

**Glass in energy**

**Glass basics II**

**MAT 498**

**Lehigh University**

# Glass properties (cont.)

- **viscosity**
- **thermal expansion**
- **annealing and tempering**
- **optical properties**
- **transport properties (diffusion, electrical conductivity, chemical durability)**

# Glass viscosity

## Viscosity ( $\eta$ )

Viscosity,  $\eta$ , is the property which more directly **controls glass-forming ability** from the melt.

It can be shown that both the rates of nucleation and crystal growth from the melt depend on  $\eta$  :

rate of homogeneous nucleation:  $I_v \propto \exp(-\Delta G_m/RT) \sim \propto 1/\eta$  (with  $\Delta G_m \sim E_\eta$ )

rate of crystal growth (m/s):  $u \propto \Delta T/\eta$

where  $\Delta T = T_m - T$  is the degree of **supercooling**.

Also, the **time needed for fining** of the melt (removal of gas bubbles), a function of the **rate of rise of bubbles** to the surface of the molten glass, is given, for spherical bubbles of **radius  $r$**  in a melt of density  $\rho$ , by Stokes law:

$$v = 2/9 g r^2 \rho/\eta$$

For a *newtonian* fluid, the **viscosity** is **constant at a given temperature** and it is defined by Newton's law as:

$$\eta = \tau / (d\varepsilon/dt) \quad (\text{in units of Pa.s})$$

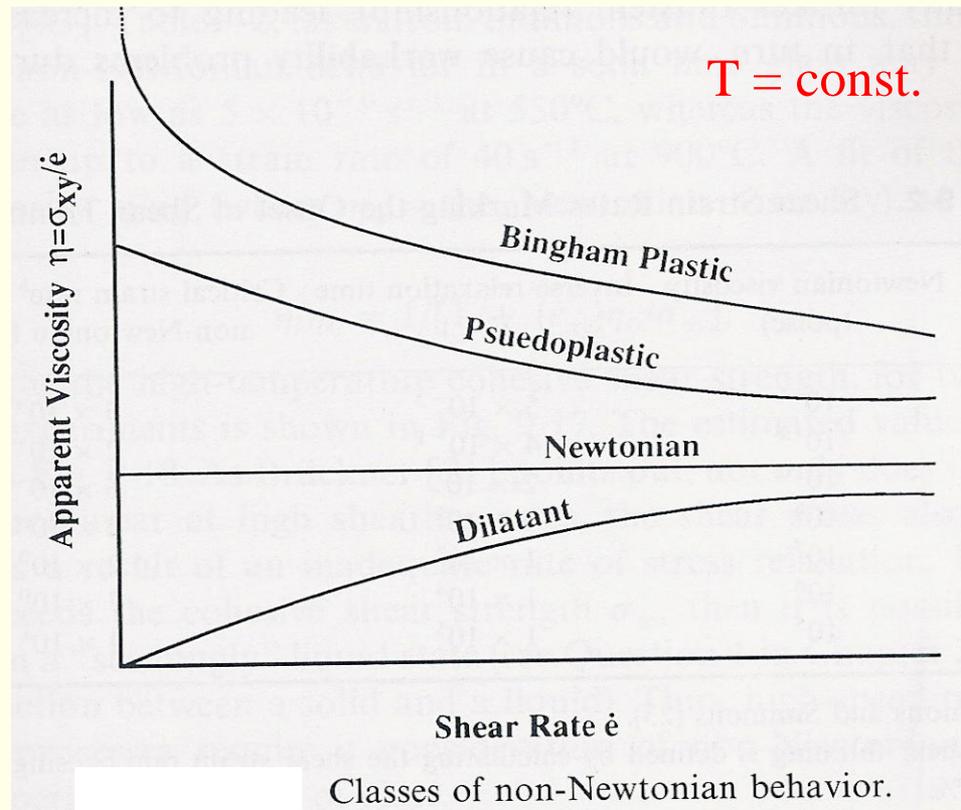
when a shear stress  $\tau$  causes a rate of shear  $d\varepsilon/dt$  ( $\varepsilon$  being the deformation).

**When the viscosity** of a fluid is not constant at a given temperature, but rather **depends on the rate of shear**, the fluid is said to be *non-newtonian*.

If the **viscosity** at a given temperature **increases with the shear rate**, the fluid is said to be *dilatant* (which is the case of mayonnaise, for example). If the **viscosity decreases with the shear rate**, rather, the fluid is said to be *pseudoplastic* (which is the case of ketchup, as another well known example).

## Newtonian and non-newtonian behaviors

Glass-forming melts at high shear stresses may approach a pseudoplastic (also called *shear thinning*) behavior. This may become important during high speed pressing and blowing operations, as typically carried out in IS machines.



(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)

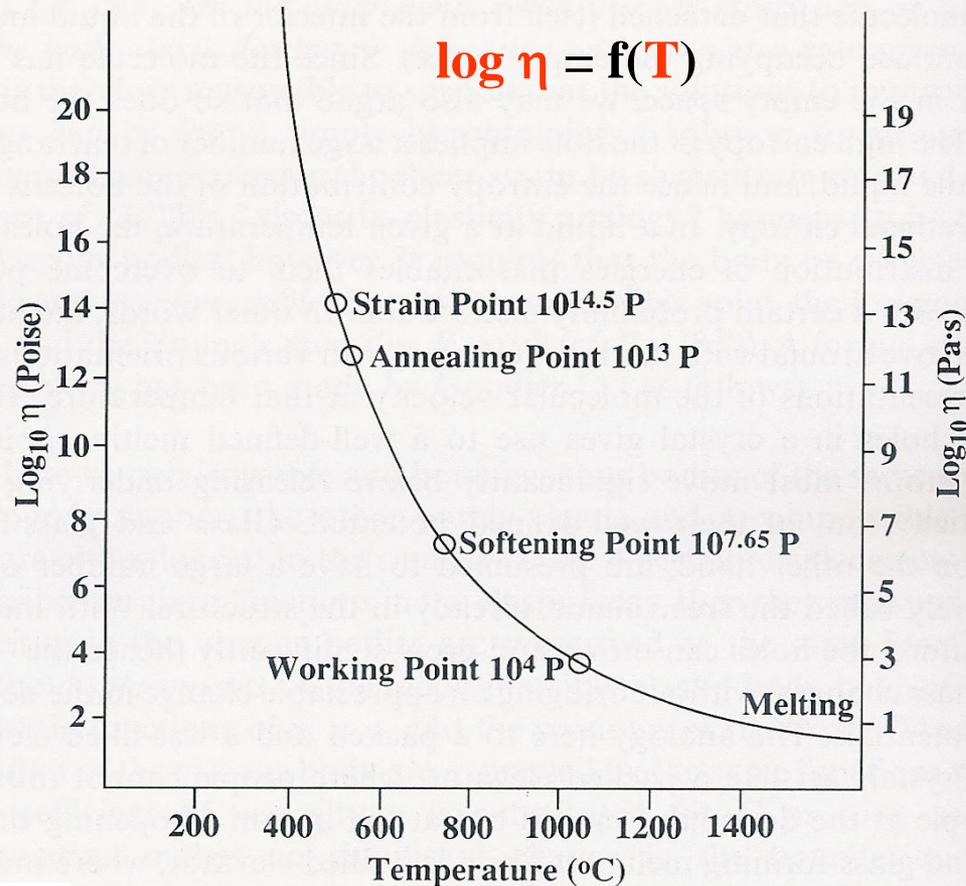
Given the importance of viscosity in glass technology, there are five standard **viscosity** reference *points* (or temperature *ranges*):

- melting (fining)      *point*                      → T @  $\eta = 10$  Pa.s
- working (forming)      “                                      → T @  $\eta = 10^3$  “
- softening (Littleton)      “                                      → T @  $\eta = 10^{6.65}$  “
- annealing ( $T_g$ )              “                                      → T @  $\eta = 10^{12}$  “
- strain                              “                                      → T @  $\eta = 10^{13.5}$  “

Stress release from the glass occurs in a matter of minutes at the annealing temperature and in a matter of hours at the strain point.

The viscosity of molten glass is a strong function of **temperature**, rapidly decreasing when the temperature increases according to Arrhenius eq.:

$$\eta = \eta_0 \exp(E_\eta/RT) \Leftrightarrow \log \eta = \log \eta_0 + E_\eta/RT$$



Variation of the viscosity of a common soda lime silica glass with temperature.

