

Recall the *Kinetic Theory* of glass formation:

- Crystallization is impeded by kinetic barrier to atomic rearrangement at high viscosity
- Glass formation is promoted by:
  - High viscosity at the melting point (liquidus), or
  - Rapid viscosity increase with  $-\Delta T$

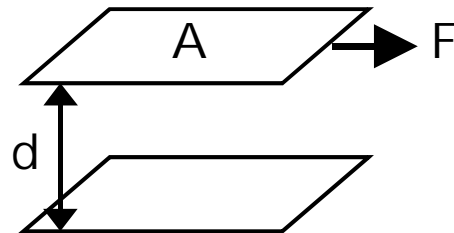
Viscosity is also a critical processing property:

- Melt conditions to form bubble-free, homogeneous melts;
- Annealing temperature to remove internal stresses;
- Forming temperature for commercial products; etc.

Definitions:

- Viscosity ( $\eta$ ) is a measure of the *resistance* of a liquid to *shear deformation*.

$F$  = difference in tangential force required to move a plane (area  $A$ ) at a constant velocity ( $V$ ) relative to a second plane a distance ' $d$ ' from the first.



Stress (or pressure)  $= \sigma = F/A$

Deformation rate  $= \dot{\epsilon} = V/d$

$$\text{Viscosity} \equiv \eta = \frac{Fd}{AV} = \frac{\sigma_0}{\dot{\epsilon}}$$

At constant applied shear stress ( $\sigma_0$ ), a *Newtonian Liquid* exhibits a constant strain rate ( $\dot{\epsilon}$ ) that is inversely proportional to a *constant* viscosity.

Viscosity Units (cgs system):

$$\eta = F \cdot d / A \cdot V = (\text{dynes}) \cdot (\text{cm}) / (\text{cm}^2) \cdot (\text{cm/s})$$

$$= (\text{dynes} \cdot \text{s}) / \text{cm}^2 = \text{Poise (P)}$$

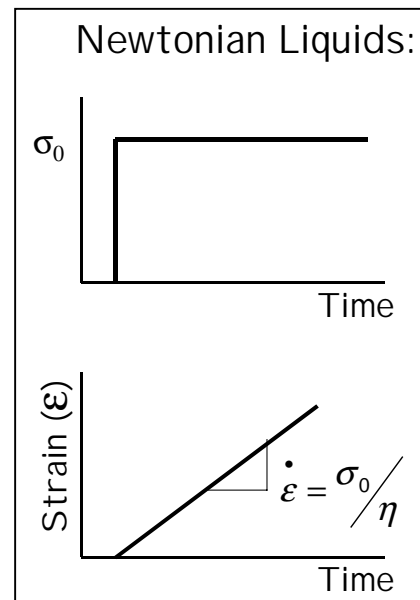
(SI units):

$$= (\text{N} \cdot \text{m}) / (\text{m}^2 \cdot (\text{m/s})) = (\text{N/m}^2) \cdot \text{s} = \text{Pascal-sec}$$

**Note:** 1 Pa-s = 10 P

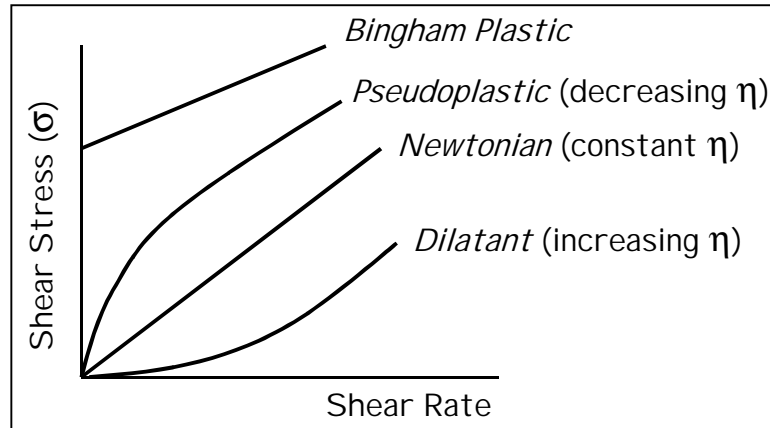
Room temperature water:  $\eta = 0.01 \text{ P} (=1 \text{ cP}) = 0.001 \text{ Pa-sec}$

NaCl (melting point) =  $1.3 \times 10^{-3} \text{ Pa-s}$ .



### Non-Newtonian Viscosity

- Non-linear stress-strain behavior



At very high shear rates, glass melts exhibit *pseudoplastic* flow (*shear thinning*)

