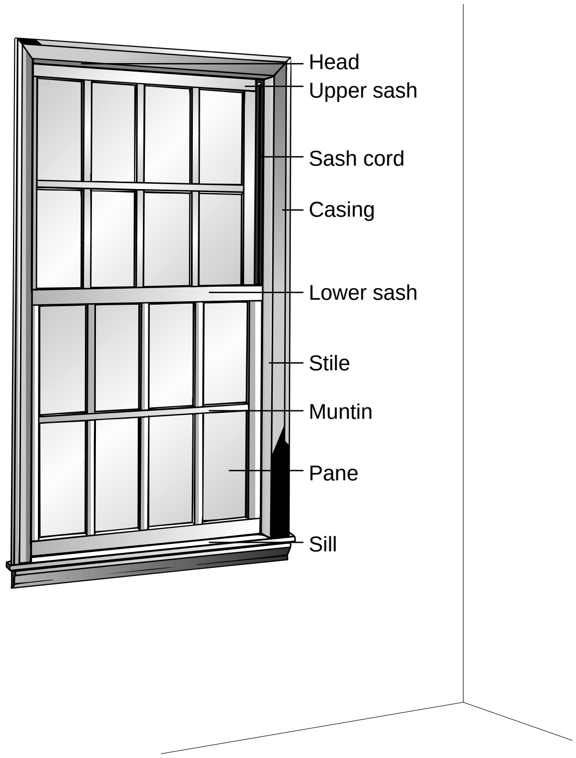

Section 16.2

Windows and Glass

When you look through a clean glass window on a sunny day, you hardly know the glass is there. Light passes through each pane with so little loss and distortion that it's difficult to see the window at all. But you have no trouble feeling glass—it's a tough, rigid material that keeps out the wind and weather while admitting light. Because glass is also a good thermal insulator, it helps to keep buildings cool in the summer and hot in the winter. Produced from cheap and plentiful raw materials with minimal effort and equipment, glass is truly a remarkable substance.

Questions to Think About: *How do they make glass sheets that are so flat and smooth? Why does some glass shatter when you heat it or cool it too rapidly? Since most solids melt suddenly at specific temperatures, why does glass become soft and pliable instead? Since most solids abruptly form narrow necks and snap when you try to stretch them, why is it possible to stretch softened glass into so many shapes? Why does tempered glass shatter completely into tiny pieces when it breaks? What colors the glass used in stained glass windows?*

Experiments to Do: *Prove to yourself that glass is a hard, brittle, elastic material. To show that glass is hard, see how difficult it is to scratch a glass bottle. Can you find anything that scratches it? To show that glass is brittle, try to dent a glass bottle without breaking it. Wrap the bottle in heavy cloth or paper and then tap it carefully with a rock or hammer. Were you able to dent it? To show that glass is elastic, push gently on a large glass mirror. Be careful not to break it! Look closely at the image to see if the glass is distorting. What happens to the glass when you stop pushing?*

Examine a piece of broken glass. You will find that the fractured surfaces are basically smooth and featureless. That's because glass has no orderly crystalline structure. Instead, *its atoms are arranged almost randomly, like those in a liquid. In fact, glass is essentially a super-thick liquid. To allow glass to flow visibly, you must heat it dangerously hot. However, you can observe similar flow in cold honey. Honey stretches and flows and sticks to itself in much the same way as softened glass. And like glass, honey doesn't crystallize as you cool it—it just gets stiffer and stiffer.*

What Is Glass?

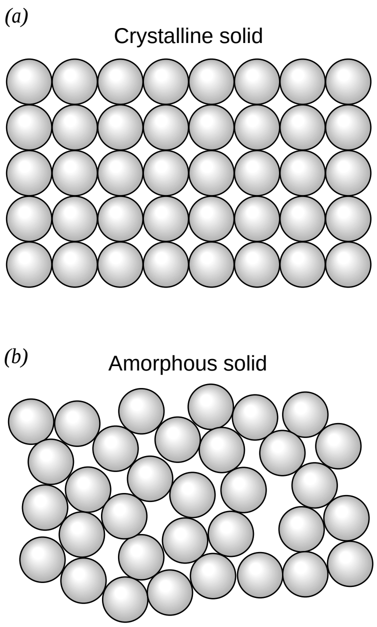

Fig. 16.2.1 - (*a*) A crystalline solid has long-range order, meaning that knowing where atoms are at one end of the crystal tells you where atoms are at the other end of the crystal. (*b*) An amorphous solid has no long-range order.

Let's begin with what glass is not—it is not a crystal. The atoms in a crystal are organized in a regular, repetitive lattice so you need only locate a few atoms in order to predict where all of their neighbors are (Fig. 16.2.1*a*). The atoms are so neatly arranged that, except for occasional crystal defects, you can predict positions for thousands or even millions of atoms in every direction. This spatial regularity is called **long-range order**.

Glass is an **amorphous solid**, a material without long-range order (Fig. 16.2.1*b*). Locating a few glass atoms tells you next to nothing about where to find any other atoms. The atoms in glass are arranged in the random manner of a liquid because glass is essentially a super-stiff liquid. Its atoms are jumbled together in a sloppy fashion but they can't move about to form a more orderly arrangement. Glass arrives at this peculiar amorphous state when hot liquid glass is cooled too rapidly for it to crystallize.

