5 STRUCTURAL MODELS FOR BORATE GLASSES

5.1 Vitreous Boric Oxide

The current model for the structure of vitreous boric oxide differs significantly from that for vitreous silica. Although boron occurs in both triangular and tetrahedral coordination in crystalline compounds, it is believed to occur only in the triangular state in vitreous boric oxide. All such triangles are connected by BO at all three corners to form a completely linked network. However, since the basic building block of this network is planar rather than 3-dimensional, the 3-dimensional linkage which occurs in a network of tetrahedra does not exist for vitreous boric oxide. A 3-dimensional structure is developed by “crumpling” of the network, in much the same way that a two dimensional drawing on a sheet of paper develops a third dimension when the paper is crumpled into a ball. Since the primary bonds exist only within the plane of the paper, bonds in a third dimension (van der Waals bonds in this case) are very weak and the structure is easily disrupted. One result of this structure, for example, can be found in the glass transformation temperature of vitreous boric oxide, which is only $\approx 260$ °C, opposed to the $T_g$ of vitreous silica, which is $\approx 1100$ °C.
The structure of vitreous boric oxide is also believed to contain a large concentration of an intermediate unit, consisting of three boron–oxygen triangles joined to form a structure known as a boroxol ring or boroxol group. These well-defined units are connected by oxygens so that the B–O–B angle is variable, and twisting out of the plane of the boroxol group can occur (see Figure 5.4).

![Diagram of boroxol rings](image)

**Figure 5.4**  *Boroxol ring structures in vitreous boric oxide and alkali borate glasses*
As noted earlier, boron is found in both 3- and 4-fold coordination in oxide crystals. Perhaps the addition of alkali oxide forces some of the boron to change from triangular to tetrahedral coordination, with no NBO formation. Such a change would actually increase the connectivity of the network, increasing $T_g$ and decreasing the thermal expansion coefficient of the glass, which is consistent with experimental observations. Formation of two boron–oxygen tetrahedra would consume the one additional oxygen provided by the $R_2O$. Since each tetrahedron would be charge deficient by $-1$ unit, the two alkali oxides would provide sufficient charge compensation for both tetrahedra, in much the same manner as discussed earlier for alkali aluminosilicate glasses. The large ($BO_{4/2}$)$^-$ units now act as anions with a loosely associated alkali cation. A continued increase in the alkali oxide concentration would result in further shift of borons from 3- to 4-fold coordination.
An interesting phenomenon occurs as even more alkali oxide is added to boric oxide. Many of the property/composition trends reverse direction, with, for example, a minimum in thermal expansion coefficient and a maximum in $T_g$ occurring at higher alkali oxide concentrations. Since such behavior was not observed for the alkali silicate glasses which had been the subject of earlier studies, this behavior was considered to be anomalous for glasses, and hence termed the **borate anomaly**. This anomaly was originally explained by assuming that the conversion of boron from 3- to 4-fold coordination only occurs until the network reaches some critical concentration of tetrahedrally coordinated boron (originally believed to occur at $\approx 16$ mol\% $R_2O$), after which additional alkali oxide causes the formation of NBO, which results in a reversal in property/composition trends. This model was widely accepted as the definitive explanation for the borate anomaly for many years.
Eventually, a number of new observations raised questions regarding the original explanation for the borate anomaly. First, and most importantly, nuclear magnetic resonance was used for the direct measurement of the concentrations of 3- and 4-fold borons in a large number of alkali borate glasses. The results of these studies clearly demonstrate that the coordination conversion process does occur as proposed, but also show that the maximum in the concentration of tetrahedrally coordinated borons, designated as $N_4$, does not occur until the composition contains $\approx 35$ to $40$ mol% alkali oxide. Since this concentration is well past the composition where the property trend reversals occur, a direct correlation between the borate anomaly and the value of $N_4$ seems doubtful.
More recent property measurements also raised new questions regarding the borate anomaly. Measurements of $T_g$ reveal that the maximum occurs at $\approx 27$ mol% $R_2O$, while the minimum in the thermal expansion coefficient for the identical samples occurs at $\approx 20$ mol% $R_2O$. Examination of trends for other properties reveals that the borate anomaly occurs at different alkali oxide concentrations for different properties, which is not consistent with the original simple model.

If the original model for the structure of alkali borate glasses is not correct, what are the structures of these glasses really like? Apparently, the original concept of a 3- to 4-fold boron coordination change, followed at higher alkali oxide concentrations by the formation of NBO is, in fact, correct.