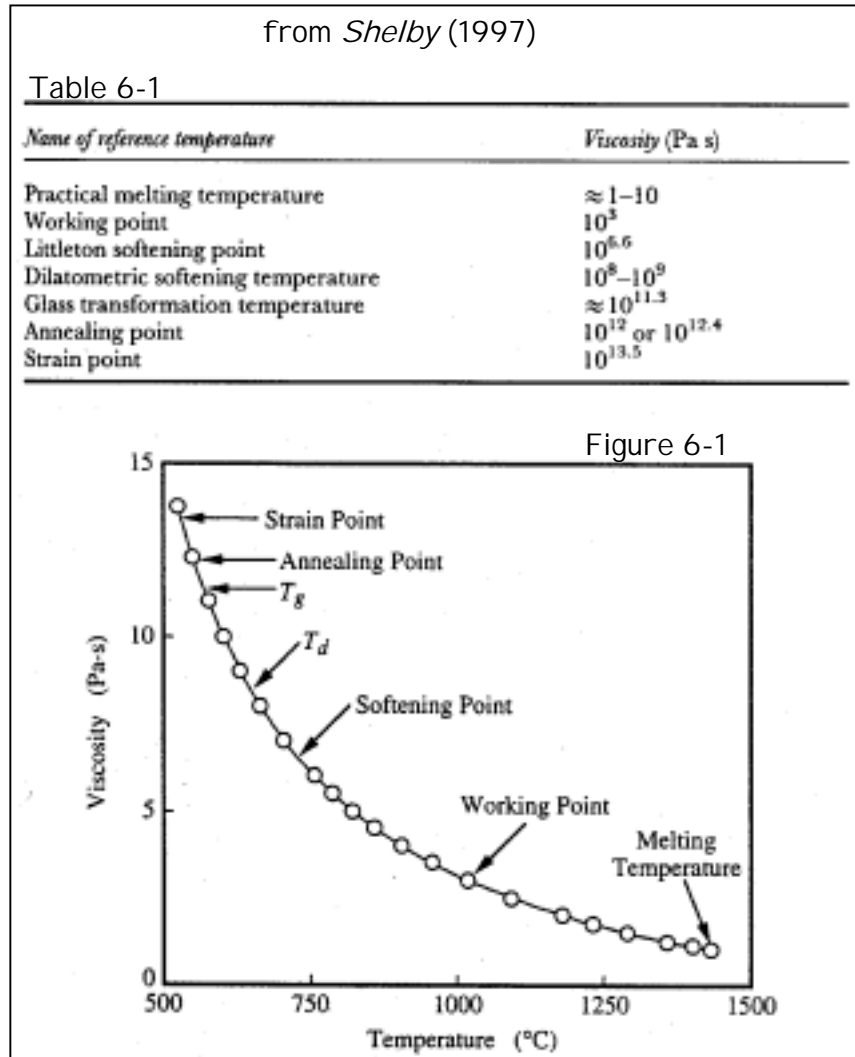
- Processing consequences: fiber drawing, controlling gob behavior, etc.

*Dilatant* Flow (*Shear Thickening*): concentrated ceramic slips (corn starch, wet beaches, etc.)

*Bingham Plastic*: no deformation until a yield point is exceeded, thereafter linear behavior (constant viscosity)- some paints, slurries behave this way.

*Thixotropic* behavior (not shown): viscosity decreases with time at constant shear rate.

There are a number of important reference points that describe the viscosity-temperature characteristics of a glass melt.



1. Typical (Practical) Melting Temperature: ( $\eta \leq 10 \text{ Pa-sec}$ ); melt is fluid enough for fining/homogenization to occur in a 'practical' amount of time.
  - This is *not* the  $T_{\text{melt}}$  associated with a crystal  $\rightarrow$  liquid phase transition
2. Working Point: ( $\eta = 10^3 \text{ Pa-sec}$ ); temperature at which the molten glass can be formed/manipulated; *viscous* gob deformed into final shape. Viscosity is low enough for some shear processing (pressing, blowing, etc.) but high enough to retain some shape after shear is removed.
3. Softening Point: ( $\eta = 10^{6.6} \text{ Pa-sec}$ ); temperature at which glass will deform under its own weight. Littleton S.P. is a standard fiber elongation test (1 mm/min).

- Processing Note:
- Working Range: temperature range where  $10^3 \leq \eta \leq 10^{6.6}$  Pa-sec
  - Wide working range (large  $\Delta T$ ): *Long Glasses*
  - Narrow working range (small  $\Delta T$ ): *Short Glasses*
  - Working range at a higher temperature than SLS glass: *Hard Glass*
  - Working range at a lower temperature than SLS glass: *Soft Glass*
- 4. Annealing Point: ( $\eta=10^{12}-10^{12.4}$  Pa-sec); temperature at which 'stress is substantially relieved' in a few minutes.
  - Measured by a standard fiber elongation test
- 5. Strain Point: ( $\eta=10^{13.5}$  Pa-sec); temperature at which 'stress is substantially relieved' in several hours.
  - Glass is essentially an elastic solid at  $T < T_{\text{strain point}}$ 
    - No significant structural rearrangements/no permanent flow

Other useful viscosity reference points? From a dilatometer curve:

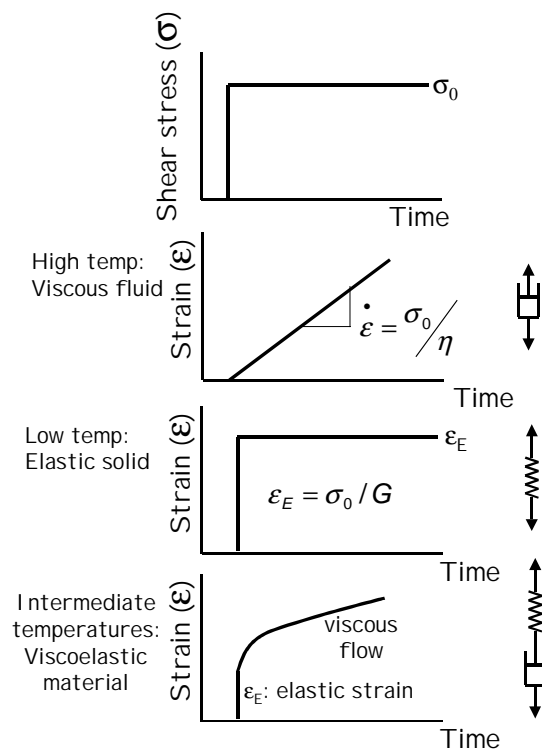
- Glass transformation temperature ( $T_g$ ):  $\eta \sim 10^{11}-10^{12}$  Pa-sec
  - Imprecise, depends on dilatometer, heating rate, etc.
- Dilatometric Softening Point ( $T_d$ ):  $\eta \sim 10^8-10^9$  Pa-sec
  - Glass squished by dilatometer; depends on the load

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**Viscoelasticity**

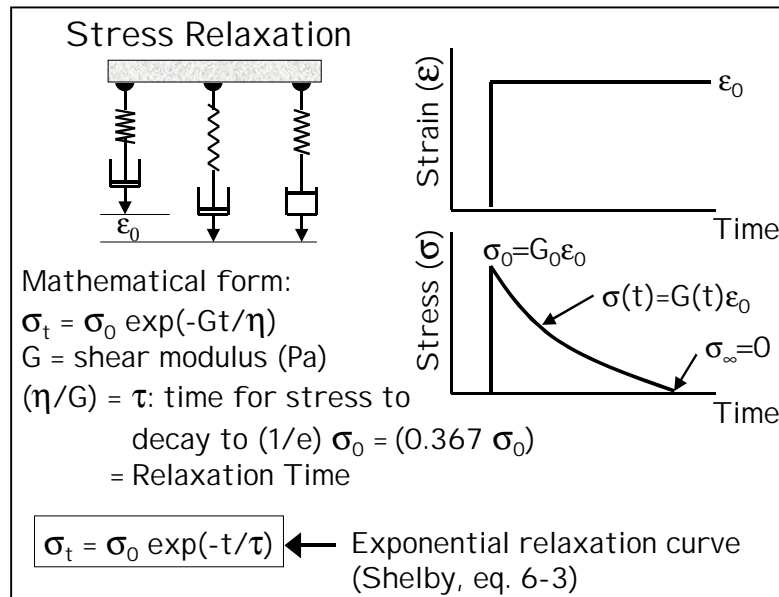
At *high temperatures*, glass melts respond to applied shear stresses ( $\sigma_0$ ) as Newtonian liquids; deformation is time dependent (deformation rate  $\sim \eta^{-1}$ ); behavior represented by the *dashpot*.

At *low temperatures* (below  $T_g$ ), glasses respond like other elastic solids; constant deformation dependent on the shear modulus ( $G$ ) and represented by a *spring*.

At intermediate temperatures (glass transform. range,  $10^8 \leq \eta \leq 10^{13}$  Pa-s), the response to an applied load will exhibit both types of behaviors, and so is described as *viscoelastic*-described by the Maxwell Element.



Consider the load required to maintain a constant deformation ( $\epsilon$ ) to a viscoelastic element. The instantaneous strain will be dependent on the elastic properties ( $G$ ). With time, the viscous component becomes increasingly important, so that progressively less stress is required to maintain the constant displacement: **stress relaxation**



Note: relaxation time and viscosity are related ( $\tau = \eta/G$ )

small  $\tau \rightarrow$  low viscosity  $\rightarrow$  fast relaxation  
 large  $\tau \rightarrow$  high viscosity  $\rightarrow$  slow relaxation

- Shear modulus,  $G$ , is (approximately) independent of temp.  $\approx 10^{11}$  Pa
  - When  $\eta = 10^{12}$  Pa-sec (annealing point),  $\tau \approx 10$  sec; 95% of relaxation occurs in  $3\tau \approx 30$  sec
- Consequences of viscoelastic relaxation time:
  - Rapidly applied stress ( $t \ll \tau$ ), too fast for viscous relaxation to occur, material behaves like an elastic solid
    - Steel ball bouncing off a melt surface (1956 study)
      - 20  $\mu$ sec contact time at  $T = T_g + 100^\circ\text{C}$
      - fire a bullet into a glass tank
        - glass cracks since applied stress  $>$  yield stress and application time  $<$   $\tau$
  - Slowly applied stresses ( $t \gg \tau$ ): deformation due to viscous flow

What about relaxation below  $T_g$ ? Does 'solid glass' flow? Is a glass a 'supercooled' liquid with a finite (albeit very large) viscosity at room temperature?

Cathedral windows (Chartes, et al.) are wavy and thicker at the bottom. Has the glass flowed standing in place for over 800 years? (An old saw- see review article by Phillips in *Physics Today*, around 1991.)

Extrapolate typical viscosity/time characteristics to room temperature and you get a characteristic relaxation time (for SLS cathedral windows) of  $10^{32}$  years (estimated age of the universe is  $10^{10}$  years). (\*see Zanotto, *Am. J. Phys.*, **66**[5] 392, 1998),

SLS glass does not flow at room temperature.