(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)

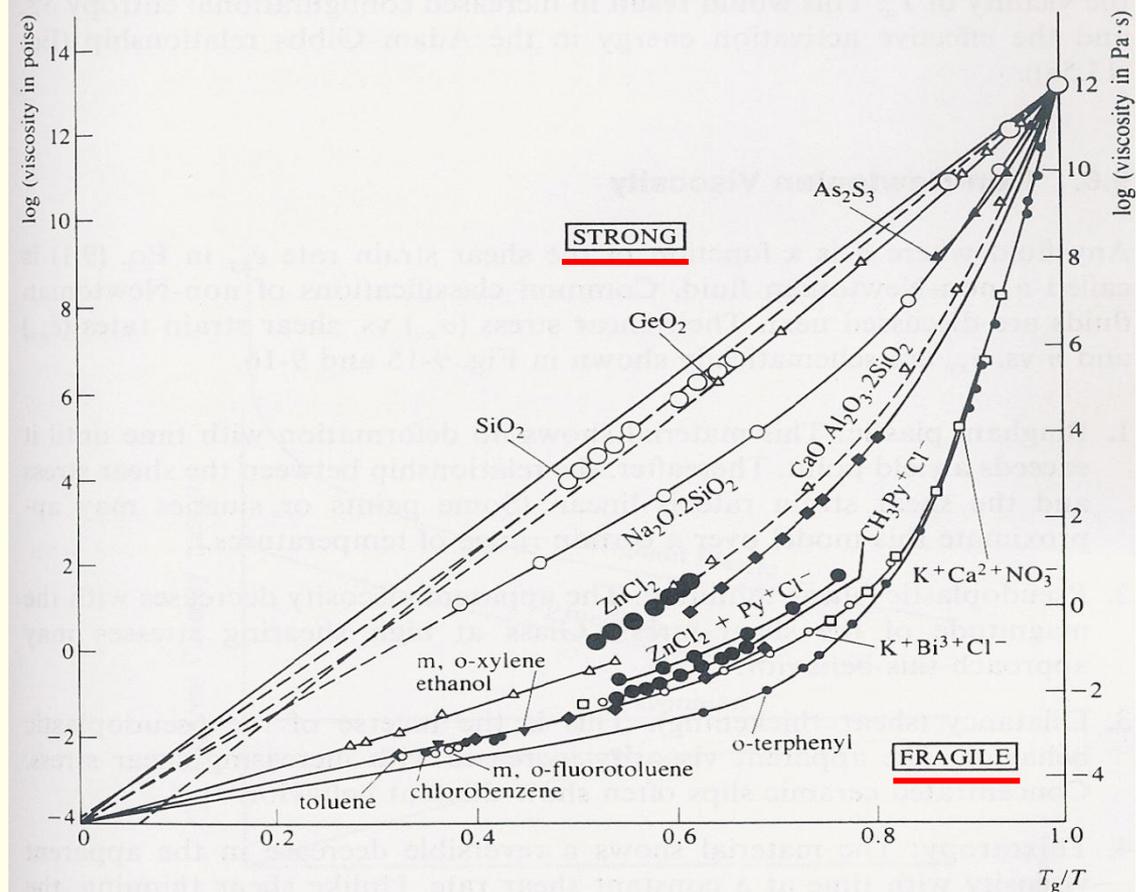
The variation of molten glass viscosity with temperature often follows the **Arrhenius law**:

$$\eta = \eta_0 \exp(E_\eta/RT) \quad (T \rightarrow \infty \Rightarrow \eta \rightarrow \eta_0)$$

where  $E_\eta$  is the **activation energy** for viscous flow (in kJ/mol), **independent of temperature** and of the order of the activation energy for diffusion across the liquid matrix/nucleous interface,  $\Delta G_m$ , in the expression of homogeneous nucleation rate,  $I_v$ .

Arrhenius behavior is the case especially with melts with **strong glass-forming ability** ( $\text{SiO}_2$ ,  $\text{GeO}_2$ ,  $\text{BeF}_2$ , ...), sometimes referred as **strong liquids**.

On the other hand, **strongly modified** melts, or melts with **weak glass-forming ability**, like most other glass-forming halides ( $\text{ZrF}_4$ -based compositions,  $\text{ZnCl}_2$ , ...), usually exhibit an activation energy for viscous flow which strongly decreases with increasing temperature, due to an accelerated depolymerization of the melt structure. Such melts are sometimes referred as **fragile liquids**, in a terminology due to C.A. Angell (1986).



Variation of  $\log(\text{viscosity})$  versus  $T_g/T$  for “strong” and “fragile” liquids. (After Angell [19]. Reproduced with permission of Elsevier Science Publishers.)

(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)

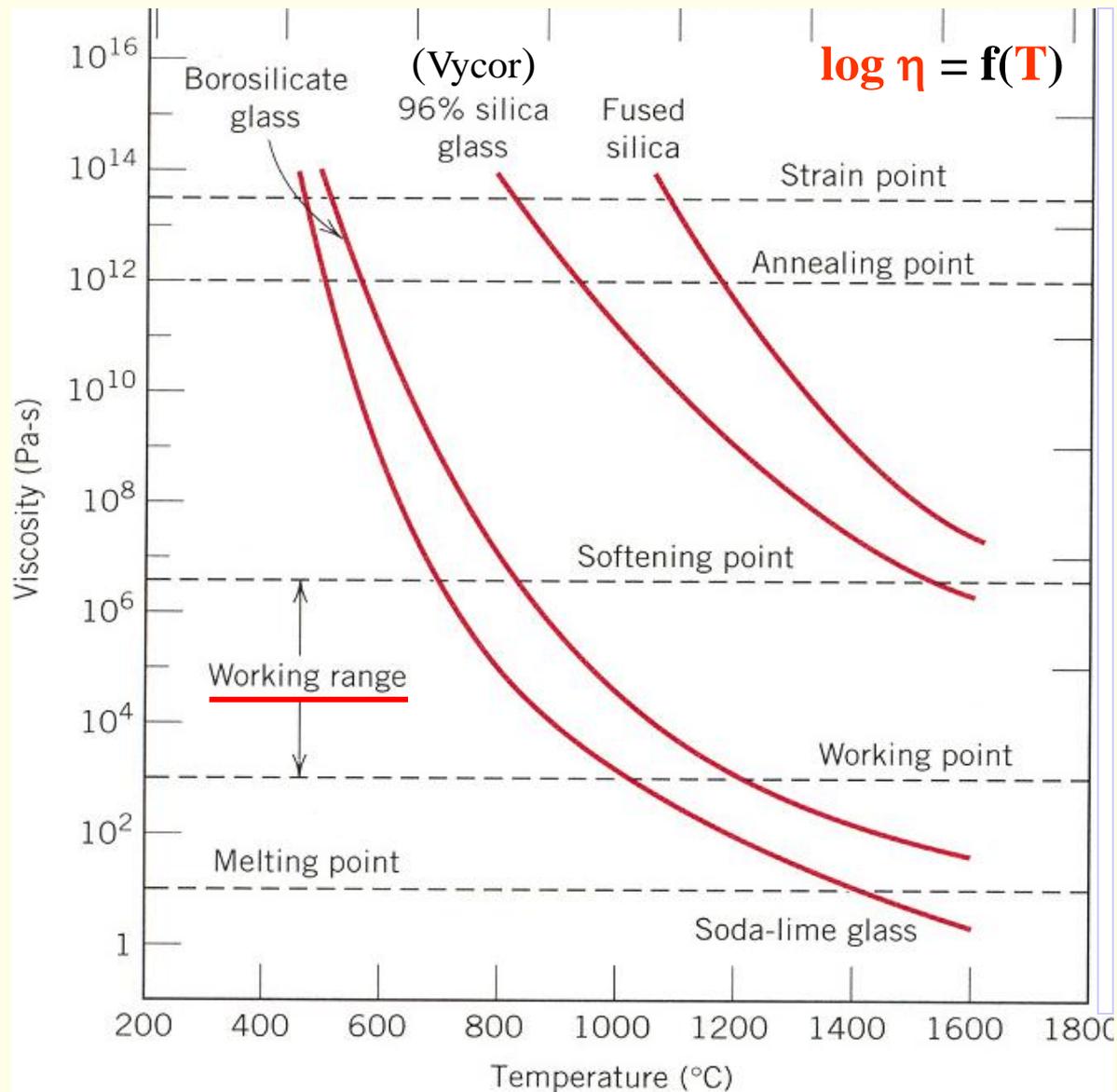
The temperature dependence of the viscosity of *fragile* liquids cannot be described by the Arrhenius equation and more complex expressions become necessary, such as the Vogel-Fulcher-Tammann equation, valid for  $T > T_0$  ( $T_0$ , adjustable parameter  $\sim T_g$ ):

$$\eta = \eta_0 \exp[Q/(T-T_0)] \quad (Q \text{ independent of } T)$$

## Viscosity standard reference points (°C)

Glass	Softening	Annealing ( $T_g$ )	Strain
v-SiO <sub>2</sub>	1600	1100	1000
Borosilicate	820	565	520
Soda-lime	700	510	470

# Effect of temperature and composition on glass viscosity



(Adapted from: *Materials Science and Engineering*, W.D. Callister, John Wiley, 1994)

## Thermal expansion of glass

Physical origin of thermal expansion: **increase in amplitude of the thermal vibrations** of the atoms/ions, as a result of their anharmonicity:

(a) *anharmonic* oscillator:

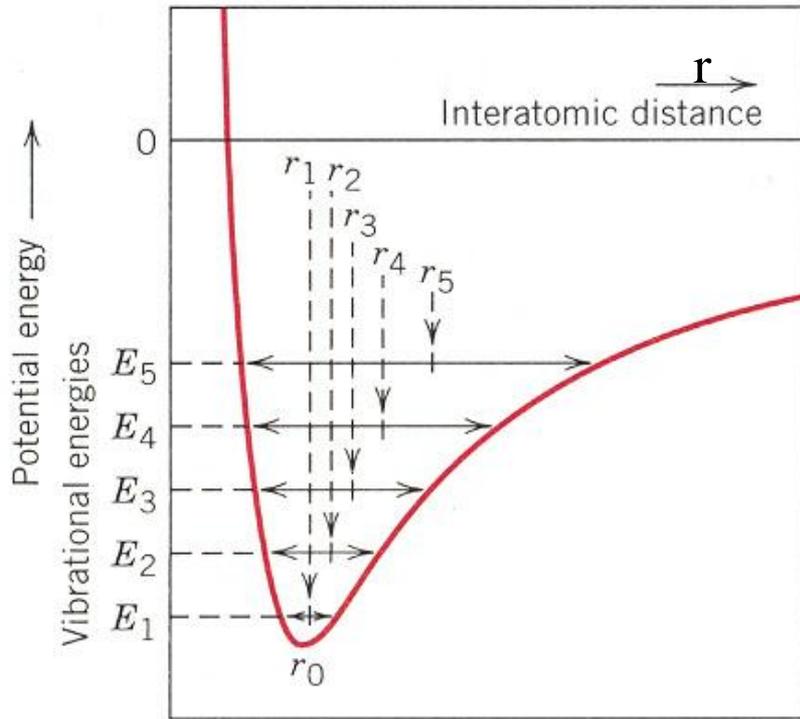
$$V = \frac{1}{2} k (r-r_0)^2 + \dots$$

$$E_v = (v + \frac{1}{2}) h\nu + \dots$$

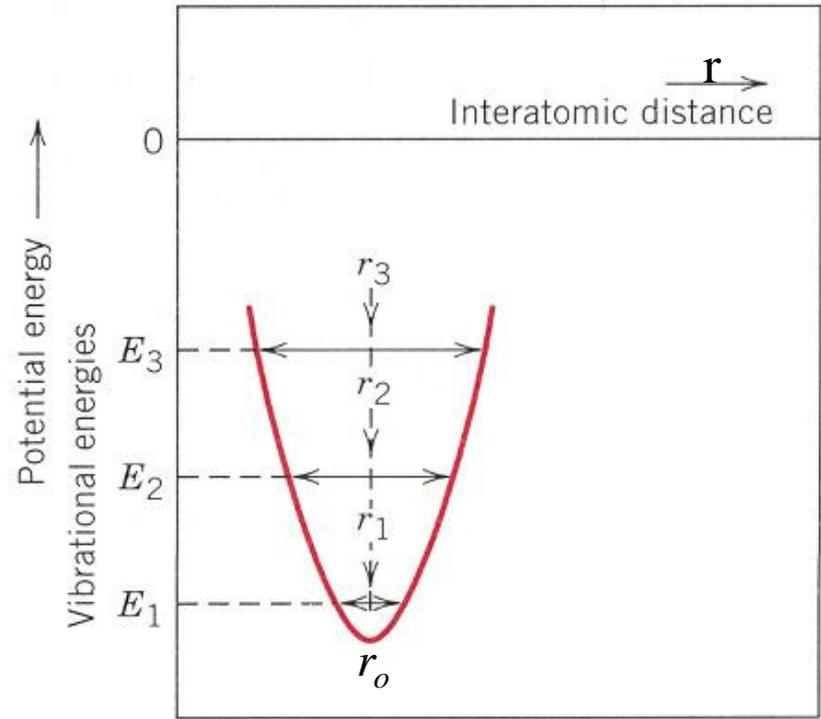
(b) *harmonic* oscillator:

$$V = \frac{1}{2} k r^2 \quad (\text{Hooke's law})$$

$$E_v = (v + \frac{1}{2}) h\nu$$



(a)



(b)

(Adapted from: *Materials Science and Engineering*, W.D. Callister, John Wiley, 1994)

For a given temperature, T:

**linear thermal expansion coefficient** of a sample of length **l**:

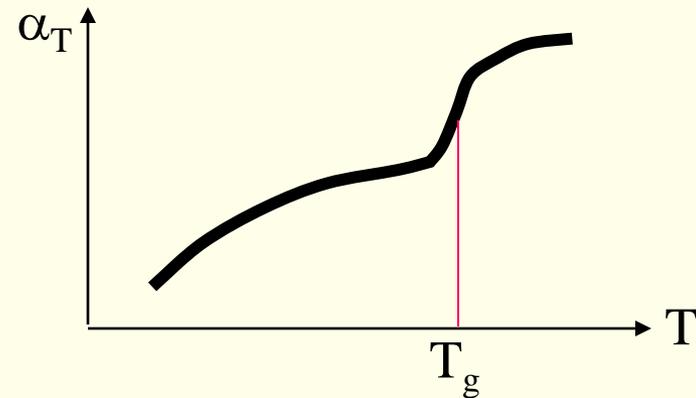
$$\alpha_T = (1/l) dl/dT \quad (\text{in units of } K^{-1})$$

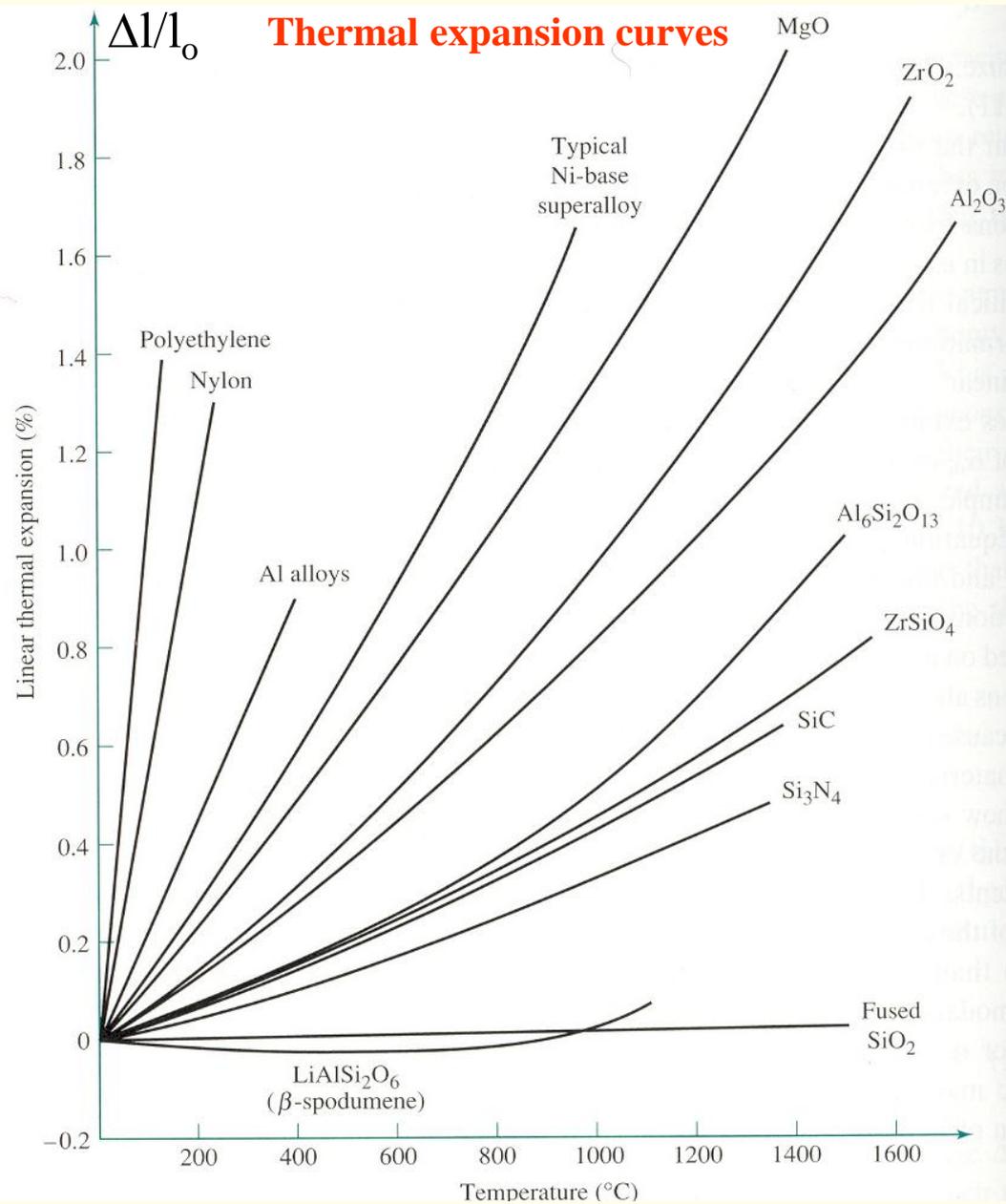
$$\alpha_T = 1/3 \alpha_T^{\text{vol}} = 1/3 (1/V) (\partial V/\partial T)_P$$

Over a small temperature range, the average value:

$$\alpha_T = (1/l_{\text{av}}) \Delta l/\Delta T \sim (1/l_o) \Delta l/\Delta T = (1/l_o) (l-l_o)/(T-T_o)$$

For a glass, the changes of  $\alpha_T$   
with T are similar to those of  $c_p$ :





