The Complete Book on Glass Technology
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Glass is an amorphous solid usually formed by the solidification of a melt without crystallisation. It is an inorganic product of melting, which has been cooled to rigid state without crystallization. Melting is in fact the sole large scale industrial method of glass making. Glass is being used worldwide and has various applications. They are typically brittle and optically transparent. It is widely used in buildings and having industrial applications. The presence of glasses in our everyday environment is so common that we rarely notice their existence. Glass, as a substance, plays an essential role in science and industry. There are various methods of glass making other than melting for example condensation of vapours, conversion of crystals to an amorphous form using mechanical means or irradiation with fast neutrons, dehydration and sintering of gels, etc. Silica (the chemical compound SiO2) is a common fundamental constituent of glass. The properties of glass can be varied and regulated over an extensive range by modifying the composition, production techniques, or both. In any glass, the mechanical, chemical, optical, and thermal properties cannot occur separately. Instead, any glass represents a combination of properties, and in selecting an individual glass for a product, it is this combination that is important. As an architectural element, glass has become the quite essential product for your home or building. The applications of glass are limited only by your imagination; glass has many applications both internal and external that play a vital role in the function and design of your project. Industrially produced glasses can be divided into groups according to various criteria: composition, appearance, properties, application, method of forming etc. According to their chemical composition glasses are classified as silica glass (quartz glass), water (soluble) glass or sodium silicate glass, crystal glass, heat resistant glass, low alkali glass etc. Glass is finding ever wider applications in modern technology; sealing glasses which have been in use for many years, serve in vacuum tight joining of glass to metal, especially in vacuum electronics, in nuclear technology (protection from radiation, immobilization of radioactive waste by fusion into a chemically, resistant glass, etc.), in agriculture (as carrier of fertilizers with long term effects) and a number of possible application in electronics and many more.

Some of the fundamentals of the book are structure of glass, structure of special melts and glasses, composition of glass, glass formation, crystallization and liquid, optical properties, theoretical strength of glasses, practical strengths of glasses, flaw sources and removal, viscosity of glass forming melts, theoretical principles of glass melting, chemical reactions occurring in glass melting, dissolution of solids in the melt, flow of glass in melting furnaces, physical chemical factors in sol gel processing, deposition of transparent non crystalline, metal oxide coatings by the sol gel process etc.

The present book covers different important parameters of glass technology. The book is comprehensive guide for researchers, technologists, new entrepreneurs and professionals.

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Sample Chapter:
Glass

Definition and Historical Summary

Most of us have stood at one time or another in awe in front of glass covered skyscrapers rose windows of medieval cathedrals or mosaics in Byzantine churches wondering about glass transparent or opaque multicolored or colorless harder than steel and yet fragile to impact. The nature of glass its preparation and its uses form the subject of this article.

Many molten materials do not crystallize to their parent crystalline phases once the thermodynamic melting temperature Tm is passed on cooling. Such melts easily supercool to a temperature far below Tm and congeal to solids without any attendant discontinuous changes in volume or entropy. These solids which are isotropic in all their properties are known as glass.

A common misconception is that all glass has the same composition. A variety of organic and inorganic materials can form glass and most of those that do exhibit a moderately sharp transition into the glassy state from the liquid.

The canonical definition of the term glass is that by Morey Glass is an inorganic substance in a condition which is continuous with and analogous to the liquid state of that substance but which as the result of a reversible change in viscosity during cooling has attained so high a degree of viscosity as to be for all practical purposes rigid. Similarly the Astm defines glass as an inorganic product of fusion that has cooled to a rigid condition without crystallizing.

Ease of glass formation is almost entirely a kinetic question. At no temperature is glass an equilibrium phase although glasses hundreds of millions of years old are not uncommon in nature. The cooling rate required to form a glass varies with composition. Some melts (e.g. those of SiO2 or B2O3) can form a glass at very slow rates of cooling whereas mixed nitrates of potassium and calcium or sulfates of potassium and zinc for instance require rapid cooling from their normal melting temperature to form glass. Glasses can even be made from melts of metals such as iron and cobalt but still higher quench rates are required than those for metal metalloid glasses. Almost any inorganic melt can apparently be quenched into a glass with a sufficiently fast quenching rate.

Glass is not merely a supercooled liquid. The distinction between a supercooled liquid and a glass lies in the ability of structural elements in the former to rearrange themselves in accordance with the thermodynamic state of the system whereas in the latter such rearrangement is not possible. This inhibition of rearrangement in glass is caused by the large increase in viscosity on cooling and gives rise to an endothermic effect on heating which occurs at the glass transition temperature (i.e. the temperature above which structural elements in the glass are sufficiently mobile to rearrange themselves according to their equilibrium configuration).

The discoverer of glass manufacture will probably remain unknown. A source of inspiration may have been the abundant occurrence of glasses in nature. Obsidian pumice (a natural foam glass) and tektites (glassy bodies probably of meteoric origin) are examples of naturally occurring glass.

Structure of Glass

Methodology in condensed matter physics and chemistry consists of identifying and relating the physical properties structure and constituent elements of a class of materials. For crystalline solids the constituents and structure can be characterized readily. In glass on the other hand understanding of the structure consists almost exclusively of negative statements no metric geometry trivial space group no Bloch states no single ground state no unique best structure. In addition the topology of glass structure is amenable only to indirect experimental investigation.
It is not surprising in light of the undetermined nature of the amorphous state of glass that competing perceptions exist with regard to its character. The principal difficulty in distinguishing between models has been the small amount of energy associated with long range ordering.

**Microcrystallite Hypothesis.** The microcrystallite cybotactic group hypothesis was constructed primarily to account for the discontinuous changes in the properties of glasses which can be correlated with similar discontinuities in the properties of associated crystalline phases. Proponents of this hypothesis were (with some) rare exceptions such as STEWART and RANDALL almost exclusively Russian the first being FRANKENHEIM and subsequently von WEIMARN who held that all matter in any state be that gas liquid or solid is crystalline. This work was followed up by LEBEDEFF who showed that vitreous amorphous silica varies considerably between 540 and 6000 °C in its double refraction refractive index and coefficient of expansion. He inferred that this variation was due to a polymorphic transformation assumed to be connected with the low high temperature transformation of quartz which occurs at 5750 °C. He furthermore suggested that vitreous silica consists of an aggregate of very minute crystals with included quartz crystals that are probably not in a pure state but in the form of a solid solution with other substances hence accounting for the temperature range over which the polymorphic transition occurs. Valenkov and Poray Koshitz analyzed the X ray diffraction curves of glasses and concluded that the observed diffraction patterns were produced by 0.75 2.5 nm crystallites that were connected to each other by an amorphous layer. These results made the microcrystallite postulate questionable because 2.5nm crystallites do not represent long range ordering in a crystallographic sense. Refinement of diffraction experiments particularly at small angles has invalidated the original microcrystallite hypothesis. Recent electron microscopy results on the other hand indicate that multicomponent glasses can be chemically inhomogeneous and contain microheterogeneities which could be taken to represent microcrystallites.

**Random Network Hypothesis.** The Zernike Prins Bernal Fowler Warren hypothesis considers the liquid a system of atomic or ionic networks designated as a random network. For glasses this implies a rigid system of continuous noncrystalline networks similar to those assumed to be present in the liquid. It remains open to debate whether there is one unique random network or ten thousand or what random really means in the context of liquid structures. The hypothesis was successful in providing qualitative explanations for the glass forming tendency of simple glass forming systems as being caused by a rapid increase in viscosity during cooling of the melt. In addition successful predictions could be made about potential glass forming systems as well as rationalizations for most of property composition relationships. Zachariasen postulated glass forming tendencies for simple oxides based on random networks and the concomitant need for flexibility in linkages. These postulates in part already phrased by Gold Schmidt are the following:

Each oxygen atom can be linked to no more than two cations the number of oxygen atoms around any one cation must be small. i.e. three or four the oxygen polyhedra must share corners not edges or faces to form a three dimensional network at least three corners must be shared. Network formers have a coordination number of 3 or 4 (Si B P Ge As Be etc.) network modifiers have coordination numbers greater than or equal to 6 (Na K Ca Ba etc.). Intermediate atoms with a variable coordination number between 4 and 6 (Li Al Mg Zn Pb Nb Ta etc.) can function as network modifiers as well as network formers the coordination change is a reflection of their amphoteric character i.e. solubility in both inorganic acids and bases. Additional refinements have been made to the random network theory. Dietzel introduced the concept of cationic field strength defined as formal cation charge divided by the cation anion distance. This concept enables a quantifiable distinction to be made between the three categories of atoms. Glass formation is favored if the difference in field strength between the cations is larger than 0.3. Smekal expanded on the cationic field strength concept by taking the bond polarity into account. Glass formation is favored if mixed bonding with a homopolar and heteropolar component occurs. Weyl postulated the
screening theory used to explain the mechanical properties of glasses. In this theory the polymerization of polyhedra to three dimensional random networks is caused by the polarization and deformation of residual valence forces. Stevels developed a theory for invert glasses which contain polyhedra with less than three connected corners in contradiction to the Zachariassen postulates. His structural parameter $Y$ is a measure of the average number of bridging anions. The properties of the glass are mainly determined by the network modifier atoms when $Y$ is smaller than 2. This is due to the fact that these network modifiers compete for the available anions thus resulting in an increased degree of disorder.

Among the less fruitful extensions of the random network theory are those by Huggins and Tilton. Huggins attempted to explain known discontinuities in properties by assuming the presence of fixed atom groups called structons. A last refinement of the network hypothesis represents the work by Tilton who postulated the presence of vitrons aggregates of silica tetrahedra primarily consisting of five membered rings which combined to form a pentagondodecahedron consisting of 20 tetrahedra. These vitrons would be connected to one another by less ordered domains.

With the advent of NMR laser Raman Spectroscopy and extended X ray absorption fine structure (EXAFS) focus has been directed to dissecting glass structure in terms of local environments avoiding any deterministic statements regarding extended structures. A current area of research involves determining the extent to which long range structural elements can be derived from such local environments.

Structure of Special Melts and Glasses

Almost all industrially manufactured glasses are silicate glasses. As a consequence these system are emphasized in the following discussion the goal being to provide a terminus ad quem for the study of amorphous materials. The viscosity of various silica containing melts is used as a reference against which structural concepts can be matched. The use of viscosity is somewhat ironic however although viscosity illustrates nicely the role of network forming atoms in comparison with network modifying atoms it is the least understood property of melts or glasses. The structural description of glasses and melts is based on $Q$ (quartz) distribution theory and $Q$ designation. The use of this model enables description of silica species in both solids and aqueous solution in terms of the distribution of local silicon environments which are amenable to investigation by NMR. These designations are as follows:

Each silicon atom is coordinated tetrahedrally to four oxygen atoms.

If all oxygen atoms in a tetrahedron are connected to two silicon atoms the local environment around the silicon atom is designated $Q4$. All four Si O bonds of the tetrahedron are therefore bridging bonds designated Si O (br).

The local silicon environments are designated $Q3$ $Q2$ $Q1$ and $Q0$ if three two one or zero oxygen atoms are connected to two silicon atoms. In $Q3$ three Si O (br) bonds and one Si O nonbridging bond designated Si O (nbr) exists. For $Q0$ all Si O bonds are Si 0 (nbr).

Designations $Q4$ to $Q0$ of local environments coincide with connectivity 4 to connectivity 0 of the extended environment.

Four reactions suffice to describe all possible rearrangements in local environments in those alkali oxide (R2O) silicate glasses in which all oxygen atoms are connected to silicon atoms.

The $Q$ distribution can in principle be determined experimentally by high resolution solidstate NMR. This distribution does not however necessarily relate glass structure to glass properties. Examination of Figure 2 makes this clear. Two hypothetical two dimensional networks each containing 45 open tetrahedra and 11 black tetrahedra are shown. The open tetrahedra represent silicon the black tetrahedra lithium in fourfold oxygen coordination. The difference in $Q$ distribution between the two networks is small. Nevertheless measurement of the transport properties of the two networks would give wildly different results the arrangement in figure 2B has very high electrical conductivity and diffusivity (and possibly low viscosity)
because of a continuous pathway through the solid in contrast to that in Figure 2A. Clearly the Q distribution does not correlate glass structure with glass properties and additional information is required to make such a connection. This additional information is obtained from Monte Carlo type computer calculations.

KEEFER recognized that the question of the structure of a silica rich alkali metal silicate glass is analogous to that of electron spin correlation in a two dimensional Ising Model. This Model attempts to explain magnetic properties of materials by constructing a lattice with two possible electron spin states up or down which allows the problem to be considered in terms of a statistical distribution. Alkali silicate and spin glasses share two characteristics (1) slow relaxation and (2) a tendency to settle into any one of a large number of atomic configurations. In silica rich alkali metal silicate glasses the two possible spin states correspond to bridging and non bridging oxygen atoms silica rich glass is required because photoelectron spectroscopy has demonstrated that only in such systems are nonbonding oxygen atoms not present. In the absence of non bonding oxygen the ratio between bridging and non bridging oxygen atoms is fixed by the stoichiometry of the sample.

As stated before connecting Q distribution with physical properties of a glass or melt requires Monte Carlo type calculations. The computational problem involves assignment of the enthalpies of formation of the four principal reactions between Q species calculation of network patterns derivation of the thermodynamic properties of the system from these patterns and use of percolation theory to compute the rheological and transport properties of melts A rule of thumb is given by Ziman with respect to site percolation site percolation occurs in a regular three dimensional assembly when favorable regions occupy ca. 15% (in the two dimensional case 45%) of the total volume.

Local silicon environments can be measured by 29Si magic angle spinning (mas) NMR. Two problems arise in using these technique variations in chemical shift for a specific silicon species and partly as a result of this limited spectral resolution. The first problem is illustrated in Figure 3 which shows the 29Si MAS NMR spectrum of Na24Y8 (Si24O72] which is a single chain silicate with 24 silica tetrahedra per unit cell (a 24er chain in the Liebau classification) and local environment Q2. The 29Si MAS NMR spectrum of this compound shows 12 peaks with a chemical shift range of 5.12 ppm. Thus small perturbations in the local environment around one Q2 species can cause a substantial chemical shift. In this case the variations are due to chain twisting. Such variations in chemical shift of a single silica species combined with the large number of species possible present (ten Q2 species are possible) and the limited NMR spectral resolution in glass render determination of the silica species distribution in glass tentative at best. Despite this some assessment of the degree of intermediate range order in lithium silicate glasses has been obtained by combining NMR and ESCA (electron spin chemical analysis) results together with the application of proper stoichiometric constraints on the system. Doing this shows clearly that the 29Si NMR spectra of such glasses indicate the presence of only a small number of local environments in contrast to the total possible number enumerated in Figure 1.

Composition of Glass

Multicomponent glass forming systems contain according to Zachariasen appreciable amounts of elements that form vitreous oxides or other elements that can replace the former isomorphously. Ternary glasses can consist of one network former and two modifiers or three network formers. Most ternary oxide systems have been sampled and investigation has been extended to quaternary and quinary systems.

The properties of complex industrial glasses tend to be rationalized in terms of simple systems. The following discussion therefore begins with vitreous silica as the canonical single component glass followed by simple two component systems the alkali metal and alkaline earth silicate borate phosphate and germinate glasses. Boro alumino and lead silicate glass is then discussed followed by two nonoxide
systems the chalcogenide and halide glasses. Finally the chemical composition of industrially important glasses is tabulated.

**Single Component Glass**
The most important single component glass is vitreous silica. The structure consists of corner sharing SiO$_4$ tetrahedra. Each oxygen atom is shared by two silicon atoms forming Q4 local silicon environments. Long range order is of course absent. Vitreous silica is an excellent dielectric with a very low equilibrium solubility (on the order of 100ppm at room temperature) in all acids except hydrofluoric. A synopsis of the properties of Corning 7940 fused silica and other amorphous silicas is given in Table 1.

The difference in structure between vitreous silica and two crystalline silicas is shown in Figure 4. Here the Frequency of occurrence of average Si–O–Si angles is illustrated by using the 29Si MAS NMR spectrum of vitreous silica and the formula of Thomas and coworkers which relates chemical shift to the Si–O–Si angle. Average Si–O–Si angles vary between 122º and 170º in vitreous silica the most common value being 147 (or 151 if the spectrum of Gladden and coworkers is used). On the other hand quartz and cristobalite each have one single Si–O–Si angle with values of 143º and 146º respectively.