- Undeformed glass vases (>2000 years old)
- Undeformed, massive astronomical mirrors- very sensitive to distortion
- Ancient geological glasses maintaining structures (fictive temperatures) that correspond to original thermal history.

Why thicker panes at the bottom? Medieval windows were blown into cylinders that were split then flattened manually- very non-uniform - architects were smart enough to (in most cases) put the thicker part on the bottom.

Deborah Number (Varshneya, 1994):  $DN = (\text{relaxation time}) / (\text{observation time})$

Prophetess Deborah (Judges 5:5): 'the mountains flowed before the Lord...'; observe 'relaxation' only over geological/supernatural time scales.

In practice, if  $DN > 10^8$  then relaxation is effectively frozen on any experimental time scale.

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Examples: Using the exponential relaxation equation: Calculating how long one needs to anneal a glass to remove stress or arrive at an 'equilibrium property'..

If the relaxation time for a glass at some temperature near  $T_g$  is 2 hours, how many minutes will be required for 90% of the residual stress to relax?

$$\sigma(\text{final}) = \sigma(\text{initial}) \exp(-t/\tau): \quad 0.10\sigma(\text{init}) = \sigma(\text{init}) \exp(-t/120 \text{ min})$$

$$\ln(0.10) = -t/120 \text{ min}; \quad t = (2.303)(120 \text{ min}) = 276 \text{ minutes}$$

If it takes 60 seconds for a property to relax to 1/2 of the difference between the initial and final states, what is the relaxation time?

$$\sigma(\text{final}) = \sigma(\text{initial}) \exp(-t/\tau): \quad 0.50\sigma(\text{init}) = \sigma(\text{init}) \exp(-60 \text{ s}/\tau)$$

$$\ln(0.50) = -60 \text{ s}/\tau; \quad \tau = 86 \text{ seconds}$$

**Derivation of the Maxwell Stress Relaxation Equation:**



Maxwell element is extended to a length,  $l_0$ , by applied force,  $F_0$ . The instantaneous extension will be elastic ( $l_s=l_0$ ) and dependent on the spring constant (k):

$$F_0=k \cdot l_s \tag{1}$$

As time elapses, tension on the spring will pull the dashpot up, reducing the spring extension and reducing the force (F) required to maintain the total extension,  $l_0$ .

At time, t, total displacement of the Maxwell element will be the sum of the extensions of the spring and the dashpot:

$$l_0 = l_s + l_p \tag{2}$$

The upward extension rate will depend on the spring tension ( $F_t$ ) and on the viscosity ( $\eta$ ) and geometry (C) of the dashpot:

$$\frac{dl_p}{dt} = \frac{F_t}{c\eta} \tag{3}$$

Differentiate equation (2) with respect to time:

$$\frac{dl_0}{dt} = \frac{dl_p}{dt} + \frac{dl_s}{dt} = 0 \tag{4}$$

from eq. (1)

$$\frac{dl_s}{dt} = K^{-1} \frac{dF}{dt} \tag{5}$$

Substitute (3) and (5) into (4):

$$K^{-1} \frac{dF}{dt} + \frac{F}{c\eta} = 0 \longrightarrow \frac{F_t}{F_0} \frac{dF}{F} = \frac{-K}{c\eta} dt \longrightarrow \ln F_t - \ln F_0 = \ln \left( \frac{F_t}{F_0} \right) = \frac{-Kt}{c\eta}$$

$$\longrightarrow F_t = F_0 \exp \left( \frac{-Kt}{c\eta} \right)$$

Replace these constants with material properties and consider shear stress instead of extension force to get Maxwell's equations:

$$\sigma_t = \sigma_0 \exp \left( \frac{-Gt}{\eta} \right) \quad \text{and} \quad \sigma_t = \sigma_0 \exp \left( \frac{-t}{\tau} \right)$$

Measuring Viscosity

- Need to measure viscosity over >12 orders of magnitude, from the practical melting point to the strain point.
- Must use different methods over different  $\eta(T)$  ranges

Measurement Methods for 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

1. Rotation Viscometers ( $10$ - $10^6$  Pa-s)

- Brookfield-type viscometer heads (to be used in Junior labs to measure room temperature slip viscosities).
- Measure the torque (T) needed to maintain a constant spindle spinning speed- or measure speed at constant applied torque (for higher viscosities). Some designs rotate the cylinder and measure the torque applied to the spindle.
- General relationship:

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



where L is the spindle length, R is the cylinder radius, r is the spindle radius, and  $\omega$  is the angular velocity.

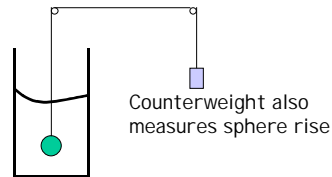
- High glass melting temperatures require that the spindle and cylinder be made of Pt/Pt-alloys.



## 2. Falling Sphere ( $10^{-10}$ - $10^6$ Pa-s)

- Stokes' Law: resistance of a liquid to motion of a falling sphere

$$\eta = \frac{2}{9} \frac{r^2 g}{V} (\rho_s - \rho_m)$$



where platinum sphere (radius  $r$  and density  $\rho_s$ ) falls at a velocity ( $V$ ) due to gravity ( $g$ ) and the melt density ( $\rho_m$ ).