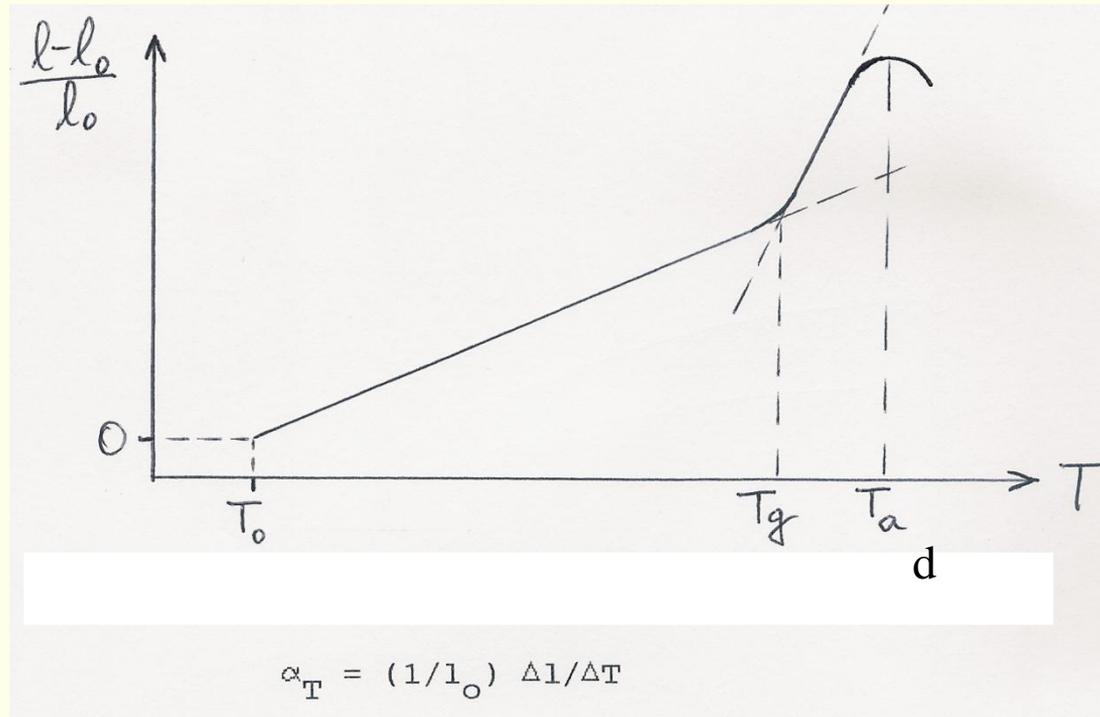
(Adapted from: *The science and design of engineering materials*, J.P. Schaffer et al., McGraw-Hill, 1999)

Coefficient of (linear) thermal expansion  $\alpha_{th}$  for selected materials.  $\alpha_T \times 10^{-6} \text{ }^\circ\text{C}^{-1}$

Material	$\alpha_{th} (\times 10^{-6} \text{ }^\circ\text{C}^{-1})$	Material	$\alpha_{th} (\times 10^{-6} \text{ }^\circ\text{C}^{-1})$
<b>Metals</b>		<b>Ceramics</b>	
Al	25	Al <sub>2</sub> O <sub>3</sub>	6.5–8.8
Cr	6	BeO	9
Co	12	MgO	13.5
Cu	17	SiC	4.8
Au	14	Si	2.6
Fe	12	Si <sub>3</sub> N <sub>4</sub> ( $\alpha$ phase)	2.9
Pb	29	Si <sub>3</sub> N <sub>4</sub> ( $\beta$ phase)	2.3
Mg	25	Spinel (MgAl <sub>2</sub> O <sub>4</sub> )	7.6
Mo	5	Soda-lime-silicate glass	9.2 (used in light bulbs)
Ni	13	Borosilicate glass	4.6 (used with Kovar)
Pt	9	Silica (96% pure)	0.8
K	83	Silica (99.9% pure)	0.55
Ag	19	<b>Polymers (unoriented)</b>	
Na	70	Polyethylene	100–200
Ta	7	Polypropylene	58–100
Sn	20	Polystyrene	60–80
Ti	9	Polytetrafluoroethylene	100
W	5	Polycarbonate	66
Zn	35	Nylon (6/6)	80
1020 steel	12	Cellulose acetate	80–160
Stainless steel	17	Polymethylmethacrylate	50–90
3003 aluminum alloy	23.2	Epoxy	45–90
2017 aluminum alloy	22.9	Phenolformaldehyde	60–80
ASTM B 152 copper alloy	17	Silicones	20–40
Brass	18		
Pb-Sn solder (50-50)	24		
AZ31B magnesium alloy	26		
ASTM B160 nickel alloy	12		
Commercial titanium	8.8		
Kovar (Fe-Ni-Co)	5		

(Adapted from: *The science and design of engineering materials*, J.P. Schaffer et al., McGraw-Hill, 1999)

Typical **thermal expansion curve for a glass**, with the relative expansion,  $\Delta l/l_0$ , plotted as a function of temperature. The **thermal expansion coefficient is the slope** of the curve. The slope increases steeply above  $T_g$ , hence this is a **good method to determine** the glass  $T_g$ . The **dilatometric softening temperature**,  $T_d$ , corresponds to  $\eta \sim 10^9\text{-}10^{10}$  Pa.s, a viscosity much higher than that of the Littleton softening point ( $10^{6.65}$  Pa.s).



Thermal expansion coefficient of alkali silicate glasses:

increases from Li  $\rightarrow$  Na  $\rightarrow$  K ...

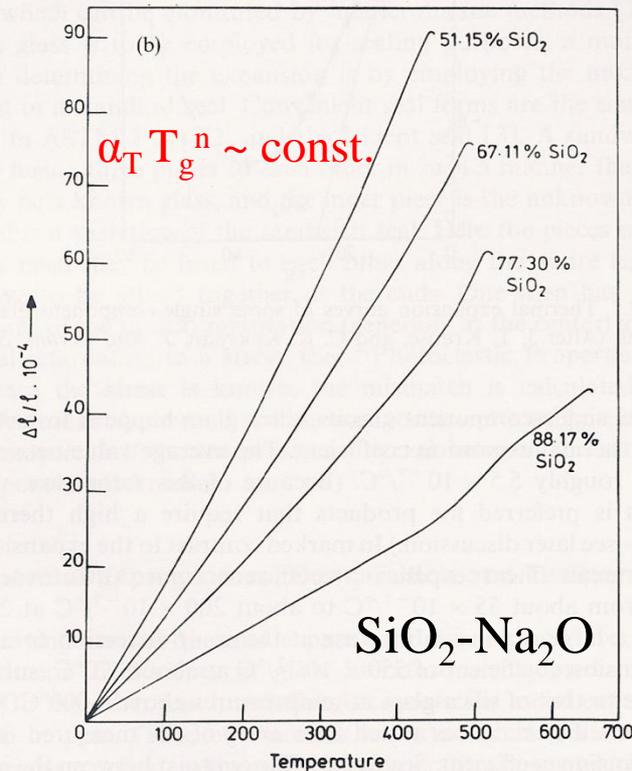
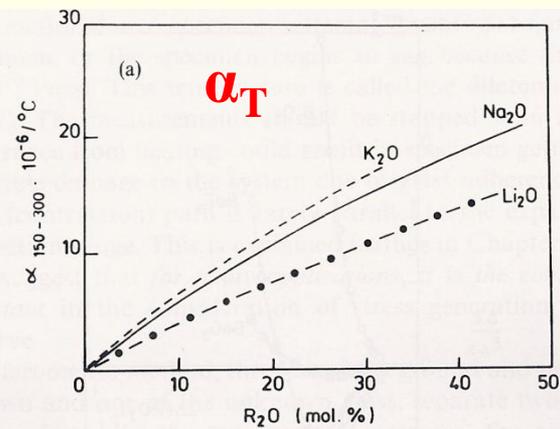
$T_g$  decreases from Li  $\rightarrow$  Na  $\rightarrow$  K ...

For  $\text{SiO}_2$ - $\text{R}_2\text{O}$  silicate glasses of increasing  $\text{R}_2\text{O}$  content,  $\alpha_T$  increases and  $T_g$  decreases, such that one has:

$$\alpha_T T_g \sim \text{constant}$$

$$\text{or } \alpha_T T_g^2 \sim \text{constant}$$

(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)



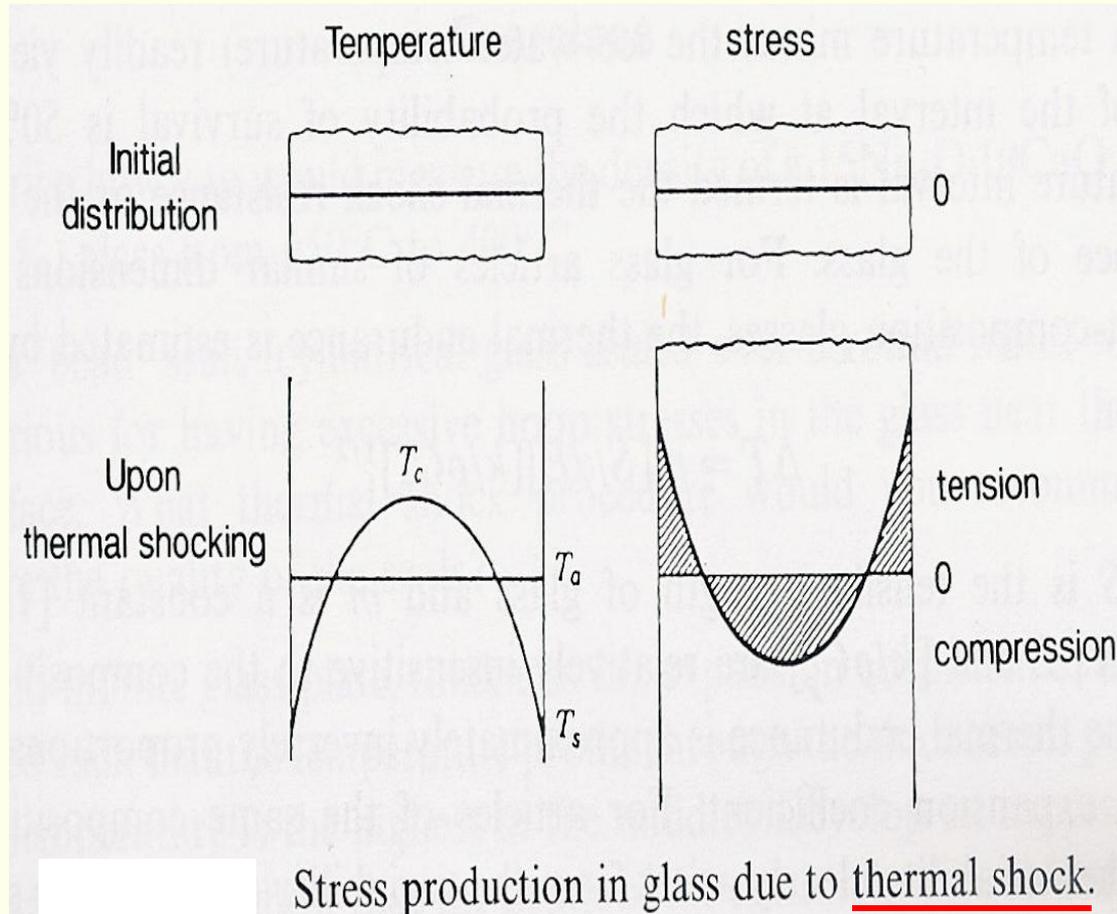
(a) Thermal expansion coefficients of  $\text{R}_2\text{O}$ - $\text{SiO}_2$  ( $\text{R} = \text{Li}, \text{Na}, \text{K}$ ) glasses as a function of composition. (b) Thermal expansion curve for  $x\text{Na}_2\text{O}$  ( $100 \times x$ ) $\text{SiO}_2$  glasses.