Superimposed on the plot of Si–O–Si angle versus frequency in Figure 4 is the two center energy taken to reflect the bond energy for a silicon oxygen bridging bond as a function of Si–O–Si angle calculated by using semiempirical molecular orbital calculations. Inspection of this curve shows that a Si–O bond with a Si–O–Si angle of 180º is stronger (i.e. has a more negative two center energy. ca. 1760kJ) than that at a Si–O–Si angle of 120º (two center energy. ca. 1530kJ). Examination of figure 4 suggests that although glasses are intrinsically less stable than their crystalline counterparts a vitreous silica more stable than quartz or cristobalite is conceivable the challenge is to make a glass with a larger percentage of Si–O–Si angles >150º. Only this angle must be considered because the energy barrier to rotation between connected silica tetrahedra is negligibly small.

Fused silica transmits light of wavelengths into the UV region and is the oxide glass most resistant to damage caused by radiation. It finds use in windows for space vehicles and wind tunnels ultrasonic delay lines crucibles for growing ultrapure silicon or germanium crystals and optical systems in spectrophotometric equipment.

Vitreous silica can be produced by several methods. These processes and the impurities associated with them are listed in table 2.

Fused quartz made by electrically fusing quartz crystals has very low moisture content and hence good IR Transmission. The disadvantage of quartz as a raw material is that even highgrade pure quartz crystals contain 1 2 ppm of aluminum alkali manganese and titanium. The presence of these elements increases the number of Si–O (nbr) bonds which thereby reduces UV transmission. Flame fusion of quartz or flame hydrolysis of SiCl$_4$ on the other hand gives glasses of very high purity except for large amounts of water which decrease IR transmission. For some applications impurities as low as 1 part in 1012 become important. An example is uranium this problem is best solved by ensuring that the silica source is biogenic rather than associated with granitic rocks or pegmatites.

**Silicate Glasses with Two components**
Two component silicate glasses are of particular interest in studying glass formation. Addition of alkali metal or alkaline earth oxides breaks Si–O–Si linkages the alkali metal or alkaline earth nestling at non bridging oxygen sites in the network hence the description network modifiers. This decrease in connectivity of the silica network manifests itself in a very large decrease in viscosity melting point and UV transmission. Modifiers also cause a decrease in resistivity an increase in thermal expansion and generally lower chemical durability.

Different alkali metal atoms have different effects on the properties of silicate glasses. Thus lithium silicate
glasses are nonhygroscopic whereas sodium potassium rubidium or cesium silicate glasses show increasingly higher hygroscopicity. Another example is the volume contraction of the silicate network in the presence of lithium and its expansion in the presence of potassium. The almost monotonic variation in cation oxygen distance as measured by X ray diffraction has led to a variety of schemes for the comprehensive compilation of the properties of alkali metal or alkaline earth silicate crystals or glasses. Among these are the cation field energy and field strength which are the formal cation charge divided by the cation anion distance and the square of the cation anion distance respectively.

Many physical properties of alkali metal or alkaline earth silicate glasses change almost monotonically as a function of cationic field strength or energy. For example, the critical liquid immiscibility temperature decreases linearly as a function of cationic field strength from magnesium to barium silicates and from lithium to cesium silicates. Similarly, the freezing point depression increases more or less monotonically from lithium to cesium silicates whereas the surface tension decreases. Viscosity, refractive index, and density show a minimum for sodium silicate melts.

Even the few 29Si MAS NMR chemical shift data on crystalline alkali metal silicates suggest a relation between chemical shift and cationic field strength less negative (downfield) chemical shifts being associated with greater cationic field strength. More sophisticated analysis of a variety of silica containing systems has been carried out. In alkali metal or alkaline earth silicate glasses most physical properties vary more or less linearly with cationic field strength with the exception of viscosity, refractive index, and density. Although it is useful as a mnemonic device no true cause and effect relations are associated with cationic field strength or energy.

**Borate Phosphate and Germanate Glasses**

Borate glasses contain planar BO3 groups as structural units rather than tetrahedral SiO4 groups. The oxygen atoms are as in silica again connected to two network forming atoms in this case boron. Radial distribution analysis describes the B2O3 glass structure as consisting of boroxyl rings i.e. planar rings containing three boron atoms and three oxygen atoms. Recent results on molecular dynamics have shown that the radial distribution pattern is consistent with structures having a low concentration of such rings. Although borate glass forms a three dimensional network its viscosity is substantially lower than that of silicate glass as shown in table 4. Again addition of alkali lowers the viscosity of the melt but the effect is by no means as dramatic as for silicate glass.

Introduction of alkali or moisture to alkali metal borate glasses causes some of the three coordinate boron atoms to become four coordinate as shown by the pioneering NMR work of Bray and O KEEFE. The ratio of three to four coordinate boron in alkali metal borate glasses has an upper limit of about 1.2.

Phosphate glasses contain tetrahedrally coordinated PO4 building blocks, however, they do not show the same type of connectivity as silicate glasses. Oxygen 1s photoelectron spectroscopy suggests that in phosphate glasses three types of oxygen atoms occur those bonded to two phosphorus atoms the bridging oxygens O(br) those bonded to one phosphorus atom and one alkali metal atom the non bridging oxygens O (nbr) and those bonded only to phosphorus the doubly bonded oxygens O (d). A characteristic oxygen 1s photoelectron spectrum of a phosphate glass is shown in figure 9. In contrast silicate glasses never contain double bonded oxygen atoms and only rarely non bonded oxygen i.e. oxygen atoms not connected to at least one silicon atom. An example of the latter is glassy Pb2SiO4.

Oxygen 1s photoelectron spectroscopy indicates both the concentration of different oxygen atoms in a material and the actual charges on these atoms. The relation between energy shift of the oxygen 1s photoelectron spectral line and charge is shown in Figure 10. According to this method quartz cristobalite and vitreous silica have an oxygen charge of 0.74. Oxygen atoms with higher negative charge are encountered for example in lead silicate glasses which show oxygen charge variations comparable to
those found for superconducting materials. Some oxygen 1s derived charges for various compounds are compiled in table 5. Assignment of charges is a partitioning problem without a unique solution. Some special phosphate glasses show a connectivity of four identical to that found in vitreous silica. Examples are ZnP2O6 and AlPO4 glasses. The structure of alkali phosphate glasses is well known because these glasses in contrast to alkali silicate glasses either do not or only at very small rates repolymerize on dissolution in aqueous solution. As a result the length of the phosphate chains remains unchanged. The relative proportions of different chains in solution analyzed chromatographically give a true measure of the distribution of extended environments in phosphate glasses. The most common chain length is three to four phosphorus atoms with a maximum chain length of seven. No analogies between the distribution of structural elements in phosphate and silicate glasses exist. This is due to the limited cross linking and branching that occur in phosphate glasses in comparison to silicate glasses due to the presence of P=O bonds.

Phosphate glasses tend to have low durability. Despite this important commercial applications exist. One of these is associated with the sharper absorption bands of iron oxide in the ultraviolet and infrared in phosphate glasses compared with silicate glasses. Iron containing phosphate glasses are therefore nearly transparent to visible light enabling the manufacture of virtually clear heat absorbing glasses containing several percent iron oxide.

Phosphate based glasses are more resistant than silicate glasses to hydrofluoric acid. Some optical glasses produced by Schott Hoya Owings Illinois and Corning France use phosphate as the primary glass former. Fluorophosphate glasses designated FK 5 and FK 50 by Schott have very low optical dispersion with Abbe numbers of 70.4 and 81.5 respectively.

### Optical Properties

#### Introduction

Glasses are among the few solids which transmit light in the visible region of the spectrum. Glasses provide light in our homes through windows and electric lamps. They provide the basic elements of virtually all optical instruments. The worldwide telecommunication system is based on the transmission of light via optical wave guides. The esthetic appeal of fine glassware and crystal chandeliers stems from the high refractive index and birefringence provided by lead oxide while the magnificent windows of many cathedrals exist only because of the brilliant colors which can be obtained in glasses. The optical properties of glasses can be subdivided into three categories. First many applications of glasses are based on the bulk optical properties such as refractive index and optical dispersion. Other properties including colour are based on optical effects which are strong functions of wavelength. Finally modern glass technology increasingly relies on the application of non traditional optical effects such as photosensitivity photochromism light scattering Faraday rotation and a host of others.

#### Bulk Optical Properties

The history of optical science closely parallels the history of the development of optical glasses. Development of early telescopes and microscopes immediately forced a search for new optical glasses with appropriate refractive index and optical dispersion characteristics. It can be argued that the development of modern astronomy biology and medical science were controlled by the ability of glass makers to develop glasses with the appropriate optical properties.

#### Refractive Index

The refractive index remains the most measured optical property of glasses as well as the most basic optical property for determination of the appropriate glass for many applications. The refractive index of any material is defined as the ratio of the velocity of light in a vacuum to the velocity of light in a medium. This
ratio can be measured by application of Snell's law which states that the refractive index \( n \) is given by the expression.

Where \( i \) is the angle of incidence and \( r \) is the angle of refraction for a beam of light striking the surface of a material. The refractive index can also be measured using methods based on the reflectivity of a surface measurement of the critical angle for total reflection or Brewster's angle or the Becke line technique. Further discussion of these methods can be found in many texts on optical properties.

The refractive index is not actually a constant but varies with the wavelength of the incident light. The most commonly quoted index is usually designated as \( n_D \) and represents the index at the yellow emission line of sodium (589.3 nm). The index at the yellow emission line of helium (587.6 nm) designated \( n_D \) is also commonly used. Since these wavelengths are nearly identical there is very little difference between these indices.

The refractive index of glasses is determined by the interaction of light with the electrons of the constituent atoms of the glass. Increases in either electron density or polarizability of the ions increases the refractive index. As a result low indices are found for glasses containing only low atomic number ions which have both low electron densities and low polarizabilities. Glass based on BeF2 has refractive indices in the range of 1.27 while vitreous silica and vitreous boric oxide have refractive indices of about 1.458. At the other extreme glasses with high lead bismuth or thallium contents may have refractive indices ranging from 2.0 to 2.5.

Since a majority of the ions in any glass are usually anions the contribution to the refractive index from the anions is very important. Replacement of fluorine by more polarizable oxygen ions or by other halides increases the refractive index. Conversely partial replacement of oxygen in oxide glasses by fluorine to form fluoroborate glasses for example reduces the refractive index. Since non bridging oxygens are more polarizable than bridging oxygens compositional changes which result in the formation of non bridging oxygens increase the refractive index of glasses while changes in composition which reduce the non bridging oxygen concentration can reduce the refractive index. The refractive indices of alkali silicate glasses thus increase with increasing alkali oxide concentration while replacement of alkali oxides by alumina which reduces the non bridging oxygen concentration can cause a reduction in the refractive index. The polarizability of the cation present increases as the field strength of the ion decreases so that glasses containing cesium have a higher refractive index than those containing sodium. Glasses which contain very high PbO concentrations such as those found in unusual systems such as the PbO Ga2O3 binary and the PbO Ga2O3 Bi2O3 ternary have refractive indices in excess of 2.5.

The density of a glass also plays a role in controlling the refractive index. Decreases in fictive temperature which increase the density of most glasses increase the refractive index. Since the fictive temperature is determined by the cooling rate through the glass transformation region the refractive index is found to increase with decreasing cooling rate. This effect can be very important for optical applications where fine annealing is essential to minimize local index variations. The refractive index also increases when glasses are eight reversibly or irreversibly compacted by pressure or by exposure to high energy radiation. Thermal expansion of glasses can result in either an increase or a decrease in the refractive index. The density of a glass will decrease if it expands upon heating which should decrease the refractive index. The polarizability of the ions however increases with temperature which increases the refractive index and may therefore offset the effect of the decreasing density. Glasses with high thermal expansion coefficients and low temperature variations in polarizability are usually found in systems containing fluorine such as the fluoride fluorophosphate or fluorosilicate systems. Glasses with low thermal expansion coefficients and higher temperature variation of polarizability as is the case for most silicate and borate glasses have positive temperature coefficients of refractive index. These variations in refractive index are reversible so long as no relaxation of the density occurs during the temperature excursion.
Molar and Ionic Refractivities

The molar refractivity is directly proportional to the polarizabilities of the constituent ions of a glass. It can be shown that the molar refractivity \( R_m \) is given by the expression

\[
R_m = \frac{n}{V_m}
\]

Where \( V_m \) is the molar volume of the glass and \( n \) is the refractive index at the wavelength of measurement. The molar volume is equal to the molecular weight of the glass divided by its density.

The molar refractivity of a compound can be calculated from the contributions of each of the constituent ions. The molar refractivity for the compound \( AxBy \) for example is given by the sum of the ionic refractivities of the constituent ions \( R_n \) times their concentration in the compound or in this case

\[
R_{AxBy} = \sum n_i R_i
\]

Although this method of estimating the molar refractivity works well for many inorganic compounds it is difficult to apply to oxide glasses. The ionic refractivity of oxygen depends upon its role in the glass structure so that the values for bridging and non-bridging oxygens are structure so that the values for bridging and non-bridging oxygens are not identical. Furthermore the ionic refractivity of oxygen ions depends on the nature of the associated cations. As a result one can only use ionic refractivities as a guideline to the choice of ions for altering the refractive index of oxide glasses and not for quantitative calculations.

The use of the molar refractivity stresses the role of ionic packing in controlling the refractive index of a glass. Since the refractive index is proportional to the molar refractivity divided by the molar volume it is obvious that a small molar volume will yield a larger refractive index for a glass consisting of ions of similar polarizabilities. An example of this effect can be found in the refractive indices of many glasses containing lithium compared to similar glasses containing sodium or potassium. Since lithium actually causes a contraction of the vitreous network in many glasses the molar volume is reduced by addition of lithium ions. This reduction in molar volume more than offsets the lower ionic refractivity of the lithium ion relative to that of sodium or potassium ions and results in a glass with a higher refractive index. In many cases apparently anomalous trends in refractive index are resolved when the data are converted to molar refractivities.

Tables of optical data for glasses often include values for the specific refractivity which is given by the expression

\[
R_s = \frac{R_m}{\rho}
\]

Where \( \rho \) is the density of the glass. The specific refractivity is primarily used for designing optical systems where the mass of glass used may be important.

Dispersion

The variation in index with wavelength known as optical dispersion or simply as dispersion is critical in the control of chromatic aberration of optical lenses. Ideally dispersion is described by the entire curve of refractive index versus wavelength over the desired wavelength range. In general however it is more convenient to measure the refractive index at a few specified wavelengths and use these measurements as the basis for terms which can be used to compare the dispersion of different glasses.

These values are nearly identical.

More detailed information regarding the dispersion curve as a function of wavelength is often provided in the form of an expression of the form.

Ultraviolet Absorption

Even transparent colorless glasses cannot transmit radiation at wavelengths beyond their inherent ultraviolet edge. This frequency is believed to be due to the transition of a valence electron of a network anion to an excited state. Conversion of a network anion from the bridging state to a non-bridging state will lower the energy required for the electronic excitation and shift the ultraviolet edge to lower frequencies. The addition of alkali oxides to silica therefore results in a shift of the ultraviolet edge toward the visible region of the spectrum. Since initial additions of alkali oxides to boric oxide result in conversion of boron from three to four-fold coordination thus strengthening the network bonds the ultraviolet edge does
not shift toward the visible. Once the concentration of alkali oxide becomes sufficient to produce non
bridging oxygens the expected shift of the edge toward the visible with increasing alkali oxide content is
observed.

The ultraviolet edge of vitreous germania is closer to the edge of the visible spectral region than that of the
other common oxide glassformers. Addition of large concentrations of alkali oxides shifts this edge to a
frequency very near the visible. If these glasses are heated they gradually become yellow with an increase
in the intensity of the color with increasing temperature. The glasses return to the colorless state on cooling.
This effect known as reversible thermochromism is due to the shift of the ultraviolet edge into the visible
region at elevated temperatures.

In reality the inherent ultraviolet edge of a glass is rarely observed. Very small concentrations of iron and
other impurities result in very intense absorption bands. Since the absorption of energy is due to the
transfer of an electron from the cation to a neighboring anion these absorptions are said to be due to a
charge transfer transition and the absorption band is called a charge transfer band. These bands are so
intense that only their tail can be detected so that the appearance of the spectrum is identical to that due to
the inherent ultraviolet absorption. The impurity iron content of most silica used in glassmaking is so great
that the inherent ultraviolet edge of silicate glasses is usually undetectable.

Visible Absorption

Absorption in the visible is perceived as color. A number of mechanisms exist for the creation of color in
glasses. The most important commercial colored glasses contain either 3d transition metal ions or 4f rare
earth (lanthanide) ions where the coloration arises from the so called ligand field effect. Other sources of
color include the formation of metal or semi conductor colloidal particles optical defects induced by
solarization or radiation and charge transfer bands in the visible region of the spectrum.