Finally, additions of more than $\approx 25$ mol% $R_2O$ eventually begin to cause the disruption of the structure and the formation of NBO.
The relative concentrations of these groups are functions of the overall glass composition, as shown in Figure 5.5, which represents a simplified version of the detailed model for these glasses. Although the complete model for these glasses contains a number of other complex intermediate units, this figure is adequate to explain the complex behavior summarized under the general term borate anomaly. The maximum in $T_g$, for example, is due to the competing effects of the maximum at about 35 mol\% $R_2O$ in the concentration of tetrahedra, which increases the connectivity of the network, and the formation of NBO, which begins at $\approx 25$ mol\% $R_2O$, which decreases the connectivity of the network. The relationship between the thermal expansion coefficient and

![Graph showing the effect of alkali oxide concentration on the relative concentrations of intermediate range units in alkali borate glasses. Dashed lines indicate simple theory. Solid lines represent experimental results.](image)
Since the structures of the alkali borate glasses only contain $Q_4$ and $Q_3$ (triangles which contain only BO) groups as short range order units at small alkali oxide contents, the calculation of the concentrations of these two species is relatively straightforward. Using the same method as before, with a general composition of $xR_2O-(100-x)B_2O_3$, we can state that:

$$x + 3(100 - x) = (2.0)Q_4 + (1.5)[2(100 - x) - Q_4]$$  \hspace{1cm} (5.15)

Solving for $Q_4$, we find that $Q_4 = 2x$ and hence $Q_3 = 200 - 4x$. In this particular case, the structure is usually discussed in terms of the fraction of network which consists of $Q_4$ units, or $Q_4/(Q_3+Q_4)$. This fraction, designated as $N_4$, is then equal to:

$$N_4 = \frac{x}{100 - x}$$  \hspace{1cm} (5.16)
The connectivity number of the alkali borate glasses in this compositional region is determined by the sum of the contributions of the $Q_3$ and $Q_4$ groups. If we consider a glass containing 10 mol% alkali oxide, Eq. 5.16 predicts that $N_4 = 0.11$ and thus $N_3 = 0.89$, where $N_3$ is the fraction of borons in 3-fold units. If we multiply the fraction of each type of unit by the number of bridges per unit and sum for all possible units, we obtain a connectivity number of 3.11 for this glass, or $3.11 = [(4)(0.11) + (3)(0.89)]$.

Data for glasses in alkali borate systems are often plotted versus the quantity $N_4$, or $x/(100-x)$ instead of the more traditional plot against the actual concentration of either $R_2O$ or $B_2O_3$. The relation expressed by Eq. 5.16 is assumed to hold until $N_4 = 0.5$, which occurs at $x = 33.3$ mol% $R_2O$. No NBO are assumed to exist in glasses containing $\leq 33.3$ mol% $R_2O$. A glass containing 33.3 mol% $R_2O$ would have a connectivity number of 3.50, which is the maximum possible in this system.

An empirical fit to the NMR data has been proposed to describe the value of $N_4$ for glasses containing $> 33.3$ mol% $R_2O$. In this compositional region, $N_4$ is given by:

$$N_4 = \frac{300 - 4x}{500 - 5x} \quad (5.17)$$

This equation predicts that a glass will contain zero $N_4$ groups when the $R_2O$ concentration equals 75 mol%.
5.3 Alkali Aluminoborate Glasses

The structures of alkali aluminoborate and alkali gallioborate glasses are not well understood at this time. A simple model would suggest that aluminum-oxygen tetrahedra would form in preference to boron-oxygen tetrahedra. It can be argued that the boron can remain in 3-fold coordination when we add alumina to the glass, but that the aluminum ions must be 4-fold coordinated and will, therefore, consume the additional oxygens from the alkali oxide in preference to the borons. Formation of boron $Q_4$ groups will occur only if there is excess oxygen after formation of the aluminum $Q_4$ groups.

5.4 Alkali Borosilicate Glasses

A large number of commercial glasses are based on alkali borosilicate systems, with a majority of these glasses primarily containing soda instead of any of the other alkali oxides. Most of the commercial glasses, while transparent, are actually phase separated with a very fine scale morphology.
6 STRUCTURAL MODELS FOR GERMANATE GLASSES

6.1 Vitreous Germania

Vitreous germania has a structure very similar to that of vitreous silica, with the basic building block of germanium–oxygen Q₄ units. Since the germanium ion is somewhat larger in diameter than the silicon ion, the Ge–O distance is also somewhat greater, with a bond length of \( \approx 0.173 \) nm. The Ge–O–Ge bond angle is smaller than the Si–O–Si bond angle. Gas diffusion studies suggest that the structure of vitreous germania is more compact than that of vitreous silica and therefore the free, or interstitial, volume of vitreous germania is slightly less than that of vitreous silica. Structural defects are more common in vitreous germania than in vitreous silica, with a measurable concentration of Ge–Ge bonds.
6.3 Alkali Germanate Glasses

