- The amount of work done in pulling two atoms apart such that two new surfaces having fracture surface energy (\(\gamma\)) are created is the theoretical strength of a flawless solid.

- Flaws in brittle solids act as stress intensifiers causing the solids break at stresses much lower in magnitudes than that theoretically required to pull atoms apart.

- Flaws generally occur on a free surface and have a wide distribution of lengths (\(c\)).

- Fracture occurs at the site of the most severe flaw like the case of weakest link in a chain.
These flaws are called Griffith Flaws as he suggested that the stress at the tip of the flaw exceeding the theoretical strength is not the only criterion for strength, the flaw must also exceed a critical length (c) before it would propagate into a fracture.

\[ \sigma_{\text{failure}} = \left[ \frac{2\gamma E}{\pi c} \right]^{1/2} \]

Although \( \gamma \) and \( E \) depend on glass composition (may be 20%) the variation in c can be of several orders of magnitude.

The strength of glass is not intrinsic to its composition but may depend generally on methods of processing.
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 of the equilibrium liquid and that of the frozen solid, is known as the glass transformation region. The frozen liquid is now a glass.
Although the glass transformation actually occurs over a temperature range, it is convenient to define a term which allows us to express the difference in thermal history between these two glasses. If we extrapolate the glass and supercooled liquid lines, they intersect at a temperature defined as the *fictive temperature*. The structure of the glass is considered to be that of the equilibrium liquid at the fictive temperature. Although the fictive temperature concept is not a completely satisfactory method for characterizing the thermal history of glasses, it does provide a useful parameter for discussion of the effect of changes in cooling rate on glass structure and properties. The changes that occur in the fictive temperature, and the properties of glasses with subsequent reheating into the glass transformation region will be discussed in detail in Chapter 6.

Finally, we need to define a term, which, while commonly used, has only a vague scientific meaning. As indicated above, the glass transformation occurs over a range of temperatures and cannot be characterized by any single temperature. It is, however, convenient to be able to use just such a single temperature as an indication of the onset of the glass transformation region during heating of a glass. This temperature, which is termed either the *glass transformation temperature*, or the *glass transition temperature*, \((T_g)\), is rather vaguely defined by changes in
Effect of temperature on the enthalpy of a glass forming melt
Principles of Glass Formation

Thus, from these two equations, both the critical radius $r^*$ and the activation free energy $\Delta G^*$ decrease as temperature $T$ decreases. (The $\gamma$ and $\Delta H_f$ parameters in these expressions are relatively insensitive to temperature changes.) Figure 11.3, a schematic $\Delta G$-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

$$n^* = K_1 \exp\left(-\frac{\Delta G^*}{kT}\right)$$  \hspace{1cm} \text{(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 $\Delta G^*$ 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, $\nu_d$. Or, the dependence of $\nu_d$ on
temperature is the same as for the diffusion coefficient—namely,

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

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 $\nu_d$. 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 $\nu_d$ (Equation 11.9); that is,

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

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.
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 \( \gamma_{SL} \) is the same surface energy as \( \gamma \) 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

\[
\Delta G_{\text{het}}^* = \Delta G_{\text{hom}}^* S(\theta) \tag{11.15}
\]

Figure 11.6, a schematic graph of \( \Delta G \) versus nucleus radius, plots curves for both types of nucleation, and indicates the difference in the magnitudes of \( \Delta G_{\text{het}}^* \) and \( \Delta G_{\text{hom}}^* \), in addition to the constancy of \( r^* \). This lower \( \Delta G^* \) 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 (\( \Delta T \)) 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

---

1 For example, for \( \theta \) angles of 30° and 90°, values of \( S(\theta) \) are approximately 0.01 and 0.5, respectively.
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,
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

\(^2\) Processes the rates of which depend on temperature as \( \dot{G} \) in Equation 11.16 are sometimes termed thermally activated.
“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).

![Temperature vs Time](image)

**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).
2 STRUCTURAL THEORIES OF GLASS FORMATION

Perhaps the earliest, and simplest, theory of glass formation was based on the observation by Goldschmidt that glasses of the general formula $R_nO_m$ form most easily when the ionic radius ratio of the cation, $R$, to the oxygen ion lies in the range 0.2 to 0.4. Since radius ratios in this range tend to produce cations surrounded by four oxygen ions in the form of tetrahedra, Goldschmidt believed that only melts containing tetrahedrally-coordinated cations form glasses during cooling. This contention was purely empirical, with no attempt to explain why tetrahedral coordination should be so favorable to glass formation.