## Thermal Expansion Coefficients of Some Commercial Glasses

Glass Code	Type	Expansion coefficient $10^{-7}/^{\circ}\text{C}$	
		<u>0–300°C</u>	Set point—25°C
GE 001	Potash soda lead	93.5	101
GE 008	Soda lime	93.5	105
GE 012	Potash soda lead	89.5	97
Corning 1720	Aluminosilicate	42	52
GE 706	Borosilicate	48	55
GE 725	Borosilicate	35.5	39
Corning 7720	Borosilicate	36	43
Corning 7740	Borosilicate	32.5	35
Corning 7913	96% silica	7.5	5.5
Corning 7940	Fused silica	5.5	3.5

(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)

Sudden cooling of a glass surface below the average specimen temperature,  $T_a$ , causes the development of **tensile stresses** which can lead to glass fracture by **thermal shock**. The **glass interior**, where the temperature is above  $T_a$  and is maximum at the center, will be **under compression**. The thermal shock resistance is strongly dependent on the value of  $\alpha_T$  and **v-SiO<sub>2</sub>** ( $\alpha_T \sim 5 \times 10^{-7} \text{ K}^{-1}$ ) has an **exceptional resistance to thermal shock**.



Thermal shock resistance:

$$\Delta T_{fr} \propto \sigma_a^{fr} / E \alpha_T$$

(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)

## Annealing and tempering

While the **annealing** of glasses at  $T \leq T_g$  is performed to promote the **release of residual thermal stresses** created during casting (generally into a mold at a temperature lower than the melt), the **mechanical resistance** of the final glass may be **increased by** means of thermal or chemical **tempering** treatments.

The most common **thermal tempering** (performed, e.g., on different types of glass windows) starts with a sudden **cooling of the surface of a glass** part (initially near its Littleton softening point), by **blowing cold air** over it, through a nozzle. The surface quickly solidifies (under a moderate tensile stress), while the **internal layers** are still hot and viscous, but these subsequently **contract upon cooling**, solidifying **under tension**, which is then compensated by a residual *surface compression*.

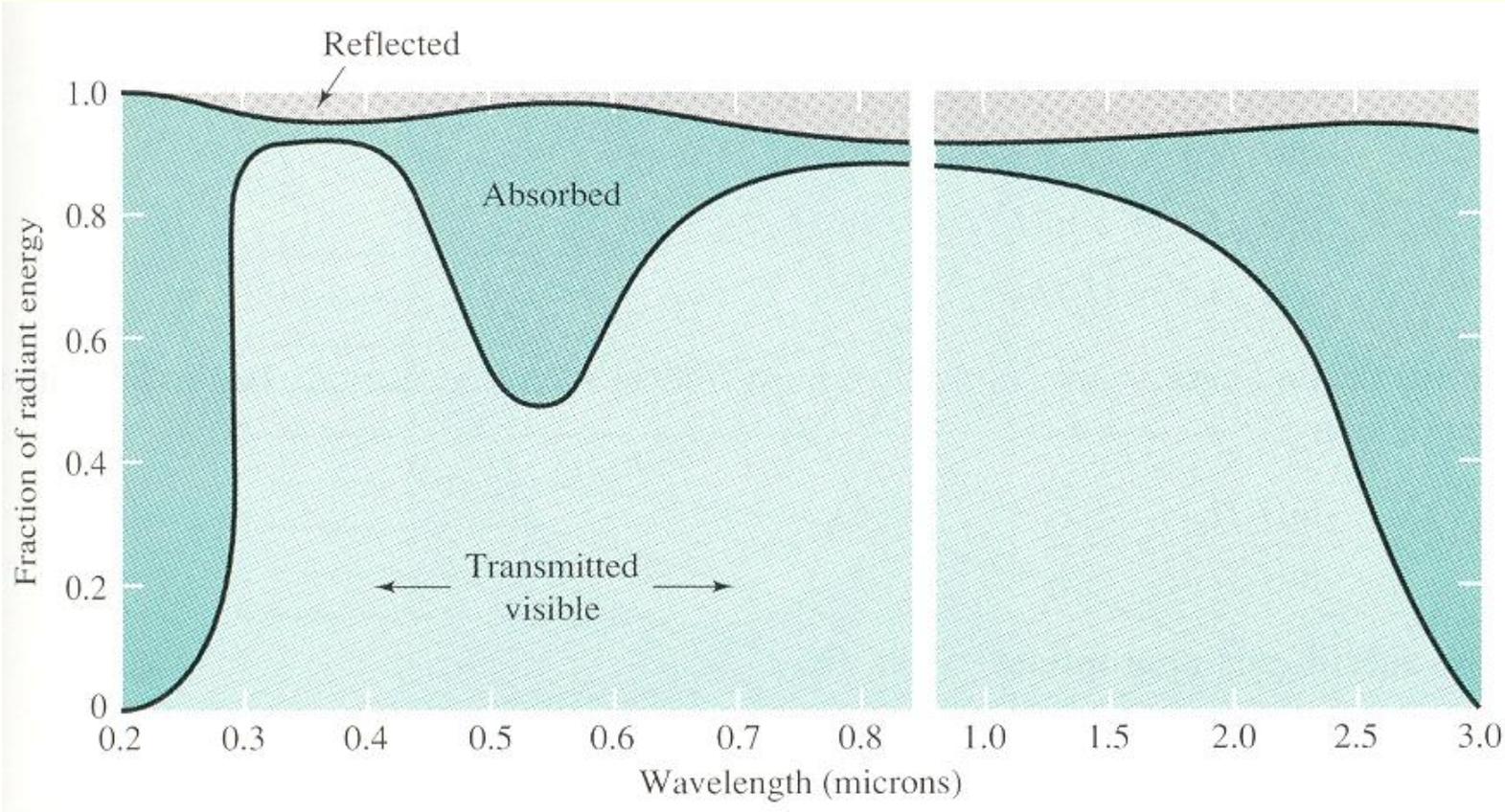
The **surface compression is the key point**, since catastrophic propagation of glass surface flaws will only occur under a tensile stress after the surface compression has been offset by the applied tensile stress, corresponding to a *strengthening* of the *glass*. (Remember that, according to Griffith's theory,  $\sigma_c = 8 \sigma_t$ ).

Thermal tempering is not possible **for very thin glass sheets**, for **glasses with very small  $\alpha_T$**  (e.g. high-silica glasses), or for **complex shapes** such as bottles, which are all cases where *chemical tempering* may be utilized.

Q.

