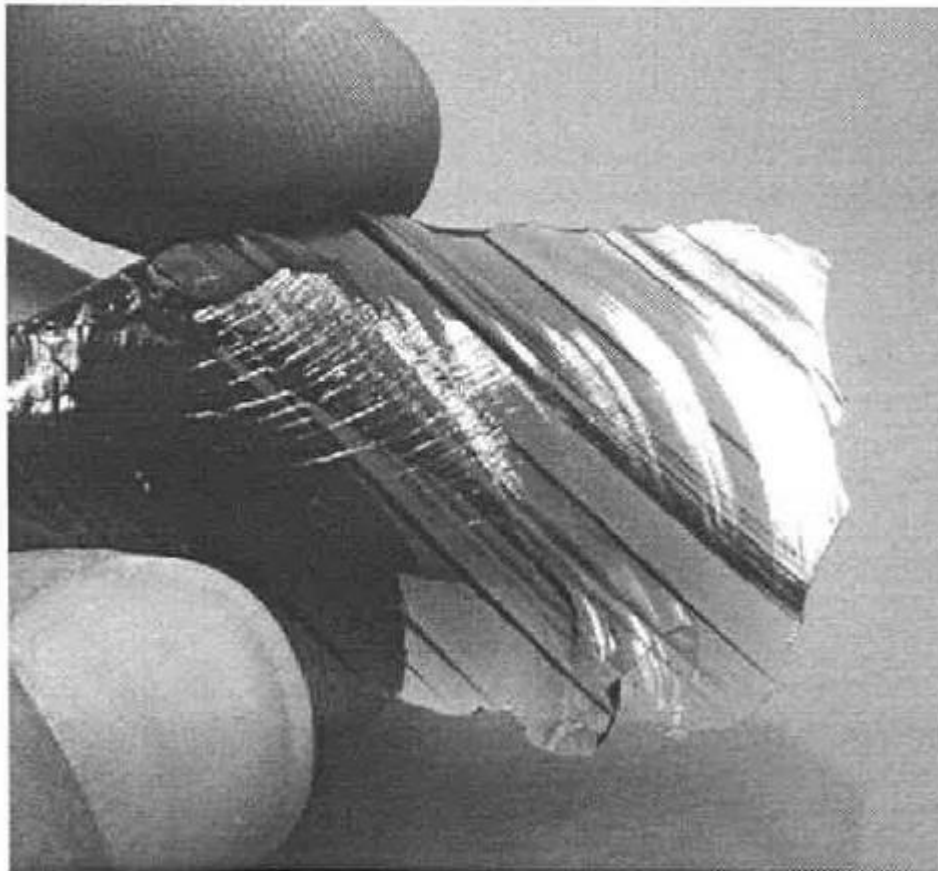# MME 2511
Glass and Glass-Ceramics

%25 Midterm 1
%25 Midterm 2
%50 Final

Textbook : James E. Shelby, '**Introduction to Glass Science and Technology**', 2005, The Royal Society of Chemistry

HISTORY

In the past, glass was the material that was created by nature itself. This kind of glass is called obsidian.


The early man used this material to make axes, knives, arrow heads and other similar tools.

However, it is not known when man learnt to make glass. It is believed that the first glass was made in Persia 7000 years ago.

The first pieces of glass melted by man were used for decorative purposes.

The most important developement in glass technology was the use of a blow pipe. This was first used approximately 100 years B.C. From this time and onwards there was a rapid development in the technique of manufacturing glass.
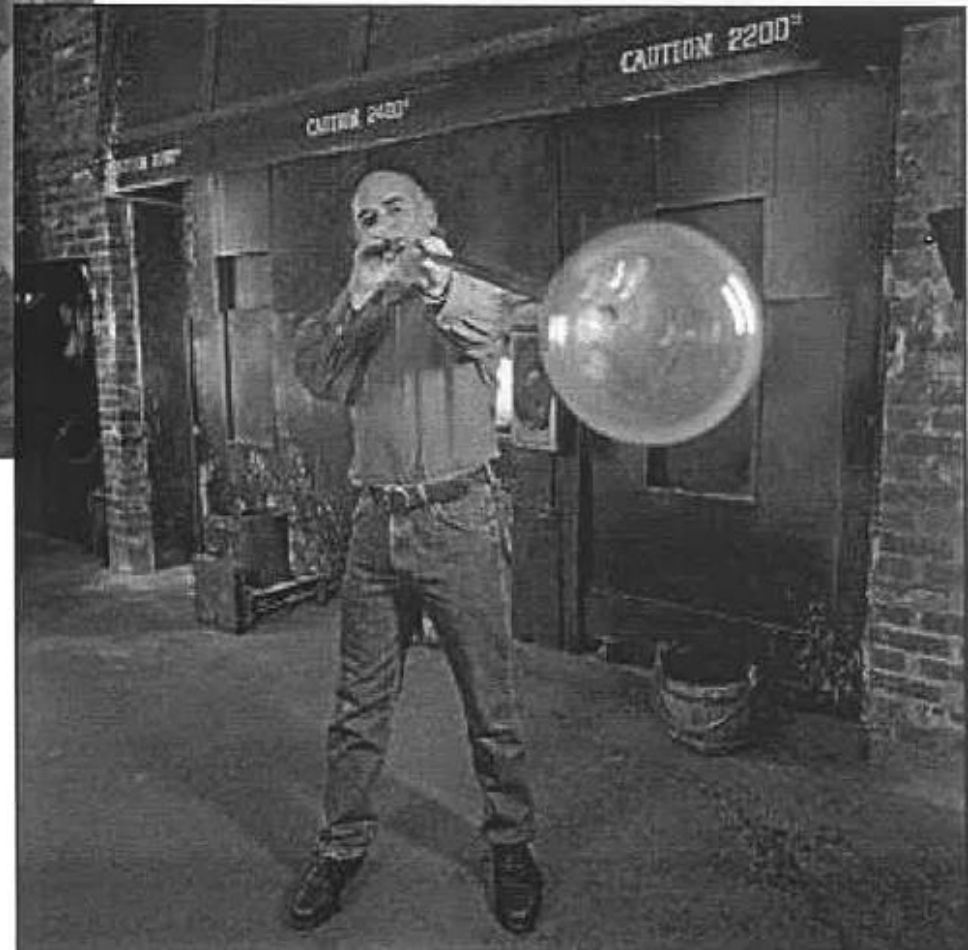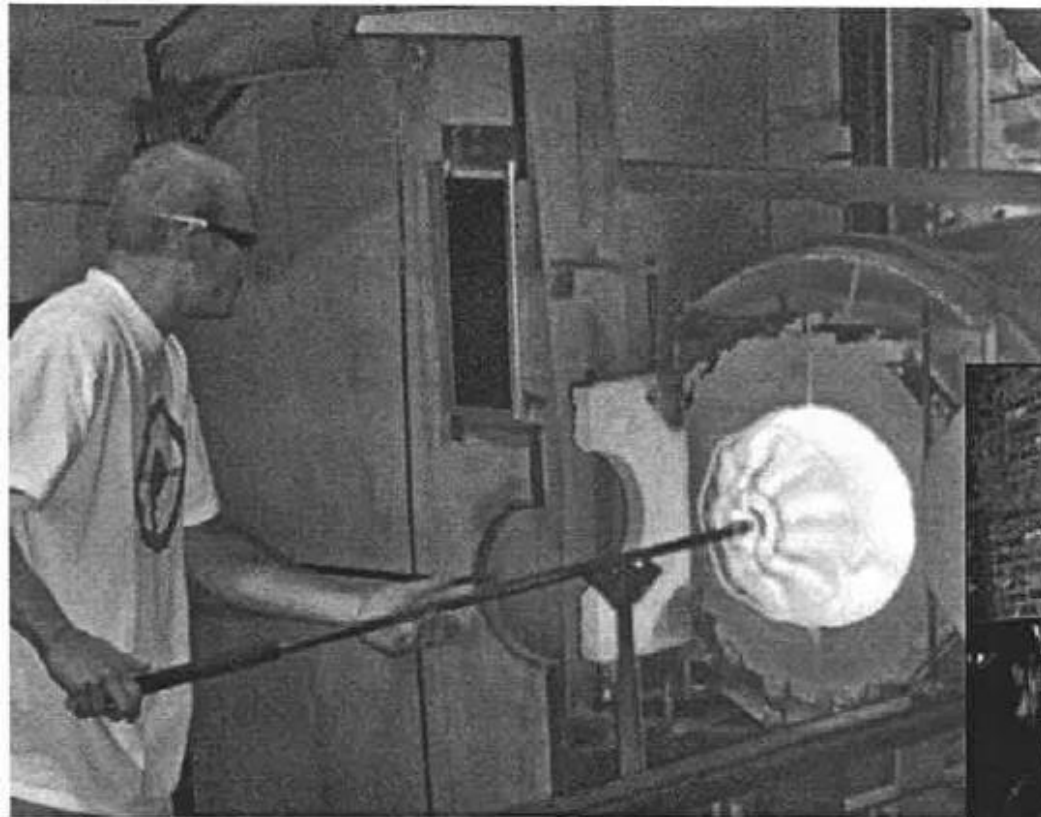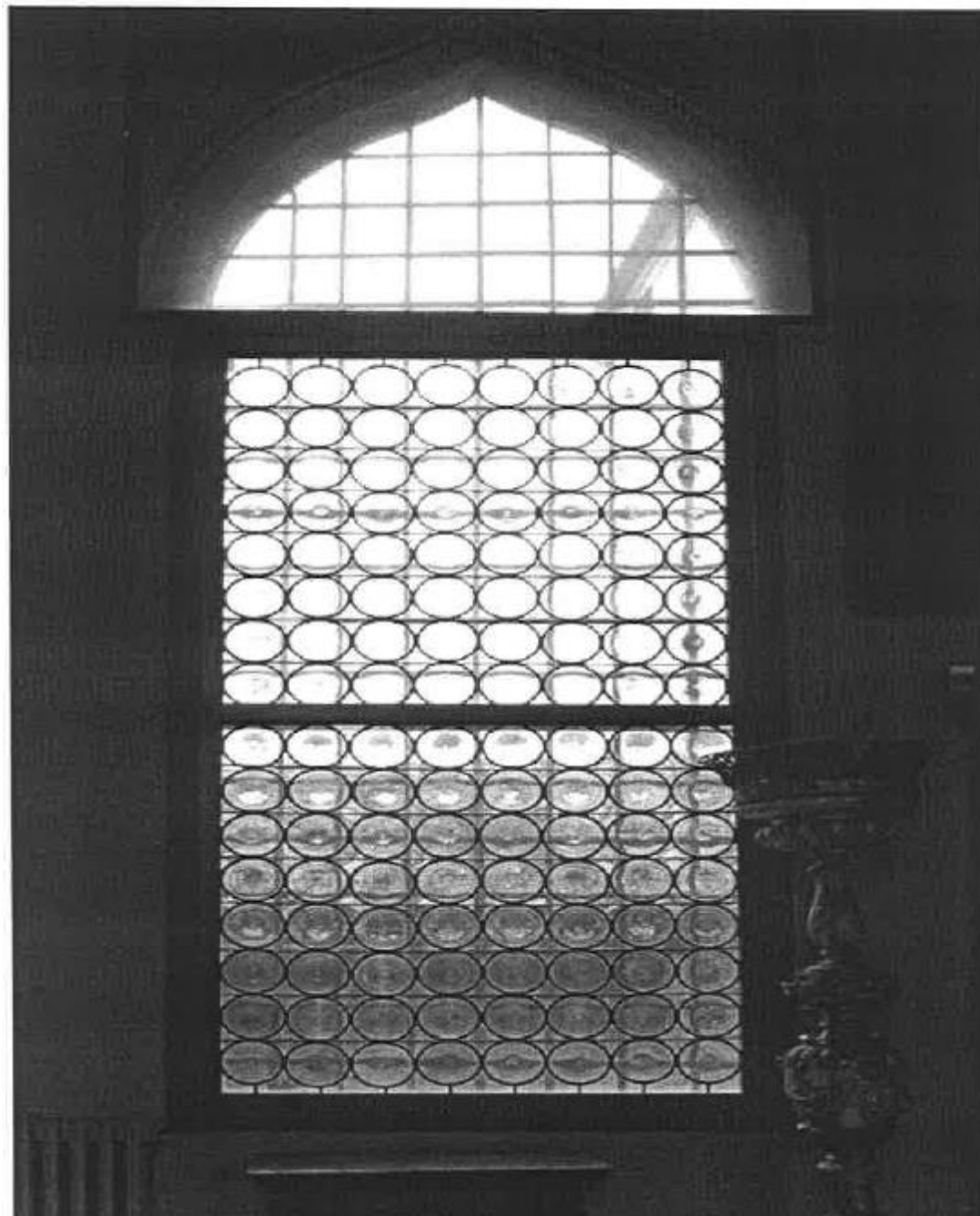
During the time of Roman Empire, glass was used in architecture, such as mosaics for walls and windows of churches.
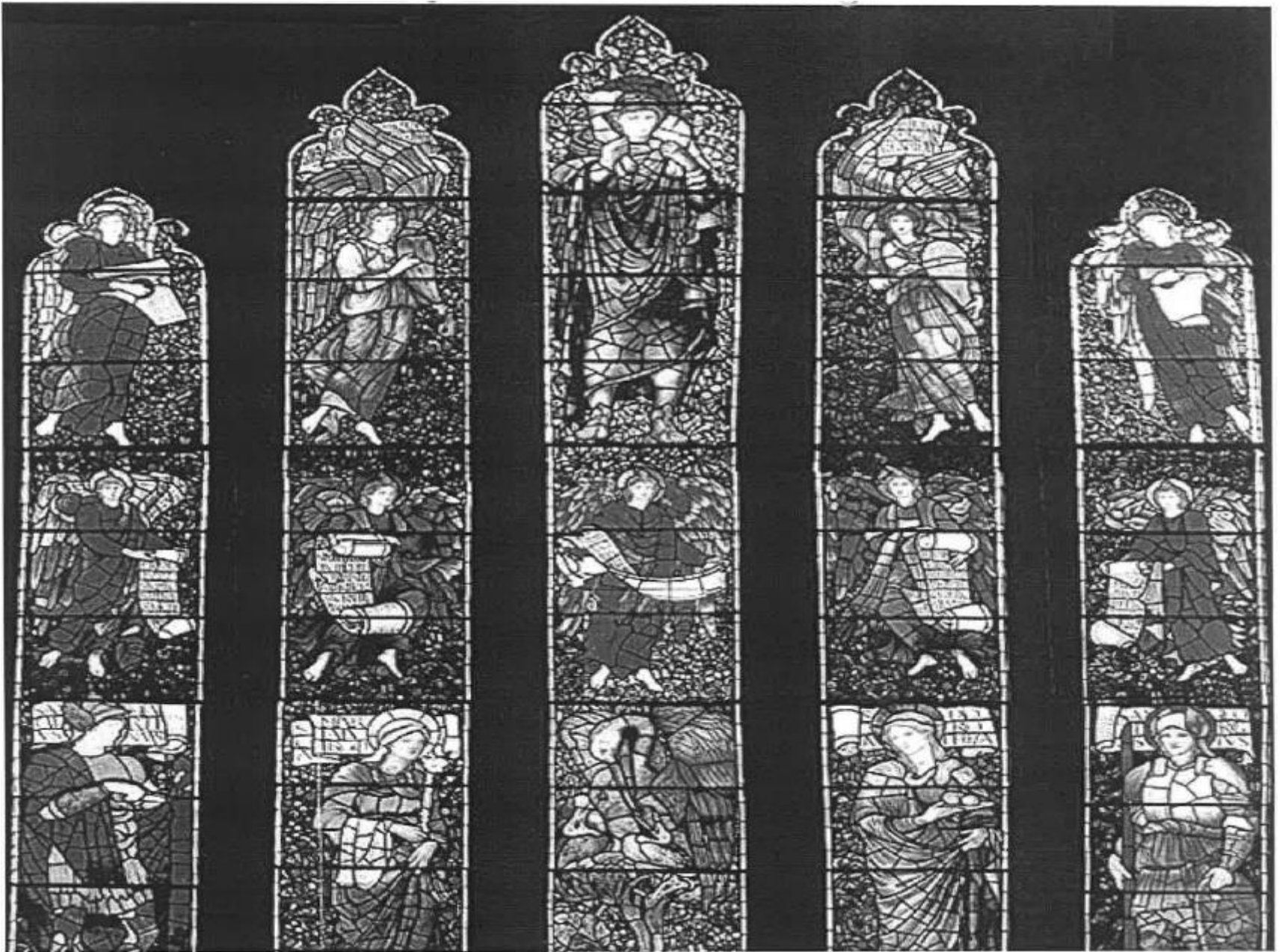
The first glasses were colored due to the presence of various impurities such as Fe_2O_3, Cr_2O_3. Virtually colorless glass was first made app. 1500 years ago.

Untill 13th century, in Roman Empire glass manufacturing was developed around Venice. After this period, many of the glass plants were moved from Venice to the nearby island Murano where is still the center for the hand made production.