A few years later, Zachariasen published a paper which extended the ideas of Goldschmidt and attempted to explain why certain coordination numbers might favor glass formation. Although intended only as an explanation for glass formation, this paper has become the basis for the most widely used models for glass structures, and is probably the most frequently cited (and misquoted) paper in the inorganic glass literature. Essentially, Zachariasen noted that the silicate crystals which readily form glasses instead of recrystallizing after melting and cooling, have network, as opposed to close-packed, structures. These networks consist of tetrahedra connected at all four corners, just as in the corresponding crystals, but the networks are not periodic and symmetrical as in crystals. These networks extend in all three dimensions, such that the average behavior in all directions is the same, i.e., the properties of glasses are isotropic. Zachariasen contends that the ability to form such networks thus provides the ultimate condition for glass formation.
<table>
<thead>
<tr>
<th>Ratio of cation radius to anion radius</th>
<th>Disposition of ions about central ion</th>
<th>Coordination number</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-0.732</td>
<td>Corners of cube</td>
<td>8</td>
</tr>
<tr>
<td>0.732-0.414</td>
<td>Corners of octahedron</td>
<td>6</td>
</tr>
<tr>
<td>0.414-0.225</td>
<td>Corners of tetrahedron</td>
<td>4</td>
</tr>
<tr>
<td>0.225-0.155</td>
<td>Corners of triangle</td>
<td>3</td>
</tr>
</tbody>
</table>

Radius ratios for various atom arrangements in ionic bonding
After establishing that the formation of a vitreous network is necessary for glass formation, Zachariasen considered the structural arrangements which could produce such a network. First, he contends that no oxygen atom can be linked to more than two network cations. Higher coordination numbers for the oxygen cations prevent the variations in cation–oxygen–cation bond angles necessary to form a non-periodic network. Zachariasen further noted that the only glasses known at the time of his work contain network cations in either triangular ($B_2O_3$) or tetrahedral (silicates, $GeO_2$, $P_2O_5$) coordination. He then generalized this observation by stating that the number of oxygen atoms surrounding the network cation must be small, specifically either at the corners and do not share either edges or faces. Finally, he states that the network can only be 3-dimensional if at least three corners of each oxygen polyhedron are shared.

The thoughts of Zachariasen can be best summarized by his statement that formation of oxide glass may occur if (1) the material contains a high proportion of cations, which are surrounded by either oxygen triangles or oxygen tetrahedra, (2) these polyhedra are connected only by their corners, and (3) some oxygen atoms are linked to only two such cations and do not form additional bonds with other cations. Essentially, item (1) states that sufficient network cations must be present to allow a continuous structure to form, item (2) states that the network is an open structure, and item (3) states that sufficient bonds linking the network polyhedra exist for the formation of a continuous network structure. It should be noted that Zachariasen only states that a glass may be formed under such conditions; he further states that the melt must be cooled under the proper conditions for glass formation actually to occur, thus anticipating the later theories based on the kinetics of the glass formation process.
Although TTT diagrams are not widely used, the general kinetic approach does provide considerable insight into the criteria for the formation of glasses. First, this approach alters our thinking from questions regarding why certain melts readily form glasses while others do not, to questions regarding the conditions necessary to force a melt to form a glass during cooling. The concept of a critical cooling rate thus leads to the simple question of HOW FAST must a sample be cooled to form a glass. We can now use this approach to consider what factors will lead to small critical cooling rates and how these factors relate to the concepts originally derived on the basis of melt structure and bonding.
4 DETERMINATION OF GLASS FORMING ABILITY AND GLASS STABILITY

Formation of a glass is a rather simple process. The appropriate batch is prepared, placed in a crucible, heated to form a crystal-free melt, and cooled to room temperature. The sample is examined to determine if it contains crystals, using methods ranging from casual visual examination, to X-ray or electron diffraction. If no crystals are detected, the sample is deemed to be a glass; if crystals are detected, it is described as either partially- or fully-crystallized, depending upon the extent of crystallization.