# Optical properties of glass

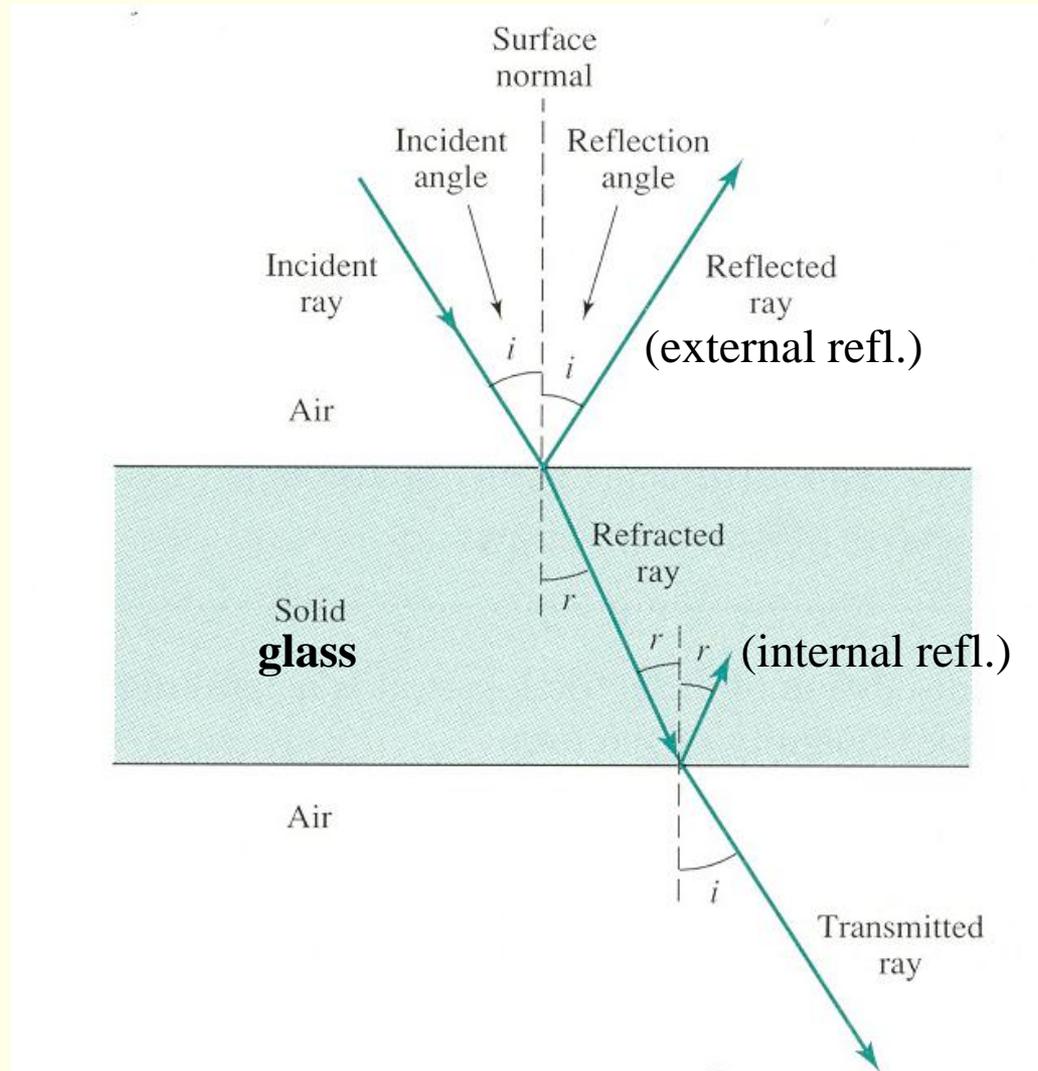
Example of the relationship between transmitted, absorbed and reflected light (in the absence of scattering, Kirchoff's law states that  $T + A + R = 1$ ), for the case of a silicate glass of blue color, due to the presence of  $\text{Co}^{2+}$  ions.



(Adapted from: *The science and design of engineering materials*, J.P. Schaffer et al., McGraw-Hill, 1999)

# Reflection and refraction

(absorption neglected at this stage)



(Adapted from: *The science and design of engineering materials*, J.P. Schaffer et al., McGraw-Hill, 1999)

# Refraction in terms of geometrical optics: Snell's law

$$[(n^2-1)/(n^2+2)] V_M = N_o \alpha_t$$

$$n = \frac{v_{\text{vac}}}{v_{\text{mat}}}$$

$$n = \frac{v_{\text{vac}}}{v_{\text{mat}}} = \frac{\lambda_{\text{vac}}}{\lambda_{\text{mat}}} = \frac{\sin i}{\sin r}$$

$$\frac{v_1}{v_2} = \frac{n_2}{n_1} = \frac{\sin i}{\sin r}$$

Refractive indices of materials.  $n \geq 1$

Material	$\lambda = 589.3 \text{ nm}$	Average refractive index
Air		1.00
Water		1.33
Ice		1.31
<b>Ceramics</b>		
Diamond		2.43
Al <sub>2</sub> O <sub>3</sub>		1.76
SiO <sub>2</sub>		1.544, 1.553
MgO		1.74
NaCl		1.55
BaTiO <sub>3</sub>		2.40
TiO <sub>2</sub>		2.71
Pyrex glass		1.47
Soda-lime-silicate glass		1.51
Lead-silicate glass		2.50
Calcite		1.658, 1.486
<b>Semiconductors</b>		
Ge		4.00
Si		3.49
GaAs		3.63
<b>Polymers</b>		
Epoxy		1.58
Nylon 6,6		1.53
Polycarbonate		1.60
Polystyrene		1.59
High-density polyethylene		1.54
Polypropylene		1.49
Polytetrafluoroethylene		1.30–1.40
Polyvinylchloride		1.54
Poly(ethylene terephthalate)		1.57

(Adapted from: *The science and design of engineering materials*, J.P. Schaffer et al., McGraw-Hill, 1999)

## Refractive indices of some glasses

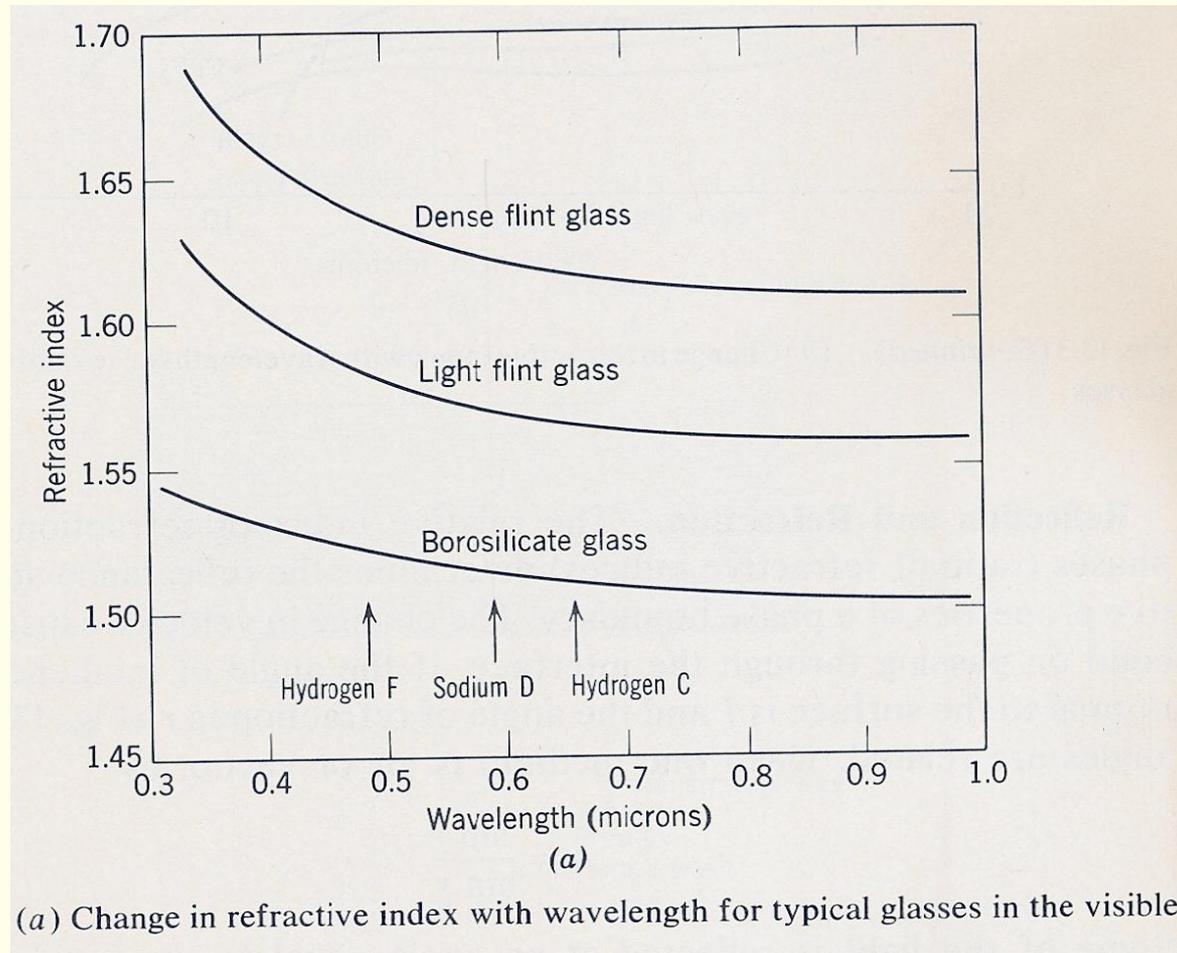
Glass composition:	$n_D$
From orthoclase ( $\text{KAlSi}_3\text{O}_8$ )	1.51
From albite ( $\text{NaAlSi}_3\text{O}_8$ )	1.49
From nepheline syenite	1.50
Silica glass, $\text{SiO}_2$	1.458
Vycor glass (96% $\text{SiO}_2$ )	1.458
Soda-lime-silica glass	1.51–1.52
Borosilicate (Pyrex) glass	1.47
Dense flint optical glasses	1.6–1.7
Arsenic trisulfide glass, $\text{As}_2\text{S}_3$	2.66
Tellurite glasses ( $\text{TeO}_2$ -based)	1.8 – 2.3

(Adapted from: *Introduction to Ceramics*, W.D. Kingery et al., John Wiley, 1976)