Ligand Field Coloration of Glasses

Coloration of glasses by 3d transition metals ions is due to electronic transitions between normally
degenerate energy levels of d electrons. Since a detailed description of the mechanism leading of these
electronic transitions (called ligand field or crystal field theory) can be found in many places only a brief
qualitative discussion will be provide here.

The 3d electronic levels are identical in energy for free ions. However when a transition metal ion is
surrounded by a few anions called ligands as in a crystal of glass the interaction of the electric fields causes
a small splitting of the energy levels. The magnitude of this splitting is a function of the field strength
number and geometric arrangement of the cation. The number of different levels formed is a
function of the electronic configuration and coordination number of the cation. Since the energy differences
which commonly result for 3d transition metal ions from ligand fields are in the range of 1-3 eV the
absorption of photons by electronic transitions between split 3d levels results in visible coloration.
Similar arguments apply to the 4f electronic levels of the rare earth ions where splitting of the 4f levels also
produces absorption bands in the visible. Differences in the nature of the 3d and 4f ions result in less
intense absorptions for the rare earth ions as well as more complex spectra which are due to the greater
number of possible configurations of the seven 4f levels compared to the five 3d levels of the transition
metal ions.

All of these electronic transitions are technically forbidden by Laporte's rule which states that electronic
transitions can only occur if the orbital angular momentum changes during the transitions. Since this does
not occur for transitions from one d state to another d state or from one f state to another f state no
absorption should occur for these ions. Fortunately Laporte's rule is relaxed in solids due to the lack of
perfect spherical symmetry which results from the presence of a limited number of point sources so that
electronic transitions can occur with a low probability between 3d or 4f levels which are split by the fields of
the neighbouring ligands. The low probability of these transitions however does reduce the intensity of the
absorption. As a result ligand field induced transitions are much weaker than the charge transfer effects which occur in the ultraviolet.

Since the coloration of glasses by transition metal and rare earth ions results from ligand field effects several general trends can be predicted. First a change in oxidation state results in a change in the number of 3d or 4f electrons resulting in a different number of possible electronic transitions for otherwise identical conditions. Since each possible electronic transition represents absorption with a different energy a difference in oxidation state will result in a different absorption spectrum.

Most 3d transition metal ions are found in either octahedral or tetrahedral coordination in oxide glasses. A change in coordination number will result in a difference in splitting energy and depending upon the number of 3d electrons present possibly a change in the number and relative positions of the potential electronic transitions.

Changes in the identity of the anions results in a change in their ligand field strength and thus a shift in the positions of the absorption bands with no change in their number or relative positions. For example the substitution of a small amount of NaCl of Na2O in a sodium borate glass containing cobalt oxide can cause the color due to CO2 ions to change from a dark blue purple to lighter blue green due to a small shift in the absorption band positions to longer wavelengths. Addition of a small amount of NaBr can result in a green glass while additions of Nal can yield a red brown glass. The CO2 ions must preferentially associate with the small number of halide ions since the color of the glass is actually due to a very small concentration of the transition metal ions.

The color is also altered by changes in concentration of the coloring cation in the identity of the network former and in the identity and concentration of the modifiers present. The effect of the concentration of the coloring ion is obvious more chromophores or coloring species result in more absorption. The effects of changes in the network former and the modifier ions present are due to alterations in bond distance and bond strength between the coloring ions and the surrounding ligands. Replacement of a small diameter modifier ion by a larger one can also occasionally cause a change in the most favorable coordination number for the coloring ion.

Details of the coloration of glasses due to ligand field effects are further complicated by the possibility of redox interactions between two or more different transition metal ions. Other elements such as arsenic and antimony which do not directly affect color may alter the oxidation state of a coloring ion and alter the color of the glass. Changes in furnace atmosphere can also inadvertently alter the oxidation state of coloring ions due to changes in the concentrations of O2, CO, CO2, and H2O vapor.

Amber Glass

Many glass containers have a brownish color popularly called beer bottle brown. This particular color occurs in glasses containing both iron and sulfur. Carbon is usually added to the batch to provide a reducing agent to insure the presence of sulfide ions. One model suggests that the coloration is due to an iron (iii) ion in tetrahedral coordination with three O2 and one S2ions. The actual absorption is due to a charge transfer process.

Control of amber browns in commercial glasses in quite difficult. The coloring agent or chromophore contains both an oxidized form of iron and a reduced form of sulphur. These forms can only co exist in a melt in a narrow range of oxygen partial pressures. Since the intensity of the color will vary with oxygen partial pressure reproducibility of the color is difficult. The oxygen partial pressure is usually controlled by varying the amount of carbon added to the melt or by controlling the redox of the combustion process.

Replacement of sulfur by selenium changes the color from brown to black.

Colloidal Metal Colors

The red color produced in many glasses containing gold known as gold ruby glasses is due to the presence of very fine colloidal gold particles. The color is not due to light scattering but rather to absorption by the
particles which cause an intense optical absorption band at about 530 nm. Doremus has calculated the shape and position of this band by assuming that the particles are spherical and using the optical properties of gold. He suggests that this band can be considered as a plasma resonance band where the free electrons in the particles are treated as bounded plasma. A similar absorption band attributed to an identical mechanism at 410 nm is obtained for glasses containing colloidal silver. The shift in band position results in a strong yellow coloration which is called silver yellow or silver stain.

A somewhat less esthetically pleasing red color can be produced in glasses containing copper. The absorption band due to copper occurs at 565 nm for these glasses and is similar in shape to those for gold and silver. While the red color of these glasses is usually attributed to copper colloids others have proposed that the color is due to colloidal crystals of Cu2O. Since both metallic copper and Cu2O are often found in copper ruby glasses it is possible that the color arises from a combination of these species. Although the solubility of both gold and silver in silicate glasses limits the concentration of colloids which can be formed the much higher solubility of copper permits the formation of a very large number of colloids. If the density of colloids is sufficiently high the glass will be opaque rather than transparent.

A number of other colloidal species including but not limited to Pb As Sb Bi Sn and Ge can be formed in glasses. The properties of the metals are such that these colloids result in brown black or gray colorations. Colloids are usually formed by producing the glass with the metal in the ionic form and subsequently reducing the ions to form atoms. These atoms diffuse through the glass until they encounter other such atoms. The atoms then agglomerate to form nuclei which grow to form the final colloids. Reduction can result from a redox reaction with other components of the glass or by reaction with an external reducing agent such as H2. Many ruby glasses contain SnO2 which provides an internal reducing agent. This reaction which is called striking occurs spontaneously upon reheating an originally colorless glass to the correct temperature. As similar process can be used to produce glasses colored by silver or copper. The color is distributed uniformly throughout the glass.

Reduction by an external agent will occur if glasses containing gold silver or copper ions are exposed to H2 gas at temperatures near the glass transformation range. Since reduction will occur in the near surface region and grow into the glass the color will occur in a layer at the glass surface. The thickness of this layer increases with the square root of time indicating that hydrogen diffusion is important in controlling the coloration process. Although formation of colloids of other metals is difficult by use of an internal reducing agent formation of a surface layer containing Pb As Sb and Bi colloids is quite easy using an external reducing agent such as hydrogen gas.

Silver colloids can also be formed in the surface region of a glass by interdiffusion of silver from an external source with sodium or other alkali ions in the glass. The silver can be supplied from either metallic silver films or from molten silver salts. Since the exchange process requires that the silver be present as ions metallic films must be heated in air or other sources of oxygen to temperatures above 150ºC to form Ag2O. Use of metallic films allows the production of complex images in the surface of the glass by sputtering the film through a mask. After ion exchange is completed the glass is exposed to hydrogen to reduce the silver and create the colloids.

Silver colloids will form spontaneously if silver films on float glass are heated in air to temperatures above 300ºC. The process involves ion exchange between the silver ions and sodium ions from the glass followed immediately by reduction of the silver by tin (II) ions in the glass surface. The tin (II) ions are present due to diffusion into the glass from the molten tin bath used in producing float glass. This reaction is highly specific to the tin surface of float glass and only occurs within the outer few micrometers of the glass surface.

Colloidal Semiconductor Colors

A number of glasses ranging in color continuously from yellow to orange to red to black can be produced by doping the melt with various combinations of CdS CdSe and or CdTe. Similar glasses are produced using a
mixture of CdS and ZnS. The as cast glasses are colorless and must be heat treated at 550-700ºC to strike the color. The optical spectra of these glasses differ from those of the colloidal metal colored glasses with a sharp cutoff of transmission in the visible or near infrared instead of the absorption bands observed for glasses colored by gold silver or copper colloids. This cutoff in transmission is due to the formation of very small semi conducting crystals of various cadmium chalcogenides. The absorption of higher frequency light is due to absorption of all photons having energies greater than the band gap of the semiconductor. Since continuous solid solutions form it is possible to adjust this band gap over a wide range of energies giving rise to a variety of colors. It has also been shown that the color is dependent upon crystallite size with a shift toward the red with increasing crystal radius.

Radiation induced Colors

An extremely large number of optical defects can be formed in glass by exposure to high energy radiation. These defects consist of trapped electrons or holes either at pre existing sites in the glass or at sites created by the bond breaking action of the radiation. Most of these defects give rise to absorption bands in the ultraviolet region of the spectrum and hence do not cause visible coloration of the glass. In general the optical absorption results from electronic states in the gap between the valence and conduction bands. Photons induce transitions between the valence band and the defect levels or from the defect levels to the conduction band. Since a number of defects are often simultaneously produced by the radiation multiple overlapping absorption bands usually occur producing complex optical absorption spectra. Although vitreous silica usually remains colorless following irradiation to very high doses doped silicas can become colored through the formation of defects associated with impurities. Purple samples for example are formed if the glass contains a small amount of aluminum due to the formation of aluminum oxygen hole centers (AlOHC). Other impurities such as germanium or titanium can also produce colored vitreous silica by formation of defect centers.

Most common silicate glasses become colored after irradiation. The color is due to formation of many defects especially hole centers associated with the non bridging oxygens present in glasses containing alkali or alkaline earth oxides.

These optical absorptions can be bleached or thermally annealed by heating to sufficiently high temperatures. The thermal stability of the defects differs widely so that the elimination of one defect may occur at room temperature while the elimination of another requires heating to near the glass transformation temperature of the glass.

Solarization

Coloration of glasses by exposure to sunlight is known as solarization. Although some of the defects produced by higher energy radiation can also be produced by ultraviolet radiation the classic solarization of glasses is due to a radiation induced change in the valence of manganese.

Many years ago manganese was frequently added to glasses to serve as a decolorizer for iron induced optical absorption. Since this practice is no longer common modern glasses do not produce the deep purple color characteristic of Mn3+ ions after long term exposure to sunlight. While less common other pairs of ions including Mn As Fe As and several couples involving cerium can also produce optical absorption changes due to solarization. Solarization of modern glasses usually produces brown shades similar to those produced by higher energy irradiation.

Infrared Absorption

Absorption of light in the ultraviolet and visible regions of the spectrum is due to electronic transitions. While there are some lower energy electronic transitions in the infrared region of the spectrum most optical absorption in this region in glasses are due to vibrational transitions. This absorption can be divided into three categories impurity absorption due to gases or bound hydrogen isotopes the infrared
cutoff or multiphonon edge and the fundamental structural vibrations.

Infrared Absorption by Bound Hydrogen Species

Virtually all oxide glasses contain hydroxyl in various forms while other molecular species may or may not be present. The primary absorption band due to Si OH bonds occurs at 2730 µm for vitreous silica. Other bands due to hydroxyl arise from the combination of the Si OH frequencies with fundamental Si O vibrations. These overtone and combination bands are relatively weak and are not of much importance for thin samples. However when one forms an extremely long (km) optical fiber from vitreous silica these bands become significant and must be eliminated to reduce optical losses to levels acceptable for telecommunication systems. Many millions of dollars have been invested in the research leading to the effective elimination of these very weak infrared absorption bands.

Replacement of hydrogen by deuterium of tritium causes all of these bands to shift toward the infrared as predicted by Equation 11. Replacement of Si4+ by B3+ Ge4 Al3 or other ions also results in shifts of the band positions with a larger shift due to germanium than due to the other elements.

Addition of alkali oxide to silica results in the formation of new bands due to hydroxyl as well as a shift in the position of the fundamental band toward the infrared. Hydroxyl bands are found at 2.75 2.95 3.35 3.85 and 4.25 µm for common sodium silicate and soda lime silica glasses. The two bands at longer wavelengths are attributed to hydroxyl groups which are hydrogen bonded to neighbouring non bridging oxygens at two different distances. Replacement of alkali oxides by alumina which eliminates the non bridging oxygens from the structure results in the elimination of the two bands attributed to hydrogen bonded hydroxyls. The hydroxyl spectra of alkali borosilicate glasses which are often phase separated with silica rich and alkali borate rich regions are also very different from those of glasses containing large quantities of non bridging oxygens.

Glasses can also contain bound hydrogen in the form of Si H B H and similar units. The fundamental vibration for Si H occurs at 4.44 µm for vitreous silica. The absorption band is much sharper than those due to hydroxyl. These groups are usually found in glasses which have been melted under a hydrogen atmosphere or which have been irradiated in the presence of H2 gas. In both cases the hydride groups can be removed by thermal treatment in air or vacuum at temperatures below the glass transformation range. Hydroxyl can be formed in glasses by many methods. The most common form of hydroxyl of course stems from melting in the presence of water vapor and thus occurs for most commercial and laboratory melts.

Formation of hydroxyl by reaction with water vapour can be described by the reaction.

The hydroxyl and hydride groups formed by these reactions are less stable than those formed by reaction with water molecules and can usually be removed at lower temperatures. The reaction described by Equation 14 can be driven either thermally during melting or by irradiation at room temperature of glasses containing dissolved hydrogen. The thermal stability of the species formed is quite different with a much lower temperature required for removal of the hydroxyl and hydride formed during irradiation.

Exposure of irradiated glasses of hydrogen gas after irradiation can also result in hydroxyl and hydride formation by reaction of H2 molecules diffusing into the glass with radiation induced defects. As a result the defects are eliminated the glass becomes colorless and the infrared transmission is reduced. If the glass contains dissolved hydrogen during irradiation no defects will be found after irradiation. This process known as chemical annealing can be used to eliminate optical defects in the ultraviolet and visible region for many glasses. Replacement of hydrogen with deuterium results in the formation of deuteroxyl instead of hydroxyl. In addition the pre existing hydroxyls in the glass will isotope exchange with the deuterium and become deuteroxyls.

Infrared Absorption by Dissolved Gases

Diatomic molecules containing only one element (H2 O2 N2 etc.) do not absorb infrared radiation in the free gaseous state. It has been found however that hydrogen molecule dissolved in glasses cause a very weak
infrared absorption band in silicate glasses in the region of 2.41 µm. This band which is relatively symmetric and narrow for an infrared band of glasses varies only slightly in position with glass composition for silicate glasses.

Dissolved carbon dioxide also causes an infrared absorption band in glasses. A narrow absorption band due to dissolved CO2 molecules is found at 4.26 µm in sodium aluminosilicate and heavy metal fluoride glasses. Bands due to carbonate species formed by reaction of carbon dioxide with oxide melts have also been reported.

Infrared Cutoffs or the Multiphonon Edge
The infrared cutoff or multiphonon edge of glasses is caused by the combinations and overtones of the fundamental infrared vibrations between the cations and anions which make up the glass structure. These extremely intense absorption bands prevent the practical application of glasses for transformation of light at longer wavelengths. The position of this edge is controlled by the strength of the bond between the atoms in the glass and the mass of those atoms. Traditional oxide glasses for infrared transmission are based on either germanate or calcium aluminate compositions which transmit to 6 µm. Recently the discovery of lead gallate and lead bismuth gallate glasses has extended the edge position for the best oxide glasses to 8 µm. The elimination of oxygen as in the heavy metal fluoride and chalcogenide glasses permits the formation of glasses which transmit further into the infrared. Fluoride glasses typically have cutoff wavelengths in the range of 6 8 µm. Unfortunately the glasses based on Br and I have such weak bonding that their physical and chemical properties are quite poor preventing widespread application to date.

Mechanical Properties
Introduction
Glasses are brittle materials. As a result their fracture behavior is usually determined by environmental factors and not by the inherent strength of the bonds forming the vitreous network. The fracture strength of glasses varies with prior surface treatment chemical environment and the method used to measure the strength. As brittle materials glasses are also quite susceptible to failure due to thermal shock.

Other mechanical properties of glasses are inherent to the material. The elastic modulus $E$ is determined by the individual bonds in the material and by the structure of the network. The hardness of glasses is a function of the strength of individual bonds and the density of packing of the atoms in the structure.

Elastic Modulus
As classic brittle materials glasses exhibit nearly perfect Hookian behavior on application of a stress. The ratio of the strain resulting from application of a stress is a constant which is known as the elastic modulus or young's modulus $E$ which is defined by the expression.