Unfortunately, while the concept of a critical cooling rate is easy to understand, the actual measurement of these rates is rather tedious. A melt must be heated to a pre-determined temperature, held for a specified time to completely dissolve any residual crystals and nuclei, and then cooled at a linear rate until it forms a solid, which is then examined to determine if it is a glass. If so, the sample, or a new, identical batch, is heated to the melt temperature and the experiment is repeated using a slower cooling rate. This procedure is repeated until the sample fails to form a glass. The slowest cooling rate which produces a glass is then defined as the *critical cooling rate*. Although only two cooling experiments are required to bracket the critical cooling rate, actual practice will usually require several experiments for each composition.
Determination of critical cooling rates can sometimes be carried out using a differential scanning calorimeter (DSC). In this case, the process can be automated, with a computer repeatedly carrying out the experiment with a series of decreasing cooling rates. Cooling rates below the critical will often be characterized by an exothermic peak in the thermal spectrum, due to the release of the heat of crystallization. Absence of such a peak in a thermal spectrum is often taken as evidence of a lack of crystal formation, *i.e.*, glass formation. This technique is best suited for low melting temperature batches, which readily crystallize with a large exothermic effect if cooled at a rate less than the critical cooling rate.

*A typical differential scanning calorimeter curve for a glass which forms a single crystalline phase on reheating*
Glass Melting

1 INTRODUCTION

Although glasses can be made by a wide variety of methods, the vast majority are still produced by melting of batch components at an elevated temperature. This procedure always involves the selection of raw materials, calculation of the relative proportions of each to use in the batch, and weighing and mixing these materials to provide a homogeneous starting material. During the initial heating process, these raw materials undergo a series of chemical and physical changes to produce the melt. Conversion of this melt to a homogeneous liquid may require further processing, including the removal of any unmelted batch remnants, impurities, and bubbles. Production of commercial products requires forming of specific shapes, as well as heat treatments to remove stresses generated during the cooling process, or to produce glasses strengthened by thermal tempering.
2 RAW MATERIALS