## 3. Fiber Elongation Viscometers ( $10^5$ - $10^{14}$ Pa-s)



- Measure elongation rate, either due to weight of the fiber (low viscosity) or due to an applied load (high viscosity).
  - Rate  $\sim dL/dt$ , fiber x-sectional area =  $A$ , applied stress =  $F/A$
  - Viscosity defined as  $\eta = LF / (3A(dL/dt))$ 
    - One source for possible error:  $A(t)$
  - Surface tension ( $\gamma$ ) opposes the applied stress (barrier against increasing the surface area of the glass when the fiber elongates). So, the downward force is a balance between gravitational load and surface tension:

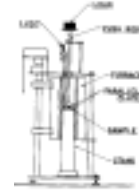
$$F = (LA\rho_g g - 2\pi\gamma r)$$

- Standard Fiber Elongation Experiments
  - Littleton Softening Point* (ASTM-C338)- gravity elongation
    - For proscribed fiber size and surface finish, the viscosity (of a soda-lime silica glass) equals  $10^{6.6}$  Pa-s when the fiber elongation rate equals 1mm/min.
      - Variations in glass density/surface tension create some uncertainty when this test is applied to other compositions.
  - Annealing Point/Strain Point* (ASTM-C336-69)
    - 1 kg weight hung on the end of the fiber
    - annealing point ( $10^{12}$  Pa-s): elongation rate =  $2.5 \times 10^{-6} l/d^2$
    - strain point ( $10^{13.5}$  Pa-s): rate = 0.0316 x rate at the annealing point (1.5 log unit increase in  $\eta$ ; related to time required to relax stresses).

4. Parallel Plate Viscometer ( $10^5$ - $10^8$  Pa-s)

- Measure the deformation rate ( $dh/dt$ ) of a glass cylinder (diameter  $d$ , height  $h$ , volume  $V$ ) under an applied load ( $M$ )

$$\eta = \frac{2\pi Mgh^5}{3V(\partial h/\partial t)(2\pi h^3 + V)}$$

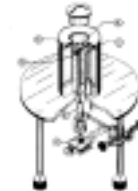


- note, sensitive to  $h^5$

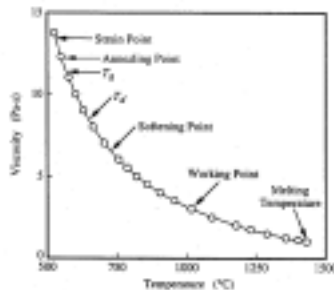
5. Beam Bending Viscometer ( $10^8$ - $10^{13}$  Pa-s)

- Measure the deflection rate ( $V$ ) on a glass (density  $\rho$ ) bar loaded ( $M$ ) in a three-point bend configuration (span  $L$ ). The bar has a x-sectional area ( $A$ ) and a moment of inertia ( $I_c$ ) dependent on beam geometry.

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



**Temperature Dependence of Viscosity**



What functional form best describes  $\eta(T)$ ?

- exponential behavior; activated process (rates increase with temperature- relaxation time becomes shorter with temperature):

$$\eta = \eta_0 \exp(\Delta H_\eta / RT) \text{ (Shelby eq. 6-8)}$$

where  $\Delta H_\eta$  is activation energy for viscous flow

Recall earlier notes about activated processes:

Notes about Activated Processes

Property vs Temperature

ln Property vs 1/Temp. (K)<sup>-1</sup>

Typical behavior for chemical reactions: rates (slope of property curve) increase with temperature.

**Arrhenius (1889)** recognized that this could be described by an exponential function

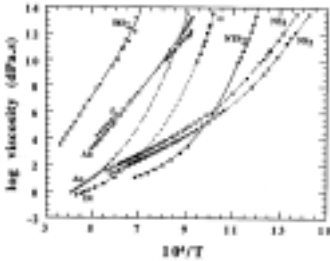
Property =  $A \exp(-E_a/kT)$

A = pre-exponential factor (intercept)

$E_a$  = activation energy (slope)

k = Boltzmann's constant (sometimes 'R')

Eyring viscosity model: flow occurs by atomic jumps into holes on a lattice; activation energy is required to move an atom from its present site before jumping. Jump rates become faster with temperature (shorter relaxation times).



From eq. 6-8, we expect a straight line (Arrhenius behavior) when plotting  $\log \eta$  vs.  $1/T$ ; slope =  $\Delta H_{\eta}$

- $\text{SiO}_2$  and framework aluminosilicates do exhibit *Arrhenian* viscosity dependencies. (Note the very high temperatures for  $\text{SiO}_2$  viscosities).
- Modifiers reduce viscosity/temperature ranges
  - These melts are *non-Arrhenian*
  - No single value for  $\Delta H_{\eta}$ ; single  $\Delta H_{\eta}$  sometimes reported over narrow ranges near  $T_g$  ( $10^9$ - $10^{13}$  Pa-s); depends on structure/network bond strengths

So, the simple Arrhenius equation (6-8) must be modified to describe the entire  $\eta(T)$  curve.