Two completely different structural models are currently proposed for alkali germanate glasses. The traditional model is based on the observation of maxima in the density and refractive index of alkali germanate glasses with increasing alkali oxide concentration. Since the existence of these maxima was believed to indicate behavior similar to that observed for alkali borate glasses, the term *germanate anomaly* was coined to describe these property trends. Furthermore, since germanium in crystalline GeO$_2$ polymorphs can be found in both tetrahedral and octahedral coordination, it seemed reasonable to propose that additions of alkali oxide cause a shift in germanium coordination from 4- to 6-fold, without any NBO formation. Each octahedron must be associated with

6.4 Alkali Aluminogermanate Glasses

Addition of alumina to alkali germanate glasses results in a shift in the position of the germanate anomaly to higher R$_2$O concentrations. The anomaly eventually disappears for glasses which contain equimolar concentrations of alkali oxide and alumina.

6.5 Fluorogermanate Glasses

Alkali germanate glasses retain fluorine in their networks at a much higher level than possible in alkali silicate glasses. Glass formation in alkali germanate systems is actually improved by replacing alkali oxides by alkali fluorides. Property trends for alkali fluorogermanate glasses are similar to those for the alkali germanate glasses, with both low alkali and germanate anomalies in $T_g$, and maxima in density and refractive index with increasing alkali fluoride concentration.
Viscosity of Glass Forming Melts

1 INTRODUCTION
The kinetic model of glass formation indicates that the temperature dependence of the viscosity plays a major role in determining the ease of glass formation for any melt. Glasses are most easily formed if either (a) the viscosity is very high at the melting temperature of the crystalline phase which would form from the melt, or (b) if the viscosity increases very rapidly with decreasing temperature. In either case, crystallization is impeded by the kinetic barrier to atomic rearrangement which results from a high viscosity.

In addition to controlling the ease of glass formation, viscosity is also very important in determining the melting conditions necessary to form a bubble-free, homogeneous melt, the temperature of annealing to remove internal stresses, and the temperature range used to form commercial products. The viscosity also determines the upper use temperature of any glass object and the conditions under which devitrification (crystallization) may occur. The very high viscosity encountered in the glass transformation range leads to viscoelastic behavior, and to time dependence in many of the properties of the melt.
2 VISCOSITY DEFINITIONS AND TERMINOLOGY

Viscosity is a measure of the resistance of a liquid to shear deformation, *i.e.*, a measure of the ratio between the applied shearing force and the rate of flow of the liquid. If a tangential force difference, \( F \), is applied to two parallel planes of area, \( A \), which are separated by a distance, \( d \), the viscosity, \( \eta \), is given by the expression:

\[
\eta = \frac{Fd}{Av}
\]  

(6.1)

where \( v \) is the relative velocity of the two planes. If the velocity varies directly with the applied shear force, the viscosity is independent of force and the liquid is said to behave as a *Newtonian* liquid. At high shear stresses, many glass forming melts exhibit an apparent decrease in viscosity with increasing shear stress. This form of non-Newtonian behavior is known as *pseudoplastic* flow, or *shear thinning*, and is important in high shear rate forming processes.

The original unit for viscosity was based on the cgs system, where the viscosity is given in dyne s cm\(^{-2}\). This unit, which is termed a *Poise* and given the symbol \( \text{P} \), is used in virtually all literature prior to 1970 and is still used extensively throughout the glass industry. In SI units, which have replaced cgs units in much of the recent literature, viscosity is given in N s m\(^{-2}\), or, since a Pascal is a N m\(^{-2}\), the viscosity is reported in Pa s. Since 1 Pa s = 10 P, the conversion of viscosity data from one unit to the other is very straightforward. The viscosity of water at room temperature is \( \approx 0.01 \) P, or 0.001 Pa s.
Fluidity is the reciprocal of the viscosity. A melt with a large fluidity will flow readily, whereas a melt with a large viscosity has a large resistance to flow. While fluidity is often used in dealing with ordinary liquids, virtually all literature dealing with glass forming melts discusses flow behavior in terms of the viscosity.

A number of specific viscosities have been designated as reference points on the viscosity/temperature curve for melts. These particular viscosities have been chosen because of their importance in various aspects of commercial or laboratory processing of glass forming melts. Several other reference temperatures which occur at approximate viscosities are also routinely used by glass technologists. These reference points are summarized in Table 6.1, and are shown on a typical curve of viscosity versus temperature for a soda–lime–silica melt in Figure 6.1.

