 μm.

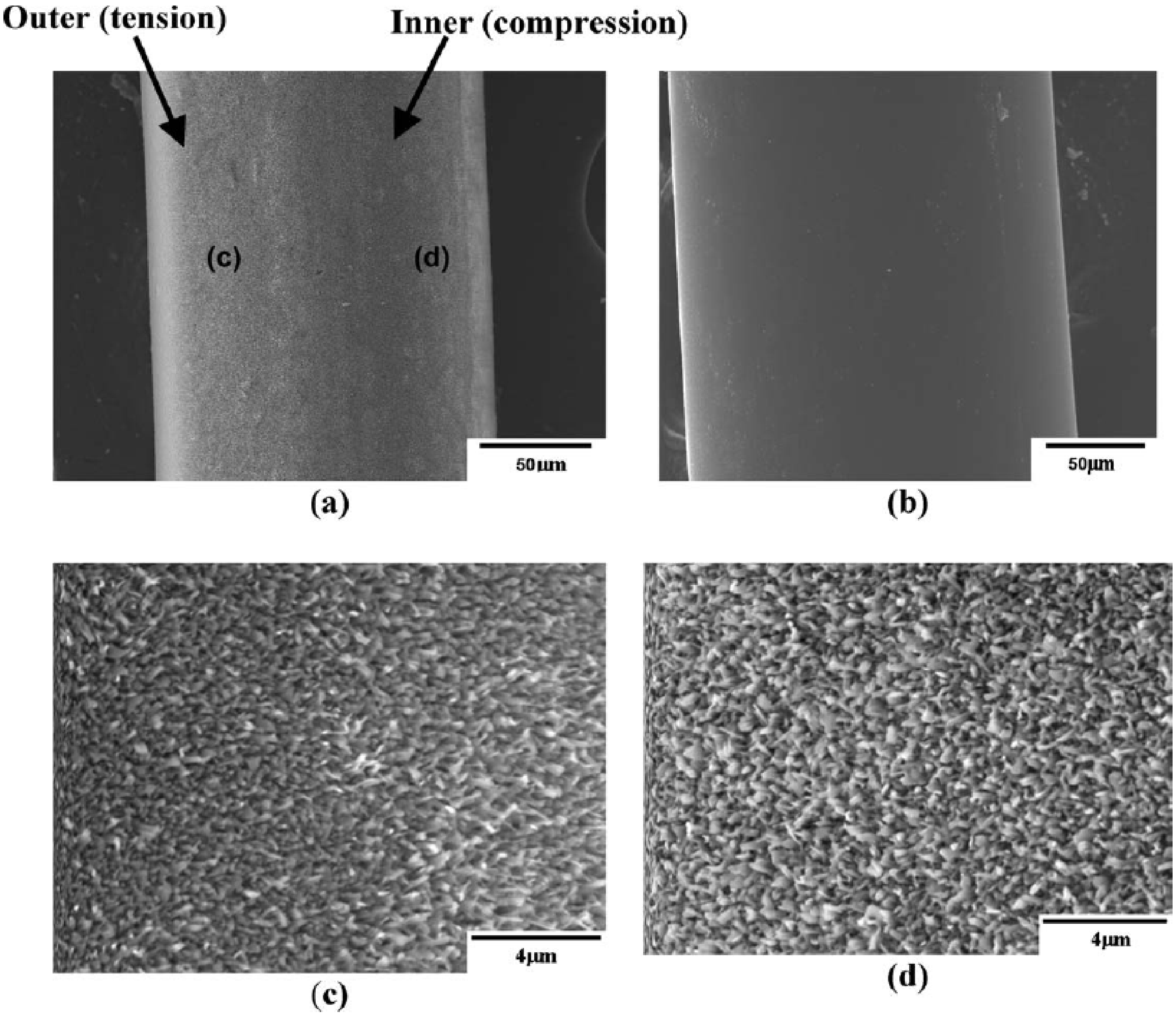

Figure 4 Scanning electron microscope pictures of the (a) stressed and (b) un-stressed (straight) LS$_{1.6}$ glass fibers after heating at 410°C for 12 h. (c) and (d) are the enlarged view of the outer and inner part of stressed fiber at locations shown in (a). No crystallization is observed on the heat treated straight fiber (b).