Vogel-Fulcher-Tamman (VFT) equation adds a third empirical fitting parameter ( $T_0$ ) to account for variability in  $\Delta H_{\eta}(T)$ :

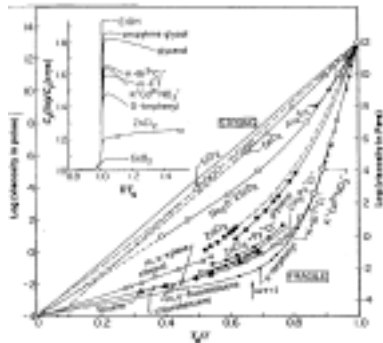
$$\eta = \eta_0 \exp \left[ \frac{B}{T - T_0} \right]$$

$$\log \eta = -A + \left[ \frac{B}{T - T_0} \right]$$

The second form is Shelby eq. 6-10.

- Note that when  $T_0 \rightarrow T_g$ , there is excessive curvature in the  $\log \eta$  vs.  $(1/T)$  curves; when  $T_0 \rightarrow 0$ , then Arrhenian behavior is observed.
- $T$  is properly given in K, although sometimes  $^{\circ}\text{C}$  is used.
- $A$ ,  $B$ , and  $T_0$  are empirical fitting parameters, with some physical meaning

**Melt Fragility:**



- A recent viscosity classification scheme proposed by Austen Angell.
- Allows direct comparison of the viscosities of vastly different melts by normalizing to  $T_g$  (defined as  $\eta=10^{12}$  Pa-s)
- Arrhenian melts are *Strong* liquids
  - Covalent, high temperature oxides
- Non-Arrhenian melts are *Fragile* liquids
  - Highly ionic, van der Waal's liquids
  - No bond directionality
  - Structures 'fall apart' when heated above  $T_g$

Note: Shelby shows an 'Angell schematic' in his Figure 6-3.

- The change in structure of fragile liquids at the glass→melt transition is reflected in the large  $\Delta C_p$  shown in the inset of the Angell figure.
- Slope near  $T_g$  in these fragility plots has been used as a measure of 'fragility'
  - 'fragility index'  $m = \partial \log \eta / \partial (T_g/T) \approx \Delta H_\eta / 2.303RT_g$

Research is underway to understand compositional dependencies of 'm' or  $\Delta H_\eta$

**Models for Viscous Flow**

- physical significance of the VFT fitting parameters?

1. Free Volume Theory

Idea: a glass has some 'ideal' close-packed structure that represents a thermodynamic minimum volume ( $V_0$ )

- Increase temperature, increase the specific volume ( $V$ ) of a material
  - New 'Free volume' ( $V-V_0$ ) within a structure becomes available to accommodate viscous flow. Higher temperatures→larger free volumes→lower viscosities.
  - Williams-Landau-Ferry (WLF) equation (polymer physics):

$$\eta = \eta_0 \exp \left[ \frac{B}{T - T_0} \right]$$

Problems: a 'hard sphere' model that does not account for directional bonds in covalent melts and does not explain why  $\eta(T)$  in constant volume experiments.

## 2. Entropy Model (Adam-Gibbs, 1965)

Idea: A liquid consists of regions that rearrange as units when experiencing a fluctuation in energy ( $\Delta T$  for structural relaxation,  $\Delta F$  for viscous flow). These regions must interact cooperatively for a material to respond to the fluctuation. The size of the unit depends on temperature and is determined by the configurational entropy of the liquid:

- High temperature  $\rightarrow$  small units  $\rightarrow$  high configurational entropy
- Decreasing temperature  $\rightarrow$  larger units  $\rightarrow$  lower  $S_c$
- At some temperature, unit size is infinite,  $S_c \rightarrow 0$ ,  $\eta \rightarrow \infty$

$$\text{configurational entropy} \Rightarrow S_c = \Delta C_p \left( \frac{T - T_0}{T} \right)$$

Substitute into the VFT equation:

$$\eta = \eta_0 \exp \left[ \frac{B}{T - T_0} \right]$$

To get the Adam-Gibbs relationship:

$$\eta = \eta_0 \exp \left[ \frac{B_2}{TS_c} \right]$$

Again, note the  $\eta(T^{-1})$  dependence and now the connection to heat capacity as seen in the Angell figure.

## Compositional Dependence of Viscosity

**Viscosity is related to structural connectivity.** In general:

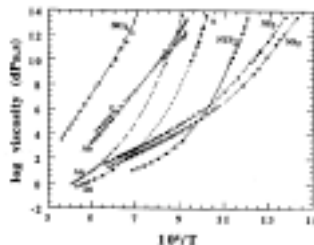
- Reduce the number of bridging oxygens, decrease viscosity
  - Concomitant changes in *fragility* may not parallel viscosity changes.