The viscosity of a typical melt under conditions where fining and homogeneity can be obtained in a reasonable time is termed as the melting temperature. Melting usually occurs at a viscosity of \( \leq 10 \) Pa s

<table>
<thead>
<tr>
<th>Name of Reference Temperature</th>
<th>Viscosity (Pa s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Practical Melting Temperature</td>
<td>( \approx 1 ) to 10</td>
</tr>
<tr>
<td>Working Point</td>
<td>( 10^3 )</td>
</tr>
<tr>
<td>Littleton Softening Point</td>
<td>( 10^{6.6} )</td>
</tr>
<tr>
<td>Dilatometric Softening Temperature</td>
<td>( 10^8 ) to ( 10^9 )</td>
</tr>
<tr>
<td>Glass Transformation Temperature</td>
<td>( \approx 10^{11.3} )</td>
</tr>
<tr>
<td>Annealing Point</td>
<td>( 10^{12} ) or ( 10^{12.4} )</td>
</tr>
<tr>
<td>Strain Point</td>
<td>( 10^{13.5} )</td>
</tr>
</tbody>
</table>
Figure 6.1  Typical curve for viscosity as a function of temperature for a soda–lime–silica melt (NIST Standard No. 710). Defined viscosity points are indicated on the figure.
Formation of a glass object from a melt requires shaping a viscous mass of liquid, termed a gob, by some process involving deformation of the material. The melt must be fluid enough to allow flow under reasonable stresses, but viscous enough to retain its shape after forming. Commercial forming methods require very precise control of the viscosity throughout the forming process, in order to achieve high throughput and high yield of acceptable products. Melt is typically delivered to a processing device at a viscosity of $10^3$ Pa s, which is known as the working point. Once formed, an object must be supported until the viscosity reaches a value sufficiently high to prevent deformation under its own weight, which ceases at a viscosity of $10^{6.6}$ Pa s, which is termed the softening point. The temperature range between the working and softening points is known as the working range. Melts which have a large working range are often referred to as long glasses, while those with a small working range are called short glasses. If the working range occurs at high temperatures relative to the working range of typical soda–lime–silica melts, the composition is termed a hard glass. On the other hand, if the working range is below that of soda–lime–silica melts, the composition is termed a soft glass. This particular terminology is often confusing since the terms hard and soft in this context do not refer to the resistance to scratching usually designated by these same terms.

The softening point is more properly termed the Littleton softening point, after the specific test used to define this reference point. The viscosity of $10^{6.6}$ Pa s does not represent the deformation temperature for all objects. This particular reference point is defined in terms of a well-specified test involving a fiber = 0.7 mm in diameter, with a length of 24 cm. The softening point is defined as the temperature at which this fiber elongates at a rate of 1 mm min$^{-1}$ when the top 10 cm of the fiber is heated at a rate of 5 K min$^{-1}$. In fact, if the density of the fiber is significantly different from that of a typical soda–lime–silica composition, the viscosity will not be exactly $10^{6.6}$ Pa s at this temperature.
Once an object is formed, the internal stresses which result from cooling are usually reduced by annealing. The annealing point (cited in various sources as either $10^{12}$ or $10^{12.4}$ Pa s), which is also determined using a fiber elongation test, is defined as the temperature where the stress is substantially relieved in a few minutes. The strain point ($10^{13.5}$ Pa s) is defined as the temperature where stress is substantially relieved in several hours. The strain point is determined by extrapolation of data from annealing point studies. Other tests are also used for these two reference points, with slightly different results.

Two other reference temperatures are often quoted for glass forming melts. While neither of these temperatures represent exact viscosities, they are convenient for relative comparison of the viscosity of different compositions. The glass transformation temperature, $T_g$, can be determined from measurements of the temperature dependence of either the heat capacity or the thermal expansion coefficient during reheating of a glass. This temperature is somewhat dependent upon the property measured, and on the heating rate and sample size used in the measurement. As a result, different studies will report slightly different values for $T_g$ for supposedly identical glasses. Moynihan has shown that the viscosity corresponding to $T_g$ for common glasses has an average value of $10^{11.3}$ Pa s. This value appears to decrease for glasses with very low glass transformation temperatures.

Another viscosity point can be obtained from thermal expansion curves. The dilatometric softening temperature, $T_d$, is usually defined as the temperature where the sample reaches a maximum length in a length versus temperature curve during heating of a glass. This temperature, which will be discussed in more detail in a later chapter, varies slightly with the load applied to the sample by the dilatometer mechanism and the sample size. The viscosity corresponding to $T_d$ lies in the range $10^8$ to $10^9$ Pa s.
At low viscosities, glass forming melts usually behave as Newtonian liquids which immediately relax to relieve an applied stress. At extremely high viscosities, however, these liquids respond to the rapid application of a stress as if they were actually elastic materials. It follows that there must exist an intermediate range of viscosities where the response of these melts to application of a stress is intermediate between the behavior of a pure liquid and that of an elastic solid. Since this behavior has aspects of both viscous flow and elastic response, it is known as viscoelasticity, or viscoelastic behavior.