Another example

- Melts prepared in micro-gravity have greater glass-forming tendencies than melts on earth at comparable quench rates
  - Hypothesis*: gravity-driven fluid-flow increases overall strain rate within melt
    - Reduced ‘local’ viscosity through shear thinning
    - Increased ‘local’ crystallization rates

*CS Ray et al, Trans. Indian Inst. Met. 60[2] 143 (2007)

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An Analysis of the Differences in the Glass Forming Tendency of Melts on Earth and in a Low - Gravity Environment

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[*]Marshall Space Flight Center, National Aeronautics and Space Administration, Huntsville, AL 35812, USA;
[*]BAE Systems, Marshall Space Flight Center, National Aeronautics and Space Administration, Huntsville, AL 35812, USA.

Calculated for LS_2 melts at 1400°C and a 5°C temperature gradient

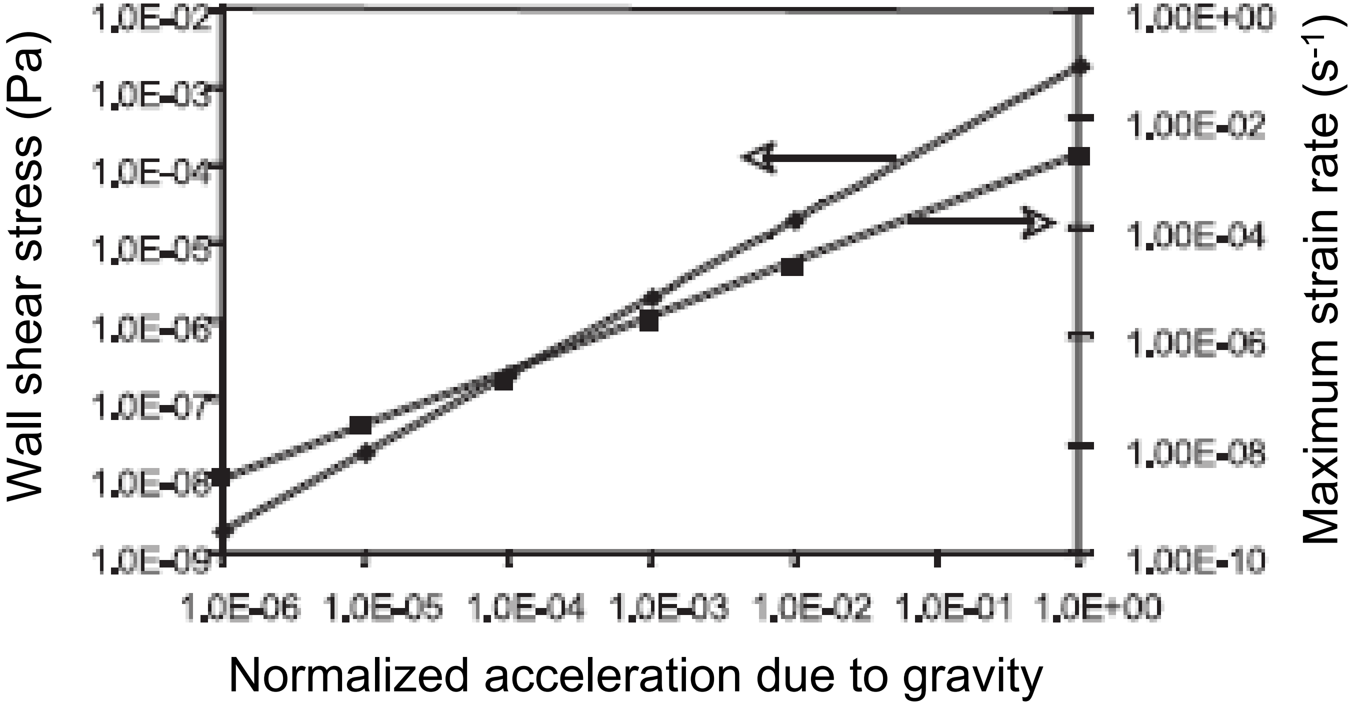

Fig. 6 : Maximum system wall shear stress and maximum system strain as a function of *g* level.