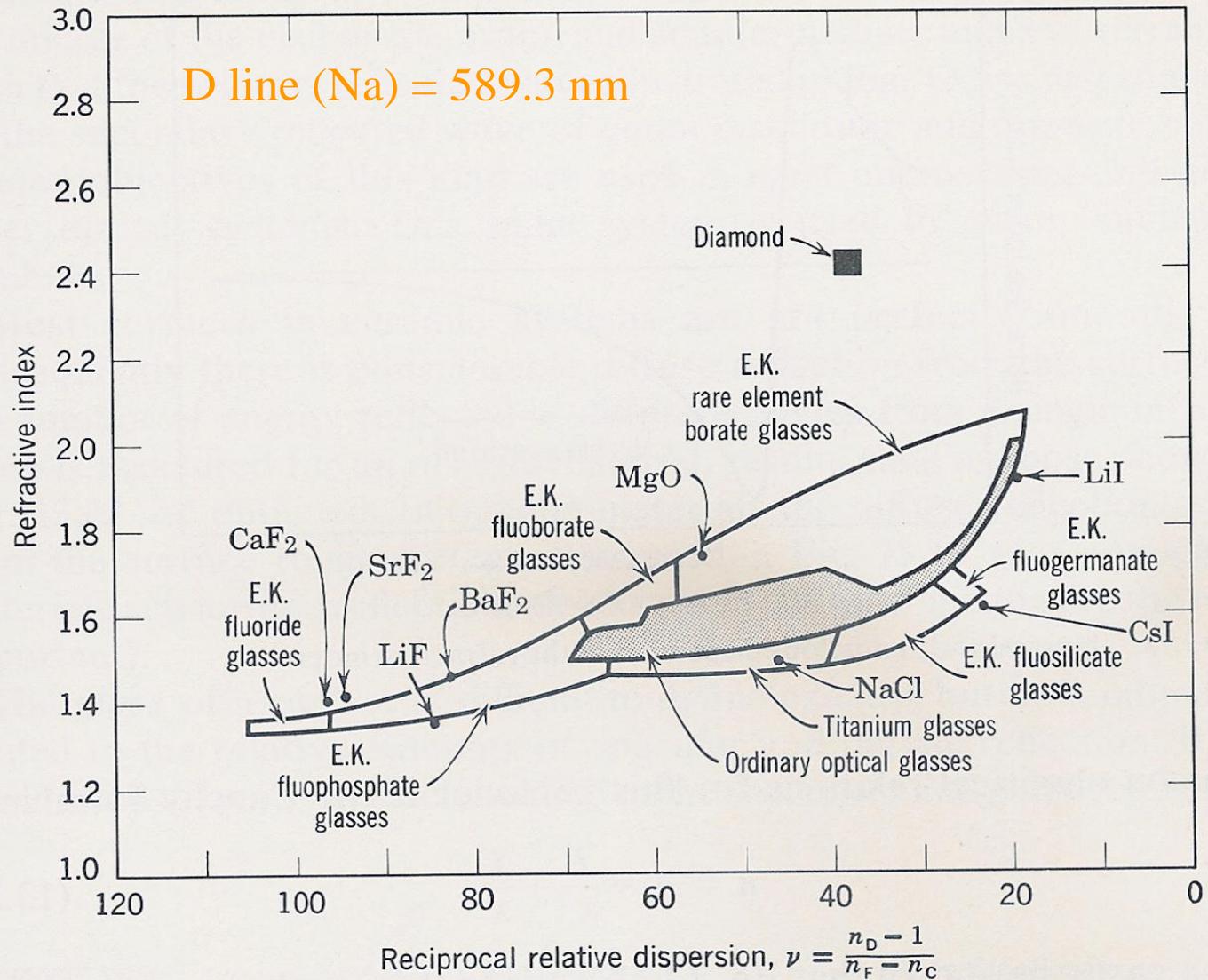
## Refractive **index dispersion** in typical glasses:

**Abbe** number:  $v_D = (n_D - 1)/(n_F - n_C)$

Cauchy equation:  $n = A + B/\lambda^2 + C/\lambda^4$



(Adapted from: *Introduction to Ceramics*, W.D. Kingery et al., John Wiley, 1976)



Range of optical properties obtained with crystals and ordinary optical glasses

(Adapted from: *Introduction to Ceramics*, W.D. Kingery et al., John Wiley, 1976)

For a glass with a “smooth” surface (whose average roughness is  $< \lambda/10$ ), the only component of the reflected light is specular (incidence angle = reflection angle).

*For normal incidence* (incidence angle =  $0^\circ$  off-normal), the Fresnel equation for the reflectivity,  $R$ , of the glass surface, is written:

$$R = \left| \frac{(n^*-1)}{(n^*+1)} \right|^2 = \frac{[(n-1)^2 + k^2]}{[(n+1)^2 + k^2]} \quad (k \sim 0 \Rightarrow R \sim (n-1/n+1)^2)$$

For a **glass parallel plate** of thickness  $x$  and absorption coefficient  $\alpha'$  ( $\alpha' = 2.303 \alpha$ ), the **transmittance** is given by **Beer's law**:

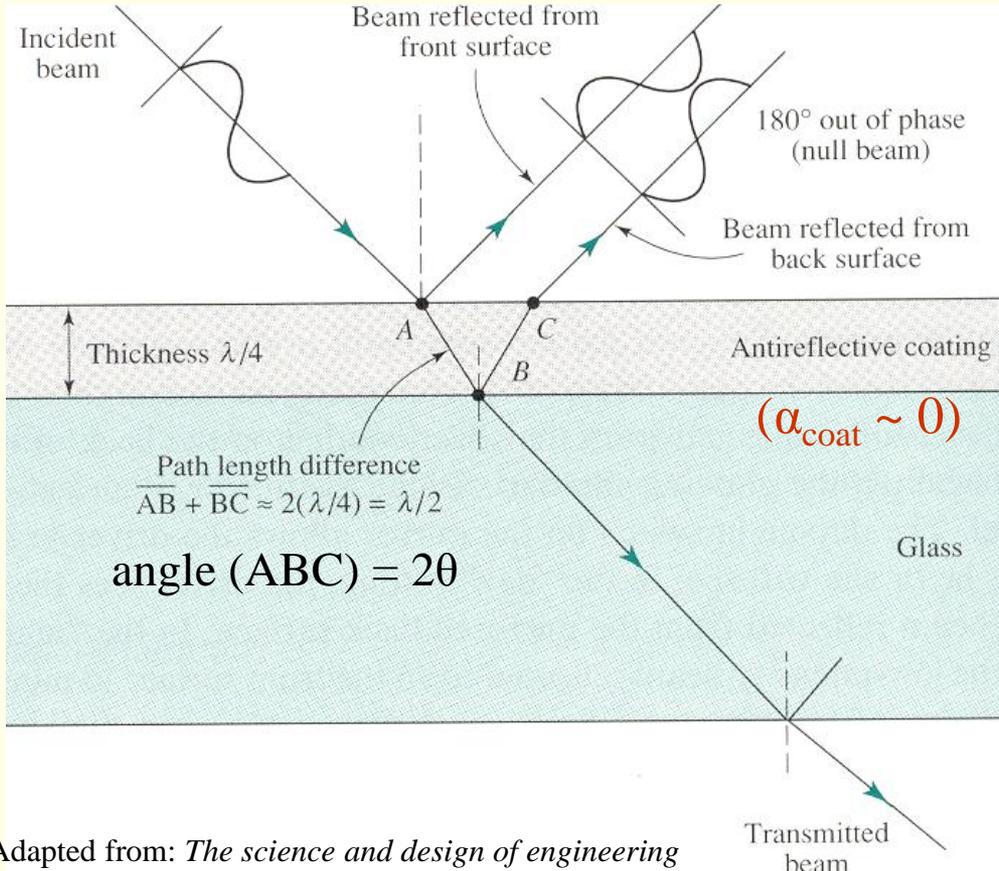
$$T = I/I_0 = \exp(-\alpha' x) \quad \text{or} \quad A = \log I_0/I = \alpha x$$

If reflection is also taken into account, the transmittance is approximately given by:

$$T = I / I_0 = (1 - R)^2 \exp(-\alpha' x)$$

If  $\alpha' \sim 0$ , there are only reflection losses:  $T = (1-R)^2 \sim 1-2R = 1-2(n-1)^2/(n+1)^2 \sim 92\%$  for common silicate glass ( $n \sim 1.5$ ) and for incidence angle below  $\sim 45^\circ$  (from normal).

In applications like ophthalmic lenses, windows or telescopes, it is important to eliminate reflection losses, by means of *anti-reflection coatings*, based on *destructive interference* of the light reflected from the top and bottom surfaces of a film of thickness  $d$  and *index*  $n$ , *lower than that of the glass*.



For normal incidence:

$$2nd = \lambda/2 \iff d = \lambda/4n$$

and one should also have  $n = n_{\text{glass}}^{1/2}$ .

Q.

(Adapted from: *The science and design of engineering materials*, J.P. Schaffer et al., McGraw-Hill, 1999)

# Transport properties of glass

## Diffusion

The **diffusion**, or transport of atoms or ions through the vitreous network **controls** glass properties such as the **chemical durability** (mass transport) and the electrical (**ionic**) **conductivity** (charge transport).

**Diffusion** refers to the **mixing between two or more species in the presence of a concentration** (or chemical potential) **gradient** between them, until chemical equilibrium is achieved. *Fick's First Law* states that the flux  $J_i$ , of species  $i$ , which crosses the unit area cross section in the perpendicular direction  $x$ , per unit time, is proportional to the gradient of its concentration,  $c_i$ , in the same direction:

$$J_i = - D_i (\partial c_i / \partial x)_T$$

the proportionality constant,  $D_i$ , is called the **diffusion coefficient** (m<sup>2</sup>/s), which varies exponentially with the temperature (T), according to Arrhenius equation:

$$D = D_0 \exp (- Q/RT)$$

$D_0$  being the pre-exponential factor and  $Q$  being the **activation energy for diffusion** in kJ/mol. A diffusion process occurring in the absence of a concentration gradient is called auto-diffusion.