Since the response of a liquid to application of an external stress is dependent upon the rate of application of that stress, viscoelasticity can occur over a wide range of viscosities. For common rates of stress application, these viscosities lie in the region of the glass transformation range, particularly in the range from $10^{13}$ to $10^8$ Pa s. The most common basic model for viscoelasticity, known as the Maxwell model, is shown in Figure 6.2. The sample is considered to consist of an elastic
If we consider the application of a force to a Maxwell element, we find that there is an instantaneous displacement of the point A at the bottom of the element to point B. If the viscosity of the liquid is infinite, the displacement is entirely due to stretching of the spring and the response is said to be perfectly elastic. If we now remove the force, the bottom of the element will return to point A.

The opposite response will occur if the viscosity of the liquid is infinitely small. The dashpot will offer no resistance to the displacement, the spring will not stretch, and point A will be permanently displaced to point B. There will be no elastic recovery upon removal of the force.

Finally, consider the case where the viscosity of the liquid has an intermediate value. Since flow requires time, the instantaneous response of the element to the displacement will be the same as that for a purely elastic material. The application of the force to the piston, however, will result in flow of the liquid to relieve the strain in the spring and the piston will rise in the dashpot. Eventually, the force will decrease to zero as the spring recovers to its original length and the displacement of the bottom of the element to point B will be permanent.
4 VISCOSITY MEASUREMENT TECHNIQUES

The viscosity of glass forming melts is highly temperature dependent, varying by 12 or more orders of magnitude between the strain point and the practical melting point of a fluid melt. As a result, the measurement of viscosity for a given composition over a wide temperature range requires the use of several different techniques, each of which is restricted to a limited range of viscosity values. Common viscometers are based on direct measurement of the viscosity using a rotation viscometer, the rate of descent of a falling sphere, or the rate of deformation of a plate, fiber, or beam. Less commonly used methods are based on the rate of penetration into the surface of a melt, the torsional deflection of a hollow tube under a torque, or the shearing of a thin disk between a cone and a flat plate.
4.1 Rotation Viscometers

Rotation viscometers are commonly used at room temperature to measure the viscosity of a wide variety of liquids in the range of 1 to $10^4$ Pa·s. Use of these viscometers at temperatures up to 1600 °C requires that the parts exposed to the melt be constructed of platinum or platinum alloys. These viscometers consist of a small cylinder, or spindle, which is rotated inside a large cylindrical crucible containing the melt. In other versions of this viscometer, the crucible is rotated and the torque exerted on the spindle by the melt is measured. The viscosity range covered by this method can be extended by measuring the time required for the spindle to rotate through a defined angle of deflection ($10^{3.5}$ to $10^{6.5}$ Pa·s), or by measuring the torque required to twist the spindle through a small angle ($10^{4.5}$ to $10^9$ Pa·s). This method requires use of a few hundred grams of glass to provide a sufficient melt size for reliable measurements.

In the most basic version, the viscosity is determined from measurements of the torque, $T$, on the spindle and use of Eq. 6.4, which relates the viscosity to the torque and the dimensions of the spindle and the cylinder:

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

(6.4)

where $L$ and $r$ are the length and radius of the spindle, respectively, $R$ is the inner radius of the cylinder holding the melt, and $\omega$ is the angular velocity of the spindle rotation.
4.2 Falling Sphere Viscometers

Viscosities can be measured directly through the determination of the resistance of a liquid to the motion of a sphere falling through the liquid under the influence of gravity. The viscosity is given by the *Stokes equation*:

\[
\eta = \frac{2}{9} \frac{r^2 g}{v} (\rho_s - \rho_m)
\]  

(6.5)

where \( r \) is the radius of the sphere, \( g \) is the gravitational constant, \( v \) is the velocity of the sphere, and \( \rho_s \) and \( \rho_m \) represent the densities of the sphere and melt, respectively. A counterbalance is frequently attached to the sphere to reverse its direction of motion, with data collected during both descent and rise of the sphere. This method yields data in the range 1 to \( 10^6 \) Pa s.

Fig: Falling Sphere Viscometer
4.3 Fiber Elongation Viscometers

The most widely used viscometers are based on measurements of the rate of elongation of a fiber of known dimensions under a known load. This method can be used for viscosities ranging from $10^5$ to $10^{12}$ Pa s. This method is also used for the determination of the Littleton softening and annealing reference points. Since the method requires formation of a long fiber for a specimen, it is well suited for many easily-worked commercial glasses, but difficulties in the formation of good fibers from many experimental compositions often limit the use of this method for basic research studies.