If a tensile stress is applied to a specimen in the direction of the x axis the specimen will elongate in that direction. This elongation will be accompanied by contraction in the y and z directions. The ratio of the transverse strain to the axial strain is called Poisson's ratio. Poisson’s ratio for oxide glasses generally lies between 0.2 and 0.3 although the value for vitreous silica is only 0.17. The shear modulus $G$ which relates shear strain to shear stress is given by the expression.

Young's modulus the shear modulus and Poisson's ratio are related by the expression.

The elastic modulus of a material arises from the relation between an applied force and the resultant change in the average separation distance of the atoms which form the structure of that material. If we consider the Condon Morse curve for force $F$ as a function of atomic separation distance $r$ we can write an expression of the form.

The simple model based on the Condon Morse curve applies quite well to highly ionic close packed structures. If we consider the structure of glasses we find that the modulus is also influenced by the
dimensionality and connectivity of the structure with a trend toward increasing elastic moduli as the structure changes from a chain structure to a layered structure to a fully connected three dimensional network. Weak bonds between chains or layers effectively offset the influence of the strong bonds between atoms within the building blocks of the structure and allow easier distortion of the structure. The presence of breaks in the linkage within a structure e.g. non bridging oxygens also allows easier displacement of atoms and reduces the elastic modulus. Replacement of modifier ions by aluminum ions which reduce the non bridging oxygen concentration and increases the connectivity of the network also increases the elastic modulus of silicate glasses. The highest elastic moduli for oxide glasses are found in glasses such as the rare earth or yttrium aluminosilicates which feature strong bonds and high packing densities. Nitriding of these glasses which provides three coordinated nitrogen linkages between tetrahedra further increases the elastic modulus with very high values found for glasses in SIALON (silicon aluminum oxynitride) systems. Values for the elastic modulus of inorganic glasses typically range for 10 to 200 Gpa.

Since the elastic modulus of glasses is related to bond strength it is not surprising to find that glasses with high glass transformation temperatures usually also have high moduli. Furthermore where it was shown that the thermal expansion coefficient is also explained using a Condon Morse diagram it should not be too surprising to learn that low expansion glasses often have high elastic moduli.

Hardness
The hardness of glasses is usually defined in terms of either the scratch hardness using the Mohs scale or indentation hardness using a Vickers indenter. Oxide glasses lie in the range of 5 to 7 on Mohs scale i.e. they will scratch apatite (hardness of 5) but will not scratch crystalline quartz (hardness of 7). The Vickers hardness of oxide glasses ranges from 2 to 8 GPA with values of over 11 Gpa for nitrided glasses. These values are much lower than the Vickers hardness of diamond which is 100 Gpa. Borate germanate and phosphate glasses are typically softer than silicate glasses. Chalcogenide glasses are much softer with Vickers hardness values in the range of 0.3 Gpa for vitreous selenium to just over 2.0 Gpa for the three dimensional structures found for Ge As S glasses. In general the effects of glass composition on hardness parallel those found for elastic modulus.

Fracture Strength
The fracture strengths of glasses are usually far less than their theoretical strengths. Fracture strength can only be described in terms of a distribution function and does not exhibit a single value characteristic of a given glass composition. The reduction in strength is attributed to surface flaws which severely weaken the glass.

Theoretical Strength of Glasses
The theoretical strength of a material is given by the force which must be applied to overcome the maximum restorative force predicted by equation 4. Once the interatomic separation distance exceeds the distance corresponding to the maximum restorative force continued application of force will extend the bond distance until the bond is broken and a crack can propagate through the material. Orowan proposed that the stress necessary to break a bond is determined by the energy necessary to create two new surfaces due to the fracture. The Orowan stress \( \sigma \) is given by the expression.

Practical Strengths of Glasses
The strengths calculated using Equation 6 are orders of magnitude greater than those found in practical applications of bulk glasses. This reduction of strength is attributed to the presence of flaws in the surface of the glass. These flaws act as stress concentrators increasing the local stresses to levels exceeding the theoretical strength and causing fracture of the glass. Griffith treated this problem in detail and derived the expression.

Where \( f \) is the failure stress and \( c \) is the critical crack length for crack growth. Attainment of the critical crack length is only a necessary condition for crack growth. It is also necessary for the stress at the crack tip of
exceed the theoretical strength of the material before the crack will grow spontaneously. Since Griffith flaws typically have curvatures approaching atomic dimensions at their tips Orowan argues that any applied stress sufficient to exceed the Griffith criterion will also exceed the theoretical strength of the material and that the Griffith criterion is usually sufficient to cause fracture. We have already argued that the elastic modulus and the fracture surface energy are relatively small functions of glass composition. Flaws which are introduced by external factors are not intrinsic to the material. Flaw lengths are determined by prior treatment of the surface and can vary over several orders of magnitude. It follows that the inherent strength of a glass is usually of little importance in determining the practical strength. The hardness of a glass can influence the practical strength through its influence on the resistance to flaw formation i.e. scratch resistance.

Flaw Sources and Removal

How are the critical or Griffith flaws introduced into glasses? Obviously contact with any material which is harder than the glass can cause a flaw. Abrasion with hard material thus degrades the strength of a glass. Actually contact with another piece to the same glass or with metal objects used to handle the glass is sufficient to generate flaws. Chemical attack can also generate flaws. Touching a glass with a fingertip will generate flaws through the attack on the surface due to the NaCl deposited from the skin. Thermal stresses induced during rapid cooling of a glass introduce flaws though thermal shock. Heating glasses for prolonged times has also been shown to reduce their strength by formation of a small number of surface crystals or by bonding of dust particles to the glass surface. In either case a thermal expansion mismatch creates local flaws during cooling.

Protection of glass surfaces against flaw formation is very difficult. The surface of a freshly produced glass has a very high coefficient of friction for contact against other materials. Flaw generation can be reduced if a lubricant is applied to the fresh glass surface before any flaws are formed. Lubricating coatings are often applied to the surfaces of glass containers just after they exit from the annealing lehr. This coating must be resistant to wear since any contact which penetrates the coating will result in flaw formation on the underlying glass.

Flaws can be removed by removing the outer surface of the material by chemical etching or mechanical polishing. Etching blunts the flaw tip and reduces the flaw length while polishing simply reduces the length of the flaw to below the Griffith criterion. Flame polishing removes flaws through viscous flow in the near surface region.

Strengthening of Glass

The strength of glasses can be increased by two methods. First we can prevent the formation of flaws and remove those which do form. Removal of flaws is only effective for short times since new flaws are readily formed while preventing their formation by use of coatings has proven to be of limited value. If we accept the fact that flaws will be present we must concentrate on the prevention of crack growth. Since crack growth requires the presence of a tensile stress at the flaw tip creation of a near surface compression region should prevent crack growth. No growth will occur until the applied stress is large enough to overcome the residual compressive stress and produces a tensile stress at the crack tip.

Compressive surfaces can be produced by ion exchange thermal tempering or by application or formation of a compressive coating. Thermal tempering involves the formation of a compressive layer by rapidly cooling a glass from at or above the upper limit of the glass transformation range. Since the interior of the glass will cool more slowly than the surface the fictive temperature of the interior will be lower than that of the surface and the equilibrium density will be greater than that of the surface region. Since the interior and surface regions are bonded together elastic strains must arise to counter the difference in equilibrium densities. The surface region is placed in compression while the interior is placed in tension. The difference in fictive temperature is a function of the difference in cooling rate between the interior and surfaces of the
glass so that the magnitude of the compressive stress increases with increasing cooling rate and glass thickness. Consideration of the volume/temperature diagram for glasses reveals that the compressive stress also increases with the thermal expansion coefficient of the glass and with the difference between the thermal expansion coefficients of the glass and the super cooled liquid. It follows that thermal tempering is not very efficient for very thin wall containers or fibers because only a small difference in cooling rate occurs or for low expansion glasses such as vitreous silica or many commercial borosilicate glasses where the volume difference as a function of fictive temperature difference is small.

A compressive surface layer can be formed if a thin layer of material having a lower thermal expansion coefficient than the bulk glass can be created. Cooling the composite will create a compressive surface layer with a balancing tension region in the bulk glass. Application of a glaze can be carried out by fusing a thin sheet of a glass with a lower glass transformation temperature to the surface of a bulk glass or by more traditional glazing methods involving application of a low melting glass frit.

A variation of the ion exchange method using an ion which is smaller than that initially present in the glass can also produce a surface region of lower thermal expansion coefficient. If for example exchange of sodium from the glass with lithium from a bath occurs at temperatures above the $T_g$ of the glass relaxation will occur and chemical stuffing stresses will not exist. Since the surface region now consists of a glass containing lithium rather than sodium the thermal expansion coefficient will usually be reduced in this region. Cooling the glass will force the lower expansion glass into compression while the bulk glass is placed in tension.

The exchange of lithium for sodium offers another route to strengthening of glasses by formation of a surface crystallized region. If the glass is an alkali aluminosilicate it may be possible to crystallize only the exchanged region forming a very low thermal expansion coefficient phase such as virgilite or spodumene. Cooling the material will place the crystallized region in compression and the substrate glass in tension. Formation of a region which can be crystallized may also be possible after ion implantation of magnesium ions or by exchange of silver for sodium to form a region with a high nucleation density where crystallization will occur more readily than in the bulk glass.

Low expansion surface regions can be obtained by removal of alkali ions from the surface region of alkali alkaline earth silicate glasses. Exposure to SO2 vapor which is often carried out to improve chemical durability leaches alkali ions from the surface producing a silica rich near surface region. The reduction in alkali concentration reduces the thermal expansion coefficient and produces a compressive layer after cooling the glass.

Many other methods of strengthening are based on formation of composites by inclusion of fibers or whiskers or by crystallization to form glass ceramics. Phase separation may also affect the strength by altering crack propagation mechanisms. Transformation toughening has also been attained by formation of a small concentration of zirconia crystals in glasses.

Statistical Nature of Fracture of Glass

Since the fracture strength of glass is usually controlled by the nature and concentration of the flaws present in the surface it is not surprising to find a wide variation in measured strengths for a set of supposedly identical samples. Furthermore since the propagation of a crack depends upon the simultaneous occurrence of a crack of sufficient length and a stress of sufficient magnitude the experimental method used to measure strength affects the outcome of the measurement. Use of a three point bend test for example yields more scatter in fracture strength data than does use of a four point bend test. Consideration of the stress distribution in a rod used in these tests reveals that the maximum stress in a three point bend test occurs at the point directly opposite the load point while the maximum stress in a four point bend test occurs over the region between the two load points. Since the area subjected to the maximum stress is much greater in the latter case the probability of a critical flaw for a given stress
occurring within the region of maximum stress is much greater. Experimental results of failure stress studies can often be represented by a \textit{Gaussian distribution}. According to Doremus the probability $P$ of finding a sample with a failure stress $S$ is given by the expression.

A second distribution function called the \textit{Weibull distribution} is often used to describe fracture strengths. In this case the fraction $F$ of samples which fail at stresses below $S$ is given by the expression. For convenience is plotting data the Weibull distribution expression given by equation 9 is often converted to the form. The data are then plotted as $\log [\ln (1 - f)]$ versus the load required for failure and the values of $m$ and $\rho$ determined from a least squares fit of the data. A plot of data in this form is called a \textit{Weibull plot}.

\subsection*{Fatigue of Glasses}

The strength of glasses usually decreases with time under normal ambient conditions. This effect known as \textit{static fatigue} is due to interaction of the glass with the surrounding atmosphere resulting in crack growth under constant load. One also finds that higher failure strength is observed when the load is increased rapidly than when it is increased slowly. Since this effect is observed under conditions of changing load it is often called \textit{dynamic fatigue}.

Both static and dynamic fatigue disappears for samples tested at liquid nitrogen temperatures. Since fatigue effectively disappears below -100ºC the use of liquid nitrogen simply provides a convenient method for obtaining very low temperatures and is not of particular relevance in fatigue studies. At higher temperatures the time to failure for a given set of conditions decreases as the temperature increases. When tests are carried out at normal room temperatures the rate of fatigue increases with increasing humidity.

Fatigue of silicate glasses is generally attributed to the \textit{stress enhanced reaction} of water with the silicate lattice at the crack tip as expressed by the reaction.

This reaction between the silicate network and water molecules results in sharpening of the crack tip instead of lengthening of the crack. Since the reaction rate is essentially zero at very low temperatures no fatigue occurs for testing at liquid nitrogen temperature (196ºC). The increase in fatigue rate at higher temperatures is consistent with the increase in reaction rate expected with increasing temperature. Increases in humidity increase the fatigue rate by providing a higher concentration of reactant. Dynamic fatigue results reflect the requirement of sufficient time for the chemical reaction. If the load rate is increased rapidly a higher stress will be reached before sufficient chemical reaction occurs to cause failure.

The simple model offered here explains the gross fatigue behavior of glasses but does not explain some of the details of the process. Several other more complex models have been offered to explain fatigue of glasses. A model proposed by Michalske and Freiman addresses the actual mechanism of the chemical reaction. Their model successfully predicts static fatigue in the presence of other molecules such as ammonia while simultaneously explaining why fatigue does not occur in the presence of N2 or CO. Another proposed mechanism known as the \textit{chemical wedge} suggests that the reacting molecules do not actually reach the crack tip. Molecules entering the crack are drawn toward the tip by capillary action. The wedging action of these molecules increases the stress at the crack tip causing rupture of the Si-O-Si bonds.

\subsection*{Thermal Shock}

\textit{Thermal shock} is a serious problem wherever glasses are rapidly cooled over extended temperature ranges. A cooling rate gradient can lead to thermal tempering of glasses by producing different fictive temperatures in the surface and bulk of the glass. Unfortunately cooling with a temperature gradient in a glass also produces temporary stresses which counter the permanent stresses due to differences in fictive temperature. If we consider a glass plate held at the glass transformation temperature no stress will exist after some finite relaxation time and the fictive temperature will be $T_g$. If we were able to cool the surface of
this plate instantaneously to room temperature the volume in the surface region should shrink due to thermal contraction (the negative of thermal expansion during heating) to the room temperature value appropriate for a fictive temperature of \( T_g \). If the center of the plate is still at the glass transformation temperature however the local volume will be considerably greater than that of the surface. After thermal equilibration at room temperature the volumes of the surface and bulk should be approximately equal since their fictive temperatures are nearly equal because little change in fictive temperature will occur for a moderately slow cooling from \( T_g \). (Remember in tempering we cool from a temperature well above \( T_g \) so that regions of different fictive temperatures can be formed.) The sample should now be relatively free of stress i.e. any stresses occurring during cooling are temporary.

Although the stresses formed during cooling are temporary failure can occurs due to the high stress which occurs when the surface and bulk temperatures differ. The maximum possible stress will be generated if the surface is instantaneously cooled while the bulk is still at the original temperature.

In practical situations one is usually more interested in the maximum possible \( T \) which can exist without failure of the glass. By rearranging Equation 13 we can write the expression. Examination of Equation 13 reveals that the temporary stress which occurs during rapid cooling for a given temperature differential increases with increasing thermal expansion coefficient and elastic modulus. The best thermal shock resistance is thus found for low expansion low modulus glasses. The maximum temperature differential which can be used without sample failure will be very high for a very low thermal expansion glass such as vitreous silica. On the other hand even high thermal expansion glasses such as vitreous boric oxide may not be susceptible to thermal shock failure if their glass transformation temperatures are very low. (As a first approximation we can assume that no stress will occur above \( T_g \) since the relaxation time will be very short at higher temperatures. This assumption becomes less valid as the cooling rate increases.)

In reality an instantaneous cooling rate cannot be obtained for a sample of finite size. If we consider the case of a plate cooled at a constant rate in \( k \) sec \(^{-1} \) we will still generate a parabolic thermal gradient through the thickness of the plate.

### 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 is separated by a distance \( d \) the viscosity \( h \) is given by the expression.
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 poise and given the symbol 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 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.

The viscosity of a typical melt under conditions where fining and homogeneity can be obtained in a reasonable time is termed the *melting temperature*. Since this temperature is not truly a melting point in the classic sense but rather simply a processing temperature the term *practical melting temperature* should be used to distinguish between the true melting points of crystals and a reference viscosity which is based entirely on pragmatic considerations.

Formation of 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 103 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 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 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 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 1012 or 1012.4 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* (1013.5 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 1011.3 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. 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 108 to 109 Pa s.

**Viscoelasticity**

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 the 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 1013 to 108 Pa s. The most common basic model for viscoelasticity known as the *Maxwell model* is shown in Figure 2. The sample is considered to consist of an elastic element represented by the spring in series with a viscous flow element represented by the piston in a cylinder filled with viscous liquid. Since the piston/cylinder arrangement is known as a dashpot models based on these two elements are frequently called spring and dashpot models. The combined spring in series with a dashpot arrangement is known as a *Maxwell element*.