In general, glasses are either produced from high quality, chemically-pure components, or from a mixture of far less pure minerals. Research specimens, optical glasses, and many glasses used for low volume, high technology applications are produced using those chemicals we might routinely encounter in any chemical laboratory. Bulk commercial products, on the other hand, are produced from minerals, which typically have names and compositions which are not familiar to the novice. The names of many of these minerals and their compositions are listed in Table 3.1. Gravimetric factors, which allow calculation of the yield of the desired glass component for each weight unit of raw material, are also listed in this table.
<table>
<thead>
<tr>
<th>Common Name</th>
<th>Nominal Composition</th>
<th>Gravimetric Factor*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albite feldspar</td>
<td>Na$_2$O–Al$_2$O$_3$–6SiO$_2$</td>
<td>Na$_2$O = 8.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al$_2$O$_3$ = 5.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SiO$_2$ = 1.45</td>
</tr>
<tr>
<td>Alumina</td>
<td>Al$_2$O$_3$</td>
<td>Al$_2$O$_3$ = 1.00</td>
</tr>
<tr>
<td>Alumina hydrate</td>
<td>Al$_2$O$_3$·3H$_2$O</td>
<td>Al$_2$O$_3$ = 1.53</td>
</tr>
<tr>
<td>Anorthite feldspar</td>
<td>CaO–Al$_2$O$_3$–2SiO$_2$</td>
<td>CaO = 4.96</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al$_2$O$_3$ = 2.73</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SiO$_2$ = 2.32</td>
</tr>
<tr>
<td>Aplite</td>
<td>Alkali lime feldspar</td>
<td>Varies with exact composition</td>
</tr>
<tr>
<td>Aragonite</td>
<td>CaCO$_3$</td>
<td>CaO = 1.78</td>
</tr>
<tr>
<td>Bone ash</td>
<td>3CaO–P$_2$O$_5$ or Ca$_3$(PO$_4$)$_2$</td>
<td>CaO = 1.84</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P$_2$O$_5$ = 2.19</td>
</tr>
<tr>
<td>Barite (barytes)</td>
<td>BaSO$_4$</td>
<td>BaO = 1.52</td>
</tr>
<tr>
<td>(Heavy spar)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Borax</td>
<td>Na$_2$O–2B$_2$O$_3$·10H$_2$O</td>
<td>Na$_2$O = 6.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B$_2$O$_3$ = 2.74</td>
</tr>
<tr>
<td>Anhydrous borax</td>
<td>Na$_2$O–2B$_2$O$_3$</td>
<td>Na$_2$O = 3.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B$_2$O$_3$ = 1.45</td>
</tr>
<tr>
<td>Boric acid</td>
<td>B$_2$O$_3$·3H$_2$O</td>
<td>B$_2$O$_3$ = 1.78</td>
</tr>
<tr>
<td>Burnt dolomite</td>
<td>CaO–MgO</td>
<td>CaO = 1.72</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MgO = 2.39</td>
</tr>
<tr>
<td>Caustic potash</td>
<td>KOH</td>
<td>K$_2$O = 1.19</td>
</tr>
</tbody>
</table>
| Material            | Formula          | Composition
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Caustic soda</td>
<td>NaOH</td>
<td>Na₂O = 1.29</td>
</tr>
<tr>
<td>Cryolite</td>
<td>3NaF–AlF₃</td>
<td>NaF = 1.67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AlF₃ = 2.50</td>
</tr>
<tr>
<td>Cullet</td>
<td>Scrap Glass</td>
<td>Varies with exact composition</td>
</tr>
<tr>
<td>Dolomite</td>
<td>CaCO₃–MgCO₃</td>
<td>CaO = 3.29</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MgO = 4.58</td>
</tr>
<tr>
<td>Fluorspar</td>
<td>CaF₂</td>
<td>CaF₂ = 1.00</td>
</tr>
<tr>
<td>Gypsum</td>
<td>CaSO₄·2H₂O</td>
<td>CaO = 3.07</td>
</tr>
<tr>
<td>Kyanite</td>
<td>Al₂O₃–SiO₂</td>
<td>Varies with exact composition</td>
</tr>
<tr>
<td>Lime (quick lime)</td>
<td>CaO</td>
<td>CaO = 1.00</td>
</tr>
<tr>
<td>(Burnt lime)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Limestone (calcite)</td>
<td>CaCO₃</td>
<td>CaO = 1.78</td>
</tr>
<tr>
<td>Litharge (yellow lead)</td>
<td>PbO</td>
<td>PbO = 1.00</td>
</tr>
<tr>
<td>Material</td>
<td>Chemical Formula</td>
<td>K_2O (wt%)</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>---------------------------</td>
<td>------------</td>
</tr>
<tr>
<td>Microcline</td>
<td>K_2O·Al_2O_3·6SiO_2</td>
<td>5.91</td>
</tr>
<tr>
<td>Nepheline</td>
<td>Na_2O·Al_2O_3·2SiO_2</td>
<td>2.84</td>
</tr>
<tr>
<td>Nepheline syenite</td>
<td>Mixture of nepheline and feldspars</td>
<td></td>
</tr>
<tr>
<td>Niter (saltpeter)</td>
<td>KNO_3</td>
<td>2.15</td>
</tr>
<tr>
<td>Potash</td>
<td>K_2O or K_2CO_3</td>
<td>1.00</td>
</tr>
<tr>
<td>Red lead</td>
<td>Pb_3O_4</td>
<td>1.02</td>
</tr>
<tr>
<td>Salt cake</td>
<td>Na_2SO_4</td>
<td>2.29</td>
</tr>
<tr>
<td>Sand (Glassmaker's sand) (Potter's flint)</td>
<td>SiO_2</td>
<td>1.00</td>
</tr>
<tr>
<td>Slag</td>
<td>Blast furnace waste glass</td>
<td></td>
</tr>
<tr>
<td>Slaked lime</td>
<td>CaO·H_2O or Ca(OH)_2</td>
<td>1.32</td>
</tr>
<tr>
<td>Soda ash</td>
<td>Na_2CO_3</td>
<td>1.71</td>
</tr>
<tr>
<td>Soda niter (Chile saltpeter)</td>
<td>NaNO_3</td>
<td>2.74</td>
</tr>
<tr>
<td>Spodumene</td>
<td>Li_2O·Al_2O_3·4SiO_2</td>
<td>12.46</td>
</tr>
<tr>
<td>Whiting</td>
<td>CaCO_3</td>
<td>1.79</td>
</tr>
</tbody>
</table>