Compositional effects on Viscosity are generally presented in two ways:

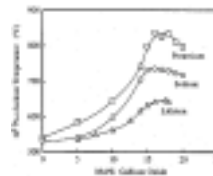
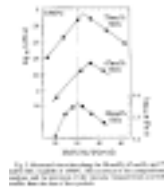
- *Isothermal Viscosity* vs. composition
- *Isokom* (constant viscosity) *Temperature* vs. composition
  - e.g., reporting the Littleton Soft. Pt. Temperature for various compositions

## Silicate Glasses

Return to the Richet data to discuss various trends:



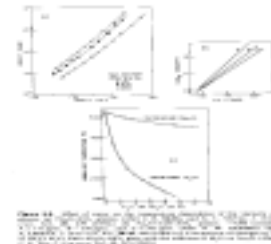
- adding Na<sub>2</sub>O to SiO<sub>2</sub> decreases the isokom temperatures by hundreds of °C (compare SiO<sub>2</sub> to NS<sub>2</sub>, NS<sub>3</sub>)
  - NBO's replace BO's; Q<sup>4</sup> → Q<sup>3</sup>
- ditto for CaO to SiO<sub>2</sub> (diopside curve)
  - Ca-silicates have greater viscosity than Na-silicates: greater Ca<sup>2+</sup> field strength
  - Alkali and alkaline earth modifiers increase silicate melt fragility.
- Adding Al<sub>2</sub>O<sub>3</sub> to sodium silicate (albite: Na<sub>2</sub>O Al<sub>2</sub>O<sub>3</sub> 6SiO<sub>2</sub>) or calcium silicate (anorthite: CaO Al<sub>2</sub>O<sub>3</sub> 2SiO<sub>2</sub>) melt increases viscosity, maybe decreases fragility
  - Replacing NBO's with Al(4)-O-Si(4) cross-links: fully polymerized networks
    - Toplis figure shows viscosity maximum when Al/Na~1.0



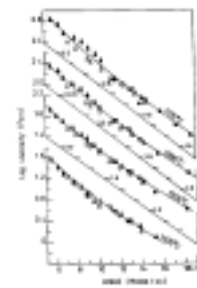
- Shelby shows similar trend when Ga<sub>2</sub>O<sub>3</sub> is added to alkali silicate glasses

Other compositional trends- handouts with data from Varshneya (1994):

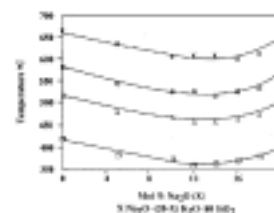
- Water reduces viscosity- has a greater effect on  $\eta$  than alkalis for some melts. (Figure 9-8)
  - Structural depolymerization:  
-Si-O-Si + H<sub>2</sub>O → -Si-OH HO-Si-
  - F<sup>-</sup> has a similar effect. (F<sup>-</sup> often used as a high temp. substitute for OH<sup>-</sup>)



- The concentration of alkali has a greater effect on viscosity than the type of alkali (figure 9-9). Note that at higher temperatures, there is little difference between viscosities of Li, Na, K-silicates.
  - The number of NBO's is more important than the field strength of the modifying alkali ion.



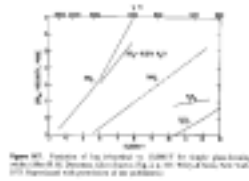
- Adding a second alkali (figure 9-10) has an effect on transport properties like viscosity. *Mixed Alkali Effect*: properties depart from additivity.



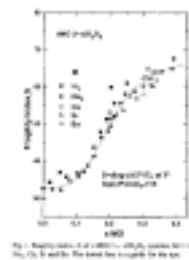
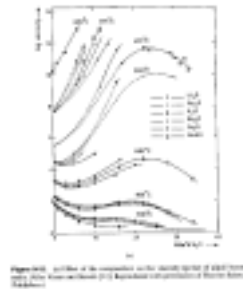
- d. Replacing  $\text{Na}_2\text{O}$  with  $\text{CaO}$  increases  $\eta$  *without* changing the number of NBO's. Here, the F.S. of  $\text{Ca}^{2+}$  is much greater than that of  $\text{Na}^+$  creating a stronger ionic bond to the NBO's that increases viscosity.
- e.  $\text{PbO}$  (on the other hand) significantly reduces melt viscosity.

Borate Glasses

- Viscosity of  $\text{B}_2\text{O}_3$  is much lower than that of  $\text{SiO}_2$ 
  - Planar boroxyl rings- less of a '3D' network
  - Lower B-O bond strength- less energy needed for structural rearrangement



- Adding alkali (or alkaline earth) oxides to  $\text{B}_2\text{O}_3$ 
  - complex composition/temperature behavior:
    - near  $T_g$ , adding  $\text{R}_2\text{O}$  increases  $\eta$ :  $\eta(\text{max})$  near 20-25 mole%  $\text{R}_2\text{O}$   
maximum concentration of B[4]  
Varshneya figure 9-12, Shelby 6-5
    - Fragility index also increases with  $\text{R}_2\text{O}$  (Chryssikos figure 1)
    - Viscosity becomes more temperature sensitive



Adding  $\text{NaF}$  instead of  $\text{Na}_2\text{O}$ ? Lower viscosities as  $\text{F}$  acts as another flux, likely replacing B-O-B bridges in the borate network with B-F bonds (Shelby figure 6-6)

Germanate Glasses

- Similar  $\eta(\text{max})$  at  $\text{R}_2\text{O} \sim 20$  mole% ( $\text{Ge}[4] \rightarrow \text{Ge}[6]$ ) (Shelby 6-7)- and increasing fragility index means that at high temperatures  $\eta$  decreases with alkali additions.

## Halide Glasses

Very fragile liquids- practical melting temperature is only a couple 1-200°C above  $T_g$  (compared to ~1000°C for stronger silicate glasses). Harder to process- must have much tighter temperature controls when casting, pulling fibers, etc- processes that depend on viscosity.

Properties like viscosity are also sensitive to thermal histories and *processing effects*.