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.

If we assume that the modulus is essentially temperature independent we can ascribe the temperature dependence of to the temperature dependence of the viscosity. Assuming a typical room temperature value of $G$ of 1011 N m$^{-2}$ the value of at a viscosity of 1012 Pa s is 10 seconds. Relaxation of approximately 95%
of the initial stress occurs by a time of 3 or 30 seconds. It follows that relaxation at temperatures in the glass transformation range would be expected to occur over times ranging from hours to seconds as the viscosity decreases with increasing temperature. Since most experimental measurements of Tg involve heating specimens at rates of 3 to 20 k min\(^{-1}\) (0.05 to 0.33 K s\(^{-1}\)) we expect that these measurements will indicate relaxation processes occurring on similar time scales and that Tg values will represent viscosities of 10\(^{11}\) to 10\(^{12}\) Pa s.

The simple Maxwell model is useful for order of magnitude calculations of relaxation times but does not adequately represent the behavior of actual glass forming melts. Better models can be obtained by including Voigt kelvin elements which consist of a spring and dashpot in parallel or by coupling a number of Maxwell elements in parallel. A Maxwell element in series with a Voigt Kelvin element (known as a Burger element) may be a better model for actual materials in the glass transformation range. A Burger element actually contains more than one relaxation time. Actual glasses may be best described by multiple Maxwell and Voigt Kelvin elements so that a spectrum of relaxation times occurs.

**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.

**Rotation Viscometers**

Rotation viscometers are commonly used at room temperature to measure the viscosity of a wide variety of liquids in the range 1 \(10^4\) Pa s. Use of these viscometers at temperatures up to 1600ºC 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 (103.5 \(10^6\) Pa s) or by measuring the torque required to twist the spindle through a small angle (104.5 \(10^9\) Pa s). This method requires use of a few hundred grams of glass to provide a sufficient melt size for reliable measurements.

**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.

**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 105 to 1012 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.

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. The large surface to volume ratio of the fiber also frequently results in compositional changes at the fiber surface either by reaction with atmospheric gases or by evaporation of melt components.
 Beam bending Viscometers
Transformation range viscosities (10^8–10^{13} \text{ 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 three point bending configuration with a load $M$ applied at the center of the beam. The viscosity is given by the expression.
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 $1 \times 1 \times 10 \text{ mm}$ which allows measurements on compositions which can only be formed as glasses by rapid quenching.

Other Viscometers
A number of other methods are occasionally used for viscosity measurements. The most common are the parallel plate viscometer used in the $10^5–10^8 \text{ Pa s}$ range the penetration viscometer used in the $10^8–10^{12} \text{ Pa s}$ range and the torsion viscometer used in the $10^{11}–10^{14} \text{ Pa s}$ range. Although each of these methods has advantages under specific conditions none has gained wide acceptance in the glass community.

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 glassforming 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.

A relatively good fit to viscosity data over the entire viscosity range is provided by a modification of Equation 8 which effectively includes 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 $T_0$ to the Arrhenian expression to account for the variability of the activation energy for viscous flow and replaces the $H$ with a less defined variable $B$ as indicated by the expression.

While the VFT equation provides a good fit to viscosity data over a wide temperature range it should be used with caution for temperatures at the lower end of the transformation region where $H$ becomes constant. The VFT equation always overestimates the viscosity in this temperature regime.
The degree of curvature of viscosity/temperature plots can vary over a wide range due to variations in the value of $T_0$ relative to $T_g$. If $T_0$ is equal to zero the viscosity, temperature curve will exhibit Arrhenian behavior over the entire viscosity region from very fluid liquid to the transformation range with a single value for $H$. On the other hand as $T_0$ approaches $T_g$ the curvature will increase and the difference between $H$ for the fluid melt and in the transformation region will become very large.

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 glassforming 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 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 this diagram range from very strong to quite fragile with curves for intermediate fragility labeled as moderately strong or somewhat fragile (no terminology has been established for intermediate fragilities). The fragility of a melt can be characterized by consideration of the slope of the viscosity, temperature curve at $T_g$ i.e. by dividing H in the transformation temperature region by $T_g$ in K to obtain the reduced activation energy for viscous flow. A fragility index which is equal to the reduced activation energy divided by 2.303 times $R$ where $R$ is the gas constant has also been proposed for ranking of melts in order of increasing fragility.

Free Volume Model for Viscous Flow

The temperature dependence of the viscosity can be treated as a function of the free volume of the melt structure. If we write a modified version of the VFT equation replacing the temperature terms with volume terms we obtain the expression

Structure of Glasses

Even though a majority of natural and manufactured solids are crystalline in nature materials which are not crystalline are of great importance for both traditional and newly developed ceramics. One important class is the liquid silicates the properties of which are an essential part of the ceramist’s knowledge in the formulation of glasses glazes and enamels. Solid glasses of which the silicates are the technologically most important group usually have a more complex structure than the liquids from which they are derived and recent studies indicate a complexity which is still not well understood although the broad structural characteristics seem reasonably clear. A more newly developed class of materials is thin films deposited as noncrystalline solids from the vapor phase about which even less is known as to structural details. In each of these classes of ceramic materials the short range order is preserved in the immediate vicinity of any selected atom that is the first coordination ring the longer range order characteristic of the ideal crystal is dissipated in a way characterized by diversity among different systems and by difficulty in precise description.

We focus our attention on glasses which are by far the most important group of inorganic noncrystalline solids. The structure of glasses may be considered on three scales (1) the scale of 2 to 10 Å or that of local atomic arrangements (2) the scale of 30 to a few thousand angstroms or that of submicrostructure and (3) the scale of microns to millimeters or more or that of microstructure and macrostructure. In this chapter we consider the atomic structure and the submicrostructure of glasses the consideration of microstructural features is deferred.

Glass Formation

Glasses are usually formed by solidification from the melt. The structure of glasses can be clearly distinguished from that of liquids since glass structure is effectively independent of temperature. This can best be seen by a plot of the specific volume of the crystal liquid and glass as a function of temperature. On cooling the liquid there is a discontinuous change in volume at the melting point if the liquid crystallizes. However if no crystallization occurs the volume of the liquid decreases at about the same rate as above the melting point until there is a decrease in the expansion coefficient at a range of temperature called the glass transformation range. Below this temperature range the glass structure does not relax at the cooling rate used. The expansion coefficient for the glassy state is usually about the same as that for the crystalline solid. If slower cooling rates are used so that the time available for the structure to relax is increased the super cooled liquid persists to a lower temperature and a higher density glass results. Similarly by heating the glassy material in the annealing range in which slow relaxation can occur the glass structure in time
approaches an equilibrium density corresponding to the super cooled liquid at this temperature.

A concept useful in discussing the properties of glasses is the glass transition temperature $T_g$ which corresponds to the temperature of the intersection between the curve for the glassy state and that for the super cooled liquid. Different cooling rates corresponding to different relaxation times give rise to a different configuration in the glassy state equivalent to different points along the curve for the super cooled liquid. In the transition range the time for structural rearrangements is similar in magnitude to that of experimental observations. Consequently the configuration of the glass in this temperature range changes slowly with time toward the equilibrium structure. At somewhat higher temperatures the structure corresponding to equilibrium at any temperature is achieved very rapidly. At substantially lower temperatures the configuration of the glass remains sensibly stable over long periods of time.

In discussing the structural characteristics of glasses reference is often made to the structure of a particular glassy material. It should be noted however that any determination of glass structure is only meaningful within limits seen from the volume temperature relations shown in Fig. 1. As the liquid is cooled from a high temperature without crystallizing a region of temperature is reached in which a bend appears in the volume temperature relation. In this region the viscosity of the material has increased to a sufficiently high value typically about $10^{12}$ to $10^{13}$ Pa so that the sample exhibits solid like behavior. As shown in Fig. 1b the glass transition temperature increases with increasing cooling rate as do the specific volumes of the glasses which are formed. In the case shown the specific volume of the glass at temperature $T_o$ can be $V_1$ or $V_2$ or $V_3$ depending on which of the three cooling rates was used in forming the glass. The maximum difference in specific volume obtainable with variations in the cooling rate is typically in the range of a few percent only within this range can one speak of the structure of a glass without carefully specifying its mode of formation.

Noncrystalline solids can be formed in other ways besides cooling from the liquid state and their structure may differ significantly from glasses formed by the cooling of liquids. Among these alternative methods the most widely used and most effective method for materials which are difficult to form as noncrystalline solids is condensation from the vapor onto a cold substrate. When a vapor stream formed by electron beam evaporation sputtering or thermal evaporation impinges on the cold substrate thermal energy is extracted from the atoms before they can migrate to their lowest free energy configuration (the crystalline state.). Another method of forming glasses is by electrode position Ta2O5 Ge and certain Ni P alloys are among the materials which have been prepared in this way. Noncrystalline solids can also be formed by chemical reactions. Silica gel for example can be manufactured from ethyl silicate by the reaction.

In this reaction the SiO2 resulting from the condensation of the silicic acid is noncrystalline. A similar silica gel can be formed by the reaction of sodium silicate with acid. These reactions are particularly effective in the case of hydrogen bonded structures in aqueous media. For example the reaction forms a noncrystalline gel in which hydrogen bonding predominates. Like silica gel it makes good inorganic cement.

On the scale of atomic structure the distinguishing structural characteristic of glasses like the liquids from which many are derived is the absence of atomic periodicity or long range order. Such a lack of periodicity does not however imply the absence of short range order on a scale of a few angstroms. The short range order which characterizes a particular glass or liquid may be described in terms of an atom centered coordinate system and is frequently represented in terms of radial distribution functions.

The radial distribution function (R) is defined as the atom density in a spherical shell of radius R from the center of a selected atom in the liquid or glass. The radial distribution function for a Ge glass determined from X ray diffraction studies is shown in Fig. 2. As shown there modulations in the radial density of atoms are observed for interatomic separations of the order of a few angstroms for large distances the observed atom density approaches the average value $p_0$. The approach of the actual radial density function to the average atom density at large distances reflects the absence of structure on such a scale. Hence a precise description can be given to the scale on which short range order is observed that is the scale on which
significant modulations are seen in the radial density function the scale of a few angstroms. Models of Glass Structure

A number of models have been suggested to describe the structure of glasses. **Crystallite Model.** X-ray diffraction patterns from glasses generally exhibit broad peaks centered in the range in which strong peaks are also seen in the diffraction patterns of the corresponding crystals. This is shown in Fig. 3 for the case of SiO₂. Such observations led to the suggestion that glasses are composed of assemblages of very small crystals termed crystallite with the observed breadth of the glass diffraction pattern resulting from particle size broadening. It is well established that measurable broadening of X-ray diffraction peaks occurs for particle sizes or grain sizes smaller than about 0.1 micron. The broadening increases linearly with decreasing particle size. This model was applied to both single component and multi-component glasses (in the latter case the structure was viewed as composed of crystallites of compositions corresponding to compounds in the particular system) but the model is not today supported in its original form for reasons discussed in the next section.

**Random Network Model.** According to this model glasses are viewed as three dimensional networks or arrays lacking symmetry and periodicity in which no unit of the structure is repeated at regular intervals. In the case of oxide glasses these networks are composed of oxygen polyhedra. Adopting the hypothesis that a glass should have an energy content similar to that of the corresponding crystal W.H. Zachariasen considered the conditions for constructing a random network such as shown in Fig. 4 and suggested four rules for the formation of an oxide glass:

1. Each oxygen ion should be linked to not more than two cations.
2. The coordination number of oxygen ions about the central cation must be small 4 or less.
3. Oxygen polyhedra share corners not edges or faces.
4. At least three corners of each polyhedron should be shared.

In practice the glass forming oxygen polyhedra are triangles and tetrahedra and cations forming such coordination polyhedra have been termed network formers. Alkali silicates form glasses easily and the alkali ions are supposed to occupy random positions distributed through the structure located to provide local charge neutrality as pictured in Fig. 5. Since their major function is viewed as providing additional oxygen ions which modify the network structure they are called network modifiers. Cations of higher valence and lower coordination number than the alkalis and alkaline earths may contribute in part to the network structure and are referred to as intermediates. In a general way the role of cations depends on valence and coordination number and the related value of single bond strength as illustrated in Table 1.

The random network model was originally proposed to account for glass formation as resulting from the similarity of structure and internal energy between crystalline and glassy oxides. Although this remains one factor to be considered we now believe that kinetic considerations preventing crystallization during cooling are more important. The model remains however as the best general picture of many silicate glasses and may readily be generalized as a random array model in which the structural elements are randomly arranged and in which no unit of the structure is repeated at regular intervals in three dimensions. In this form the model may be used to describe a variety of liquid and glass structures both oxide and nonoxide in which three dimensional networks is not possible.

**Other Structural Models.** Several other models have been suggested to represent the structures of glasses. One of these termed the pentagonal dodecahedron model views silicate glasses as composed of pentagonal rings of SiO₄ tetrahedra. From a given tetrahedron the rings extend in six directions to include the six edges and form twelve sided dodecahedral cavities. Because of their fivefold symmetry these dodecahedral cages cannot be extended in three dimensions without an accompanying strain which ultimately prevents maintenance of the silicon oxygen bonds. Although pentagonal rings of SiO₄ tetrahedra may indeed exist in the structure of glasses such as fused silica there is little reason to believe that the
structure is composed entirely of such elements. According to another model glasses are composed of micelles or paracrystals characterized by a degree of order intermediate between that of a perfect crystal and that of a random array. These paracrystalline grains may themselves be arranged in arrays with differing degrees of order. The degree of order in the grains should be large enough to discern their mutual misorientation in an electron microscope and small enough to avoid sharp Bragg reflections in X ray diffraction patterns. Although such models seem plausible the evidence for the existence of such structures at least in oxide glasses is marginal.

The Structure of Oxide Glasses

In discussing the structures of oxide glasses it should be emphasized that these structures are not known to anything like the confidence with which the crystal structures have been determined. Recent advances in experimental techniques and means of analyzing data have opened a new era of glass structure studies and the next decade should be marked by significant advances in our knowledge of such structure. Even the best experimental techniques are inadequate however for establishing any particular model as the structure of a given glass. Rather the results of structural investigations of glasses should be regarded as providing information with which any proposed structure must be consistent.

Silica. Early controversies between proponents of the crystallite and random network models of glass structure were generally decided in favor of the random network model based largely on the arguments advanced by B.E. Warren. From the width of the main broad diffraction peak in the glass diffraction pattern the crystallite size in the case of SiO$_2$ was estimated at about 7 to 8 Å. Since the size of a unit cell of cristobalite is also about 8 Å any crystallites would be only a single unit cell in extent and such structures seem at variance with the notion of a crystalline array. This remains a powerful argument even if the estimate of crystallite size were only accurate to within a factor of 2. Further in contrast to silica gel there is no marked small angle scattering from a sample of fused silica. This indicates that the structure of the glass is continuous and is not composed of discrete particles like the gel. Hence if crystallites of reasonable size are present there must be a continuous spatial network connecting them which has a density similar to that of the crystallites.

A more recent X ray diffraction study of fused silica was carried out with advanced experimental techniques and means of analyzing data. In this study the distribution of silicon oxygen silicon bond angles was determined. As shown in Fig. 6b these angles are distributed over a broad range from about 120 to about 180° centered about 145°. This range is much broader in the glass than in the corresponding distribution for crystalline cristobalite. In contrast the silicon oxygen and oxygen distances are nearly as uniform in the glass as in the corresponding crystal.

The essential randomness of the SiO$_2$ glass structure results then from a variation in the silicon silicon distances (the silicon oxygen silicon bond angles). Beyond this direct joining of the tetrahedra over a range of Si O Si angles the structure of fused silica seems to be completely random. X ray diffraction work by G.G. Wicks provides strong evidence for a random distribution of rotation angles of one tetrahedron with respect to another. That is there appears to be no pronounced preference in fused silica for edge to face sharing to tetrahedra which is often found in crystalline silicates.

The structure of fused silica seems then to be well described by a random network of SiO$_4$ tetrahedra with significant variability occurring in silicon oxygen silicon bond angles. Such a random network is however not necessarily uniform and local variations in density and structures are to be expected.

B$_2$O$_3$. X ray diffraction and nuclear magnetic resonance studies of glassy B$_2$O$_3$ indicate clearly that the structure is composed of BO$_3$ triangles. Less clearly defined is the way in which these triangles are linked together in the structure. A random network of triangles provides a poor representation of the diffraction data. A better description is provided by a model in which the triangles are linked in a boroxyl configuration. A still better representation of the data is obtained from a model based on a distorted version of the crystal
structure in which the triangles are linked in ribbons. The distortions are such as to destroy the essential symmetry of the crystal and the notion of discrete crystallites embedded in a matrix is not appropriate.