*Quantity required to yield one weight unit of the glass component.
Regardless of the source of the components used to produce a specific glass, the batch materials can be divided into five categories on the basis of their role in the process: **glassformer**, **flux**, **property modifier**, **colorant**, and **fining agent**. The same compound may be classed into different categories when used for different purposes. Alumina, for example, serves as a glassformer in aluminate glasses, but is considered a property modifier in most silicate glasses. Arsenic oxide may be either a glassformer or a fining agent, depending upon the purpose for which it has been added to the batch.
The primary glassformers in commercial oxide glasses are silica (SiO$_2$), boric oxide (B$_2$O$_3$), and phosphoric oxide (P$_2$O$_5$), which all readily form single component glasses. A large number of other compounds may act as glassformers under certain circumstances, including GeO$_2$, Bi$_2$O$_3$, As$_2$O$_3$, Sb$_2$O$_3$, TeO$_2$, Al$_2$O$_3$, Ga$_2$O$_3$, and V$_2$O$_5$. With the exception of GeO$_2$, these oxides do not readily form glasses by themselves unless very rapidly quenched or vapor deposited, but can serve as glassformers when mixed with other oxides. The elements S, Se, and Te act as glassformers in chalcogenide glasses. Although halide glasses can be made in many systems, with many different compounds acting as glassformers, the two most common halide glassformers are BeF$_2$ and ZrF$_4$.

Although the number of possible glass compositions is effectively unlimited, the vast bulk of commercial glasses are based on silica as the glassformer. While silica itself forms an excellent glass, with a wide range of applications, the use of pure silica glass for bottles, windows, and other bulk commercial applications would be prohibitively expensive, due to the high melting temperature (>2000 °C) required to produce vitreous silica. Production of silicate glasses requires the addition of a flux to reduce the processing temperature to within practical limits, e.g., <1600 °C. The most common fluxes are the alkali oxides, especially Na$_2$O (soda) and PbO. Most commercial glasses contain soda, including those used for containers and window glasses. Potassium oxide is also used extensively in commercial glasses, while lithium oxide is used in a number of commercial glass-ceramics. Rubidium and cesium oxides are frequently used in laboratory studies of trends in behavior due to changes in the identity of the alkali oxide present in glasses, but are very rarely used in commercial products, due to their high cost. PbO, which is an excellent flux, is becoming much more limited in use due to concerns regarding toxicity of heavy metals. PbO is especially useful in dissolving any refractory or other impurity particles which might otherwise result in flaws in the final glass.
While addition of fluxes to silica lead to decreased cost of glass formation, the addition of large amounts of alkali oxides results in serious degradation in many properties. In particular, the chemical durability of silicate glasses containing large concentrations of alkali oxides is degraded to the point where they can no longer be used for containers, windows, or insulation fibers. The degradation in properties is usually countered by addition of property modifiers, which include the alkaline earth and transition metal oxides, and, most importantly, aluminum oxide (alumina). While these oxides partially counter the reduction in processing temperature obtained by addition of fluxes, they also improve many of the properties of the resulting glasses. The properties are thus modified, or adjusted, by careful control of the amount and concentration of these oxides to obtain precisely the desired results. Since many of these oxides are actually very weak fluxes for silica, and the property modifiers are usually added in lesser quantities than the fluxes, their use does not lead to excessively high processing temperatures.
Colorants are used to control the color of the final glass. In most cases, colorants are oxides of either the 3d transition metals or the 4f rare earths. Uranium oxides were once used as colorants, but their radioactivity obviously reduces their desirability for most applications. Gold and silver are also used to produce colors by formation of colloids in glasses. Colorants are only used if control of the color of the glass is desired, and are usually present in small quantities. Iron oxides, which are common impurities in the sands used to produce commercial silicate glasses, act as unintentional colorants in many products. When colorants are used to counteract the effect of other colorants to produce a slightly gray glass, they are referred to as decolorants.