Fiber elongation measurements are based on the rate of elongation, $dL/dt$, where $L$ is the fiber length, of a fiber of cross-sectional area, $A$, which is suspended vertically in a furnace. The elongation rate is determined by the viscosity of the melt and the applied stress, $F/A$, where $F$ is the force applied to the fiber. The viscosity is then given by the expression:

$$\eta = \frac{LF}{3A(dL/dt)}$$  \hspace{1cm} (6.6)

Since the area of the fiber is continually decreasing as the fiber elongates, a correction for the changing fiber area must be applied throughout the measurement.
4.4 Beam-Bending Viscometers

Transformation range viscosities (10^8 to 10^{13} Pa s) are often measured by the *beam-bending* method, in which a small beam of known cross-sectional area, A, is placed in a 3-point bending configuration with a load, M, applied at the center of the beam. The viscosity is given by the expression:

\[
\eta = \frac{gL^3}{2.4I_eV}\left( M + \frac{AL\rho}{1.6} \right)
\]  

(6.7)

where L is the length of the specimen between the support spans, I_e is the moment of inertia of the beam, V is the deflection rate at the mid-point of the beam, and \( \rho \) is the density of the material. The second term in parentheses, AL\( \rho \)/1.6, accounts for the contribution of the mass of the beam to the bending load. This term is frequently negligible when compared to the added mass, M, and is often neglected in the calculation, especially for viscometers which use very small samples.

The ease of sample preparation for the beam-bending method makes this technique particularly suitable for research studies. Any beam shape, including rods or tubing in addition to square or rectangular bars, can be used, provided the moment of inertia can be calculated. Viscometers have been designed which use samples as small as 1 \( \times \) 1 \( \times \) 10 mm, which allow measurements on compositions which can only be formed as glasses by rapid quenching.
VIS 401 Beam Bending Viscometer

The dynamic viscosity ($\eta$) is determined using the bending speed of a beam at uniformly increasing or constant temperature.

The beam must show Newtonian behaviour, and be non-porous, homogeneous and non-tensioned.

Only for investigating the measurement accuracy reference glasses are available.
5 TEMPERATURE DEPENDENCE OF VISCOSITY

Two mathematical expressions, the Arrhenian equation and the Vogel-Fulcher-Tamman equation, are commonly used to express the temperature dependence of the viscosity of glass forming melts. At one extreme, we find that the viscosity can often be fitted, at least over limited temperature ranges, by an Arrhenian expression of the form:

\[ \eta = \eta_o e^{\Delta H_\eta / RT} \]  \hspace{1cm} (6.8)

where \( \eta_o \) is a constant, \( \Delta H_\eta \) is the activation energy for viscous flow, \( R \) is the gas constant, and \( T \) is the temperature in K. In general, Arrhenian behavior is observed within the glass transformation range (10^{13} to 10^9 \text{ Pa s}) and at high temperatures where melts are very fluid. The activation energy for viscous flow is much lower for the fluid melt than for the high viscosity of the transformation region. The temperature dependence between these limiting regions is decidedly non-Arrhenian, with a continually varying value of \( \Delta H_\eta \) over this intermediate region.
A relatively good fit to viscosity data over the entire viscosity range is provided by a modification of Eq. 6.8, which effectively includes a varying activation energy for viscous flow. This expression was derived independently by several workers, and is usually called the Vogel–Fulcher–Tamman (or VFT) equation in recognition of each of their contributions. However, since a paper by Fulcher provided most of the early recognition of the utility of this equation, it is also often simply called the Fulcher equation, particularly within the glass industry. The VFT equation adds a third fitting variable, \( T_o \), to the Arrhenian expression to account for the variability of the activation energy for viscous flow, and replaces the \( \Delta H_\eta \) with a less defined variable, \( B \), as indicated by the expression:

\[
\eta = \eta_o e^{B/(T-T_o)}
\]  

(6.9)

This expression is most often written in the form actually used by Fulcher:

\[
\log\eta = -A + \frac{B \times 10^3}{T-T_o}
\]  

(6.10)

where the constant \( A \) replaces \( \eta_o \) and \( T \) and \( T_o \) are given in °C rather than K. The value of \( T_o \) for a given composition is always considerably less than the value of \( T_e \) for that composition.
5.1 Fragility of Melts

The large range of variation in the curvature of viscosity/temperature plots has been used as the basis for a system of classification of glass forming melts. Angell has proposed that compositions which exhibit near-Arrhenian behavior over their entire viscosity range be termed strong melts, while those which exhibit a large degree of curvature be termed fragile melts. In general, strong melts have well-developed structural units with a high degree of short range order, at least partially covalent bonds, and only gradually dissociate with increasing temperature. Strong melts usually display only small changes in heat capacity upon passing through the glass transformation region. Fragile melts are characterized by less well defined short range order, high configurational degeneracy, and ionic bonds. Their structures disintegrate rapidly with increases in temperature above $T_g$. Fragile melts are usually characterized by large changes in heat capacity at $T_g$.