The rate of change of the concentration with time at a given distance into the sample is given by *Fick's Second Law*:

$$(\partial c / \partial t)_T = D (\partial^2 c / \partial x^2)_T$$

If the **diffusing species is a gas**, such as hydrogen or helium and if one face of a glass plate of thickness  $L$  is exposed to a known gas pressure, while the other remains at zero pressure, a steady state flow can be reached for which:

$$J = - D \Delta c/L$$

where  $\Delta c/L$  represents the slope of the linear concentration gradient from the front to the rear surface. If the gas concentration is expressed by *Henry's Law*,  $c = SP$  (where **S** is the **solubility** and  $P$  is the gas pressure) and a vacuum is maintained on the inside face of the glass sample, then:

$$JL/P = \mathbf{K} = \mathbf{DS}$$

where **K** is the **gas permeability through the glass** plate, whose knowledge allows the calculation of the steady-state flow rate of gas through a known area of a sample of known thickness, when exposed to a known pressure of gas.

# Electrical conductivity

Charge transport in a glass may be due to the **motions of ions** or **electrons**. While special glasses, like the chalcogenides or glasses with appreciable concentrations of certain transition metal oxides, exhibit electronic conductivity and semiconducting behavior, **most conventional oxide and halide glasses are ionic conductors**, behaving as reasonably **good electrical insulators**. In particular, **common silicate glasses** exhibit ionic conductivity due to alkali cations like **Na<sup>+</sup>** or **Li<sup>+</sup>**, while fluoride glasses are usually anionic conductors by means of F<sup>-</sup> motions.

The electrical conductivity,  $\sigma$ , is by definition the current density (or charge flux),  $J$ , by unit applied electric field,  $\mathcal{E}$ :

$$\sigma = J/\mathcal{E} = n e \mu \quad (J = nev ; \quad \mu = v/\mathcal{E})$$

where  $n$  is the **concentration of charged particles** (m<sup>-3</sup>),  $e$  is their charge (Coulomb) and  $\mu$  is the drift **mobility** (m<sup>2</sup>/(V.s)).

If the conductivity of a glass is the result of field-induced diffusion of a **single ionic species** (e.g. **Na<sup>+</sup>** in window glass), the electrical conductivity and the diffusion coefficient are related by *Nernst-Einstein* equation:

$$\sigma = Z^2 F^2 D c / f RT$$

where  $Z$  is the ionic charge (+1 for Na<sup>+</sup>),  $F$  is the Faraday constant (96500 Coulomb/equivalent-gram),  $c$  is the concentration of the diffusing species (mols of ions/m<sup>3</sup> of glass),  $R$  is the gas constant and  $f$  is an empirical adjustment factor  $\sim 0.2 - 1.0$  for most glasses.

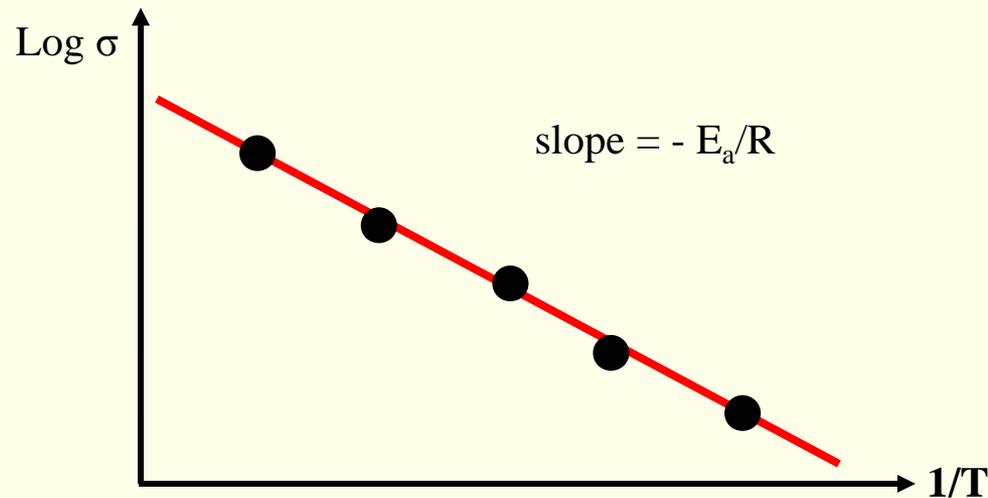
# Electrical conductivity

The **ionic conductivity** varies exponentially with temperature according to the Arrhenius equation:

$$\sigma = \sigma_0 \exp(-E_a / RT)$$

where the activation energy for electrical conductivity,  $E_a$ , has a value similar to the activation energy for diffusion of the conducting species (e.g.  $\text{Na}^+$ ), i.e.  $E_a \sim Q$ .

Both activation energies may be calculated from a plot of  $\log \sigma$ , or  $\log D$ , as a function of  $1/T$ . For example:



## Electrical conductivity

Divalent ions like  $\text{Ca}^{2+}$  have very low mobility and they will contribute very little to the overall ionic conductivity of a glass in the presence of alkali ions, in particular the smaller ones ( $\text{Na}^+$  and  $\text{Li}^+$ ). In fact, the addition of  $\text{Ca}^{2+}$  to a sodium silicate glass will **block** the **diffusion of the  $\text{Na}^+$**  ions and will decrease the electrical conductivity of the glass, as shown by the Fulda experiment. In a sodium silicate glass where  $\text{Na}^+$  is the only species with significant ionic mobility,  $\text{Na}^+$  undergoes *self-diffusion*.

It is interesting to notice that the **sodium diffusion coefficients in sodium silicate glasses** are found to **increase with increasing  $\text{Na}^+$  concentration**, primarily due to a simultaneous decrease in the activation energy for diffusion,  $Q$ , with little variation in  $D_0$ .

## Chemical durability and weathering

Most non-silicate glasses are quite susceptible to dissolution in water. Even glasses which exhibit excellent chemical durability in water may be readily dissolved in highly acidic or highly basic solutions. **Silicate glasses**, e.g., despite their **excellent resistance to neutral water**, are **readily attacked by HF**.

If a glass contains alkali ions like  $\text{Na}^+$ , **ion-exchange** occurs **between the alkali and  $\text{H}_3\text{O}^+$  ions from the surrounding liquid**. **Congruent dissolution may also occur** in the presence of a liquid, when this directly attacks the glass network bonds. Layers of reaction products may also deposit on the surface of the glass, which may influence the subsequent rate of dissolution.

Since the **ion-exchange** process **is diffusion-controlled**, it is found that, for glasses containing alkali cations like  $\text{Li}^+$  or  $\text{Na}^+$ , the **depth of H penetration into the glass increases with the square root of time** ( $x \propto \sqrt{Dt}$ ) during exposure to the H-containing liquid. On the other hand, congruent dissolution, which may occur simultaneously with ion-exchange, occurs at a constant rate and will thus dominate the dissolution process at longer times. If one characterizes the **glass** chemical durability by a weight loss measurement, the **initial rate of weight loss varies with the square root of time**, changing to a **linear rate** of loss with time, **at longer times**.

In general, **silicate glasses dissolve** rapidly **at pH levels higher than 9 or less than 1**, when the attack starts to occur directly on the Si-O bonds and the rate of congruent dissolution becomes so high that ion-exchange becomes unimportant.

## Chemical durability and weathering

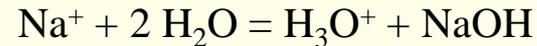
In neutral solutions, additions of alumina or CaO increase the chemical durability of alkali silicate glasses, while zirconia usually improves durability at high pH values. In fact, the addition of an alkaline earth modifier like  $\text{Ca}^{2+}$  to an alkali silicate glass blocks the motions of the alkali ions, decreasing their diffusivity and improving the chemical durability.

Phase separation may also have a significant effect on the chemical durability of a glass. A typical example are the alkali borosilicate glasses, which owe their very good chemical durability to the fact that they consist of a dispersion of isolated alkali borate droplets within a continuous silica-rich phase, such that the durability of the bulk glass is determined by that of the silica-rich phase, which is usually quite high.

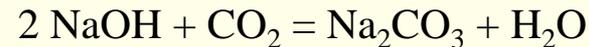
# Chemical durability and weathering

**Weathering** refers to the interaction of a glass with water vapor, while *chemical durability* usually refers to the interaction with liquids.

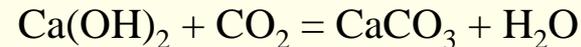
When a glass surface is exposed to water vapor, the water concentration is insufficient for congruent dissolution, but ion exchange can still occur. In the absence of liquid, the ions leached from the glass remain on its surface, where they can react with the surrounding atmosphere. Namely, hydroxides of Na and Ca can form at the surface of common silicate glass:



These hydroxides then react with carbon dioxide from the atmosphere to form carbonates:



or, in the case of Ca:



These carbonates precipitate as discrete particles on the glass surface, which scatter light and give glass a frosted appearance and cannot be easily removed without permanent damage to the glass surface.

Reduction in alkali concentration by treatment with  $\text{SO}_2$  (dealkalization), as done for glass bottles, not only leads to mechanical strengthening due to surface compression upon cooling, but also improves weathering resistance. In the case of float glass, when exposed to water vapor, the tin-rich surface exhibits much reduced weathering phenomena compared to the tin-poor surface.

Q.

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