Finally, fining agents are added to glass forming batches to promote the removal of bubbles from the melt. Fining agents include the arsenic and antimony oxides, potassium and sodium nitrates, NaCl, fluorides such as CaF₂, NaF, and Na₃AlF₆, and a number of sulfates. These materials are usually present in very small quantities (<1 wt%), and are usually treated as if they have only minor effects on the properties of the final glasses. Their presence, however, is essential in many commercial glasses, which would be prohibitively expensive to produce without the aid of fining agents in reducing the content of unwanted bubbles in the final product.
3 COMPOSITIONAL NOMENCLATURE

Historically, oxide glass compositions were expressed in terms of weight percentages of the oxide components, in what is known as oxide formulations. A composition for a soda–lime–silicate glass might thus be given as 15% soda, 10% lime, and 75% silica. The reader is assumed to know that the percentages are based on weights of each component, and that soda is Na₂O and lime is CaO. While use of a weight fraction basis simplifies preparation of batches and is very useful in commercial production, it does little to aid in understanding the relative effect of various components on glass or melt properties. On the other hand, use of a molar fraction or percentage basis, while very useful in understanding compositional effects and currently used in most of the literature, complicates batch preparation. In either case, oxide formulations suggest that the components of the glass somehow exist as distinct, separate oxides in the melt or glass, which is certainly not the case.

Atomic fraction, or stoichiometry, formulae are routinely used to express the composition of chalcogenide glasses and for certain simple oxide compositions. A glass containing 40 atom% arsenic and 60 atom% sulfur, for example, might be designated as either As₂S₃, As₁₀S₆₀, or As₀.₄S₀.₆. Since the chalcogenide glasses are usually based on elements
4 BATCH CALCULATIONS

Glass batch calculations can range from very simple to very complex, as a function of the complexity of the composition and the raw materials used to prepare the mixture. Batches containing only oxides in their exact state as expressed by the glass formula, for example, involve very simple calculations, while batches using a number of different minerals, where a glass component may be present in two or more raw materials, require much more complicated calculations.

All batch calculations follow the same procedure. First, determine the weight fraction of each component required to produce the desired molar composition. Begin by multiplying the mole fraction of each component by the molecular weight of that component. Next, total these contributions to determine the molecular weight of the glass, and then divide each individual contribution by the molecular weight of the glass to determine the weight fraction of each component. Finally, multiply the weight fraction of each component by the amount of glass to be produced (Example 3.1). The batch weight of any component which decomposes during melting is adjusted by multiplying the weight fraction of that component by the appropriate gravimetric factor for the raw material actually used in the batch (Example 3.2). Use of raw materials which supply more than one batch component requires additional calculations, as illustrated in Example 3.3.
Example 3.1

Glass composition: $65\text{CaO} - 35\text{Al}_2\text{O}_3$
Molecular weights of components (in g mol$^{-1}$):
  \[
  \text{CaO} = 56.08 \quad \text{Al}_2\text{O}_3 = 101.96
  \]
Molecular wt of glass: $(0.65 \times 56.08) + (0.35 \times 101.96) = 72.14$ g mol$^{-1}$
Weight fraction of each component:
  \[
  \text{CaO} = (0.65 \times 56.08) \div 72.14 = 0.505
  \quad \text{Al}_2\text{O}_3 = (0.35 \times 101.96) \div 72.14 = 0.495
  \]
For 100 grams of glass: \[
\begin{align*}
\text{CaO} & = 0.505 \times 100 = 50.5 \text{ g} \\
\text{Al}_2\text{O}_3 & = 0.495 \times 100 = 49.5 \text{ g}
\end{align*}
\]

Example 3.2

Glass composition: $20\text{Na}_2\text{O} - 80\text{SiO}_2$
Molecular weights of components (in g mol$^{-1}$):
  \[
  \text{Na}_2\text{O} = 61.98 \quad \text{SiO}_2 = 60.09
  \]
Molecular wt of glass: $(0.20 \times 61.98) + (0.80 \times 60.09) = 60.47$ g mol$^{-1}$
Weight fraction of each component:
  \[
  \text{Na}_2\text{O} = (0.20 \times 61.98) \div 60.47 = 0.205
  \quad \text{SiO}_2 = (0.80 \times 60.09) \div 60.47 = 0.795
  \]
For 100 grams of glass: \[
\begin{align*}
\text{Na}_2\text{O} & = 0.205 \times 100 = 20.5 \text{ g} \\
\text{SiO}_2 & = 0.795 \times 100 = 79.5 \text{ g}
\end{align*}
\]