Trans. Indian Inst. Met. 60[2] 143 (2007)

Normalized acceleration due to gravity

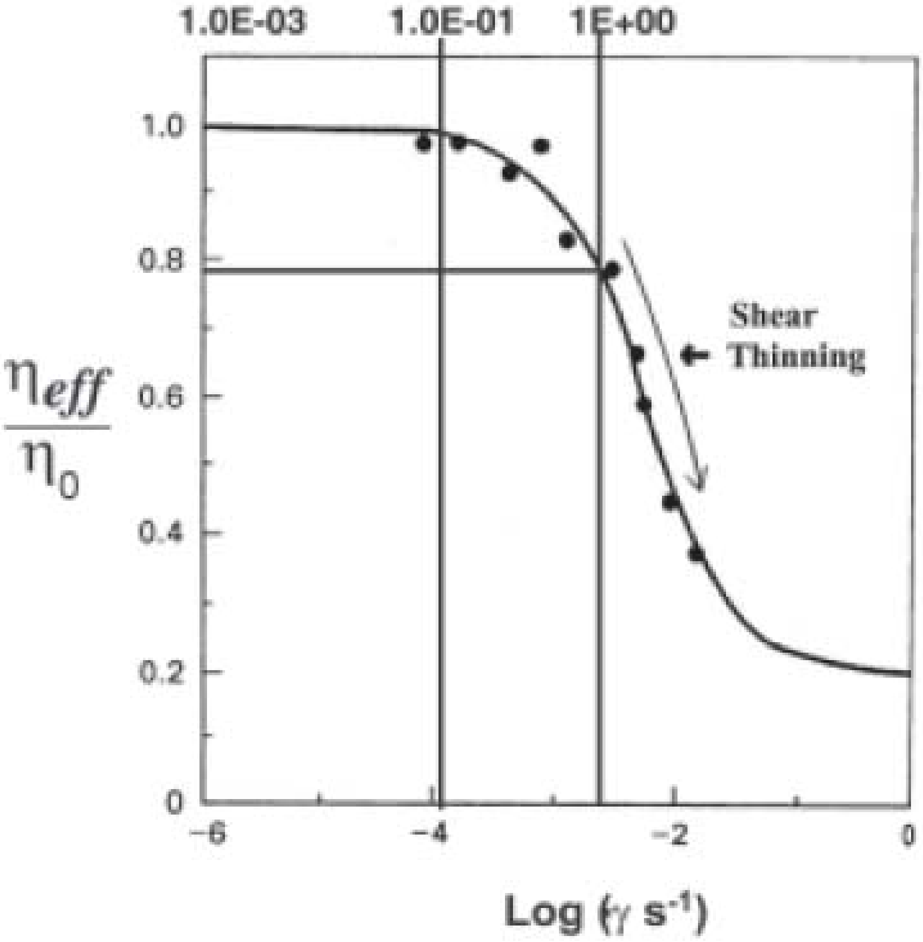

Fig. 7 : Superimposition of calculated strain rate from present study on experimental measurements [15] of viscosity as a function of strain rate.

Shear-thinning behavior is reduced when gravitational effects are reduced.

From J. H. Simmons, in *Experimental Techniques of Glass Science*, (1993), p. 383-432.