The concept of fragile–strong melt behavior is summarized in a fragility diagram, as shown in Figure 6.3. A plot of log viscosity against $T_g$ (which is defined here as the temperature for a viscosity of $10^{12}$ Pa s) divided by the experimental temperature allows direct comparison of the curvature of various glass forming melts. Examples shown on
Figure 6.3  Fragility diagram for typical melts
6 COMPOSITIONAL DEPENDENCE OF VISCOSITY

The compositional dependence of the viscosity of glass forming melts is closely related to the connectivity of the structure. In general, changes in composition which reduce connectivity reduce the viscosity, while those which increase connectivity increase the viscosity. These changes are accompanied by changes in fragility which may or may not follow the trend in viscosity, but which are very important in discussion of the temperature dependence of viscosity.

Viscosity data are usually presented in one of two forms. The first form of presentation, which is termed the isothermal viscosity, reports the viscosity at specified temperatures. The second form of presentation reports the temperature at which specified viscosities occur, e.g., the values of the Littleton softening temperature or the glass transformation temperature. In general, temperatures referring to a specified viscosity are termed isokom temperatures for that viscosity. If a series of curves showing the isokom temperatures are presented on a figure, the individual curves are termed isokoms (lines of constant viscosity).
6.1 Silicate Melts

Vitreous silica is the most viscous of all common glass forming melts. The glass transformation temperature of vitreous silica, which is strongly influenced by hydroxyl and other impurity concentrations, lies in the range of 1060 to 1200 °C. The viscosity of silica, which is one of the least fragile melts, varies very slowly with temperature. Production of commercial vitreous silica requires processing temperatures in the range of 2200 °C in order to obtain bubble-free glass.

Addition of alkali oxides to silica results in the formation of non-bridging oxygens and a reduction in the connectivity of the structure. It is not surprising that this reduction in connectivity results in a rapid, monotonic decrease in viscosity with small additions of alkali oxide to silica. The effect of further alkali oxide additions decreases with increasing alkali oxide concentration, and eventually becomes quite small for concentrations exceeding 10 to 20 mol% R₂O. The decrease in viscosity is accompanied by an increase in fragility, which is evidenced by an increase in the reduced activation energy for viscous flow, \( \Delta H_\eta/T_g \), in the transformation region and a decrease in \( \Delta H_\eta \) in the fluid melt region.
The identity of the alkali oxide present has a relatively small effect on the viscosity of the melt. Although the isothermal viscosity does decrease in the order Cs > Rb > K > Na > Li, the differences among the alkali oxides are small as compared to the effect of alkali oxide concentration. In fact, if low viscosity data (< $10^3$ Pa s) are plotted against the concentration of alkali per cm$^3$ of melt instead of against mol% R$_2$O, one finds that the data for lithium, sodium, and potassium silicate melts essentially lie on the same line for any given temperature between 1100 and 1400 °C.

Viscosities of melts containing a mixture of two or more alkali oxides are lower than those of corresponding melts containing the same total molar concentration of a single alkali oxide. If we plot isokoms as a function of the ratio of the concentrations of the alkali oxides present, for melts containing a constant total concentration of alkali oxides, we might expect a linear variation, or additivity, in the isokom temperature as a function of the composition of the melt. In general, however, we find a small negative deviation from additivity whenever we make such a plot for glasses containing a mixture of alkali oxides. Such a departure from additivity in a property is often considered to be anomalous. Since this particular anomaly is observed in compositions containing a mixture of alkali oxides, it is termed the mixed alkali effect.
The viscosities of alkaline earth silicate melts are significantly greater than those of alkali silicate melts. The glass transformation temperature, which occurs at a viscosity around $10^{12}$ Pa s, is $> 200$ K higher for a calcium silicate glass than for a sodium silicate glass containing the same molar concentration of modifier oxide. Replacement of a modest amount of alkali oxide by an alkaline earth oxide, as is often done in commercial silicate glasses, results in small increases in viscosity due to changes in the field strength of the modifier ion. Although a direct replacement of Na$_2$O, for example, by an equimolar concentration of CaO does not alter the non-bridging oxygen concentration, the greater field strength of the divalent calcium ion strengthens the bond to neighboring oxygens, thus slightly increasing the strength of the network.