Crown glass process

1. Gather molten glass

2. Blow to pear shape

3. Attach "punty" rod, cut off blow pipe and reheat

4. Spin to form disc

5. Open, reheat, spin again etc. Cut off.

6. Anneal
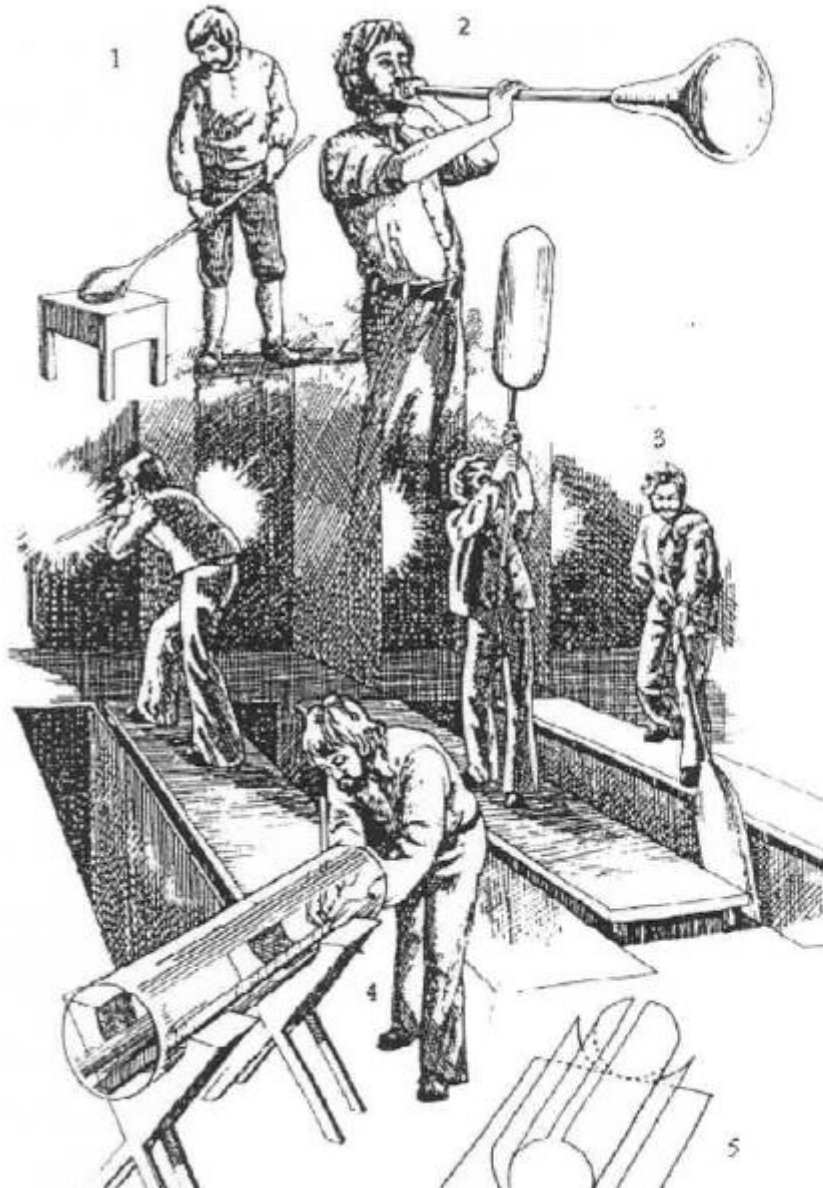
Original "sheet"

1. Reheat, blow, rotate
2. Reheat and swing in pit to form cylinder
3. Gather molten glass
4. Cut off, cool, cut longitudinally, inside
5. Reheat again, open cut, flatten with wet wooden block. Anneal.

DEFINITION

Glass is an amorphous material, and the most important properties can be counted as;

- it is transparent,
- it is inert to reactions with most of the chemicals; and
- it is strong and rigid.
- it is non-porous

The worst property of glass is its fragility.

The most accepted definition of glass is the one suggested by ASTM at 1945:

"Glass- an inorganic product of fusion that has cooled to a rigid condition without crystallization."

1 DEFINITION OF A GLASS

What is a "glass"? The glasses used by mankind throughout most of our history have been based on silica. Is silica a required component of a glass? Since we can form an almost limitless number of inorganic glasses which do not contain silica, the answer is obviously, "No, silica is not a required component of a glass." Glasses are traditionally formed by cooling from a melt. Is melting a requirement for glass formation? No, we can form glasses by vapor deposition, by *sol-gel* processing of solutions, and by neutron irradiation of crystalline materials. Most traditional glasses are inorganic and non-metallic. We currently use a vast number of organic glasses. Metallic glasses are becoming more common with every passing year. Obviously the chemical nature of the material cannot be used to define a glass.

What, then, is required in the definition of a glass? All glasses found to date share two common characteristics. First, no glass has a long range, periodic atomic arrangement. And even more importantly, every glass exhibits time-dependent *glass transformation* behavior. This behavior occurs over a temperature range known as the glass transformation region. A glass can thus be defined as "an amorphous solid completely lacking in long range, periodic atomic structure, and exhibiting a region of glass transformation behavior." Any material, inorganic, organic, or metallic, formed by any technique, which exhibits glass transformation behavior is a glass.

ATOMIC ARRANGEMENT (in solids)

Depending partially on their bonding between them, atoms (ions) can be arranged in space with different degrees of **order**.....

    In noble gases → complete lack of order (argon gas)

Bonds between the atoms in a molecule or directional bonds between nearest neighbor atoms will force a **short range order** between atoms like in a water molecule between oxygen and hydrogen atoms, or like in the silicon oxygen tetrahedra in **glass**
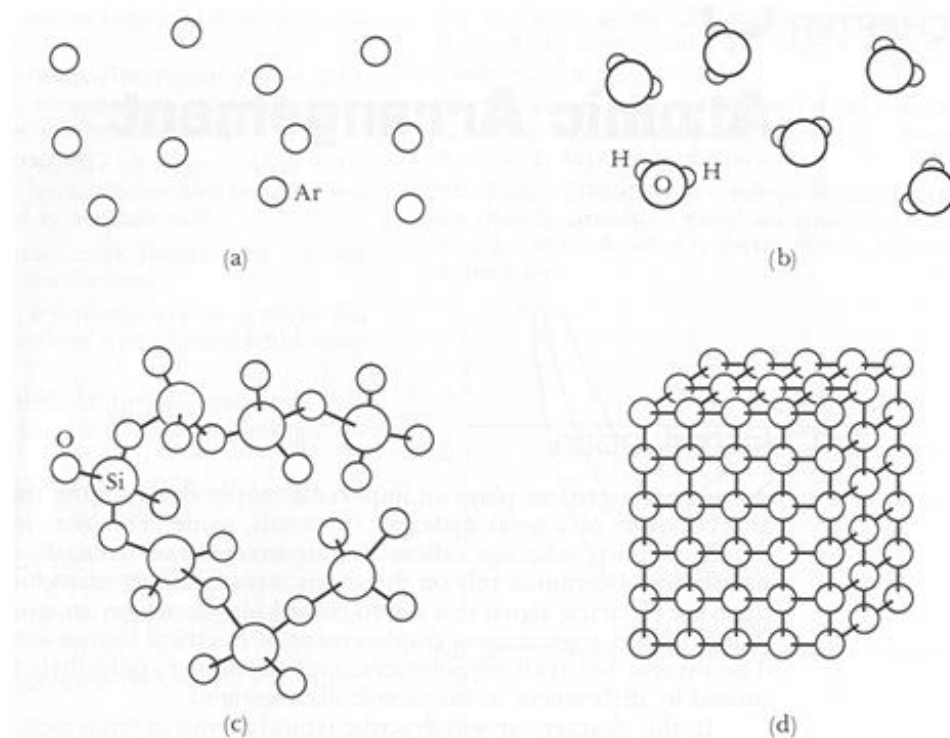

FIG. 3-1   The levels of atomic arrangement in materials. (a) Inert gases have no regular ordering of atoms. (b) and (c) Some materials, including steam and glass, have ordering only over a short distance. (d) Metals and many other solids have a regular ordering of atoms that extends throughout the material.

This short range order is typical of liquids or in the structure of so-called amorphous (amorph = lacking organization, or regular periodicity) materials.

The atomic arrangement in melts and amorphous solids are very similar. A major difference is their viscosities:

In amorphous solids the **disordered** structure is <u>frozen in</u>.

Crystalline solids exhibit "**long range order**" in the position and stacking sequence of atoms, molecules, or "**lattice points**"

In crystalline solids, each atom or molecule has <u>identical</u> surroundings in the crystal (except for the surface atoms)

Crystal Lattice Concept

Crystalline structure → consists of regular array of "points" in 3 dimensional space
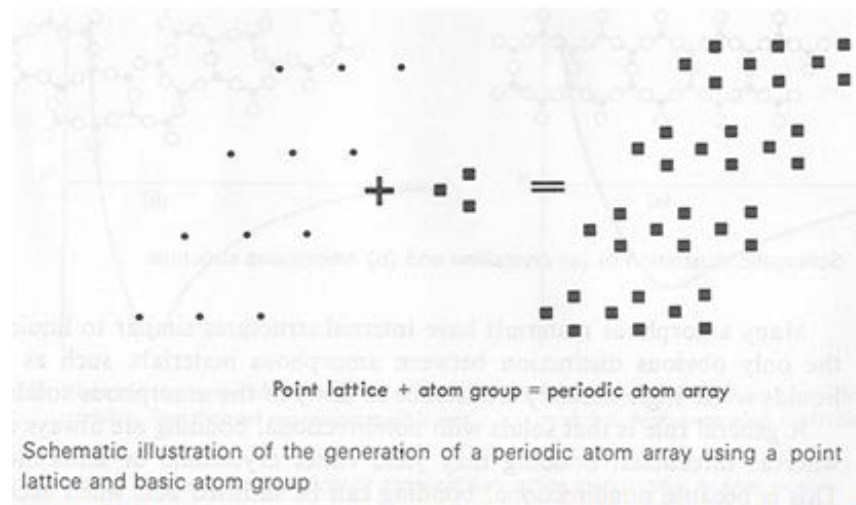
With each of the **lattice points**,

there may be *none*, *one* or *more atoms* associated

e.g. with each lattice point is one molecule of the above kind associated

Point lattice + atom group = periodic atom array

Schematic illustration of the generation of a periodic atom array using a point lattice and basic atom group

point lattice + atom group = periodic array of atoms

Crystalline and amorphous structures are built from exactly the same basic building blocks (short range order):

Schematic illustration of (a) crystalline and (b) amorphous structure
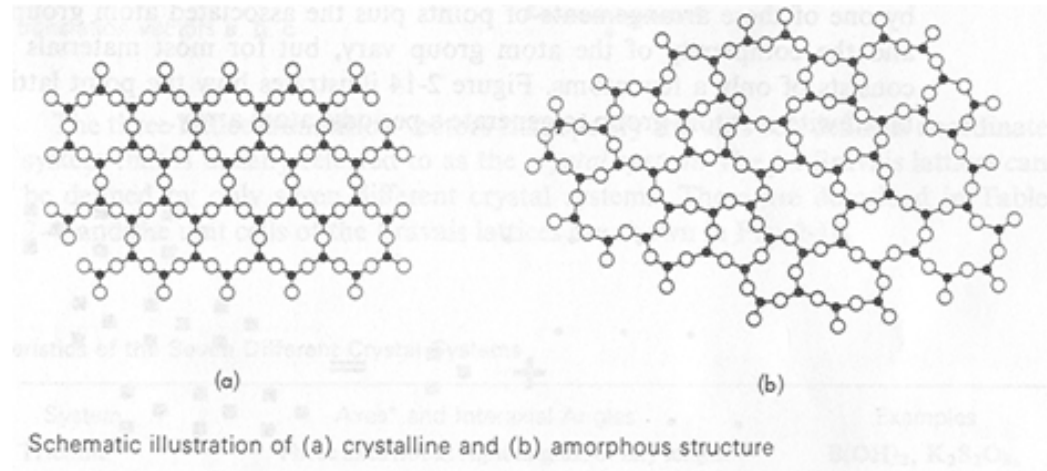
how many ways to pack atoms in regular self repeating units???

Fortunately, there is only limited number of ways that one can pack lattice points in 3-D space such that each point has identical surroundings.
All the crystalline solids in the world can be described by these 14 ways of packing lattice points in space. (plus the local atoms group arrangement associated with each lattice point.)
Most of the time we have one or few atoms associated with one lattice point……BUT in a polymer this could be many atoms per lattice point!!!!!!!!!!!!!

The 14 different ways of packing ➔ 14 **BRAVAIS** lattices distributed to 6 (or 7) **crystal systems**.

Each **Bravais** lattice described by the smallest repeating unit:

UNIT CELL

Unit cell is defined by the three lattice translation vectors, $\vec{a}$, $\vec{b}$ and $\vec{c}$.
The magnitude of $\vec{a}$, $\vec{b}$ and $\vec{c}$ are called "lattice parameters".
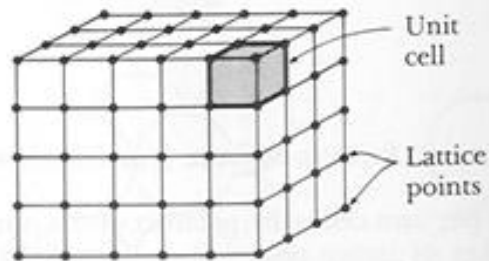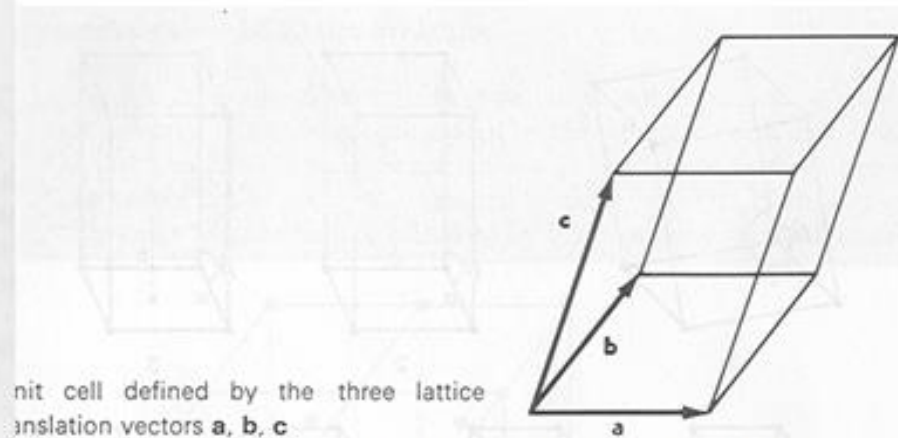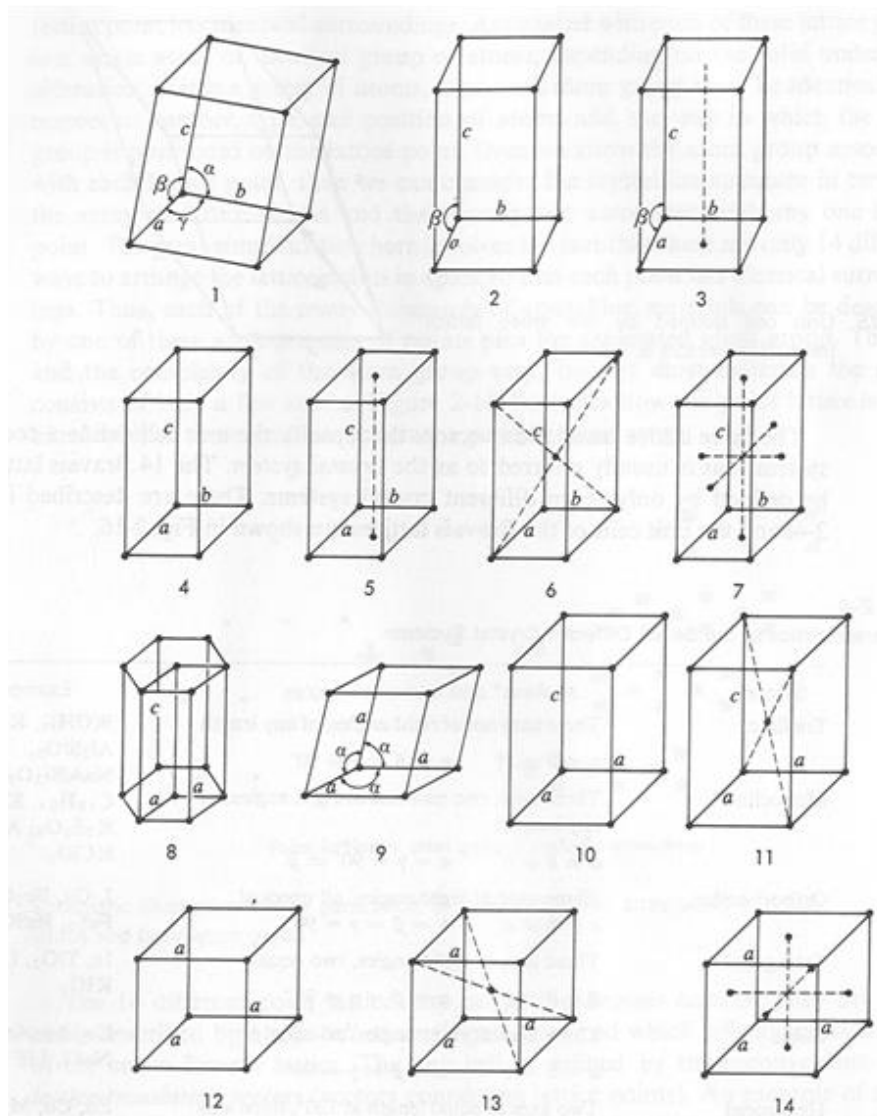

FIG. 3-2 A lattice is a periodic array of points that define space. The unit cell (heavy outline) is a subdivision of the lattice that still retains the characteristics of the lattice.

nit cell defined by the three lattice nslation vectors **a**, **b**, **c**

Depending on the ratio of a, b, and c and the angle between them, each unit cell is assigned to one of the 6 (or 7) crystal system.

The 14 point lattices illustrated by a unit cell of each: (1) triclinic, simple; (2) monoclinic, simple; (3) monoclinic, base centered; (4) orthorhombic, simple; (5) orthorhombic, base centered; (6) orthorhomic, body centered; (7) orthorhombic, face centered; (8) hexagonal; (9) rhombohedral; (10) tetragonal, simple; (11) tetragonal, body centered; (12) cubic, simple; (13) cubic, body centered; (14) cubic, face centered.
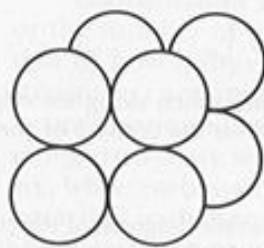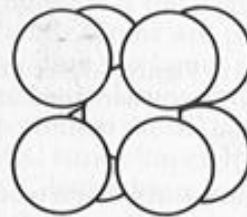
Simple cubic   Body-centered cubic   Face-centered cubic

FIG. 3-5 The models for simple cubic (SC), body-centered cubic (BCC), and face-centered cubic (FCC) unit cells assuming only one atom per lattice point.