Phase separation affects viscosity

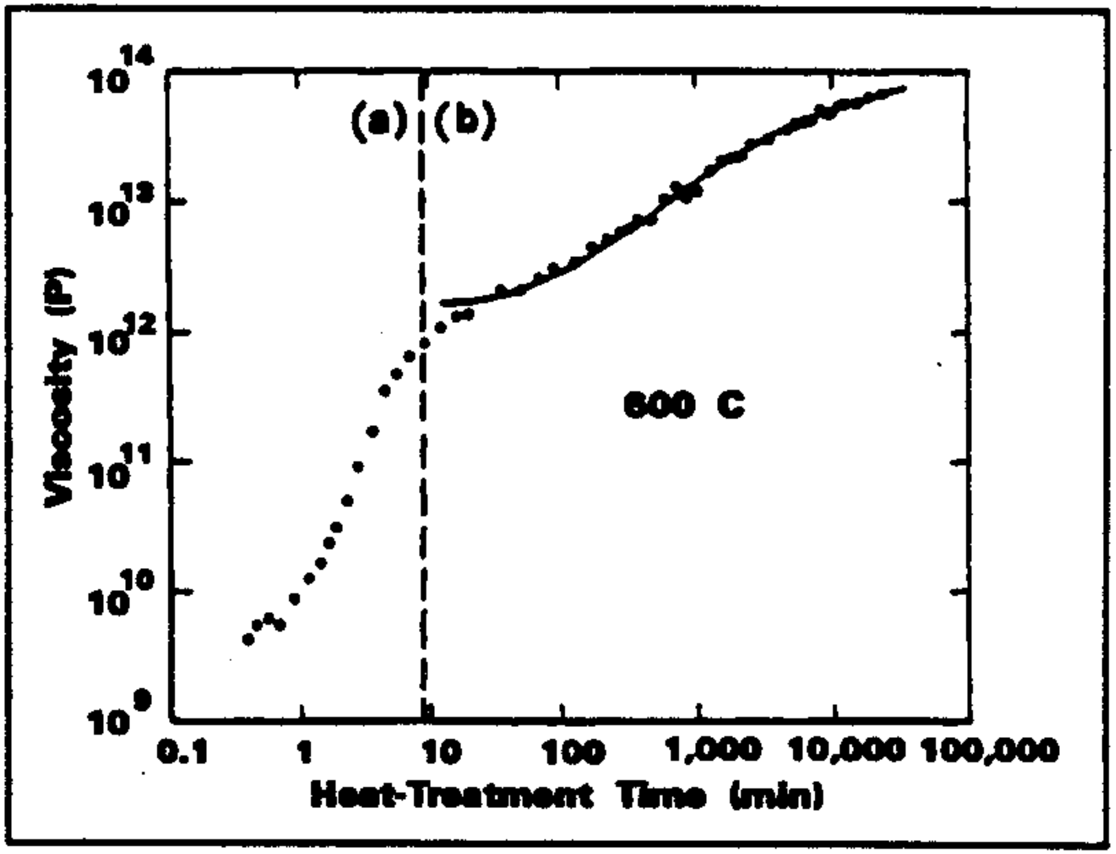

Figure 11 - Viscosity change in Pyrex due to phase separation. Period (a) is dominated by spinodal decomposition. Period (b) is dominated by coarsening[92].

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Crystallization affects viscosity