Addition of PbO to silicate melts almost always reduces their viscosity. The viscosity of binary lead silicate melts, for example, decreases monotonically with increasing PbO concentration. These melts also become more fragile with increasing PbO content. Lead oxide also increases the dissolution rate into the melt for impurity particles such as refractory fragments, so that a small concentration of PbO improves the quality of many melts.
Figure 6.4  Effect of composition on the $10^{11}$ Pa·s isokom temperature for alkali galliosilicate melts containing 15 mol% of the oxides of potassium, sodium, or lithium.

Replacement of an alkali or alkaline earth oxide by alumina or gallia reduces the concentration of non-bridging oxygens and increases the connectivity of the network. As a result, the viscosity increases significantly if these intermediate oxides are added to a melt, as is shown in Figure 6.4. The effect of the intermediate oxide is very small for small
6.2 Borate Melts

The viscosity of vitreous boric oxide is among the lowest reported for common oxide glasses. Boric oxide melts are also considerably more fragile than those of silica, germania, or phosphoric oxide. Since the network of vitreous boric oxide consists of 2-dimensional boron–oxygen triangles, with no strong bonding in 3-dimensions, the connectivity of the network is low. Many of the boron–oxygen triangles are grouped into boroxol rings. Raman spectroscopy has shown that these boroxol rings dissociate with increasing temperature, resulting in a large thermal expansion coefficient for boric oxide melts. It is probable that the fragility of boric oxide melts is a result of the rapid dissociation of the network, which occurs as the boroxol rings open and allow much easier movement within the melt.
Addition of alkali oxides to boric oxide results in considerably more complex behavior than that found for alkali silicate melts. First, even though the connectivity of the melt is increased through conversion of boron–oxygen triangles to tetrahedra with no non-bridging oxygen formation, the fragility of the melt increases with increasing alkali oxide concentration. Second, if we consider the behavior of the viscosity in the transformation region, we find that initial additions of alkali oxide increase the viscosity, while further additions decrease the viscosity, so that maxima in the viscosity versus composition curves occur at 25 to 30 mol% alkali oxide for all 5 alkalis (Figure 6.5). If we examine these curves at high temperatures ($>1000$ °C), where the viscosity is $<10^3$ Pa s, we find that these maxima have disappeared and that the viscosity decreases monotonically with increasing alkali oxide content. Finally,

![Graph showing the effect of composition on the 10^11 Pa·s isokom temperature for lithium borate melts.](image)

**Figure 6.5** Effect of composition on the $10^{11}$ Pa·s isokom temperature for lithium borate melts.

we also find that the viscosity in the transformation region decreases in the order Li > Na > K > Rb > Cs, which is the reverse of the order observed for alkali silicate melts.
The addition of intermediate oxides such as $\text{Al}_2\text{O}_3$ and $\text{Ga}_2\text{O}_3$ to alkali borate melts has very little effect on the viscosity. The transformation range viscosity still passes through a maximum with increasing alkali oxide content. Similar maxima are also observed for $\text{Sb}_2\text{O}_3$–$\text{B}_2\text{O}_3$ and $\text{Bi}_2\text{O}_3$–$\text{B}_2\text{O}_3$ melts for viscosities in the transformation range, even though these binary systems are believed to consist of two network oxides. In fact, the only common binary borate melts which do not display viscosity maxima are those containing either $\text{SiO}_2$ or $\text{GeO}_2$, where the viscosity increases monotonically with increasing concentration of the second glass forming oxide. The viscosity of binary borosilicate melts displays a large, negative departure from additivity, while that of binary borogermanate melts approaches additivity, with only a very small, negative departure from additivity.

One final group of binary borate systems is worthy of note. Glasses can be formed over a wide compositional range in the $\text{RF–B}_2\text{O}_3$ systems, where $\text{R}$ is any alkali ion. The viscosity of melts in these systems exhibits the same behavior as that of the corresponding $\text{R}_2\text{O–B}_2\text{O}_3$ melts, but the isokom temperatures are considerably reduced for any given viscosity for the same alkali ion, as shown in Figure 6.6 for melts containing either $\text{Na}_2\text{O}$ or $\text{NaF}$. The maxima are less distinct for the
Figure 6.6 Effect of composition on the $10^{11}$ Pa s isokom temperature for sodium borate and sodium fluoroborate melts
SUMMARY

The viscosity of a glass forming melt varies over 14 to 15 orders of magnitude during the production of a glass. As a result, several different techniques must be used to measure a complete viscosity/temperature curve. The viscosity/temperature curve has a complex shape, which is commonly described by the Vogel–Fulcher–Tamman equation or by discussion of the fragility of the melt. Compositional changes which decrease the connectivity of the vitreous network decrease the viscosity, while changes which increase the connectivity increase the viscosity. Hydroxyl, fluorine, and PbO all act as fluxes and reduce the viscosity of oxide melts.