**Silicate Glasses.** The addition of alkali or alkaline earth oxides to SiO₂ increases the ratio of oxygen to silicon to a value greater than 2 and breaks up the three dimensional network with the formation of singly bonded oxygens which do not participate in the network. The structural units found in crystalline silicates are shown for different oxygen silicon ratios in Table 2. For reasons of local charge neutrality the modifying cations are located in the vicinity of the singly bonded oxygens. With divalent cations two singly bonded oxygens are required for each cation for univalent alkali ions only one such oxygen is required.

An X-ray diffraction study of a number of K₂O SiO₂ glasses by G.G. Wicks indicates systematic changes in the structure as the alkali oxides are added to SiO₂. The data seem to indicate a random network structure in which the alkali ions are distributed in pairs at random through the structure but located adjacent to singly bonded oxygens. In the case of a Ti₂O SiO₂ glass containing 29.4 mole % Ti₂O Blair and Milberg suggest clustering of the modifying cations with an average cluster diameter of about 20 Å.

It is sometimes convenient to describe the network character of silicate glasses in terms of the average number \( R \) of oxygen ions per network forming ion usually the oxygen silicon ratio. For example \( R=2 \) for SiO₂ for a glass containing 12 g atom% Na₂O 10 g atom% CaO and 78 g atom % SiO₂.

In the case of silicate glasses containing more alkali and alkaline earth oxides than Al₂O₃ the Al³⁺ is believed to occupy the centers of AlO₄ tetrahedra. Hence the addition of Al₂O₃ in such cases introduces only 1.5 oxygens per network forming cation and nonbridging oxygens of the structure are used up and converted to bridging oxygens. This is shown in Table 3 in which the values of \( X \), \( Y \) and \( R \) are given for a number of glass compositions.

The parameter \( Y \) gives the average number of bridges between the oxygen tetrahedra and their neighbors. For silicate glasses with \( Y \) values less than 2 no three dimensional network is possible since the tetrahedra have fewer than two oxygen ions in common with other tetrahedra. Chains of tetrahedra of various lengths are then expected as the characteristic structural feature.

In crystalline silicates the SiO₄ tetrahedra are found in a variety of configurations depending on the oxygen to silicon ratio as shown in Table 2. Such configurations may also occur in glasses of the corresponding compositions and mixtures of these configurations may occur in glasses of intermediate compositions. Occurrence in the crystalline phases indicates that these structural units represent low energy configurations. However since glasses are derived from supercooled liquids in which the greater entropy of more random arrays may be controlling the analogy between crystalline and glassy structural units should be pursued with caution.

For a variety of glazes and enamels it is typically found that the oxygen to network former ratio is in the range of 2.25 to 2.75 as shown in Table 4. Usually soda lime silica glasses have an oxygen to network former ratio of about 2.4. The compositions of these and other commercial glasses are shown in Table 5.

**Borate Glasses.** It has been established that the addition of alkali or alkaline earth oxides of B₂O₃ results in the formation of BO₄ tetrahedra. The variation of the fraction of four coordinated borons with the concentration of alkali oxide is shown in Fig. 9. The smooth curve shown in the figure represents the assumption that each of the oxygens added with the alkali ions converts two triangles to tetrahedra. Up to alkali oxide concentrations of about 30 mole % nearly all the modifier oxides have the effect of converting BO₃ triangles to BO₄ tetrahedra. Beyond this composition range the experimentally determined fractions of four coordinated borons depart significantly from the indicated curve and this suggests that singly bonded oxygens are produced in appreciable numbers. These singly bonded oxygens are presumably associated with BO₃ triangles rather than with BO₄ tetrahedra since the requirements for local charge compensation by the modifying cations is simpler in the case of the triangular arrangements.

**Germanate and Phosphate Glasses.** Glassy GeO₂ is composed of GeO₄ tetrahedra with a mean
germanium oxygen germanium bond angle of about 138°. The structural model of a random network of oxygen tetrahedra seems reasonable for this material. In contrast to fused silica however the distribution of intertetrahedral angles (Ge-O-Ge in this case) for vitreous germania is quite sharp. The essential randomness of glassy GeO2 apparently results from a random distribution of the rotation angles of one tetrahedron with respect to another and this represents a second mode of generating random tetrahedral networks (in addition to the mode based on the broad distribution of intertetrahedral angles). Measurements of physical properties such as density suggest that the addition of alkali oxide to GeO2 may result in the formation of GeO6 octahedra up to about 15 to 30 g atom% alkali oxide. For larger additions of alkali oxide a rapid return to tetrahedral configurations seems indicated presumably accompanied by the formation of singly bonded oxygens in large numbers. These structural changes remain however to be confirmed by diffraction studies.

Information on the structure of phosphate glasses has been determined largely from chromatographic studies. Like silicate and most germanate glasses phosphate glasses are composed of oxygen tetrahedra but unlike the silicate and germanate analogs a PO4 tetrahedron can be bonded to at most three other similar tetrahedra. The most familiar structural units in phosphate glasses are rings or chains of PO4 tetrahedra. The results of the chromatographic studies have elucidated the change in average length of chains as the P2O5 concentration of phosphate glasses is varied. With other additions such as alumina it is possible to simulate the characteristics of network based silicate or germanate glasses.

Submicrostructural Features of Glasses

For several decades after the pioneering work of Warren glasses were regarded as homogeneous materials and the conceptual picture of the random network was widely accepted as the best structural model for glasses. Despite this wide acceptance however it was known that several glass systems such as the alkaline earth silicates exhibited miscibility gaps in their phase diagrams and it was also known that heterogeneities provided the structural basis for the commercial Vycor process. In this process a glass containing about 75 wt% SiO2 20 wt% B2O3 and 5 wt% Na2O is melted formed into desired shapes and then heat treated in the range of 500 to 600° C. Such heat treatment results in the glass separating into two distinct phases one almost pure SiO2 and the other rich in Na2O and B2O3. On exposure to a suitable solvent at modest temperatures the latter phase may be leached out leaving a SiO2 rich framework containing a network of pores on a scale of 40 to 150 Å. Subsequent compaction at elevated temperatures (in the range of 900 to 1000°C) results in a transparent glass containing 96 wt % SiO2.

The introduction of electron microscopy as a tool for investigating materials revolutionized the field of glass structure when submicroscopic features on a scale of a few hundred Å were observed in many glasses using both replication and direct transmission electron microscopy. It has now been well established that submicro structures on a scale of 30 to a few hundred Å are characteristic of many glass systems. Such submicro structural features have been observed in silicate borate chalcogenide and fused salt glasses. These submicrostructures have been shown to result from a process of phase separation in which a liquid which is homogeneous at high temperatures separates into two or more liquid phases on cooling.

**Glass Technology**

In the current sense of the term glass is an inorganic product of melting which has been cooled to a rigid state without crystallizing. Melting is in fact the sole large scale industrial method of glass making. In the following chapters attention will therefore be paid to the melting process with special emphasis on the theoretical principles and general rules with references to literature concerned with details of a specific nature. Other glass making operations following the melting process will be dealt with in a similar way. The properties and practical applications of glass will be described briefly to provide a general picture of glass technology.
The literature dealing with the individual fields of glass making technology is extremely extensive and will be referred to in the individual chapters. There are relatively few monographs devoted to the technology of glass as a whole. Of the authors of older wide ranging monographs we should mention R. Dralle and E. Keppeler and of the more recent ones books by F.V. Tooley P. Beyerdorfer H. Salmang I.I. Kitaigorodskii P.J. Doyle are particularly noteworthy.

The Characteristics of Glass

Glass is an amorphous solid usually formed by the solidification of a melt without crystallization. Compared with crystals the structure of glass is devoid of regular arrangement of atoms in a periodic lattice. This basic difference between the structure of glasses and crystalline substances is well demonstrated on SiO2 which is known both in vitreous and crystalline states. In both instances the (SiO4) tetrahedra constitute the basic building unit in which the distance from the silicon atoms to oxygen atoms is 0.16 nm however according to X ray analysis at distances larger than 1 nm glass exhibits deviations from regular mutual arrangement of the tetrahedra characteristic for crystalline forms. At the same time the distances between Si and O atoms in vitreous SiO2 show some variation.

There exist a number of both inorganic and organic substances which form glass when cooled from the liquid state at a rate that does not provide conditions from the formation of a regular structural lattice. The number of compounds capable of forming glass can be increased by taking into account special preparation techniques. Extremely rapid quenching of very small particles can yield vitreous (amorphous) state of a number of further substances which are generally not considered to be glass forming. Only systems exhibiting a marked glass forming tendency under current conditions of cooling are of significance for usual practical purposes.

With some exceptions inorganic glasses finding practical application are not stoichiometric compounds but represent more complex systems with a variable ratio of components supplemented by substances that do not form glass by themselves. A very extensive variety of compositions can thus be obtained. According to the prevailing component silicate and borosilicate glasses constitute the largest groups among commercially produced glasses. Smaller amounts of fluoride phosphoric chalcogenidic (based on the system S Se Te) glasses are manufactured for special purposes.

Besides the amorphous structure both inorganic and organic glasses exhibit another characteristic property the so called transformation (glass transition). Transformation of glass may be demonstrated on the diagram of temperature dependence of some physical property for instance specific volume.

When proceeding from the liquid state with most current substances one encounters solidification and crystallization at the melting point simultaneously the volume decreases abruptly and becomes temperature dependent according to a relationship which differs from that of the liquid state. A liquid capable of readily forming glass does not undergo any such abrupt change at the melting point (or at the liquidus temperature). Below this temperature it behaves as an undercooled liquid and its specific volume then decreases continuously (the metastable equilibrium range). Only after attaining a viscosity of the order of 10 dPa s (i.e. after considerable undercooling when the substance passes from a plastic state to a rigid one) does there appear a distinct deflection on the temperature volume curve. Up to this point the given substance can be considered as a metastable undercooled liquid at the lower temperatures the substance is regarded as glass or being in vitreous state which is a non equilibrium state. The transition from the undercooled liquid to the vitreous state is called transformation and the respective temperature is designated the transformation temperature.

However the temperature pertaining to the deflection mentioned above depends on the rate of cooling as indicated by Fig. 1. The lower the rate of cooling the lower the temperature and vice versa. For this reason preference is given to the term transformation range within which the substance being cooled begins to exhibit properties characteristic for solid state (elasticity strength). Having chosen a certain standard rate of cooling the transformation range can be determined by measuring the temperature corresponding to the deflection on the temperature specific volume curve.
cooling for instance 10ºC min¹ one obtains the so called transformation point designated Tg in the literature.

Figure 1 also indicates that the final specific volume and the other properties depend on the cooling rate or on the thermal history of the glass. When reheating a rapidly cooled glass to the transformation range temperature its volume will change in the direction indicated by arrows in Fig. 1 that is in the direction corresponding to a metastable liquid.

Stabilization is a result of spontaneous structural changes through which the substance passes from the non equilibrium state into the metastable one. The transformation range is a temperature region within which the changes occur at a measurable rate. The transformation point appears on the temperature dependence curve of the particular property at a temperature where the time required for a distinct change in property is commensurable with the period for which the glass is held at this temperature.

In order to describe the degree of stabilization Tool suggested the term fictive temperature. It is the temperature at which the properties of the given glass should correspond to the properties pertaining to the metastable state. In other words, on cooling down the glass freezes with a structure corresponding to a certain higher fictive temperature. For example, thin glass fibres cooling very rapidly during manufacture show a high fictive temperature; the same glass cooled by the procedure usual with optical glasses has a low fictive temperature which also determines its room temperature properties. Introduction of the term fictive temperature is useful practically but represents a considerable simplification because a single parameter is not sufficient to describe the state of a glass.

The above considerations imply that the glass is formed by a continuous transition from the liquid state. This continuity can also be demonstrated on the atomic structure of glass as has been established by X ray diffraction and other methods.

The lack of periodicity of the structural arrangement is explained in that the (SiO₄) tetrahedra are mutually bound only by common corners and not by edges or planes. In this geometrical concept the Si-O-Si bond in glassy SiO₂ has a mean angle of 152 degrees; however, this angle is variable over the 120°-180° range. This results in the formation of a non regular structure. The random arrangement in the more complex glasses is also due to the presence of cations situated in the cavities of the silica network. This is demonstrated by the planar projection in Fig. 2.

The concept of random structure of oxidic glasses was first suggested by Zachariasen and later on confirmed by X ray studies by Warren et al. Zachariasen has formulated crystallochemical postulates with which the given oxide has to comply to be glass forming, that is, it forms glass readily on cooling down. Zachariasen’s rules for glass formation of oxides RxOy: An oxygen atom is not linked to more than two R atoms.

The number of oxygen atoms surrounding an R atom must be small (3 or 4).

The oxygen polyhedra share corners with each other not edges or faces.

At least three corners in each oxygen polyhedron must be shared.

This is also the basis of the classification of oxides to network formers capable of forming glasses by themselves (for example SiO₂, B₂O₃, P₂O₅, GeO₂) and network modifiers (for example CaO, BaO, Na₂O, K₂O). The latter do not form glass by themselves and only modify the silicate lattice. Introduction of network modifiers disrupts the Si-O-Si bonds according to the schematic equation.

The Zachariasen - Warren theory also explained the anomalies in the behaviour of glasses containing B₂O₃ as a network former. This oxide may be present in coordination 3 or 4 that is in the form of triangular (BO₃) or tetrahedral (BO₄) formations. Introduction of Na₂O brings about conversion of (BO₃) to (BO₄) and strengthening of the network as a result of creation of further B-O-B bonds. Up to a certain concentration the effect of the alkali oxide is therefore quite the opposite to that in the case of SiO₂. The coordination change results in anomalous changes in properties. The more recent results obtained by the nuclear
magnetic resonance method have confirmed a change in the coordination of boron due to the introduction of alkalis however the structural changes are not in full agreement with the anomalies in the physical properties.

The present concepts on the structure of oxidic glasses differ from the random network hypothesis particularly in that existence of regularly arranged or heterogenous regions is admitted. Their presence has been proved by new more sensitive methods and is in no disagreement with the X ray structural studies by Warren. The Zachariasen model of a quite disarranged continuous lattice is in this sense a limit case while real glasses contain regularly arranged or heterogenous regions of various sizes and in various amounts according to glass composition and the thermal history. With single component and stoichiometric glasses the nature of these regions may approach the crystalline arrangement in that the structure changes continuously without any phase boundary from the centre of the more regularly arranged regions into the less arranged ones. These regions have a character of frozen density and structural fluctuations. This concept is based on the so called crystallite theory of glass structure suggested by Lebedev and has been modified by further Soviet authors.

A number of multicomponent glasses have in recent years been found to show a tendency to metastable separation into two or more liquid phases. The resulting microheterogenous regions impair the structural continuity by more or less distinct phase boundaries. The phenomenon of phase separation will be dealt with later.

Research of new types of glass has also brought about corrections in the classification of oxides to network forming and modifying ones it has been shown that glass can be formed in more complex systems even in absence of a typical glass forming oxide for example in the system Al2O3 - CaO.

The properties of glass can be adjusted continuously by continuously changing the composition within the range given by the glass forming limits of a given system. Within a narrow composition range the general property V may be expressed by the additive function.

**NITRIDATION OF SILICA Sol Gel Thin Films**

*Introduction*

There have been many investigations of thin film preparation using sol gel processes. In almost all of those studies the objective was to optimize and control the optical properties of the films. Nonetheless oxide films and coatings made with sol gel processes may also offer advantages for the preparation of dielectric films scratch resistant coatings and oxidation or diffusion barriers. In the case of silica based films and coatings all of these properties should be enhanced by partial nitridation.

Currently there is very specific interest in the direct nitridation of silicon and silicon dioxide for advanced integrated circuits. That work has shown that thermally grown silicon dioxide films on silicon are converted to an oxynitride in ammonia at 1200ºC. However the reaction with these dense silica films occurs predominantly at the surface and produces a nitrided silica film whose nitrogen fraction decreases with depth. It is suggested herein that the metastable structure of the initially microporous sol gel films enhances the thermodynamics and kinetics of nitridation in ammonia. Therefore it is likely that they can be nitrided at lower temperatures and with greater in depth uniformity than dense silica films.

It was demonstrated that a thermal treatment in ammonia can be used to nitride gels. These investigators observed large increases in sintering temperature and microhardness which were attributed to chemically dissolved nitrogen. They limited their studies however to bulk gels in a multicomponent alumina borosilicate system.