Sodium oxide is not stable in air, so we must use a batch component such as $\text{Na}_2\text{CO}_3$, which yields $\text{Na}_2\text{O}$ after decomposition. It is necessary to multiply the desired quantity of $\text{Na}_2\text{O}$ by the gravimetric factor for $\text{Na}_2\text{CO}_3$ (1.71), to obtain the weight of $\text{Na}_2\text{CO}_3$ (35.05 g) to be used to yield the desired 20.5 g of $\text{Na}_2\text{O}$.
Example 3.3

Glass composition: 20Na₂O–5Al₂O₃–75SiO₂
Molecular weights of components (in g mol⁻¹):
  Na₂O = 61.98  Al₂O₃ = 101.96  SiO₂ = 60.09
Molecular wt of glass:
  \((0.20 \times 61.98) + (0.05 \times 101.96) + (0.75 \times 60.09) = 62.56\) g mol⁻¹
Weight fraction of each component:
  Na₂O = \((0.20 \times 61.98) / 62.56 = 0.198\)
  Al₂O₃ = \((0.05 \times 101.96) / 62.56 = 0.0815\)
  SiO₂ = \((0.75 \times 60.09) / 62.56 = 0.720\)
For 100 grams of glass: Na₂O = 0.198 × 100 = 19.8 g
  Al₂O₃ = 0.0815 × 100 = 8.15 g
  SiO₂ = 0.720 × 100 = 72.0 g

If we use albite feldspar as the source of alumina, we also obtain some of the soda and silica needed for the batch. Using the gravimetric factors for albite in Table 3.1, we find that we that 41.89 g of albite will yield the required 8.15 g of alumina. This amount of albite also yields 4.95 g of soda and 28.89 g of silica (divide the weight of albite by the gravimetric factor to find the yield for a given amount of albite). After subtracting these quantities from the required amounts of soda and sand, we find that we must add 14.85 g of soda and 43.11 g of sand. If we use Na₂CO₃ as the source of the additional soda, we will require 14.85 × 1.71 = 25.39 g of Na₂CO₃.
Final Batch: Na₂CO₃ = 25.39 g
  Albite = 41.89 g
  Sand = 43.11 g
5 MECHANISMS OF BATCH MELTING

5.1 Release of Gases

Initial heating of a glass forming batch usually results in the release of some moisture, which may have been absorbed on the particles, or combined as water of hydration or as hydroxyl. Many of the components of common glass forming batches are somewhat hygroscopic, readily absorbing some water from the surroundings. Boric oxide may partially convert to boric acid ($\text{H}_3\text{BO}_3$), CaO may form Ca(OH)$_2$, etc. Other components already contain water, e.g., NaOH, clays, hydrated alumina, Na$_2$B$_4$O$_7$·10H$_2$O, which will be released at moderate temperatures. The temperature at which this water is released will depend upon the nature of its bonding to the materials, i.e., physical or chemical, and the strength of these bonds. Removal of this water carries heat from the batch and increases the cost of processing.

Far more gas is released during the decomposition of carbonates, sulfates, and nitrates. The gases released expand to volumes much greater than that of the starting batch, resulting in considerable mixing and stirring action, which aids in homogenization of the melt. The creation of so much gas, however, also leads to the formation of an extremely large number of bubbles, which must be removed from the melt before processing is completed. If we consider limestone (calcium carbonate), with a density of $\approx 2.7$ g cm$^{-3}$, we find that decomposition of one mole of limestone, which has a volume of $\approx 37$ cm$^3$, produces 22,400 cm$^3$ of CO$_2$ gas, i.e., an expansion in volume of a factor of $\approx 600$. Since a single 1 mm diameter bubble per m$^3$ of glass is often considered to be a serious flaw in production of commercial glasses, we find that the gas concentration of the melt must be reduced by 10 to 12 orders of magnitude relative to that of the starting batch!
5.2 Formation of Liquid Phases