TABLE 2-4

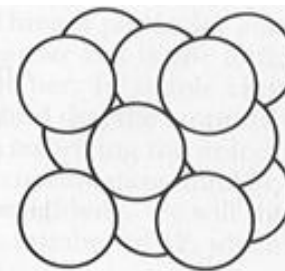The Characteristics of the Seven Different Crystal Systems

System	Axes* and Interaxial Angles	Examples
Triclinic	Three axes not at right angles, of any length $a \neq b \neq c$† $\alpha \neq \beta \neq \gamma \neq 90°$	$B(OH)_3$, $K_2S_2O_8$, Al_2SiO_5, $NaAlSi_3O_8$
Monoclinic	Three axes, one pair not at right angles, of any lengths $a \neq b \neq c$ $\alpha = \gamma = 90° \neq \beta$	$C_{18}H_{24}$, KNO_2, $K_2S_4O_6$, As_4S_4, $KClO_3$
Orthorhombic	Three axes at right angles, all unequal $a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$	I, Ga, Fe_3C, FeS_2, $BaSO_4$
Tetragonal	Three axes at right angles, two equal $a = b \neq c$ $\alpha = \beta = \gamma = 90°$	In, TiO_2, $C_4H_{10}O_4$, KIO_4
Cubic	Three axes at right angles, all equal $a = b = c$ $\alpha = \beta = \gamma = 90°$	Cu, Ag, Ar, Si, Ni, NaCl, LiF
Hexagonal	Two axes of equal length at 120°, third axis at 90° to these $a = b \neq c$ $\alpha = \beta = 90°$ $\gamma = 120°$	Zn, Cd, Mg, NiAs
Rhombohedral	Three axes equally inclined, not at right angles, all equal $a = b = c$ $\alpha = \beta = \gamma \neq 90°$	Hg, Sb, Bi

*a, b, and c refer to the lattice parameters or dimensions of the unit cell.
†In this table $\neq$ means "not necessarily equal to, and generally different from."

2 THE ENTHALPY/TEMPERATURE DIAGRAM

We have established that any material which exhibits glass transformation behavior is a glass. What, then, is glass transformation behavior? We traditionally discuss glass transformation behavior on the basis of either enthalpy or volume versus temperature diagrams, such as that shown in Figure 1.1; (this diagram will be discussed in considerably more detail in Chapter 6). Since enthalpy and volume behave in a similar fashion, the choice of the ordinate is somewhat arbitrary.
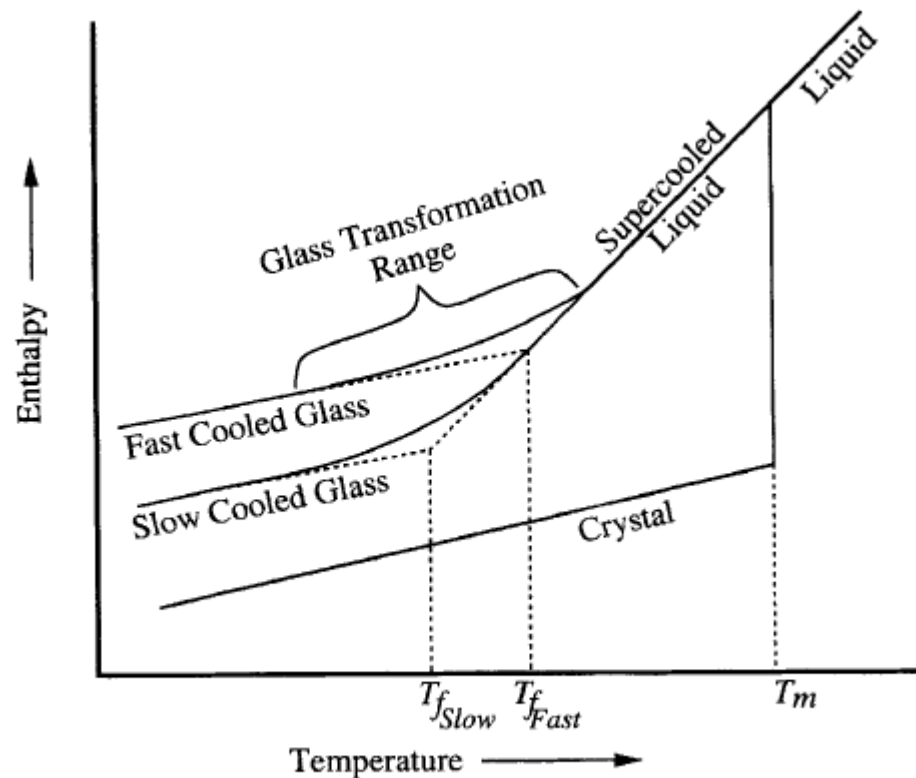

Figure 1.1 *Effect of temperature on the enthalpy of a glass forming melt*

characteristic of the exact temperature at which the melt is held. Cooling to any temperature below the melting temperature of the crystal would normally result in the conversion of the material to the crystalline state, with the formation of a long range, periodic atomic arrangement. If this occurs, the enthalpy will decrease abruptly to the value appropriate for the crystal. Continued cooling of the crystal will result in a further decrease in enthalpy due to the heat capacity of the crystal.

If the liquid can be cooled below the melting temperature of the crystal without crystallization, a supercooled liquid is obtained. The structure of the liquid continues to rearrange as the temperature decreases, but there is no abrupt decrease in enthalpy due to discontinuous structural rearrangement. As the liquid is cooled further, the viscosity increases. This increase in viscosity eventually becomes so great that the atoms can no longer completely rearrange to the equilibrium liquid structure, during the time allowed by the experiment. The structure begins to lag behind that which would be present if sufficient time were allowed to reach equilibrium. The enthalpy begins to deviate from the equilibrium line, following a curve of gradually decreasing slope, until it eventually becomes determined by the heat capacity of the frozen liquid, *i.e.*, the viscosity becomes so great that the structure of the liquid becomes fixed and is no longer temperature-dependent. The temperature region lying between the limits where the enthalpy is that

Crystalline Silica

If silica (SiO_2) which is a highly viscous liquid, is cooled very slowly, it can form a crystalline solid material called quartz.

In crystalline silica, Silicon ion (Si^{4+}) forms a constraction unit, together with 4 oxygen ions (O^{2-}) around it.

In this construction unit, silicon takes place in the center of the unit and it is surrounded by oxygens to form a tetrahedron.
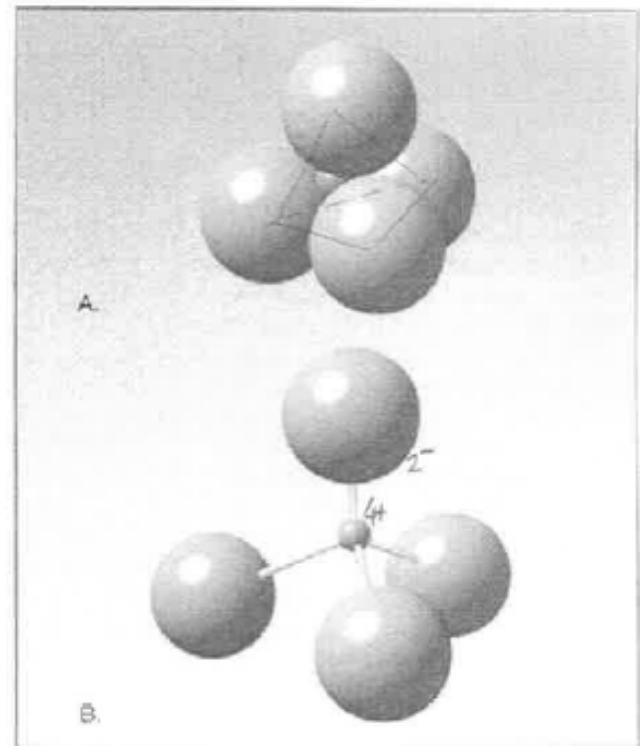
If these tetrahedra can arrange themselves through sufficiently slow cooling, a regular structure will emerge.
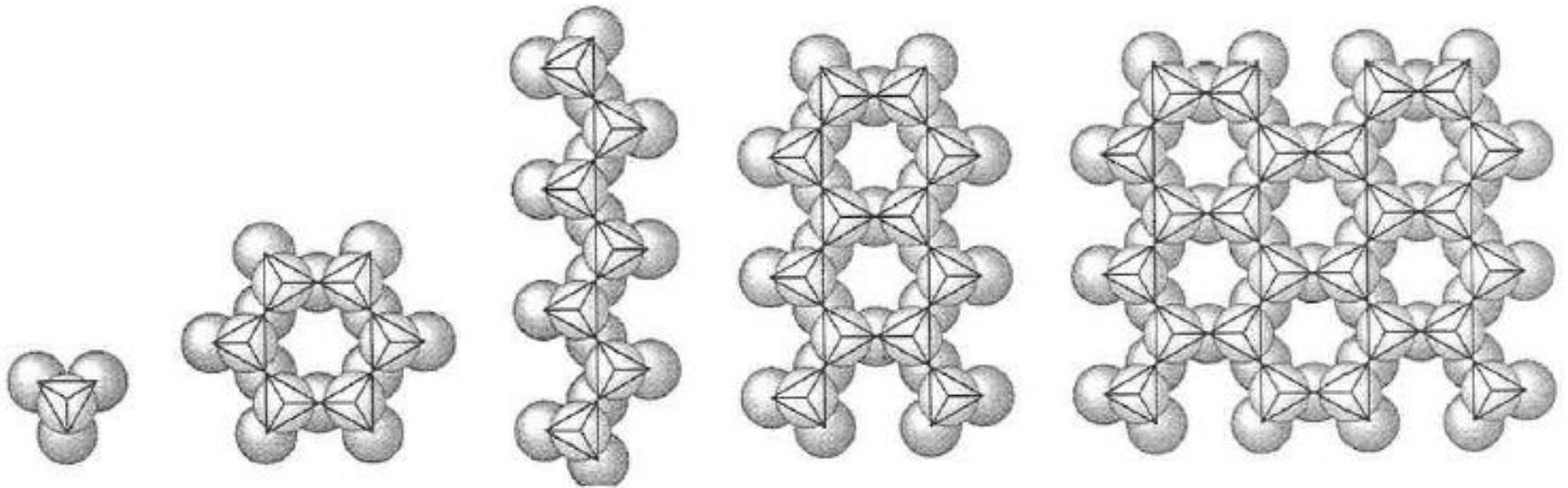
Silica
tetrahedron

Crystalline silica
(quartz)

Vitreous Silica

When a rapid cooling is applied, silica tetrahedra can not arrange themselves accordingly. In this way, the glass state will develop.

In two dimensional scheme
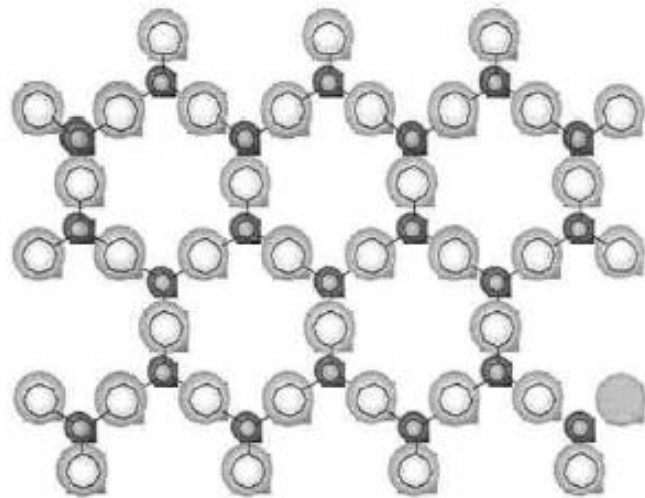
Crystalline silica
(quartz)
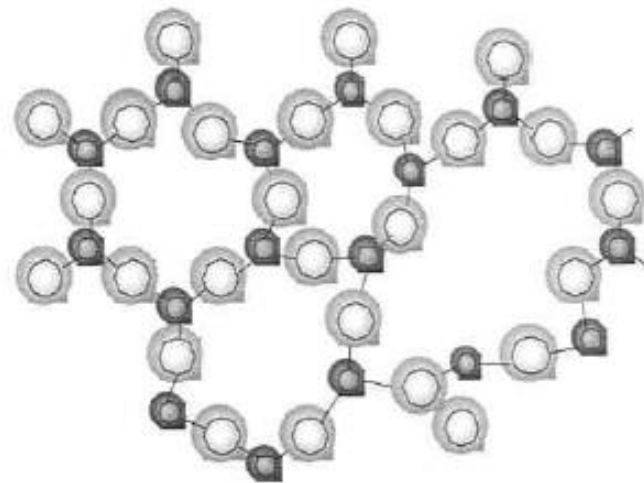
Vitreous silica

Although there are irregular holes between the structural units of vitreous silica, Si-O-Si bonds are very strong bonds.

These oxygens, taking place in the network, are called bridging oxygens.
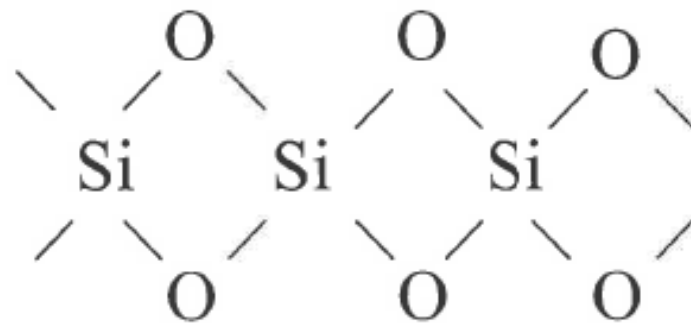
Bridging oxygens

Silicate Glasses

Several ions can be added to the silica network in order to develop the glass properties. These ions are called (network-) modifiers and intermediates.

in order to change glass properties of glass

Periodic Table of the Elements
© www.elementsdatabase.com

Legend:
- hydrogen
- alkali metals
- alkali earth metals
- transition metals
- poor metals
- nonmetals
- noble gases
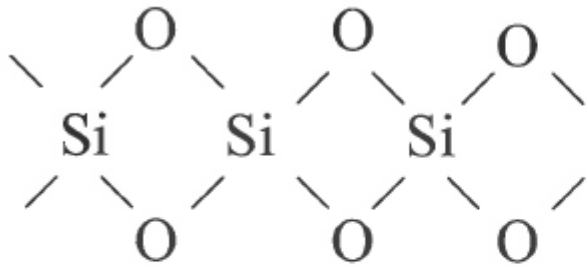- rare earth metals

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une	110 Unn								

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Alkali Metals (Li, Na, K)

(Network Modifiers)

- They are at the first column (IA) of periodic table.

- They have one single electron at their last orbit. So they can easily give this electron and form an ionic bond with the oxygen in the network.

- They break the strong covalent bonds of the network, Si-O-Si (Bridging property) and form weak ionic bonds. Oxygen ions which take place in these ionic bonds called non-bridging oxygens.

- They called as modifiers.

Bridging oxygen
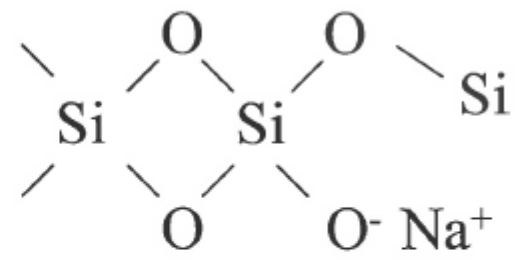
Non-bridging oxygen
(bonded to alkali ion)

Alkali ions (Li, Na, K)

Attraction force

$Li^+ < Na^+ < K^+$

Ionic radius
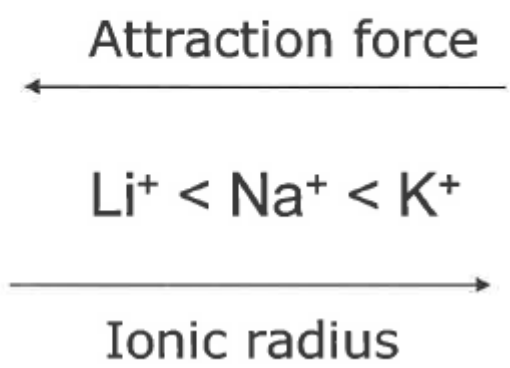
Alkaline Earth Metals (Mg, Ca, Sr, Ba)

(Network Modifiers)

• They are at the second column (IIA) of periodic table.

• They have two electrons at their last orbit, so they can give these electrons (gain +2 charge) and form two ionic bonds with two oxygens in the network. They are modifiers as well.

• They break the strong covalent bonds of the network like alkali metals, and they form two ionic bonds. Since they are bonded to two non-bridging oxygens, they hang on the network more strongly than alkali ions.