- Example: crystallizable sealing glass

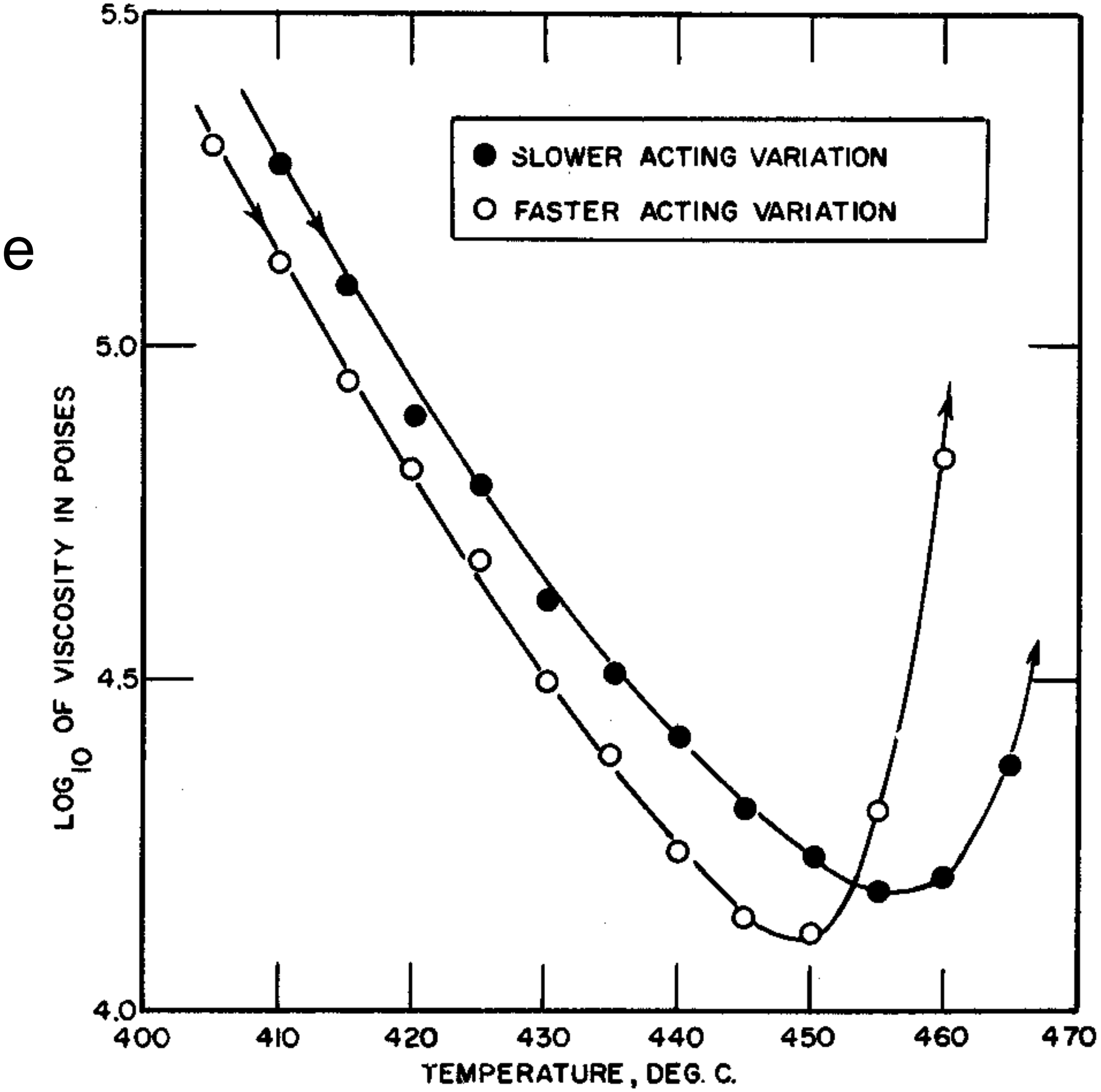


Figure 12. Parallel plate viscometer data for frit glasses.

From H. E. Hagy, in *Introduction to Glass Science*, (1972), p. 343-371

Viscosity Summary

- Viscosity is the most important melt property
  - Critical for processing, from melting through annealing
- Compositional dependence can be understood in terms of melt/glass structure
  - Stronger networks = greater viscosity
    - Fraction of NBO’s on silicate tetrahedra
    - Aluminosilicate networks
    - Borate ‘anomaly’- tetrahedral sites
  - Viscosity is sensitive to changes in melt structure
- Temperature dependence is non-Arrhenian
  - VFT equation is a useful empirical description
  - Fragile/strong classification can be related to configurational changes
- Shear-thinning has processing consequences

Glass formation is 'crystallization avoidance'

$$\dot{T}_c \approx \underbrace{\frac{AT_m{}^2}{\eta(at\ 0.77T_m)}}_{\textit{Kinetic barrier}} \cdot \underbrace{\exp(-0.212B)}_{\textit{Nucleation barrier}} \cdot \left[1-\underbrace{\exp\left(-\frac{0.3\Delta H}{RT_m}\right)}_{\textit{Free energy driving force}}\right]^{3/4}$$

Reduce critical cooling rate to improve glass formation

- Lower T_m
- Increase η at T_m

If T_g ($\eta=10^{13}$ P) is near T_m, then $\eta(T_m)$ will be high

Glass formation expected when $T_g/T_m>2/3$

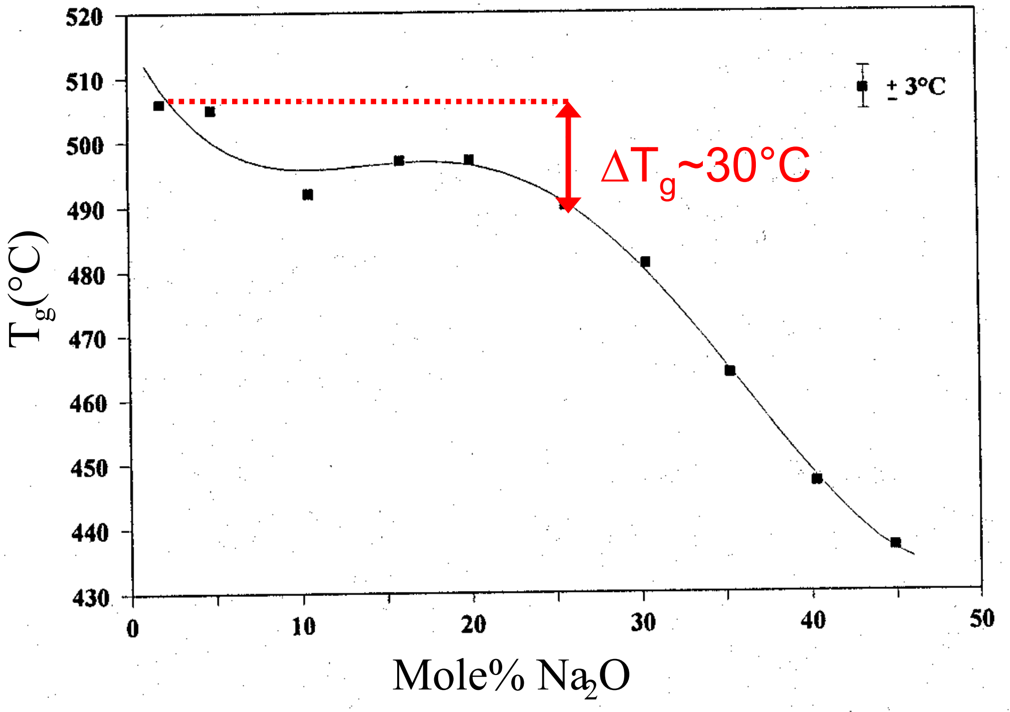
	T_m(°C)	$\eta(T_m)$
BeF_2	540	>10^6 P
B_2O_3	460	10^5 P
GeO_2	1150	10^7 P
SiO_2	1710	10^7 P
LiCl	613	0.02 P
Zn	420	0.03
Fe	1535	0.07