In this chapter the nitridation of silica sol gel films on silicon is discussed. The films were prepared using an acid catalyzed solution of silicon alkoxide and water. A gel that is not highly condensed and that possesses
a fine pore microstructure is produced under these conditions. Thus the dried gel films used in this study were especially reactive and capable of densification at relatively low temperatures. The densification and refractive index of the films treated in nitrogen and ammonia were examined as a function of temperature using ellipsometry. Some of the films were pretreated in chlorine at low temperatures to enhance the reaction with ammonia at higher temperatures. The composition and in depth profiles of the films were determined with Auger electron spectroscopy (AES) and secondary ion mass spectroscopy (SIMS).

Experimental Methods
The solutions used to prepare the silica sol gel films consisted of 43% tetraethyl orthosilicate (TEOS) 43% ethanol and 14% water (by volume). This corresponds to a 4 1 molar ratio of water to tetraethoxysilane. A small amount of 1 M HCl acid was added to catalyze the hydrolysis. The mixture was heated and stirred in a closed reaction vessel equipped with a reflux condensor. After 1 hr at 60ºC the solution was cooled to 30ºC. The cooled solution was diluted with ethanol in the ratios 2 1 3 1 and 4 1. These diluted solutions were used to spin coat silicon wafers. The polished p type silicon wafers (1¼ in diameter) were cleaned using electronic grade reagents and methods standardized by the semiconductor industry. A photo resist spinner uniformly distributed 250 µL of solution over the surface of the wafer. The spinning time was 15 sec. The coated wafers were placed in covered petri dishes and stored in a desiccating cabinet prior to characterization and thermal treatment. Figure 1. shows the variation in film thickness caused by the spinning rate and solution dilution. The film thickness was measured with an ellipsometer at an incident angle of 70º. The uniformity of film thickness increased with the spinning rate although the thickness variation across the wafer was typically 2% or less. The films were thermally treated in a silica tube furnace equipped with a gas manifold and individual flowmeters. The temperature variation in the hot zone of the furnace was less than 10ºC. None of the gases used for this study received any special treatment or purification. Since a wide variety of thermal treatments was used in this study the details are presented in the appropriate sections of the text.

Results and Discussion
Film Shrinkage
The first set of film shrinkage curves was obtained in the following manner. A set of silicon wafers was spin coated at 4000 rpm with a solution diluted 3 1 with ethanol. The initial film thickness and its variation across the wafer was measured and the wafers were fractured. In some cases the initial film thickness and its variation across individual fragments was measured. The fragments were placed within the hot zone of the tube furnace under flowing nitrogen or ammonia. The temperature was raised in approximately 100ºC increments and held at each temperature for 30 min. (An independent set of experiments showed that the maximum film shrinkage at each temperature occurs within 5-10 min). One of the fragments was withdrawn under the flowing atmosphere at each temperature increment. The final film thickness on each fragment was measured and compared with the initial film thickness. Figure 2 shows that film shrinkage as a function of temperature for both the nitrogen and anhydrous ammonia atmospheres. It is apparent that the ammonia atmosphere enhances the shrinkage behaviour at the lower temperatures. The maximum film shrinkage and the temperature where it is attained is increased. An apparent increase in thickness was observed repeatedly for the films treated in nitrogen at temperatures in excess of 900ºC. It is caused by either oxidation of the substrate or bloating of the film. In the ammonia atmosphere no such behavior has been observed at least up to temperatures of 1200ºC. Since the initial density of these films should be identical one might conclude that the final density of the films treated in ammonia is greater. The difference in the low temperature shrinkage behavior is related in part to the greater degree of dehydration achieved in the ammonia atmosphere. The most important contribution at high temperatures may be chemical incorporation of nitrogen in the silica structure.
A second set of studies was done to determine the film density achieved after thermal treatment in nitrogen and ammonia. The temperature dependence of both the film shrinkage and the weight loss were measured. Three silicon wafers were cleaned and weighed on a microbalance. The wafers were then spin coated with the silica solution. The film thickness and weight gain were recorded. One wafer was then heated in the tube furnace to 100°C at 10°C/min. It was removed and its thickness and weight were remeasured. This procedure was repeated at 100°C increments for each of the three wafers in air nitrogen and ammonia. Great care was taken to minimize exposure of the porous film to the atmosphere where water adsorption would occur. In many instances the coated wafers were weighed while warm. Nonetheless although the film shrinkage curves were reasonably smooth and continuous the weight loss curves were erratic. The calculated densities fluctuated between 2.20 and 3.00 g/cm³. The lack of precision in these density determinations precludes any quantitative interpretation. However it showed that most of the weight loss in the films occurs at temperatures less than or equal to 250°C. In addition this thermal treatment—which involved cycling the temperature and intermittent exposure to the ambient atmosphere—also resulted in greater shrinkage in ammonia than in nitrogen or air. The maximum shrinkage in nitrogen exceeded the maximum shrinkage in air. The onset of substrate oxidation occurred at 750°C in air.

The densified films were examined in the scanning electron microscope (SEM). With the exception of some gross particulate contamination none of the films showed microstructure topography or discontinuities. Some of the films have been further characterized with capacitance voltage (CV) measurements. The initial CV data have verified the continuity and integrity of these films.

Refractive Index

Figure 3 shows the temperature dependent changes in refractive index for the nitrogen and ammonia treated films. In nitrogen there is an initial decrease in the refractive index at low temperature. This is attributed to the release of water and carbonaceous species that increase the porosity of the film. In the temperature range 600–800°C the refractive index rises due to densification of the porous film. The final refractive index of 1.44 is slightly less than that of a thermally grown silicon oxide film on silicon which is typically 1.45.

The films treated in ammonia have higher refractive indices at all temperatures. Although the chemical incorporation of nitrogen in silica is expected to increase the refractive index it is surprising that the effects are prevalent at low temperatures. This may be caused partly by the presence of residual carbon in the ammonia treated films. At temperatures in excess of 400°C the measured carbon content of the films treated in ammonia was comparable with the carbon content of the films treated in nitrogen. Moreover others have found that treatment of bulk gels in ammonia at 460°C actually enhanced the removal of carbon. Thus it seems doubtful that the large increase in refractive index for the films treated in ammonia is due to residual carbon or alkoxy groups.

The refractive index of dense Si₃N₄ is about 2.02–2.04 the refractive index of the stoichiometric oxynitride (Si₂N₂O) has not been reported. In any event silicon oxides that have been partially nitrided are expected to exhibit refractive indices between 1.45 and 2.04. The results of Ito et al are of special interest. They showed that ammonia treatment of dense silicon oxides-thermally grown on silicon-increased the refractive index from 1.45 to 1.65. They used anhydrous ammonia to carry out the treatment at 1200°C for 1hr. Figure 3 shows that the silica sol gel film treated in anhydrous ammonia at 1100°C exhibits a refractive index of 1.65.

SIMS Depth Profiles

The films treated at each temperature increment in nitrogen and ammonia were subjected to a depth profiling analysis with SIMS. Figures 4–6 present SIMS depth profiles for a dried SiO₂ film a SiO₂ film treated to 900°C in N₂ and a SiO₂ film treated to 900°C in NH₃ respectively. The profile for the dried
SiO2 film reveals the presence of carbon with an average signal intensity through the film more than an order of magnitude greater than the background C+ signal. It is also noteworthy that the C+ intensity in particular seems to increase with distance from the film surface. The amount of hydrolysis/polymerization-and consequent evolution of alkoxy groups-is probably impeded in the subsurface of the film.

It was found however that the intensity of the 42 amu line was highest in the untreated films and decreased upon thermal treatment in either nitrogen or ammonia. Moreover the intensity of this line always decreased rapidly near the surface of the films regardless of their thermal history. Presumably the presence of the adsorbed water nitrogen or oxygen at the surface of the films and in particular within the pore spaces of untreated films enhances the secondary emission of SiN (and, or some other cluster) at 42 amu. This apparent matrix effect precluded the use of this line for qualitative analysis.

Although the film thickness is reduced by the thermal treatments the time required to sputter through the films has not changed appreciably. The total number of atoms sputtered is greater for the dried film than for the heated films. A comparison of Fig 4 with Fig 5 or 6 shows the elimination of water and carbon after heating. Thus the number of atoms sputtered per incident argon ion (the absolute sputter yield) has decreased after thermal treatment. This reduction in sputter yield is presumably due to polymerization of the molecular silica structure.

The effect of the thermal treatment upon polymerization of the gel film structure can be related at least qualitatively to the number of SiOH species detected in the film.

Auger Analyses

While the SIMS analyses provided an excellent means for characterizing the composition depth profiles in these films the incorporation of nitrogen in the films could not be directly verified. Therefore the same series of films treated at various temperatures in nitrogen and ammonia were subjected to Auger analysis. Figure 7 presents the Auger spectra and corresponding refractive indices for the dried film and the film heated to 900ºC in nitrogen. Only silicon oxygen and a small quantity of carbon were detected on these surfaces. The films treated at temperatures less than 900ºC in nitrogen showed similar spectra. Because of the dehydration produced by the ultrahigh vacuum in which the Auger analysis is performed and additional potential for electron beam stimulated desorption of adsorbed water and carbonaceous species these spectra are only qualitatively significant. All the spectra were recorded in the same way. That is a low current density beam was used it was stabilized on the periphery of the sample and the sample was translated to present a new region where the spectra were immediately recorded.

Figure 8 presents the Auger spectra and corresponding refractive indices for the films treated in ammonia. The films treated at 600ºC or lower showed only the presence of silicon oxygen and carbon in the Auger spectra. The films treated at 700 and 800ºC exhibited traces of nitrogen. However the film treated at 900ºC in ammonia showed very distinctly the presence of nitrogen the films treated at 1100ºC showed the highest nitrogen content. The nitrogen Auger signal intensity was stable under the electron beam irradiation suggesting that it is not the result of physically adsorbed ammonia.

It is apparent that the carbon concentration at the surface of the ammonia treated films has increased at the higher treatment temperatures. However the carbon signal was reduced dramatically upon sputtering the film for 60 sec with argon ions. This is consistent with the SIMS profiles which showed carbon only at the surface of the films after a high temperature treatment.

After 60 sec of sputtering (30 60 Å) the nitrogen signal was reduced by 30% and then stabilized through the films. However it is not yet known whether this represents a real concentration gradient for nitrogen or is a consequence of the ion bombardment. We have reported severe distortions associated with Auger sputter profiling of multicomponent insulators and therefore hesitate to present any quantitative interpretation of the depth profiles obtained here. Perhaps the most important observation made during the Auger sputter profiling of these films was the obvious and reproducible increase in vacuum pressure. This indicated that...
there was a significant quantity of gas trapped in these films.
An attempt was made to semiquantitatively interpret the nitrogen Auger intensity in the unsputtered ammonia treated films. A CVD Si3N4 film \((n=1.95)\) was examined for comparison the resulting Auger spectrum is presented in Fig. 9. The Si3N4 films exhibits both carbon and oxygen at the surface because of its exposure to the ambient atmosphere and the formation of a native oxide. The nitrogen to oxygen Auger signal ratio for the sol gel film treated ammonia at 1100ºC is approximately one half the ratio for this Si3N4. The uncertain characteristics of the native oxide on this Si3N4 film and the matrix difference between the CVD nitride and sol gel oxide preclude more than speculation. Ito et al. suggested that the atomic nitrogen content of their ammonia treated silica film \((n=1.65)\) was about one half the nitrogen content in Si3N4. These results for the ammonia treated sol gel film \((n = 1.65)\) are qualitatively consistent with their observation.

**Modification of Oxides by Polymerization Process**

**Introduction**

In most alkoxide systems hydrolysis and condensation reactions rapidly proceed until one of the reacting groups OR and OH is finally exhausted. Under a given hydrolysis condition the relative concentration of OH and OR depends on the availability of water aging dilution and type of alkoxide and the host liquor. In silicon alkoxides for example the hydroxyl and alkyl groups can coexist in significant numbers. Given sufficient time and availability of water \(y\) becomes small enough to be negligible for compositional purposes. When this occurs the hydrolyzation product can be considered as an inorganic polymer whose main skeleton is an oxide network framed in hydroxyl groups.

**Introduction of Chemical Structural Variations In Inorganic Polymers**

**Theoretical Bases**

Equations expressing the chemical makeup of polymeric particles having an oxide skeleton framed by hydroxyl groups as a function of polymerization can readily be derived. Such equations must take into account the type of polymerization for example linear or planar. Generally a diluted and unrestricted hydrolysis of metal alkoxides in a liquid environment produces spherical polymers.

For a polymerization expanding spherically the volume of the particle can be expressed in terms of the total atoms \(n\) polymerized in such units.

If we use hydrolysis of silicon alkoxides as a model those silicon atoms located on the surface will each have an OH bond whose number (and therefore the number of OH groups) can also be expressed in terms of the total number of silicon atoms \((n)\) in the polymer units by expressing the radius \((r)\) in terms of \(n\) in Eq. (4) and plugging into the surface area equation.

Equations for other systems and for non spherical shapes may also be derived similarly. Computer analysis shows that a moderate deviation from perfectly spherical polymerization does not significantly affect the compositional results given by Eq. (7).

Figure 1 shows the dependence of the oxide content on polymer size for three types of polymerization in the silica system. The rate of change of the oxide content for each polymer as a function of size is significantly different for different polymerizations. To achieve 99% of the maximum oxide content requires polymerization of 18 silicons in the case of linear polymerization and \(2 \times 10^3\) in the case of planar and \(4 \times 10^5\) in the case of spherical polymerization (referred to as critical size \(n_c\)).

Since the number of silicons in the molecule and the oxide content are related the size of the particles the average network connectivity and so forth can be calculated from the equivalent oxide content.

Table 1 gives some calculated values for \(n_r\) and connectivity in terms of equivalent oxide content of the polymers.
The discussion developed here in terms of silica is general in nature and applied to all similar systems (e.g. Ti Al etc.) and non spherical geometrical configurations with necessary adjustments.

Experimental
The theoretical discussion predicting the variability of oxide content of polymers obtained by hydrolysis of metal alkoxides can be demonstrated experimentally. A controlled hydrolysis can be performed in a liquid medium where both alkoxide and water are diluted in a neutral solvent for example ethyl alcohol. In these cases the basic parameters affecting the kinetics of hydrolysis and polymerization which determine the nature of the polymer are

Water/alkoxide ratio.

Dilution of reacting species in the carrier solvent.

Temperature.

Electrolyte.

The amount of water and its dilution determines the degree of hydrolysis and type of initial species formed for example Si(OR)\(_3\)(OH) or Si(OR)\(_2\)(OH)\(_2\) thus influencing the secondary polymerization reactions. These in turn affect the chemical and structural makeup of resultant polymer molecules. For example it is structurally important whether a partially hydrolyzed specie in the liquor [e.g. Si(OR)\(_3\) (OH)] next comes into contact with a water molecule a partially hydrolyzed specie or an unhydrolyzed alkoxide specie [Si(OR)\(_4\)]. In each case a different molecule with a different capability for further reactions with other species result. Consequently the water/alkoxide ratio along with its dilution determines the structurally important statistical probabilities.

Figure 2 shows the oxide content of the hydrolysis products as a function of hydrolysis water. Concentration of hydrolysis water strongly affected the chemical makeup of the product. Thus remarkable similarities occur between the theoretical curve which shows oxide content versus polymer size and the experimental curve which shows oxide content versus hydrolysis water.

Electron micrographs show that the hydrolysis of alkoxides produces spherical polymeric units whose diameter varies from 30 to 300 Å depending on the alkoxides and hydrolysis conditions. Theory predicts the diameters of these spherical units reasonably well. Polymerization appears to maximize the oxide content of the molecule. This driving force however diminishes rapidly as the polymerization proceeds and eventually limits the particle size within 5 30% of the optimum. Overall connectivity increases with increasing molecular size and with oxide content. This was confirmed by IR investigations that showed a higher ratio of bridging oxygens with increasing hydrolysis water in silica system. Infrared spectroscopy also shows molecular structural variations in TiO\(_2\) as a function of hydrolysis conditions and these structural variations are not transient or limited to low temperatures.

Hydroxide polymers of Al Ti or Si can be formed to contain from 65 to over 90% equivalent oxide by weight when calcined. Note that the hydroxyl content is inversely related to the amount of water used during hydrolysis indicating that these groups are not merely absorbed species but are part of the structural composition. The hydrolysis product of zirconium alkoxide contains about 80% ZrO\(_2\) by weight regardless of the amount of water used during hydrolysis. The hydrolysis of zirconium alkoxides by atmospheric moisture yields a similar composition. The zirconium atom does not give up electrons instead electrons may either be bound to its ligands covalently or accepted by the zirconium producing a negative charge that repels hydroxyl groups and leads to preferential formation of oxo and aquo groups.