• Like the alkali ions, they break the network continuity.
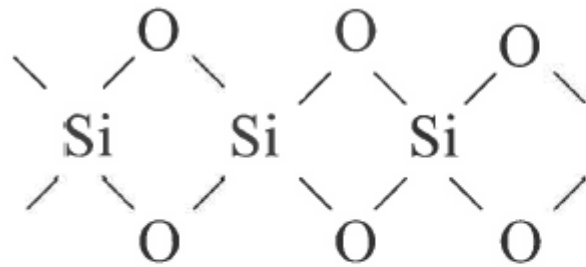
Bridging oxygen
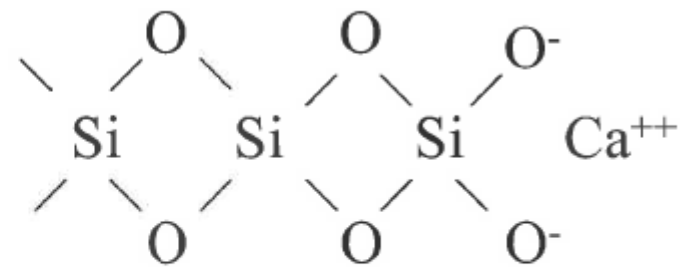
Non-bridging oxygen

(bonded to alkaline earth ion)

Alkaline earth ions (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+})

Attraction force

$\longleftarrow$

Mg < Ca < Sr < Ba

$\longrightarrow$

Ionic radius
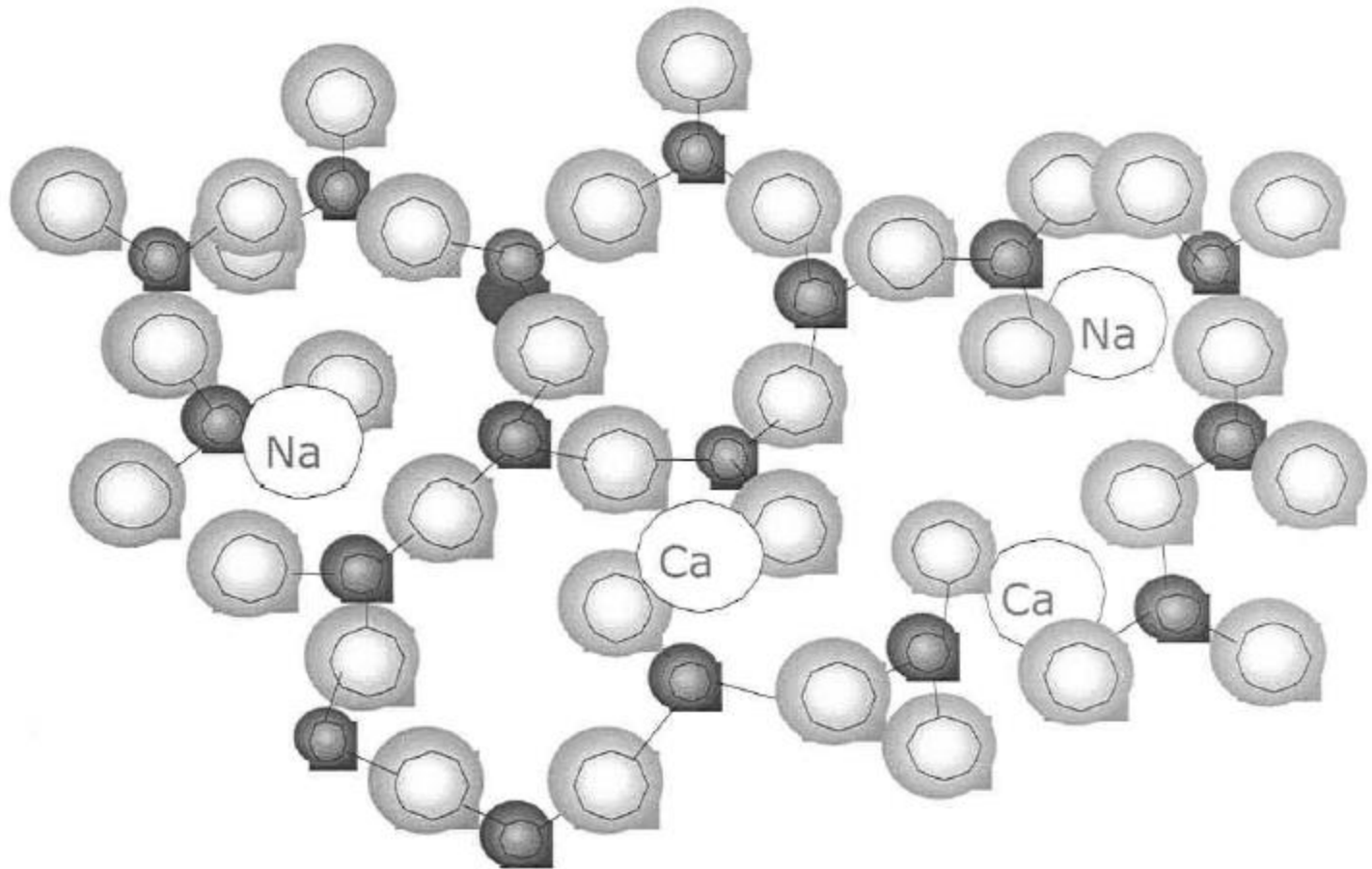
Structure of soda-lime-silicate glass

Aluminum

(Intermediate)

• It stays on the third column (IIIA) of the periodic table.

• It shows both covalent and ionic character (amphoteric). As a result of having small ionic radius and high electronic charge (3+), it forms strong bonds with oxygen.

• Since it is amphotheric it can form AlO_4^{-5} tetrahedron at the similar size of the tetrahedron of SiO_4^{-4}. So it can show similar properties to silica but Al can not form construction units itself.

• It is not a network former but can take place a former role in the silica network. So it is an intermediate.
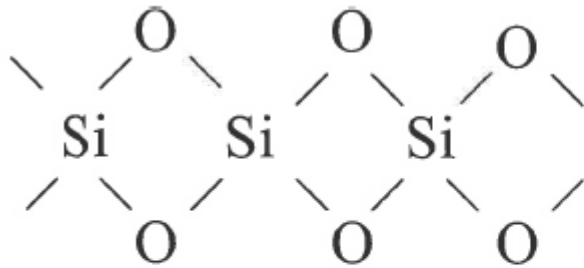
Tetrahedral structure
of silica
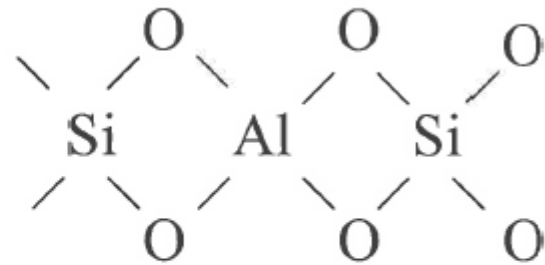
The position of alumina
(AlO_4^{-5}) in the silica
network

Boron

(network former)

• It stays at the third column (IIIA) of the periodic table like Al.

• It is both a network former like silica and can take place in the silica network as well.

• The coordination number can be three or six fold depending on the network modifiers in the structure whereas silica has a fourfold coordination.

• It has a high attraction force on oxygen in both coordinations resulting a strong B-O bond.

• On the other hand, B-O-B construction units are weaker at higher temperatures. This property brings easier melting and lower viscosity. B keeps this property on both borate glasses (as network former itself) and silicate glasses (as an intermediate).
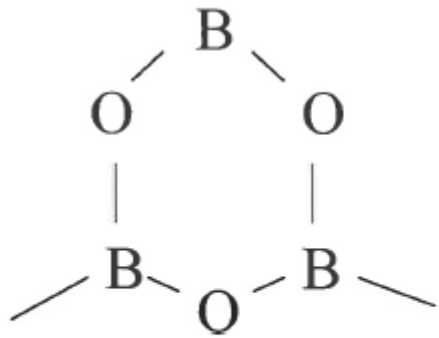
BO₃ network
(trigonal structure)
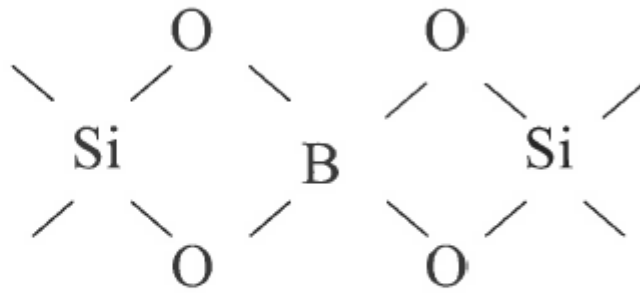
The position of boron in
the silica network

CRYSTALLIZATION

Crystallization is the result of two processes:

- Nucleation
- Crystal growth

THE KINETICS OF PHASE TRANSFORMATIONS

With phase transformations, normally at least one new phase is formed that has different physical/chemical characteristics and/or a different structure than the parent phase. Furthermore, most phase transformations do not occur instantaneously. Rather, they begin by the formation of numerous small particles of the new phase(s), which increase in size until the transformation has reached completion. The progress of a phase transformation may be broken down into two distinct stages: **nucleation** and **growth.** Nucleation involves the appearance of very small particles, or nuclei of the new phase (often consisting of only a few hundred atoms), which are capable of growing. During the growth stage these nuclei increase in size, which results in the disappearance of some (or all) of the parent phase. The transformation reaches completion if the growth of these new phase particles is allowed to proceed until the equilibrium fraction is attained. We now discuss the mechanics of these two processes, and how they relate to solid-state transformations.

Nucleation

There are two types of nucleation: *homogeneous* and *heterogeneous*. The distinction between them is made according to the site at which nucleating events occur. For the homogeneous type, nuclei of the new phase form uniformly throughout the parent phase, whereas for the heterogeneous type, nuclei form preferentially at structural inhomogeneities, such as container surfaces, insoluble impurities, grain boundaries, dislocations, and so on. We begin by discussing homogeneous nucleation because its description and theory are simpler to treat. These principles are then extended to a discussion of the heterogeneous type.

Homogeneous Nucleation

A discussion of the theory of nucleation involves a thermodynamic parameter called **free energy** (or *Gibbs free energy*), G. In brief, free energy is a function of other thermodynamic parameters, of which one is the internal energy of the system (i.e., the *enthalpy, H*), and another is a measurement of the randomness or disorder of the atoms or molecules (i.e., the *entropy, S*). It is not our purpose here to provide a detailed discussion of the principles of thermodynamics as they apply to materials systems. However, relative to phase transformations, an important thermodynamic parameter is the change in free energy ΔG; a transformation will occur spontaneously only when ΔG has a negative value.
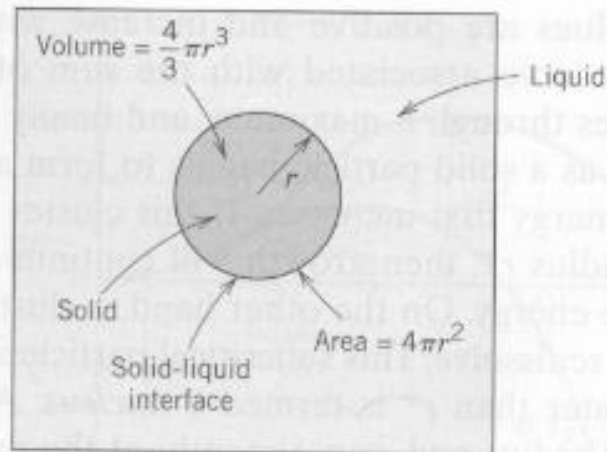
Figure 11.1 Schematic diagram showing the nucleation of a spherical solid particle in a liquid.

For the sake of simplicity, let us first consider the solidification of a pure material, assuming that nuclei of the solid phase form in the interior of the liquid as atoms cluster together so as to form a packing arrangement similar to that found in the solid phase. Furthermore, it will be assumed that each nucleus is spherical in geometry and has a radius r. This situation is represented schematically in Figure 11.1.

There are two contributions to the total free energy change that accompany a solidification transformation. The first is the free energy difference between the solid and liquid phases, or the volume free energy, ΔG_v. Its value will be negative if the temperature is below the equilibrium solidification temperature, and the magnitude of its contribution is the product of ΔG_v and the volume of the spherical nucleus (i.e., $\frac{4}{3}\pi r^3$). The second energy contribution results from the formation of the solid–liquid phase boundary during the solidification transformation. Associated with this boundary is a surface free energy, γ, which is positive; furthermore, the magnitude of this contribution is the product of γ and the surface area of the nucleus (i.e., $4\pi r^2$). Finally, the total free energy change is equal to the sum of these two contributions—that is,

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma \qquad (11.1)$$

These volume, surface, and total free energy contributions are plotted schematically as a function of nucleus radius in Figures 11.2a and 11.2b. Here (Figure 11.2a) it will be noted that for the curve corresponding to the first term on the right-hand side of Equation 11.1, the free energy (which is negative) decreases with the third power of r. Furthermore, for the curve resulting from the second term in
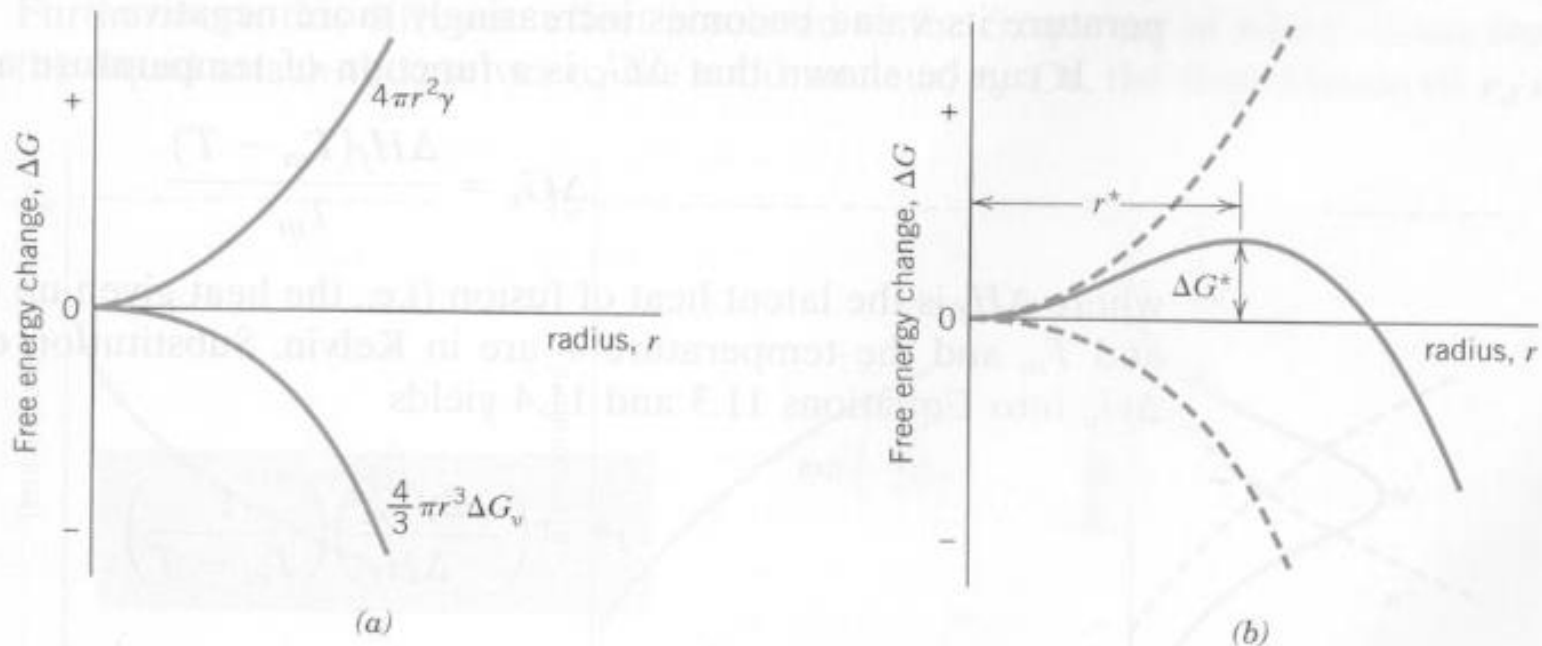

Figure 11.2 (a) Schematic curves for volume free energy and surface free energy contributions to the total free energy change attending the formation of a spherical embryo/nucleus during solidification. (b) Schematic plot of free energy versus embryo/nucleus radius, on which is shown the critical free energy change (ΔG^*) and the critical nucleus radius (r^*).

Equation 11.1, energy values are positive and increase with the square of the radius. Consequently, the curve associated with the sum of both terms (Figure 11.2b) first increases, passes through a maximum, and finally decreases. In a physical sense, this means that as a solid particle begins to form as atoms in the liquid cluster together, its free energy first increases. If this cluster reaches a size corresponding to the critical radius r^*, then growth will continue with the accompaniment of a decrease in free energy. On the other hand, a cluster of radius less than the critical will shrink and redissolve. This subcritical particle is an *embryo*, whereas the particle of radius greater than r^* is termed a *nucleus*. A critical free energy, ΔG^*, occurs at the critical radius and, consequently, at the maximum of the curve in Figure 11.2b. This ΔG^* corresponds to an *activation free energy*, which is the free energy required for the formation of a stable nucleus. Equivalently, it may be considered an energy barrier to the nucleation process.

Since r^* and ΔG^* appear at the maximum on the free energy-versus-radius curve of Figure 11.2b, derivation of expressions for these two parameters is a simple matter. For r^*, we differentiate the ΔG equation (Equation 11.1) with respect to r, set the resulting expression equal to zero, and then solve for r ($= r^*$). That is,

$$\frac{d(\Delta G)}{dr} = \tfrac{4}{3}\pi \Delta G_v (3r^2) + 4\pi\gamma(2r) = 0 \tag{11.2}$$

which leads to the result

$$r^* = -\frac{2\gamma}{\Delta G_v} \tag{11.3}$$

Now, substitution of this expression for r^* into Equation 11.1 yields the following expression for ΔG^*:

$$\Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2} \qquad (11.4)$$

This volume free energy change ΔG_v is the driving force for the solidification transformation, and its magnitude is a function of temperature. At the equilibrium solidification temperature T_m, the value of ΔG_v is zero, and with diminishing temperature its value becomes increasingly more negative.