- Phase separation-  $\eta$  of Pyrex changes as the morphology changes from a spinodal-like structure to a coarse droplet-in-matrix structure (Simmons figure)
- Crystallization- most melts will crystallize in the viscosity range  $10^4$ - $10^8$  Pa-sec (below the liquidus, far enough above  $T_g$  so that kinetics will not impede crystallization).
  - Slight crystallization will change viscosity because of changes in residual glass composition.
  - Massive crystallization will change viscosity because of interlocking crystals (Hagy figure).

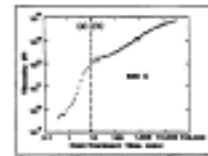


Figure 11 - Viscosity change in Pyrex due to phase separation. Period (a) is dominated by optical densification, Period (b) is dominated by coarsening (D).

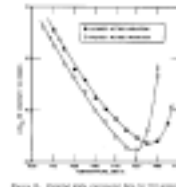


Figure 12 - Viscosity change in Pyrex due to crystallization.

### **Viscosity Summary:**

- The viscosity of a glass forming melt can change over 14-15 orders of magnitude, from the melt through the glass transition.
  - Need several different techniques to measure  $\eta(T)$  over entire range
- The  $\eta(T)$  dependence is complex
  - Best described by the VFT fit and characterized in terms of 'melt fragility'
- Compositional changes that increase structural connectivity (increase the numbers of bridging oxygens) generally increase viscosity, particularly near  $T_g$ .
  - Alkalis,  $H_2O$ ,  $PbO$ ,  $F$  are all effective 'fluxes'
  - Temperature dependence of  $\eta$  (fragility) is also sensitive to composition
- Phase separation and crystallization will alter a melt viscosity
  - The effective viscosity depends on the connectivity of the vitreous phase(s)



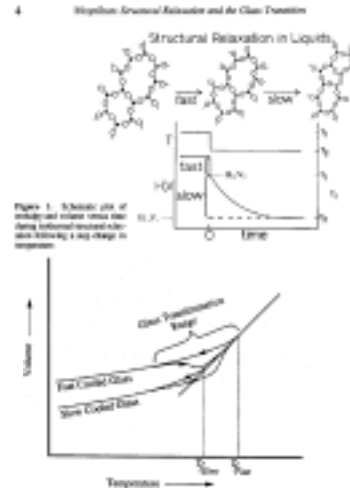
## Thermal History Effects on Viscosity and Density

*Observation:* glasses have time-dependent properties near  $T_g$

- 'Structural Relaxation' caused by change in temperature (different from the 'stress relaxation' that is due to a change in applied stress-  $\Delta\sigma$ ).

Moynihan's figure: step change in temperature yields:

- fast response: thermal lattice vibrations change; akin to elastic response to  $\Delta\sigma$
- slower response: structure relaxes towards 'equilibrium supercooled liquid' (Shelby figure 7-4)- akin to the 'viscous response' to  $\Delta\sigma$



## Fictive Temperature

In the transformation range, relaxation rates decrease with cooling until they become compatible with the cooling rate. At some temperature, one reaches the condition where the structure falls out of equilibrium with the supercooled liquid as relaxation can no longer keep pace with cooling. A glass is said to possess a *fictive temperature* that represents that last equilibrium structure.

- Glasses cooled quickly fall out of equilibrium at higher temperatures
  - Possess greater  $T_{fictive}$  and lower densities
- Glasses cooled more slowly remain in equilibrium to lower temperatures
  - Possess lower  $T_{fic}$  and greater densities

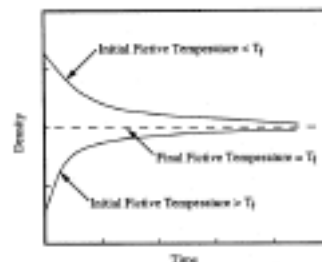
*Fictive temperature depends on thermal history.*

Other properties (including viscosity) are sensitive to the fictive temperature (and so the thermal history) of a glass.

- Higher  $T_{fic}$ , more open structure
- Lower refractive index
- Lower viscosity (think about the greater free volume into which material can flow)

Reheating a glass into the transformation range can change its fictive temperature, and so change the glass properties (as a function of time), as the structure relaxes back towards equilibrium (and a new fictive temperature).

- $T_{fic}(init) > T_{fic}(final)$ : relaxes *faster* because of the more open initial structure.



Same behavior seen in viscosity response; the amount of time needed for rearrangement to occur (for  $T_f(\text{init})$  to reach  $T_f(\text{final})$ ) depends on the melt viscosity- which varies with  $T_f$ .

In Shelby's fig 6-8:  $T_f(1) > T_f(2) > T_f(3)$  (right); sample 1 has the more open structure and so has the lowest initial viscosity. When heated to a temperature represented by  $T_f(3)$ , sample 1 will *initially* relax faster than sample 2, but both will eventually reach the  $T_f(3)$  equilibrium viscosity.

Similarly, in Shelby figure 6-9 (right), a sample with  $T_f > T_3$  will exhibit a more rapid increase in  $\eta$  for a given  $\Delta T$  than the decrease in  $\eta$  for a sample with  $T_{fic} < T_3$ . (The sample with the lower  $T_f$  has a less dense structure that inhibits viscous rearrangement).