Liquid phases are formed by the direct melting of batch components, by melting of decomposition products, and by melting of eutectic mixtures formed from the batch components. In soda–lime–silicate batches, we find eutectic mixtures of sodium and calcium carbonates, which melt at 775 °C, and sodium disilicate and silica, which melt at \( \approx 800 \) °C. At this point, the liquid phases are very fluid, the release of gases occurs rapidly, and the mixture of liquid and solids is very turbulent. As the temperature increases, the rates of dissolution of the refractory particles such as sand, alumina, and feldspars increase. The increase in concentration of these components causes a rapid increase in viscosity, and the release of additional gases as the solubility of CO\(_2\) and other gases decrease with increasing silica concentration in the melt. Since the viscosity increases rapidly as the silica content of the liquid increases, the temperature must be increased even further to keep the melt fluid enough for thorough mixing between liquid and remaining solids. The final stage of the melting process, in which the remaining silica and other refractory components are completely dissolved and the melt becomes homogeneous, occurs much more slowly due to the high viscosity of the melt.
The time required to completely dissolve the original batch is known as the *batch-free time*. Although the definition of the batch-free time is straightforward, determination of the exact time at which the last remaining trace of batch remains in the melt is difficult. In general, determination of the batch-free time is subject to a variety of errors, including prejudice on the part of the researcher.

Studies of the batch-free time have, not unexpectedly, shown the great importance of temperature on the rate of melt formation. Other factors include overall glass composition, specific batch components used to obtain that composition, batch homogeneity, grain size of batch components, and the grain size and amount of *cullet* added to the batch. The use of cullet, or scrap glass, not only reduces waste, but also aids in reducing batch-free time by both reducing the amount of refractory material in the batch, and by providing additional liquid throughout the melting process.

The overall glass composition is by far the most important factor in controlling the batch-free time. Simple oxide mixtures, such as those used to produce calcium aluminate glasses, often form eutectic mixtures which melt directly with very short batch-free times. Many non-silicate melts are very fluid at any temperature above the melting point of their components and rapidly dissolve all batch particles. Borate, phosphate, and germanate melts can be formed at much lower temperatures than are typically required for silicate melts. As a result, it is usually easier to decrease their viscosity by increases in temperature, *e.g.*, an increase in temperature from 1000 to 1200 °C is more easily attained than an increase from 1400 to 1600 °C.
Changes in particle size can seriously affect the batch-free time for melts. While fine particles melt more rapidly, they can also agglomerate to form larger, porous particles, which effectively prevent penetration of the viscous liquid to the particle surfaces. Since these agglomerations have a low bulk density, they can float to the surface of the melt, which significantly slows the dissolution process. Escape of gases is inhibited when very fine particles are used, since the channels between the particles are reduced in size. Use of very fine particles can result in the blockage of these channels in the early stages of the melting process, which can suppress decomposition reactions.
5.3 Melting Accelerants

A number of methods can be used to decrease the batch-free time. The most important methods for accelerating the melting process are based on changes in batch raw materials. Replacement of a small portion of sodium carbonate by sodium sulfate, for example, speeds the dissolution of sand by forming additional, lower melting eutectic mixtures. As more silica dissolves into the melt, sulfates separate from the melt in the silica-rich regions surrounding the silica particles. These sulfates decompose as the temperature increases, reacting with the silica particles to release sodium and form sodium metasilicate, which melts readily to form a fluid liquid. The release of SO$_3$ creates a vigorous stirring effect which aids in homogenization of the melt, and improves the contact between silica particles and the surrounding liquid.

Other melting accelerants are also based on replacement of some of the sodium carbonate by more easily melted compounds such as NaOH, NaF, or NaCl, all of which form very fluid liquids upon melting. When melts are formed under an atmosphere containing oxygen, halides will gradually exchange with the oxygen in the surrounding atmosphere, the melt composition will revert to the desired oxide composition, and the viscosity will increase. Since the batch has
Components which force water to enter the melt are especially effective in accelerating melting processes. Water is very efficient in reducing the viscosity of oxide melts. The source of the water is unimportant, so long as it is in direct contact with the liquid. Water can be provided by use of components such as $\text{H}_3\text{BO}_3$ instead of $\text{B}_2\text{O}_3$, or $\text{NaOH}$ instead of $\text{Na}_2\text{CO}_3$, by wetting the initial batch, or by changes in the furnace atmosphere, which increase the partial pressure of water vapor in the combustion gases. Changes from gas–air combustion to gas–oxygen combustion result in higher water vapor contents in furnace atmospheres, which may lead to reductions in overall melting times.