It can be shown that ΔG_v is a function of temperature as

$$\Delta G_v = \frac{\Delta H_f(T_m - T)}{T_m} \qquad (11.5)$$

where ΔH_f is the latent heat of fusion (i.e., the heat given up during solidification), and T_m and the temperature T are in Kelvin. Substitution of this expression for ΔG_v into Equations 11.3 and 11.4 yields

$$r^* = \left(-\frac{2\gamma T_m}{\Delta H_f}\right)\left(\frac{1}{T_m - T}\right) \qquad (11.6)$$

and

$$\Delta G^* = \left(\frac{16\pi\gamma^3 T_m^2}{3\Delta H_f^2}\right)\frac{1}{(T_m - T)^2} \qquad (11.7)$$
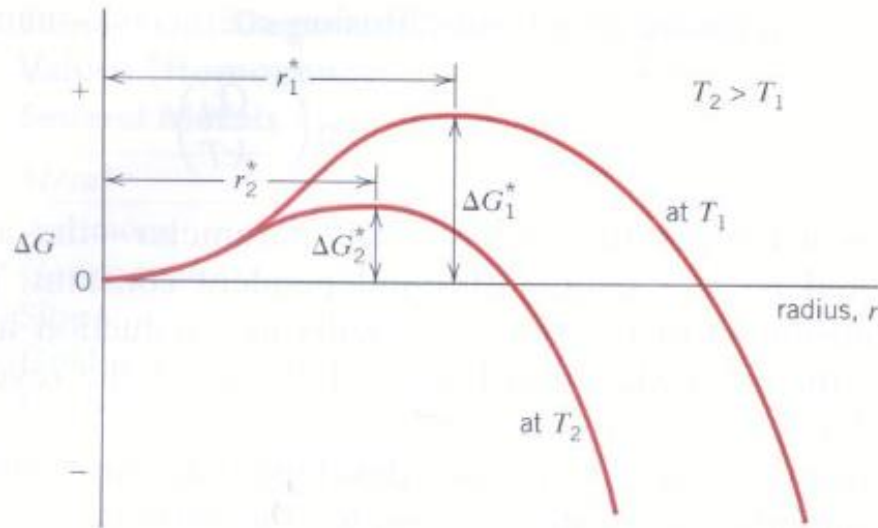
Figure 11.3 Schematic free-energy-versus-embryo/nucleus-radius curves for two different temperatures. The critical free energy change (ΔG^*) and critical nucleus radius (r^*) are indicated for each temperature.

Thus, from these two equations, both the critical radius r^* and the activation free energy ΔG^* decrease as temperature T decreases. (The γ and ΔH_f parameters in these expressions are relatively insensitive to temperature changes.) Figure 11.3, a schematic ΔG-versus-r plot that shows curves for two different temperatures, illustrates these relationships. Physically, this means that with a lowering of temperature at temperatures below the equilibrium solidification temperature (T_m), nucleation occurs more readily. Furthermore, the number of stable nuclei n^* (having radii greater than r^*) is a function of temperature as

$$n^* = K_1 \exp\left(-\frac{\Delta G^*}{kT}\right) \qquad (11.8)$$

where the constant K_1 is related to the total number of nuclei of the solid phase. For the exponential term of this expression, changes in temperature have a greater effect on the magnitude of the ΔG^* term in the numerator than the T term in the denominator. Consequently, as the temperature is lowered below T_m the exponential term in Equation 11.8 also decreases such that the magnitude of n^* increases. This temperature dependence (n^* versus T) is represented in the schematic plot of Figure 11.4a.

There is another important temperature-dependent step that is involved in and also influences nucleation: the clustering of atoms by short-range diffusion during the formation of nuclei. The influence of temperature on the rate of diffusion (i.e., magnitude of the diffusion coefficient, D) is given in Equation 6.8. Furthermore, this diffusion effect is related to the frequency at which atoms from the liquid attach themselves to the solid nucleus, ν_d. Or, the dependence of ν_d on

Figure 11.4 For solidification, schematic plots of (a) number of stable nuclei versus temperature, (b) frequency of atomic attachment versus temperature, and (c) nucleation rate versus temperature (also shown are curves for parts a and b).
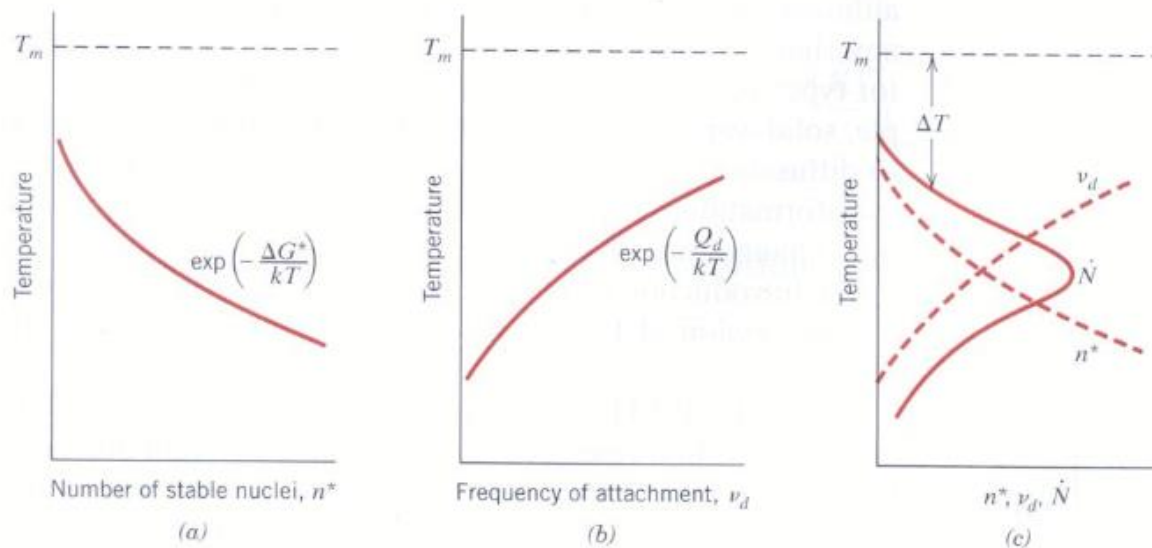
temperature is the same as for the diffusion coefficient—namely,

$$\nu_d = K_2 \exp\left(-\frac{Q_d}{kT}\right) \tag{11.9}$$

where Q_d is a temperature-independent parameter—the activation energy for diffusion—and K_2 is a temperature-independent constant. Thus, from Equation 11.9 a diminishment of temperature results in a reduction in ν_d. This effect, represented by the curve shown in Figure 11.4b, is just the reverse of that for n^* as discussed above.

The principles and concepts just developed are now extended to a discussion of another important nucleation parameter, the nucleation rate $\dot{N}$ (which has units of nuclei per unit volume per second). This rate is simply proportional to the product of n^* (Equation 11.8) and ν_d (Equation 11.9); that is,

$$\dot{N} = K_3 n^* \nu_d = K_1 K_2 K_3 \left[\exp\left(-\frac{\Delta G^*}{kT}\right) \exp\left(-\frac{Q_d}{kT}\right) \right] \tag{11.10}$$

Here K_3 is the number of atoms on a nucleus surface. Figure 11.4c schematically plots nucleation rate as a function of temperature and, in addition, the curves of Figures 11.4a and 11.4b from which the $\dot{N}$ curve is derived. Note (Figure 11.4c) that, with a lowering of temperature from below T_m, the nucleation rate first increases, achieves a maximum, and subsequently diminishes.

The shape of this N curve is explained as follows: for the upper region of the curve (a sudden and dramatic increase in $\dot{N}$ with decreasing T), ΔG^* is greater than Q_d, which means that the $\exp(-\Delta G^*/kT)$ term of Equation 11.10 is much smaller than $\exp(-Q_d/kT)$. In other words, the nucleation rate is suppressed at high temperatures due to a small activation driving force. With continued diminishment of temperature, there comes a point at which ΔG^* becomes smaller than the temperature-independent Q_d, with the result that $\exp(-Q_d/kT) < \exp(-\Delta G^*/kT)$, or that, at lower temperatures, a low atomic mobility suppresses the nucleation rate. This accounts for the shape of the lower curve segment (a precipitous reduction of $\dot{N}$ with a continued diminishment of temperature). Furthermore, the $\dot{N}$ curve of Figure 11.4c necessarily passes through a maximum over the intermediate temperature range where values for ΔG^* and Q_d are of approximately the same magnitude.

Several qualifying comments are in order regarding the above discussion. First, although we assumed a spherical shape for nuclei, this method may be applied to any shape with the same final result. Furthermore, this treatment may be utilized for types of transformations other than solidification (i.e., liquid–solid)—for example, solid–vapor and solid–solid. However, magnitudes of ΔG_v and γ, in addition to diffusion rates of the atomic species, will undoubtedly differ among the various transformation types. In addition, for solid–solid transformations, there may be volume changes attendant to the formation of new phases. These changes may lead to the introduction of microscopic strains, which must be taken into account in the ΔG expression of Equation 11.1, and, consequently, will affect the magnitudes of r^* and ΔG^*.

From Figure 11.4c it is apparent that during the cooling of a liquid, an appreciable nucleation rate (i.e., solidification) will begin only after the temperature has been lowered to below the equilibrium solidification (or melting) temperature (T_m). This phenomenon is termed *supercooling* (or *undercooling*), and the degree of supercooling for homogeneous nucleation may be significant (on the order of

Table 11.1 Degree of Supercooling (ΔT) Values (Homogeneous Nucleation) for Several Metals

Metal	$\Delta T(°C)$
Antimony	135
Germanium	227
Silver	227
Gold	230
Copper	236
Iron	295
Nickel	319
Cobalt	330
Palladium	332

[From D. Turnbull and R. E. Cech, "Microscopic Observation of the Solidification of Small Metal Droplets," *J. Appl. Phys.*, **21**, 808 (1950)].

several hundred degrees Kelvin) for some systems. In Table 11.1 is tabulated, for several materials, typical degrees of supercooling for homogeneous nucleation.

EXAMPLE PROBLEM 11.1

Computation of Critical Nucleus Radius and Activation Free Energy

(a) For the solidification of pure gold, calculate the critical radius r^* and the activation free energy ΔG^* if nucleation is homogeneous. Values for the latent heat of fusion and surface free energy are -1.16×10^9 J/m^3 and 0.132 J/m^2, respectively. Use the supercooling value found in Table 11.1.

(b) Now calculate the number of atoms found in a nucleus of critical size. Assume a lattice parameter of 0.413 nm for solid gold at its melting temperature.

Solution

(a) In order to compute the critical radius, we employ Equation 11.6, using the melting temperature of 1064°C for gold, assuming a supercooling value of 230°C (Table 11.1), and realizing that ΔH_f is negative. Hence

$$r^* = \left(-\frac{2\gamma T_m}{\Delta H_f}\right)\left(\frac{1}{T_m - T}\right)$$

$$= \left[-\frac{(2)(0.132 \text{ J/m}^2)(1064 + 273 \text{ K})}{-1.16 \times 10^9 \text{ J/m}^3}\right]\left(\frac{1}{230 \text{ K}}\right)$$

$$= 1.32 \times 10^{-9} \text{ m} = 1.32 \text{ nm}$$

For computation of the activation free energy, Equation 11.7 is employed. Thus

$$\Delta G^* = \left(\frac{16\pi\gamma^3 T_m^2}{3 \Delta H_f^2}\right)\frac{1}{(T_m - T)^2}$$

$$= \left[\frac{(16)(\pi)(0.132 \text{ J/m}^2)^3(1064 + 273 \text{ K})^2}{(3)(-1.16 \times 10^9 \text{ J/m}^3)^2}\right]\left[\frac{1}{(230 \text{ K})^2}\right]$$

$$= 9.64 \times 10^{-19} \text{ J}$$

(b) In order to compute the number of atoms in a nucleus of critical size (assuming a spherical nucleus of radius r^*), it is first necessary to determine the number of unit cells, which we then multiply by the number of atoms per unit cell. The number of unit cells found in this critical nucleus is just the ratio of critical nucleus and unit cell volumes. Inasmuch as gold has the FCC crystal structure (and a cubic unit cell), its unit cell volume is just a^3, where a is the lattice parameter (i.e., unit cell edge length); its value is 0.413 nm, as cited in the problem statement. Therefore, the number of unit cells found in a radius of critical size is just

$$\text{\# unit cells/particle} = \frac{\text{critical nucleus volume}}{\text{unit cell volume}} = \frac{\frac{4}{3}\pi r^{*3}}{a^3} \qquad (11.11)$$

$$= \frac{\left(\frac{4}{3}\right)(\pi)(1.32 \text{ nm})^3}{(0.413 \text{ nm})^3} = 137 \text{ unit cells}$$

Inasmuch as there is the equivalence of four atoms per FCC unit cell (Section 3.4), the total number of atoms per critical nucleus is just

(137 unit cells/critical nucleus)(4 atoms/unit cell) = 548 atoms/critical nucleus

Heterogeneous Nucleation

Although levels of supercooling for homogeneous nucleation may be significant (on occasion several hundred degrees Celsius), in practical situations they are often on the order of only several degrees Celsius. The reason for this is that the activation energy (i.e., energy barrier) for nucleation (ΔG^* of Equation 11.4) is lowered when nuclei form on preexisting surfaces or interfaces, since the surface free energy (γ of Equation 11.4) is reduced. In other words, it is easier for nucleation to occur at surfaces and interfaces than at other sites. Again, this type of nucleation is termed *heterogeneous*.

In order to understand this phenomenon, let us consider the nucleation, on a flat surface, of a solid particle from a liquid phase. It is assumed that both the liquid and solid phases "wet" this flat surface, that is, both of these phases spread out and cover the surface; this configuration is depicted schematically in Figure 11.5. Also noted in the figure are three interfacial energies (represented as vectors) that exist at two-phase boundaries—γ_{SL}, γ_{SI}, and γ_{IL}—as well as the wetting angle θ (the angle between the γ_{SI} and γ_{SL} vectors). Taking a surface tension force balance in the plane of the flat surface leads to the following expression:

$$\gamma_{IL} = \gamma_{SI} + \gamma_{SL} \cos \theta \tag{11.12}$$

Now, using a somewhat involved procedure similar to the one presented above for homogeneous nucleation (which we have chosen to omit), it is possible to
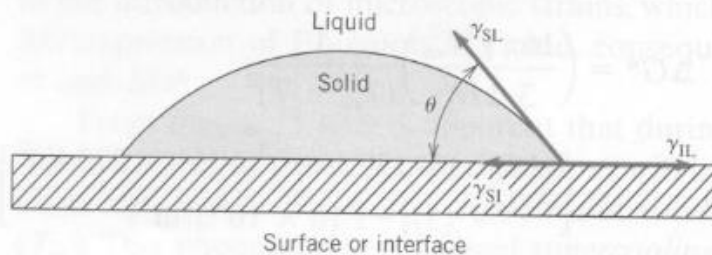

Figure 11.5 Heterogeneous nucleation of a solid from a liquid. The solid–surface (γ_{SI}), solid–liquid (γ_{SL}), and liquid–surface (γ_{IL}) interfacial energies are represented by vectors. The wetting angle (θ) is also shown.
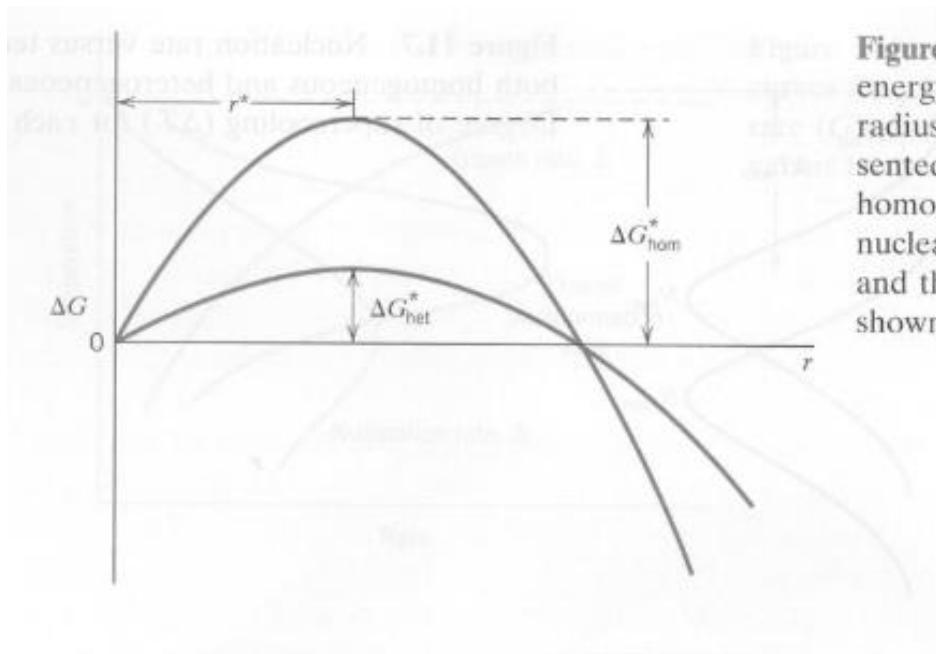
Figure 11.6 Schematic free-energy-versus-embryo/nucleus-radius plot on which are presented curves for both homogeneous and heterogeneous nucleation. Critical free energies and the critical radius are also shown.

derive equations for r^* and ΔG^*; these are as follows:

$$r^* = -\frac{2\gamma_{SL}}{\Delta G_v} \tag{11.13}$$

$$\Delta G^* = \left(\frac{16\pi\gamma_{SL}^3}{3\Delta G_v^2}\right)S(\theta) \tag{11.14}$$

The $S(\theta)$ term of this last equation is a function only of θ (i.e, the shape of the nucleus), which will have a numerical value between zero and unity.[1]

From Equation 11.13, it is important to note that the critical radius r^* for heterogeneous nucleation is the same as for homogeneous, inasmuch as γ_{SL} is the same surface energy as γ in Equation 11.3. It is also evident that the activation energy barrier for heterogeneous nucleation (Equation 11.14) is smaller than the homogeneous barrier (Equation 11.4) by an amount corresponding to the value of this $S(\theta)$ function, or

$$\Delta G^*_{het} = \Delta G^*_{hom} S(\theta) \tag{11.15}$$

Figure 11.6, a schematic graph of ΔG versus nucleus radius, plots curves for both types of nucleation, and indicates the difference in the magnitudes of ΔG^*_{het} and ΔG^*_{hom}, in addition to the constancy of r^*. This lower ΔG^* for heterogeneous means that a smaller energy must be overcome during the nucleation process (than for homogeneous), and, therefore, heterogeneous nucleation occurs more readily (Equation 11.10). In terms of the nucleation rate, the $\dot{N}$ versus T curve (Figure 11.4c) is shifted to higher temperatures for heterogeneous. This effect is represented in Figure 11.7, which also shows that a much smaller degree of supercooling (ΔT) is required for heterogeneous nucleation.