Drying and Firing Monolithic Silica Shapes from Sol Gels
Introduction
To form monolithic shapes from solutions of tetraethylorthosilicate (TEOS) ethanol and water requires careful drying. Solutions of various ratios of water to TEOS have been reacted that is hydrolyzed and polymerized cast into shapes gelled and dried to transparent undistorted single pieces. Likewise tetramethyl orthosilicate (TMOS) TEOS with trimethyl borate and multicomponent solutions have been treated to form monoliths. In all cases the pieces have been made with one thin dimension typically as disks or sometimes as rods. For example disks have been made that are 4 or 5 cm in diameter and 5 mm thick. Though solutions with various ratios of water to alkoxide have given dried monolithic shapes only ratios of about 10 or greater have resulted in shapes that densified on firing intact.

The ability to convert dried silica gels to a chemical and physical equivalent of fused silica without melting in a crucible is one of the advantages of the sol gel process. When the dried gel densifies without the need for a supporting container there is no chance for the container to contaminate the sample or for the sample to pick up its surface features. Consequently the question to be asked is why one dried gel has the structural integrity to hold together during firing and another falls apart? Some clues to the answer should be obtained from systematic studies of the physical properties of dried gels including their density weight loss and porosity.

First the density of the dry gel can be used as an indication of its microstructure. Recently very low density gels have been dried using hypercritical evacuation. Though the dried gels were not transparent owing to greater than 50% porosity in the size range that scatters light they were converted routinely to dense glass at about 1050ºC. The same high porosity gels could be converted rapidly by hot pressing. The texture of these gels with greater than 50% porosity was described as spongy.

Second control of the weight loss during drying which is as high as 40 70% with another 25% of the dry weight lost during firing is necessary to control the gel to glass conversion. The rate of drying monoliths is usually extremely slow except in critical point drying. Only one report on fabricating rods estimates a drying rate. According to this patent the recommended rate is less than 40% weight loss/day and preferably no more than 10 20% weight loss/day. Presumably the same factors surface tension and capillary stresses that operate during the drying of colloidal systems are operating during the drying of gels. When these factors are balanced the gel can dry uniformly without cracking.

Third the porosity of dried gels has received a great deal of attention regarding pore morphology pore distribution and internal surface area. The dried gels have high surface areas but it is not clear how the surface area or its addition to free energy affects the densification on firing.

There is a fundamental difference between the microstructure of colloidal gels and that of polymer gels. Similarly there is a difference between base catalyzed and acid catalyzed gels. The acid catalyzed gels are characterized by high dry densities which decrease with increasing water in the original solution. The base catalyzed gels are characterized by low dry densities which vary more with amount of base than amount of water. The base catalyzed gels are probably not the same as colloidal gels. The base catalyzed gels are made up of more condensed regions and less condensed regions in an overall polymer framework rather than compact spheres. In contrast the acid catalyzed gels seem to have a more flexible uniformly cross linked polymer. However it is difficult to generalize for all cases because the interactions of electrolyte solvent and amount of water are fairly complicated.

To get some idea of the nature of the microstructure of dried gels this chapter concentrates on acid catalyzed gels. The picture of the microstructure of dried gels used as a starting point is a sponge where the skeleton is silica separating pores that are cylindrical uniformly distributed and interconnected. The skeleton may or may not have the density of fused silica. The surface may be covered with hydroxyls or a combination of hydroxyls and alkoxy groups. By considering the density weight loss and porosity of acid catalyzed gels
catalyzed gels prepared with 2, 4, 8, and 16 moles water/mole TEOS the picture of the dried gel microstructure can be refined and these observations can be compared to a proposed structural model for gels.

**Sol Gel Derived INDIUM TIN Oxide Coatings**

**Introduction**

In this time of increasing energy costs and limited resources the development of energy saving windows by special coatings is one of the more challenging tasks. These coatings should be highly transparent for solar radiation and highly reflective for long wave IR radiation. Such a double insulating glass unit with one pane coated is a good passive solar collector possessing high solar energy input combined with excellent heat insulating properties.

Sol gel chemistry enables the production of oxide coatings. At Schott Glaswerke titania coatings for sun shielding purposes are produced on a large industrial scale. This is done in a dip coating sol gel process with 12 m² float glass panes as shown in Fig 1.

About 1970 a process for making well defined multicomponent oxide coatings by dipping was developed published and patented by Schott. We then began discussion on how to use this process for developing heat mirror coatings.

This is not only a chemical question but also a technical one. A heat mirror coating on glass panes should have the properties listed in Table 1. Because it seemed likely that these properties could be achieved using the sol gel dip coating process we first prepared cadmium stannate as shown in Fig. 2.

The result was not good enough for technical use but helped us to understand the chemical problems as shown in Table 2.

In preparing such ITO dip coatings many difficulties had to be overcome. The main steps of this process are shown in Table 3.

**Properties of Sol Gel Derived ITO Coatings**

A combination of optical mechanical chemical and aesthetic properties is necessary if such a coating is to have practical value in energy saving windows. It makes only limited sense to compare single properties. One must compare the combined properties. For example a very high IR reflectivity is not satisfactory if the coating is unstable or the homogeneity is too poor for building requirements.

In the following section the basic properties of the ITO layer are discussed and their influence on the performance of window systems is illustrated.

**Characteristic Properties of ITO Coatings for Window Systems Derived from Dip Coating**

It is generally known that solar transmittance and IR reflectivity of single layer semiconductor films are related by the free carrier concentration the film thickness and the carrier mobility. By increasing conductivity the infrared reflectance increases and the plasma frequency shifts to shorter wavelengths. At the same time solar transmittance decreases because of increased absorption in the film. Absorption in the visible range is due to free charge carriers and lattice defects. To maximize transmission the thickness must be as small as possible but below a critical thickness the infrared reflectivity degrades. It is therefore desirable to have high mobility and conductivity to ensure proper IR reflectivity. These properties are shown in Table 4.

**Optical Properties**

Reflection and transmission of an ITO coating with the properties listed in Table 4 are shown in Fig. 3. The comparison of ITO coated glass with presently available commercial heat mirror systems is illustrated in Fig. 4. At present the best available system in Europe is a heat mirror system based on silver. However the new ITO system as it is shown in Fig. 4 has a superior combination of properties.
Architectural Properties
These properties are homogeneity over large areas (= constant thickness) no spots and no changing of the color of transmitted light. Neutral grey reflection may also be desired. Thus far all of these requirements can be fulfilled.

Mechanical Properties
The coating cannot be scratched by a brass or iron stylus only slight abrasion from the stylus occurs. Adhesion of the layers to the glass is excellent. ITO coated glass can be handled and stored without problems. This is preferable to metal coated glass which must be handled and stored with special care.

Chemical Properties
The chemical properties of the ITO coatings depend heavily on the production process. The sol gel ITO coating process uses 400 500°C and this leads to good chemical stability. Table 5 lists the stability of ITO coatings against several agents.
Because the dip coating process coats both sides of the plate one side is always exposed to the atmosphere. Therefore this coating must be stable.

Relationships Between the Sol to Gel and Gel to Glass Conversions
Multicomponent gels were prepared with a wide range of pH water combinations so that the skeletal structure of the desiccated gels varied from being less highly (low pH low H2O) to more highly (high pH high H2O) polymerized. The apparent value of isothermal viscosity determined by isothermal shrinkage experiments increased with time presumably owing to polymerization and structural relaxation of the skeletal framework. This increase was dramatic (>200×) for less highly polymerized gels but occurred in all cases and therefore is predicted to be a general property of metal alkoxide derived gels.

Introduction
The sol gel process is now a well accepted technique for preparing monolithic glass articles without melting. This technique has been applied not only to the preparation of single component oxide glasses for example SiO2 but also more recently to the preparation of multicomponent oxide and oxynitride glasses. For processes that use metal alkoxides as glass precursors monolithic glass formation consists of (1) growth and linkage of polymer units to form a gel (2) desiccation of the gel under ambient or hypercritical conditions to form respectively a porous xerogel or aerogel and (3) heat treatment of the porous gel at a temperature sufficiently high to convert it to a dense glass like solid. In this chapter we review the concepts of gel formation and present evidence of how gelation conditions affect gel structure and ultimately the kinetics of the thermal conversion of gels to glass.

Gelation
Gelation involves the growth and linkage together of polymeric units to form a continuous network that extends through (and thus incorporates) a liquid. In systems based on metal alkoxides polymer growth involves polymerization of hydrolyzed metal alkoxides in alcoholic solutions.
The hydrolysis reaction is catalyzed by the addition of acid or base. Depending on pH and water content the hydrolysis of tetraethylorthosilicate (TEOS) (Si(OC2H5)4) can result in the formation of polymeric species ranging from polysiloxane chains to colloidal particles of essentially pure SiO2. Gelation conditions employed in the preparation of monolithic glasses normally consist of the hydrolyzation of the alkoxide precursors with a small to large excess of water (in Eq. 1 x > n/2) at low to intermediate pH (~1 9). These conditions can result in structures that are intermediate between linear chains and colloidal particles. For example small and intermediate angle X ray scattering has shown that hydrolysis of 1 mole of TEOS with
~4 moles of water results in primarily linear or randomly branched polymers at pH 1 and in discrete more highly branched polymeric clusters at pH 7.

These differences in structure occur for the same addition of water because at low pH (< ~2.5) hydrolysis occurs by a mechanism involving electrophilic attack on an alkoxide oxygen and at intermediate to high pH (> ~2.5) hydrolysis and polymerization occur by a mechanism involving nucleophilic attack on silicon. It is important to note that polymer growth did not result in the formation of colloidal silica in either case. Colloid formation is expected however for hydrolysis carried out in a large excess of water and at high pH. Under these conditions hydrolysis and polymerization are extensive and the siloxane network is quite soluble so that depolymerization is also likely to occur. Because small polymers are more soluble than larger ones the polymers grow in average size and diminish in number as the smaller ones dissolved and the silica is deposited monomer by monomer on the larger ones (Ostwald ripening). Colloidal particles of essentially anhydrous silica are formed for example when an aqueous solution of monosilicic acid is polymerized at 80ºC and above pH 7.

Gelation occurs when the growing polymers aggregate or entangle and cross link to form extensive three dimensional networks. Because of the sharp increase in viscosity accompanying gelation it may be considered a rapid solidification process that is a structure at a given state of polymerization is essentially frozen in at the gel point. Under conditions in which the polymer is relatively insoluble (e.g. low temperature, low water and low pH) this frozen in structure does not change appreciably with duration of aging if solvent is not allowed to evaporate. However aging under conditions in which appreciable polymer solubility occurs (e.g. high temperature, high water and high pH) can result in extensive restructuring of the gel. In addition to Ostwald ripening polymer surfaces exhibiting positive radii of curvature dissolve and polymer is redeposited on surfaces exhibiting negative radii of curvature such as interparticle contacts. Thus interparticle necks are formed causing the skeletal morphology to become more fibrillar and because of the solution-redeposition process that occurs in both ripening and neck formation the skeletal framework changes toward a more anhydrous dense oxide.

Structural changes can also occur during gel desiccation. Removal of solvent by evaporation results in surface tension forces which in effect exert an external positive pressure on the gel structure. More weakly cross linked gels exhibit greater shrinkage in response to surface tension forces than do more highly cross linked gels formed under conditions in which solution redeposition can occur to dehydrate the skeletal framework and reinforce particle particle contacts. Thus acid catalyzed gels prepared with low water contents dry to a relatively dense structure (xerogel) exhibiting extremely fine continuous porosity. As the water content and especially the pH is increased during gelation and aging xerogel density decreases (owing to the large pores formed on removal of solvent) while the skeletal structure becomes more glass like that is more highly polymerized. These effects of gelation conditions and aging on gel density and pore size are shown in Fig. 2 for multicomponent borosilicate gels.

Gel to Glass Conversion

The physical and chemical structure of a desiccated gel is a result of the sequential gelation aging and drying conditions under which it was prepared. Compared with a glass of the same oxide composition formed by melting desiccated gels exhibit higher structural energies as shown schematically in Fig. 3. At least three structural characteristics unique to gels contribute to this high free energy. Surface area created by the formation of microspores during desiccation makes the largest contribution 30 300 J/g (this corresponds to 100 1000 m²/g of surface).

The final contribution to free energy results from additional free volume (compared with the melted glass). This is a consequence of the low cross link density which may be frozen in by gelation and subsequent aging and drying (especially at low pH and low H₂O content). Thus during the thermal conversion to gel to glass the desiccated gel exothermically changes to become more highly polymerized while reducing its
The more polymeric nature of gels formed by the sol gel process (i.e. low cross link density and high free volume) results in a higher associated structural energy than that found for colloidal gels (formed e.g. from LUDOX which contribute primarily a surface energy term to free energy. The polymeric nature of gels has a significant impact on the kinetics of gel densification. Both low cross link density and free volume reduce the activation energy for viscous flow. Therefore if polymerization and/or reduction of free volume occur simultaneously with viscous sintering the apparent viscosity is not merely a function of temperature but also of the polymeric state of the gel.

The temperature range over which each of these exothermic mechanisms contribute to gel shrinkage is probably dependent on numerous chemical and physical properties such as oxide composition pore size polymer state and heating rate that is there are both thermodynamic and kinetic dependencies. Some of these dependencies are demonstrated in Fig 4 which shows shrinkage curves measured at 1°C/min for a series of borosilicate glasses prepared under similar gelation conditions (pH and H2O content) with soda contents ranging from 0 to 6.3 wt%. Shrinkage is relatively independent of oxide composition at low temperature whereas at higher temperatures extensive shrinkage commences at a temperature that scales with decreasing soda content (increasing $T_g$). All of these mechanisms however are dependent more or less on material transport and as such are kinetically limited. Based on kinetic considerations increased heating rates are expected to increase the temperature at which sintering occurs however because the polymeric structure (i.e. low cross link density and free volume) is retained to higher temperatures (at higher heating rates) the activation energy for viscous flow and the absolute viscosity are decreased. For example we have recently observed that increasing the heating rate from 10 to 15°C min actually reduces the sintering temperature.

Experimental

To demonstrate the significant effect of the polymeric nature of the skeletal framework on the kinetics of gel densification we prepared gel compositions of the nominal oxide content (in wt. %)

Results and Discussion

Physical Properties

The effect of gelation conditions on physical properties is evident from measured values of bulk density and pore size. Whereas most pH water combinations produced gels with densities of approximately 1.1–1.3 g cm$^{-3}$ the two compositions produced at pH 9.2 exhibited densities less than 0.8 g cm$^{-3}$ with correspondingly larger pores. This pH is apparently sufficiently high to cause reinforcement of the skeletal framework so that it can resist deformation under the force of surface tension.

The various pH water combinations also influenced the oxide composition of the desiccated gel. All samples showed loss of boron which decreased with increased pH presumably because the rate of reesterification (and subsequent evaporation as B(OR)$_3$) of borate was reduced. Analyzed compositions are listed in Table 2.

For purposes of comparison conditions that represent the two extremes of the processing matrix (LpH5 and HpH12) were chosen to demonstrate the effect of polymer character on gel densification. To make the comparison more valid in terms of oxide composition some samples of MpH5 were also used.

Shrinkage and Densification

The linear shrinkage of HpH12 is compared with that of MpH5 in Fig. 5. Because these two gel samples are of similar oxide composition the differences in shrinkage are due only to gel structure. Sample MpH5 exhibits considerably more shrinkage at low temperatures and considerably less shrinkage at high temperatures than does HpH12. Corresponding densification curves are shown in Fig. 6. It is apparent that MpH5 undergoes significant densification at temperatures much lower than predicted for viscous sintering. Because MpH5 was prepared with low pH and water content compared with HpH12 it is reasonable to
suspect that this low temperature densification results from polymerization and reduction of free volume that is the skeletal structure becomes more like the anhydrous oxide. HpH12 was formed under conditions in which the skeletal structure is expected to be highly polymerized. It therefore undergoes less skeletal densification at low temperatures.

It might be argued that low temperature densification is a viscous sintering process involving a subset of smaller diameter pores than those involved at higher temperatures. However the pores involved would have to be at least an order of magnitude smaller to have a significant effect and thus would be of the dimensional scale of free volume.

Isothermal Shrinkage Experiments

To determine the effect of polymer character of the skeletal phase on sintering kinetics isothermal shrinkage experiments were performed in the temperature region where viscous sintering was expected to be the predominant shrinkage mechanism. Samples of LpH5 and HpH12 were heated at 2°C min to temperatures between 700 and 800°C and held isothermally for up to 5000 min. LpH5 exhibited shrinkage behavior quite similar to MpH5 except that the shrinkage curves were displaced toward higher temperatures because of low B2O3 content.