Good glass formers

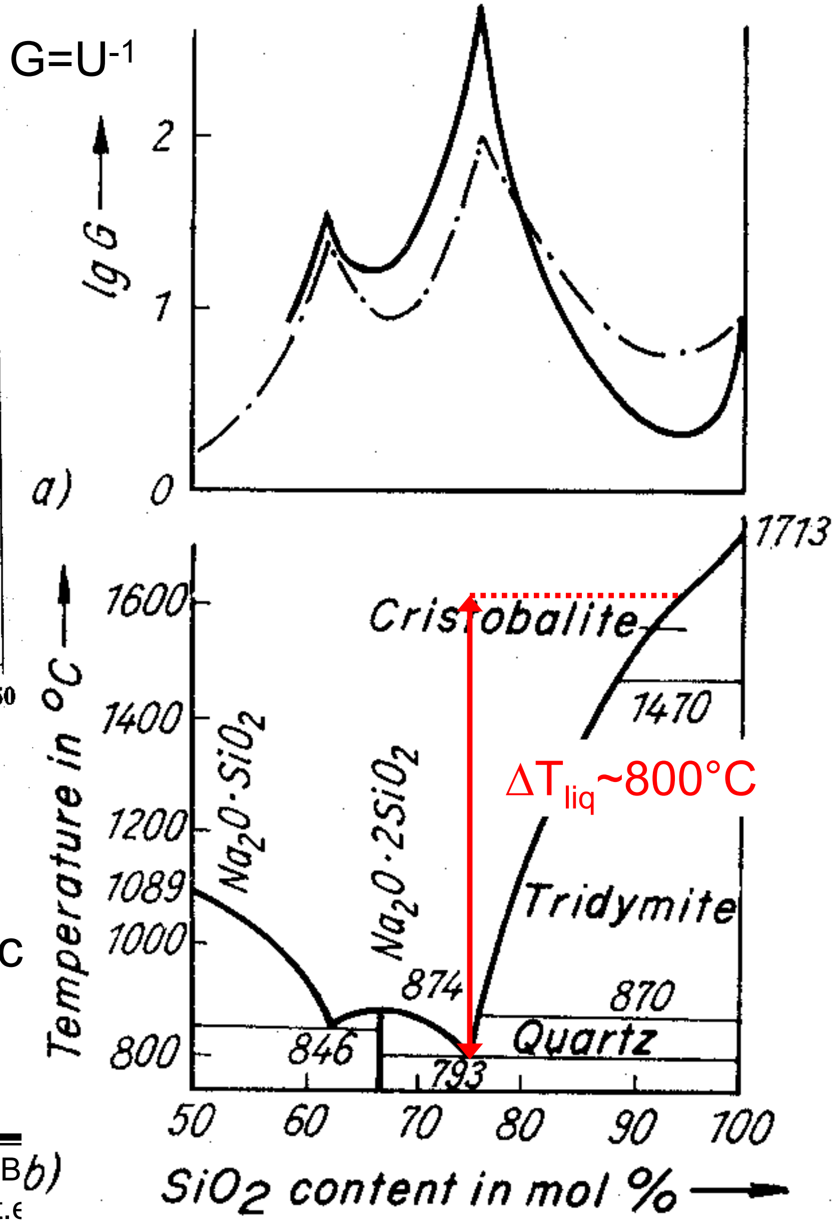
Poor glass formers

Eutectic compositions are good glass-formers

From Dingwell in *Rev. Mineral.* **32** (1995)



W. Vogel, *Chemistry of Glass*, 1985



T_g/T_{liq} is a maximum (~0.7) at the eutectic

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