Growth

The growth step in a phase transformation begins once an embryo has exceeded the critical size, r^*, and becomes a stable nucleus. Note that nucleation will continue

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[1] For example, for θ angles of 30° and 90°, values of $S(\theta)$ are approximately 0.01 and 0.5, respectively.
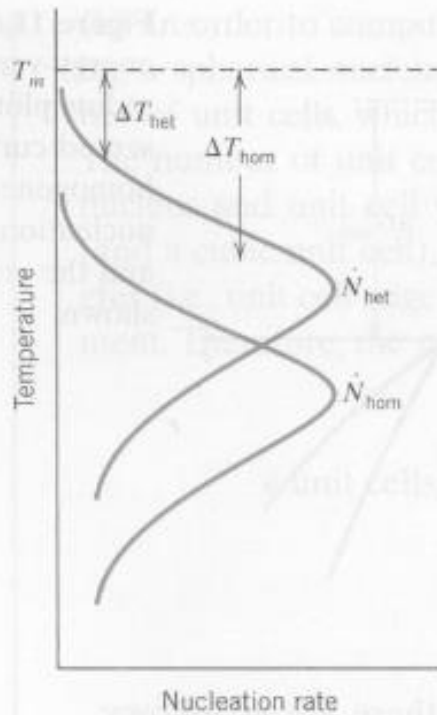
Figure 11.7 Nucleation rate versus temperature for both homogeneous and heterogeneous nucleation. Degree of supercooling (ΔT) for each is also shown.

to occur simultaneously with growth of the new phase particles; of course, nucleation cannot occur in regions that have already transformed to the new phase. Furthermore, the growth process will cease in any region where particles of the new phase meet, since here the transformation will have reached completion.

Particle growth occurs by long-range atomic diffusion, which normally involves several steps—for example, diffusion through the parent phase, across a phase boundary, and then into the nucleus. Consequently, the growth rate $\dot{G}$ is determined by the rate of diffusion, and its temperature dependence is the same as for the diffusion coefficient (Equation 6.8)—namely,

$$\dot{G} = C\exp\left(-\frac{Q}{kT}\right) \tag{11.16}$$

where Q (the activation energy) and C (a preexponential) are independent of temperature.[2] The temperature dependence of $\dot{G}$ is represented by one of the curves in Figure 11.8; also shown is a curve for the nucleation rate, $\dot{N}$ (again, almost always the rate for heterogeneous nucleation). Now, at some temperature, the overall transformation rate is equal to some product of $\dot{N}$ and $\dot{G}$. The third curve of Figure 11.8, which is for the total rate, represents this combined effect. The general shape of this curve is the same as for the nucleation rate, in that it has a peak or maximum that has been shifted upward relative to the $\dot{N}$ curve.

Whereas this treatment on transformations has been developed for solidification, the same general principles also apply to solid–solid and solid–gas transformations.

As we shall see below, the rate of transformation and the time required for the transformation to proceed to some degree of completion (e.g., time to 50% reaction completion, $t_{0.5}$) are inversely proportional to one another (Equation 11.18). Thus, if the logarithm of this transformation time (i.e., log $t_{0.5}$) is plotted versus temperature, a curve having the general shape shown in Figure 11.9b results. This

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[2] Processes the rates of which depend on temperature as $\dot{G}$ in Equation 11.16 are sometimes termed **thermally activated**.
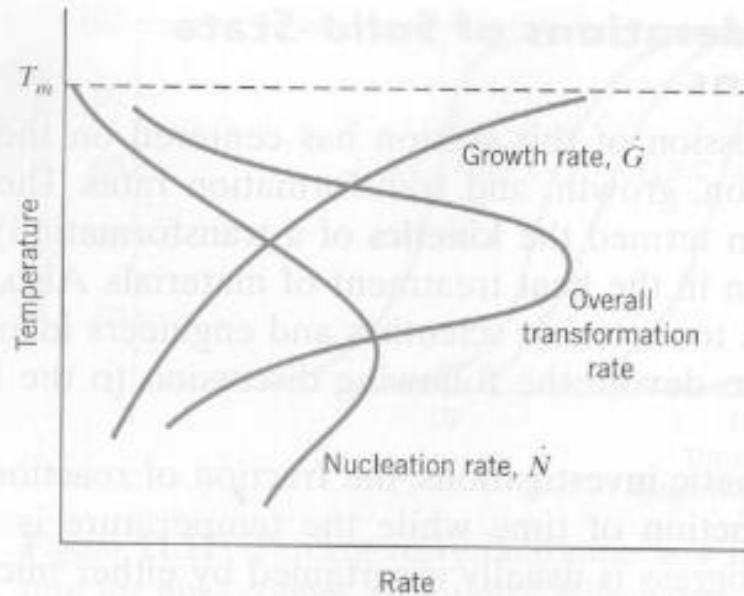
Figure 11.8 Schematic plot showing curves for nucleation rate ($\dot{N}$), growth rate ($\dot{G}$), and overall transformation rate versus temperature.

"C-shaped" curve is a virtual mirror image (through a vertical plane) of the transformation rate curve of Figure 11.8, as demonstrated in Figure 11.9. It is often the case that the kinetics of phase transformations are represented using logarithm time- (to some degree of transformation) versus-temperature plots (for example, see Section 11.5).

Several physical phenomena may be explained in terms of the transformation rate-versus-temperature curve of Figure 11.8. First, the size of the product phase particles will depend on transformation temperature. For example, for transformations that occur at temperatures near to T_m, corresponding to low nucleation and high growth rates, few nuclei form that grow rapidly. Thus, the resulting microstructure will consist of few and relatively large phase particles (e.g., coarse grains). Conversely, for transformations at lower temperatures, nucleation rates are high and growth rates low, which results in many small particles (e.g., fine grains).

Also, from Figure 11.8, when a material is cooled very rapidly through the temperature range encompassed by the transformation rate curve to a relatively low temperature where the rate is extremely low, it is possible to produce non-equilibrium phase structures (for example, see Sections 11.5 and 11.11).
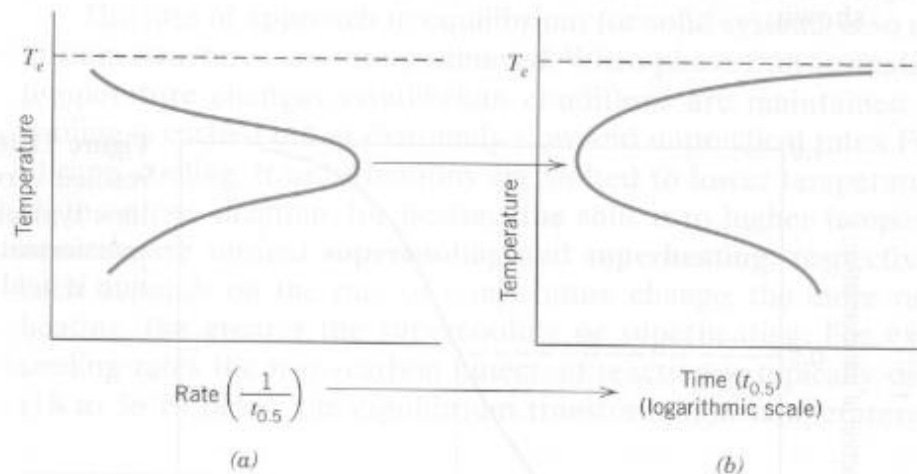

Figure 11.9 Schematic plots of (a) transformation rate versus temperature, and (b) logarithm time [to some degree (e.g., 0.5 fraction) of transformation] versus temperature. The curves in both (a) and (b) are generated from the same set of data—i.e., for horizontal axes, the time [scaled logarithmically in the (b) plot] is just the reciprocal of the rate from plot (a).

Glass Chemistry and Properties "Density"

Density (Definition and Unit)

Density is defined as the mass per unit volume and is expressed as g/cm^3.

A related quantity is the specific gravity which is a dimensionless number being the ratio of the density at a specified temperature to the density of water at 4^oC.

Density depends on chemical composition of glass. The densities of commercial glasses can vary from $2.2g/cm^3$ to $3\ g/cm^3$.

Densities of Typical Glasses

Glass Type	Density (g/cm³)
Fused silica	2.20
Borosilicate	2.25
Soda-lime-silicate glass	2.50
Lead crystal glass	2.545

The density of most glasses decreases with temperature. "Negative expansion" materials would show an increase in density with temperature. The change in volume and hence the change in density will be three times the linear change in dimension with temperature.
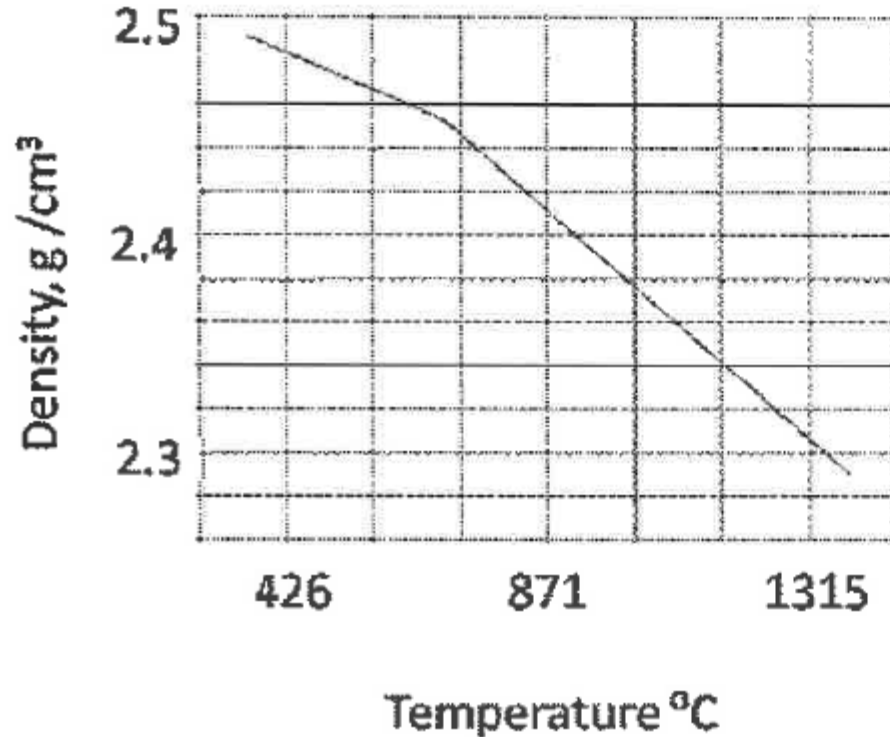
The change in density with temperature for a soda-lime silicate glass.

In the temperature range of 1000-1500°C the temperature dependancy of the density described with a volumetric expansion coefficient.

$$\rho_T = \rho_{To} \cdot \{1 - \beta(T - T_o)\}$$

ρ: density

β : volumetric expansion coeff.

(Mostly this coeff. İs assumed to have a constant value at this temperature range.)

T : temperature (oC)

To: refrance temp. (oC)

The density of liquid glass is important for the melting technology.

Glass Chemistry and Properties "Viscosity"

The viscosity is one of the most important properties of glass.

- At melting temperature, the viscosity is relatively low. This makes it possibble to mix and to homogenize the glass.

- During cooling, the viscosity increases continuously, which makes forming possibble.

- With the proper forming process conditions, the viscosity just after forming has become so high that the product will retain its shape.

- By cooling further, the viscosity increases tremendously: the product stiffens and will become rigid.
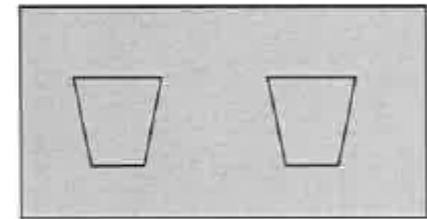
Glass Manufacturing Process
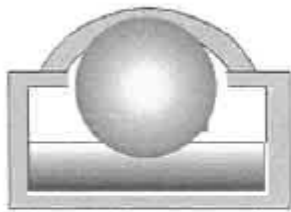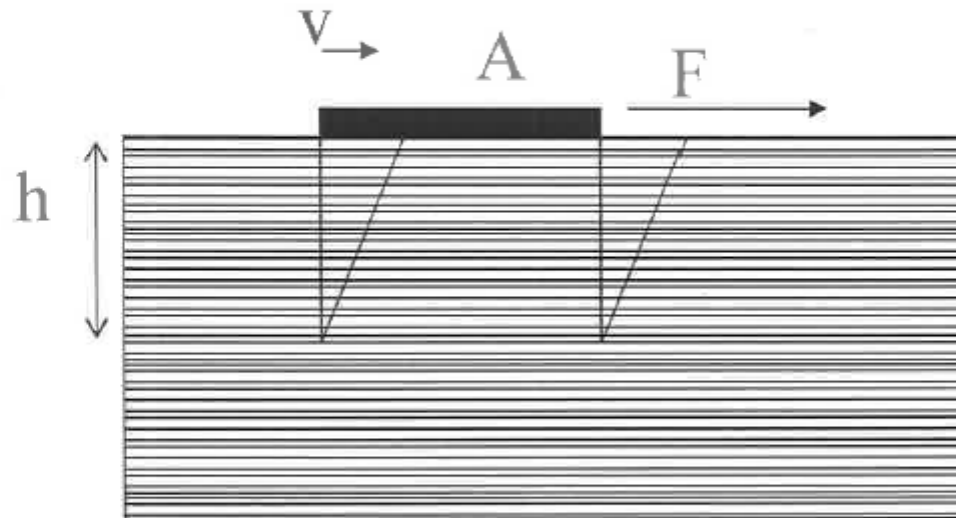

Melting and Fining
(1500-1200°C)

Forming
(1200-800°C)

Annealing
(600-300°C)

Definition of viscosity

In fluids (liquids and gasses), viscosity can be defined as internal friction.

$$\eta = \frac{F/A}{v/h}$$

η : viscosity (Poise)

F: Force (dyn)   v: velocity (cm²/s)

A: Area (cm²)   h: height (or depth) (cm)

Unit of viscosity

$$\eta = \frac{F/A}{v/h}$$

$$\eta = \frac{dyn/cm^2}{\frac{cm}{s}/cm} = dyn.s/cm^2 = 1 \text{ Poise}$$

$$1 \text{ Pa.s} = 10 \text{ Poise}$$

Temperature dependancy of viscosity

Fulcher – Tamman Equation

$$\eta = \exp\left(-A + \frac{B}{T - T_o}\right)$$

T: Temperature (K)

To: Initial temperature (K)

A, B : constants (depending on the glass composition)

Critical Viscosity Points

Melting Point ($\eta = 10^2$ poise) The melting temperature is defined as the temperature at which the glass melt has become a viscosity low enough to allow for well mixing.

Gob Temperature ($\eta = 10^3$ poise) Around this temperature most forming processes take place.

Softennig point, T_S ($\eta = 10^{7.65}$ poise) At this temperature glass deforms with a reasonable rate by its own weight (ASTM C 338-57).

Annealing point, T_A ($\eta = 10^{13}$ poise) At this temperature the internal thermal stresses present in the glass are relieved by viscous relaxation with in 15 minutes.

Strain point, T_{St} ($\eta = 10^{14.5}$ poise) Below this temperature reieving the internal stresses is practically imposibble(at this point it may last about 15 hours).

Relationship between Viscosity and Temperature
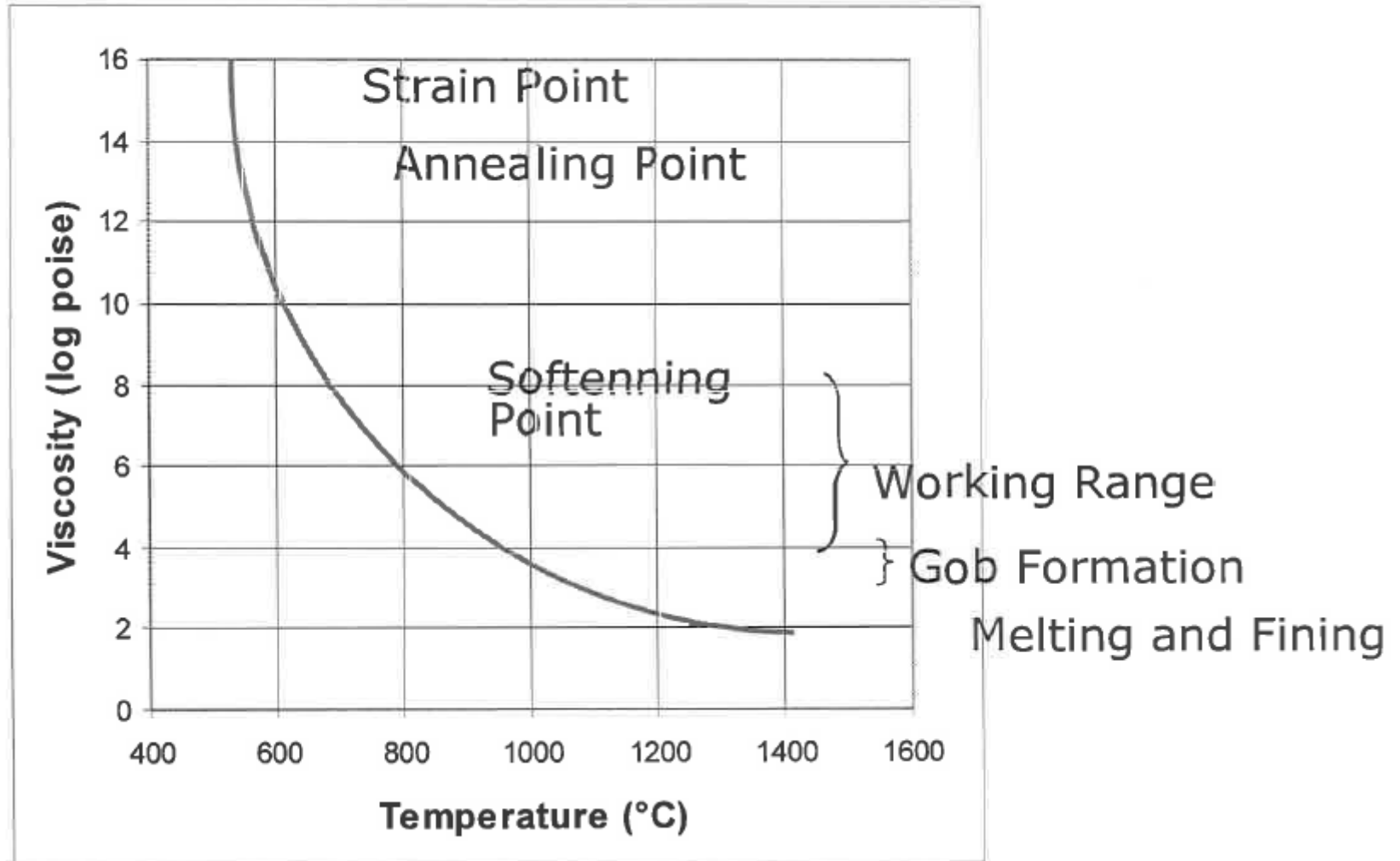
Workability

The forming ability of the glass is called workability. The slope of the viscosity-temperature curve between log $\eta=10^3$-$10^{7.65}$ defined as working range and in these temperaures forming process can take place. This behaviour is directly depends on the chemical composition of the glass.

Influence of Composition on Viscosity

The vicsosity is a measure for the shear resistance and therefore it is directly related to the mutual binding forces. These forces depend on the molecules of the glass components and the way they are interconnected.

1. Moleculer attraction forces: The bonding power is much stronger in Si-O than other oxides including other network formers. The higher the molecular attraction in the structure; the higher the viscosity.

2. The coordination number of the cations: This property shows bonding ability (SiO_2 fourfold, forming tetrahedron; B_2O_3 threefold, forming trigonal structure).

3. The number of non-bridging oxygen atoms: The amount of network modifiers (alkali oxides and alkaline eart oxides). Ionic bond→easy to break; making lower viscosity.

Network Formers:

1. SiO_2: SiO_2 has a high melting point (1710^0C) and it increases viscosity at the whole temperature range. This property is directly related to the strength of the Si-O bonds.

2. B_2O_3: B_2O_3 is another network forming oxide, but its effect on viscosity is somehow different than SiO_2. It increases the viscosity at lower temperatures than softenning point while it reduces sharply at higher temperatures.
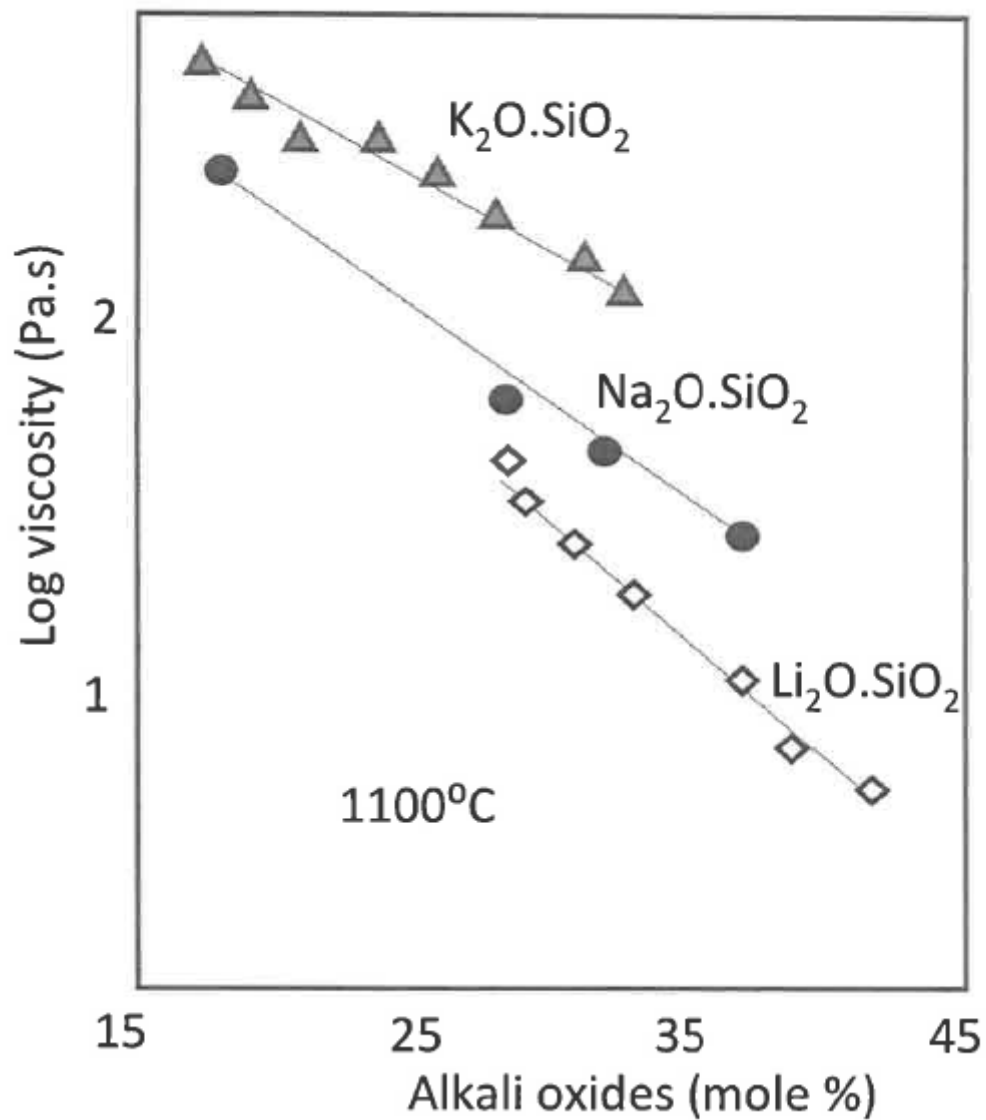
Influence of R_2O

Alkali oxides reduce the viscosity at every point. Because they break strong bridging bonds and weaken the structure.

In silicate network, their effect on viscosity occurs in an increasing order of while the ionic radii decrease.

$$K_2O < Na_2O < Li_2O$$

Influence of Alkali Oxides on Viscosity

Influence of RO:

- At higher temperatures;

A softening of the structure due to more ruptures caused by the R atoms, resulting in a lower viscosity.

- At lower temperatures;

An increase of viscosity, because the R^{2+} ion uses the floating O^{2-} ions for the coordination resulting in more bridging(more than alkali ions).

- Concequence;

They make the viscosity curve steeper, the glass becomes shorter.

Effect of Chemical Composition

Alkaline oxides disturb the symmetry of the tetrahedral and weakens the strong $Si - O$ bonds by forming non-bridging oxygen bonds and thus increase the non–harmonic vibrations. The effect is stronger as the bond strength becomes weaker.

$$K > Na > Li$$

Alkaline earth oxides like CaO and MgO increase the thermal expansion coefficient but not as much as the alkaline oxides due to the stronger bond strengths.

$$Ba > Sr > Ca > Mg$$
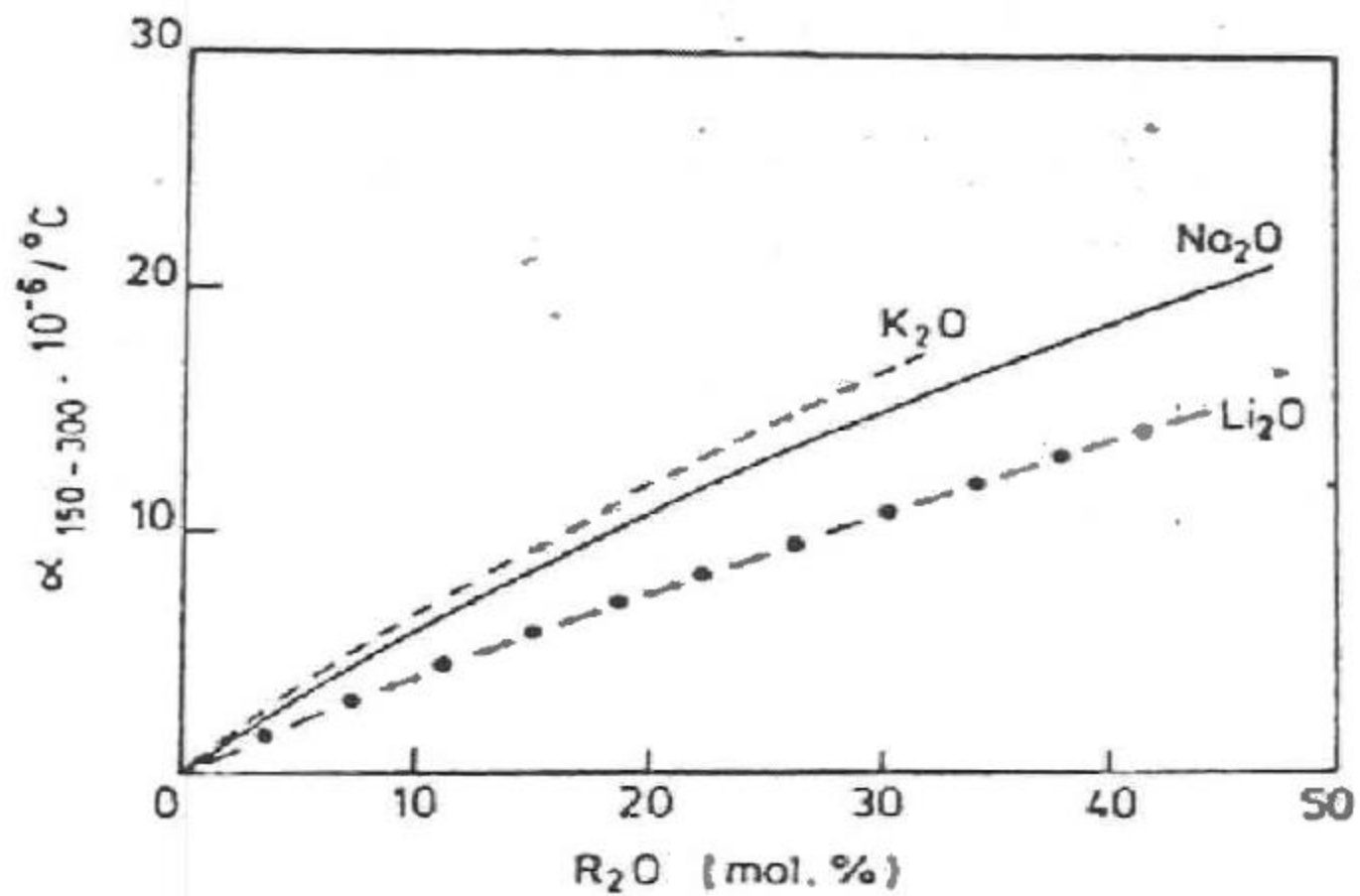
Glass type	Thermal Exp. Coeff. ($\times 10^{-7}$/°C)	Glass Type	Thermal Exp. Coeff. ($\times 10^{-7}$/°C)
Vitreous Silica	5.5	Borosilicates	33
%96 Silica	8.0	Soda Lime Silica	85– 92
Alumino silicates	33	Lead Silicate	100

Thermal Shock Resistance

The most important parameter that affects the thermal shock resistance of the glasses is their thermal expansion coefficient.

Lower the coefficient, higher the temperature differences that the glass articles can stand.

Therefore the heat resistant ovenware products are produced from borosilicate glasses with low expansion coefficients.

Tempering is another tool for increasing the thermal shock resistance.

During tempering surface of the glass undergoes through fast cooling and the molecules of the structure do not have enough time to rearrange themselves and thus the density of the surface remains lower than the bulk. In order to keep the molecules together, the surface creates compression stress which in turn lowers the expansion coefficient.

Therefore tempered items have higher thermal shock resistances.

- Commercial soda lime silicate glasses have ΔT ranging in between 80°C-90°C depending upon their chemical composition.

- Tempered SLS glasses have ΔT around 120°C.

- Borosilicate glasses with expansion coefficient 33 $\times 10^{-7}$/°C have ΔT ranging in between 130°C -140°C.

- Tempered borosilicate glasses have ΔT values higher than 220°C.

MECHANICAL PROPERTIES

Mechanical properties of glasses which are different than all the other materials we know, originate from their molecular structure that does not allow permanent (plastic) deformation or ductility.

Due to this basic property, glasses ;

- have low fracture toughness (ability to absorb energy prior to failure),
- are brittle,
- have strengths which are susceptible to surface flaws,
- may cause injuries when fractured.

When a force with a magnitude enough to move is applied to a solid, it accelerates according to Newton's Law. The movement is prevented if the applied forces create stresses inside the solid.
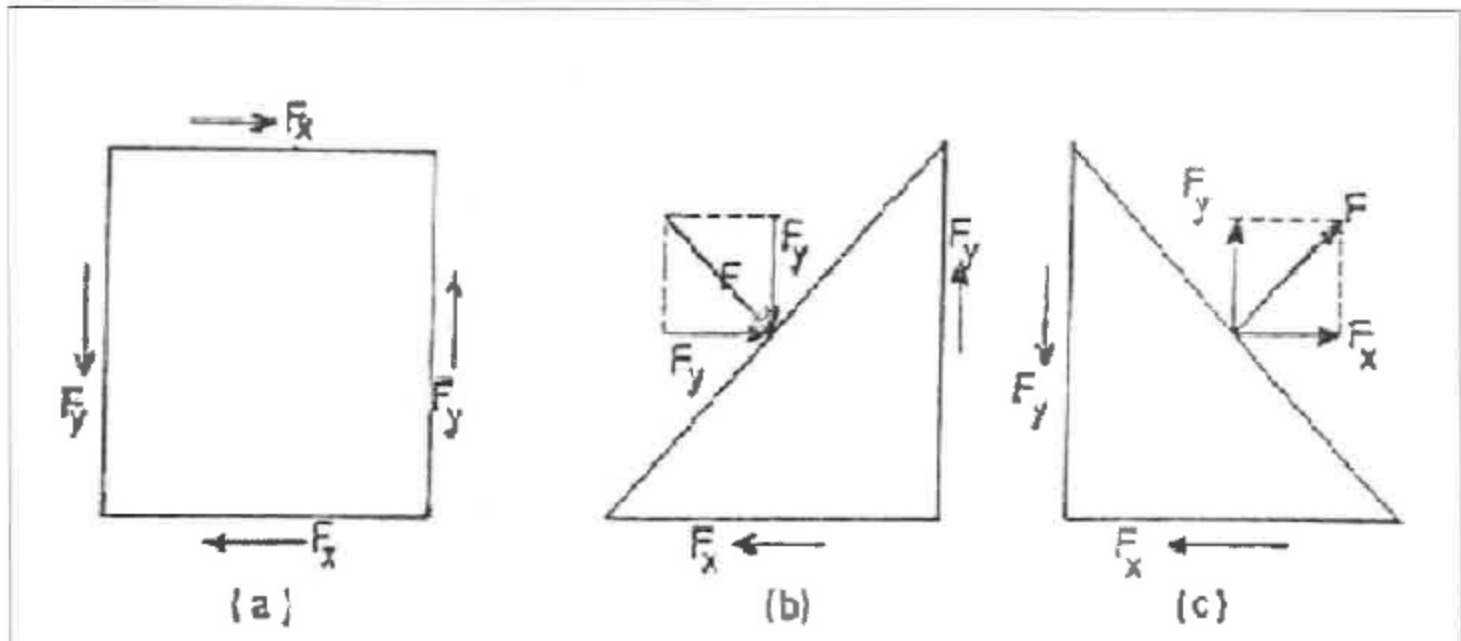

$$\sigma = F/A$$
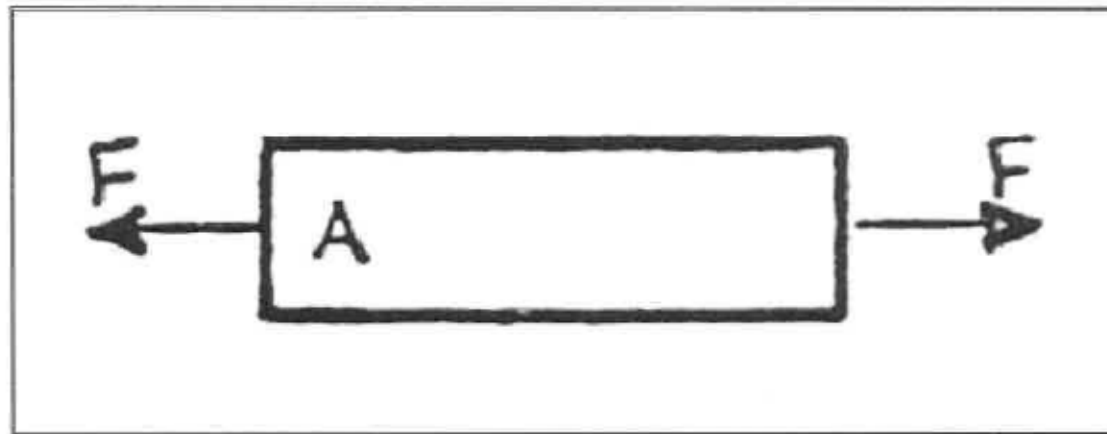
Stress (σ) Newton/m², dyn/cm² or lb/ft²

The solids are subjected to 3 types of stressing
• shear,
• compression
## • tension

(a) (b) (c)

shear   compression   tension

Change in length per unit length under the applied force is called as

(Strain) (ε)

- All the stressed solids are strained.
- When the elasticity limit is not exceeded, strain is reversible if the stress is removed (Hooke's Law)
- Glasses are considered as linear elastic solids obeying Hooke's Law at temperatures below the glass transition range.
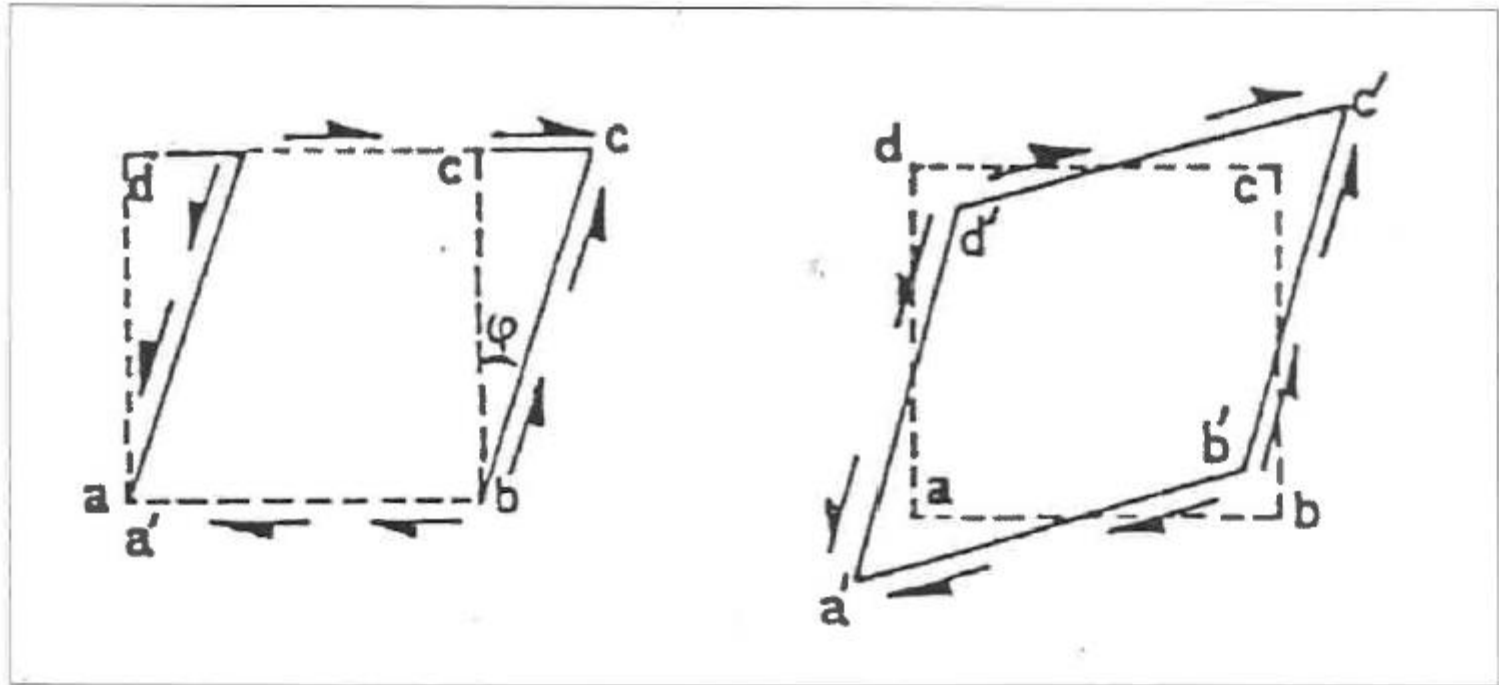
Different types of stresses cause different types of strains.
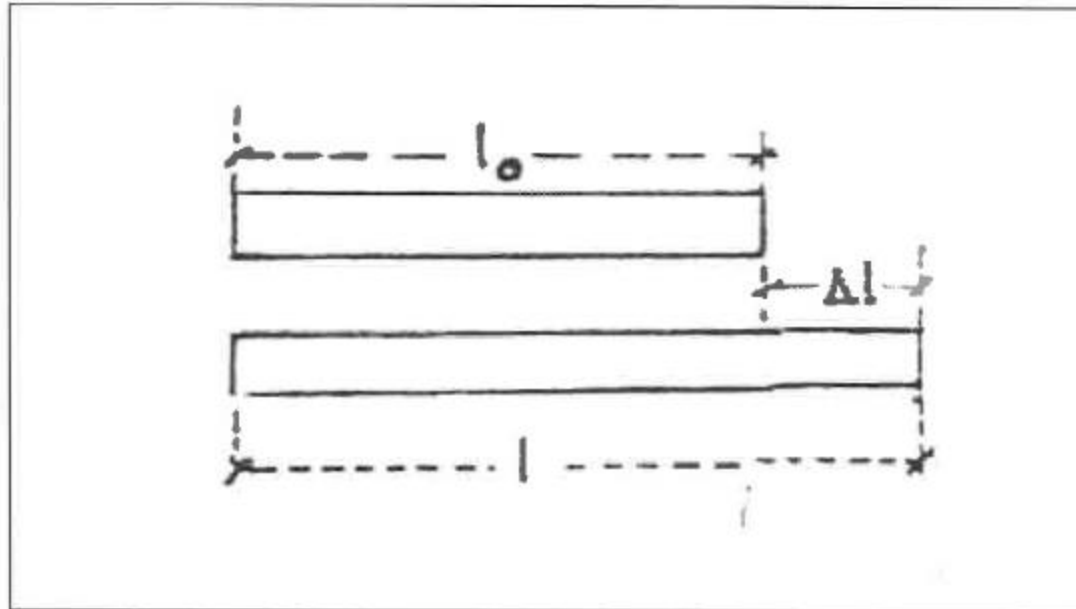
Tensile strain

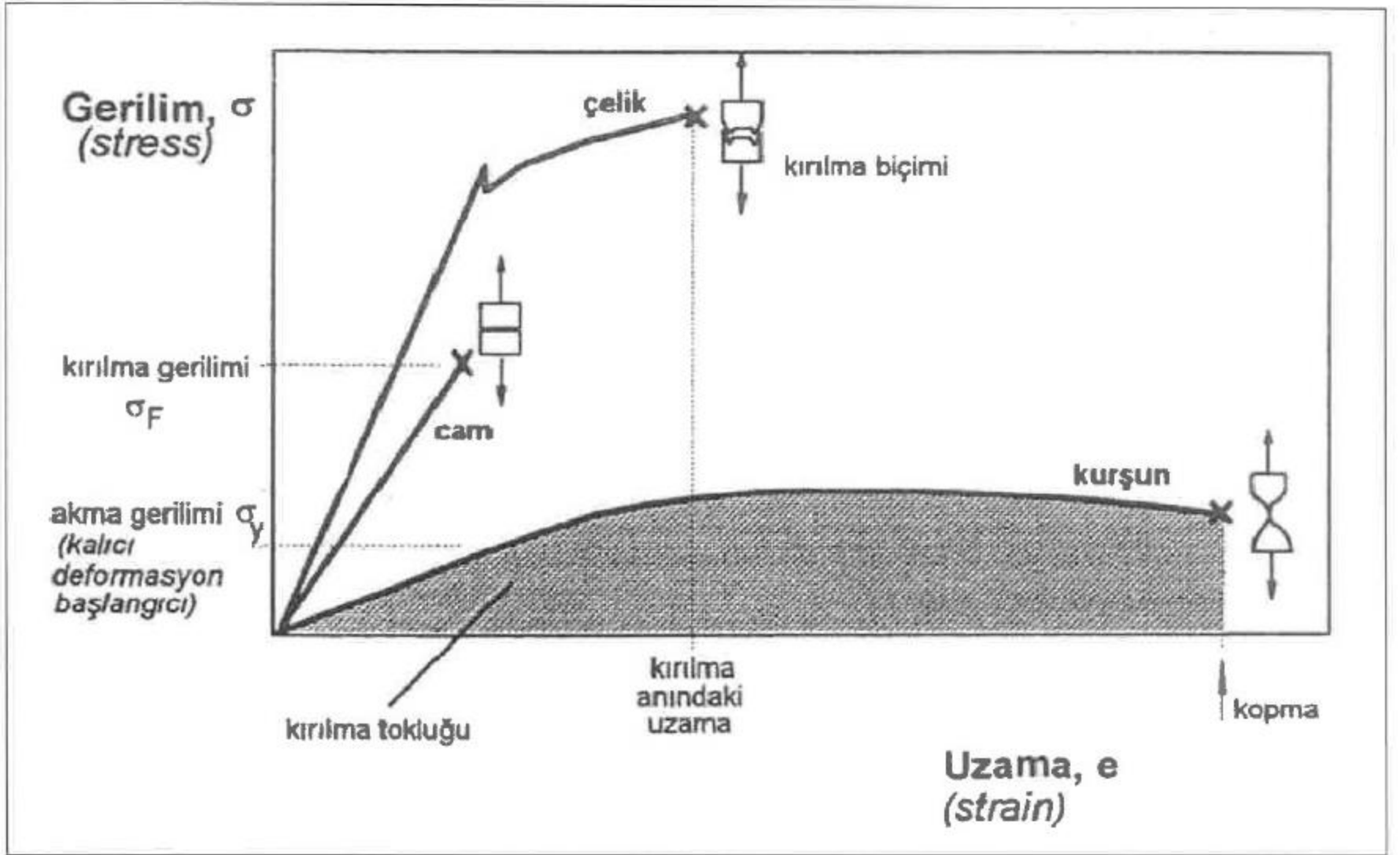$$\Delta l = l - l_o$$

$$\varepsilon = \Delta l / l_o$$

Shear Strain

Upon application of a stress (force/unit area) solids undergo instantaneous deformation such that the ratio of the stress to the resulting strain (change in length per unit length) is a constant called

Modulus of Elasticity

which is independent of the magnitude of strain.

Slope of the stress strain curve before fracture yields the

modulus of elasticity σ/ε;

- Ratio of tensile stress to tensile strain; Young's Modulus E

- Ratio of shear stress to shear strain; Rigidity Modulus G

- Ratio of compression stress (pressure) to volumetric strain;   Bulk Modulus K, the inverse is called Compressibility κ

Positive tensile stress produces elongation in the applied direction. Accompanying this elongation in the x direction, contraction occurs in the y and z directions.

The ratio of the transverse strain ($\Delta d/d_o$), to longitudinal strain ($\Delta l/l_o$) is called

Poisson Ratio μ

These elasticity moduli may change according to the;

• State of the glass structure i.e. Temperature, phase separation.

• Bond strength, packing density of the oxides, molar volume and ionic radii.

Al, Be, La, Mg, Ti, Zr increases the elestic moduli by increasing the packing density.

• In contrast to the case of ionic crystals, in glasses where bonding is partially ionic, theoretical consideration must include the possibility that not all the external force applied is used in pulling the ions apart. Some portion of this force is used to straighten the Si-O-Si bond angles between the two adjacent tetrahedra.

• Some researchers suggest that E should be proportional to the number of the Si-O-Si bridging bonds per unit volume and that the modifier oxides should contribute little to E since they only fill up the voids.

- Although the addition of Na_2O and K_2O does decrease Young's Modulus, such is not true with Li_2O addition to the silica network.

- Likewise, the addition of CaO to a sodium silicate increases the modulus.

- In dual SiO_2-R_2O system, replacement of SiO_2 by K_2O or Na_2O decreases E where as, replacement of Na_2O by K_2O increases Young's Modulus.

- While the addition of other high valence oxides increase E, replacement of them with each other may affect differently. e.g. replacement of CaO by ZrO_2 decreases Young's Modulus.
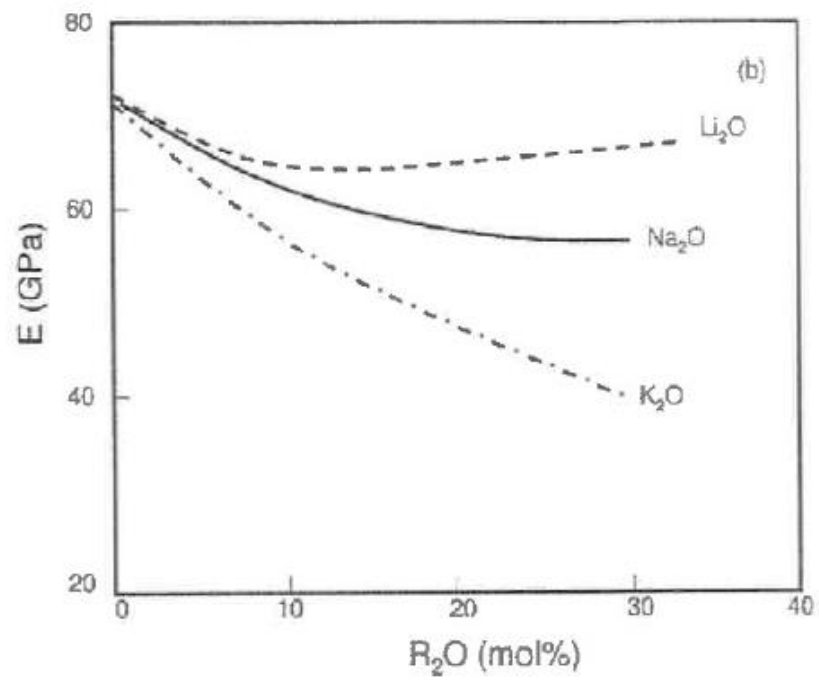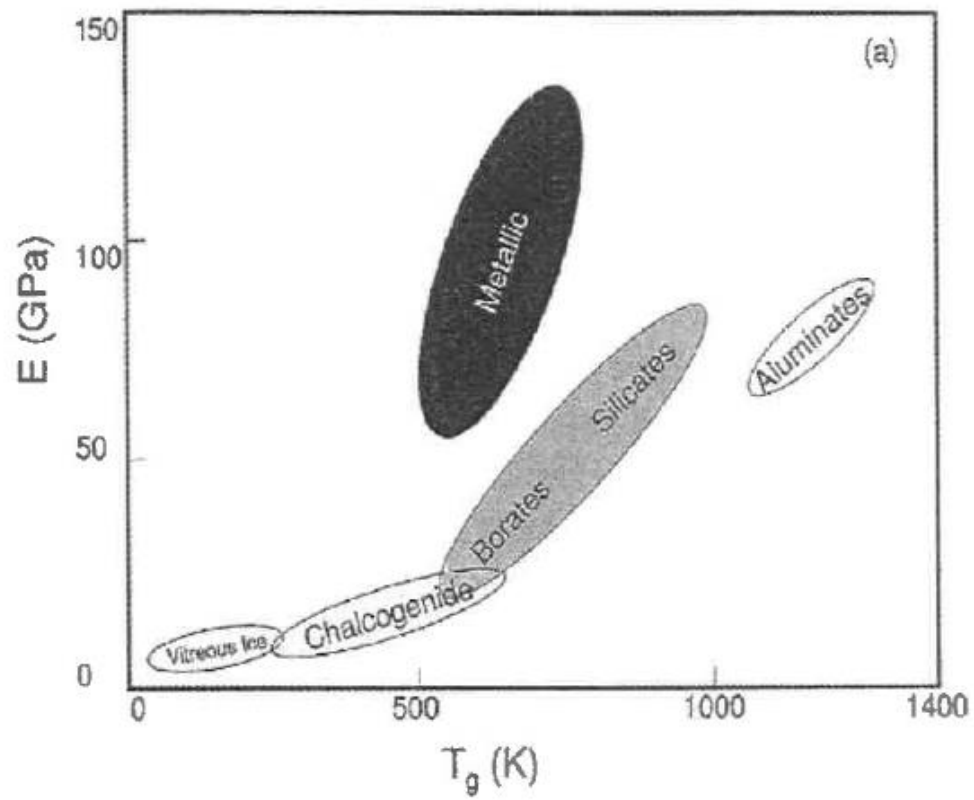
When a force exceeding the elasticity limit is applied to glasses breakage occurs.

Therefore even though it looks like glasses with higher elastic moduli may resist to higher forces, hence higher strength, this can not be generalized.

Mechanical Strength of Glasses primarily depends on;

• their surface conditions,
• presence of the micro cracks and
• the interaction of them with humidity, gases and impurities

MECHANICAL STRENGTH

• Applied stress at the point of failure is termed the strength.

• Measurement of strength is done by applying increasing magnitude of stress in a defined geometry system until fracture.

• In brittle materials like glass, fracture occurs under tensile stresses, meaning that glass breaks under tension.

• Bulletproof glass and glass fibers are considered as stronger than steel.

Contrasts Between Metal and Glass Failure

- Metals yield plastically before actual failure.

- Glasses show no ductility, they show brittle failure.

- Metal specimens prepared identically show narrow distribution of yield stress.

- Similar glass specimens display a large variation of strength.

- Crystalline structures like metals contain large number of defects which can move readily and new dislocations are created by applied stresses.

- The irreversible movement of dislocations causes ductility or plastic deformation.

- In glasses there are no structural dislocations hence no ductility upon the application of stress.

- Strength of brittle solids like glasses is compromised by structural flaws.
- The micro cracks present at the glass surface propagates without the obstruction of plastic deformation under applied stresses.
- In metals or plastics these surface flaws get blunt and leave a trace of permanent deformation area.