If molten glass were an ordinary liquid, it would begin to solidify abruptly during cooling once it reached its freezing temperature. At that point, its atoms would begin to arrange themselves in crystals that would grow in size until there was no liquid left. That's what's normally meant by freezing.

However some liquids are slow to crystallize when you cool them slightly below their freezing temperatures. While they may be cold enough to grow crystals, they must get those crystals started somehow. If crystallization doesn't start, a material's atoms and molecules will continue to move about and it will behave as a liquid. When that happens, the liquid is said to be **supercooled**.

Supercooling is common in liquids that have difficulties forming the initial **seed crystals** on which the rest of the liquid can crystallize. Because almost all of the atoms in a seed crystal are on its surface, it has a relatively large surface tension and surface energy. Below a certain critical size, a crystal is unstable and tends to fall apart rather than grow. However once the first seed crystals manage to form, a process called **nucleation**, the rest of the supercooled liquid may crystallize with startling rapidity.

Just below its freezing temperature, the atoms in glass don't bind to one another long enough to form complete seed crystals and nucleation takes almost forever. The glass is a supercooled liquid. At somewhat lower temperatures, seed crystals begin to nucleate, but glass's large viscosity (thickness) prevents these crystals from growing quickly. The glass remains a supercooled liquid for an unusually long time. At even lower temperatures, glass becomes so viscous that crystal growth stops altogether. The glass is then a stable supercooled liquid, one that will remain in that form indefinitely. At this temperature range, glass still pours fairly easily and can be stretched or molded into almost any shape, including windowpanes.

However, when you cool the glass still further, it becomes a ***glass***. Here the word *glass* refers to a physical state of the material—a type of amorphous solid. To distinguish this use of the word *glass* from the common building material, it is italicized here and elsewhere in this section. Glass, the material, becomes a *glass*, the state, at the ***glass* transition temperature** (T_g). Below T_g, the atoms in the glass rarely move past one another; they continue to jiggle about with thermal energy but they don't travel about the material.

It's hard to tell by looking at the glass just when this *glass* transition takes place. It generally occurs when the glass's viscosity exceeds about 10^{12} Pa·s, where the Pa·s is the SI unit of viscosity. At that point, the great difficulty the fluid has flowing past itself reflects the microscopic difficulty the atoms have in rearranging. The atoms are practically frozen in place and the fluid flows so slowly that the glass is almost indistinguishable from a solid.

To see that glass behaves like a solid, let's look at how viscous fluids and solids respond to shear stress. If you exert shear stress on a viscous fluid, by pushing its top right and its bottom left, the top portion will flow right and the bottom portion will flow left (Fig. 16.2.2). But if you exert shear stress on a solid, it will experience shear strain. It won't flow anywhere. To get the top half of a steel bar to "flow" right while the bottom half "flows" left, you'd have to break it. In contrast, even a small shear stress will eventually cause a liquid to flow. Thus there seems to be a fundamental difference between solids and liquids in their responses to shear stress: solids undergo shear strain while liquids flow.

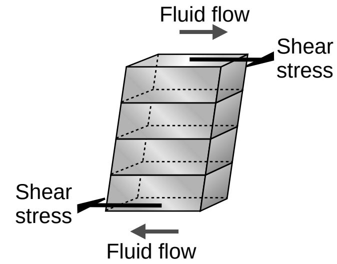

Fig. 16.2.2 - Viscosity measures the difficulty a fluid has flowing past itself. The higher this fluid's viscosity, the more shear stress it must experience to keep its bottom layer flowing quickly to the left and its top layer flowing quickly to the right.

But what happens when you suddenly expose an extraordinarily viscous liquid to shear stress? The liquid has so much trouble flowing that it undergoes shear strain instead. It bends elastically, just like a crystalline solid! If you release the stress quickly enough, the liquid will spring back almost to its original shape. However if you wait a while before releasing the stress, the liquid will have time to flow and the stress will go away on its own. You can see this effect by bending a stick of taffy. If you bend it briefly, the taffy is almost as springy as a solid. But if you bend it and wait, the taffy flows to relieve the shear stress.

The time a liquid takes to relieve shear stress by flowing increases with that liquid's viscosity. Thin liquids such as water relieve stresses quickly, but with a viscosity of 10^{12} Pa·s, it takes glass minutes or hours to relieve stresses and you would have to be very patient to detect anything non-solid about that glass. It would feel just as hard and elastic as an ordinary crystalline solid unless you were willing to wait for hours to see it flow (Fig. 16.2.3).

There is one more change that occurs as the *glass* transition takes place: the glass stops shrinking like a liquid with decreasing temperature and starts shrinking like a solid. Liquids shrink rapidly as you cool them because their mobile atoms pack together more tightly as their thermal energies decrease. Solids shrink less rapidly as they're cooled because their atoms can't rearrange. Above the glass transition temperature, glass shrinks quickly as it's cooled, like a liquid. Below the glass transition temperature, glass shrinks slowly as it's cooled, like a solid.

CHECK YOUR UNDERSTANDING #1: Flash Frozen
If you sprinkle some small ice crystals into supercooled liquid water, what will happen?

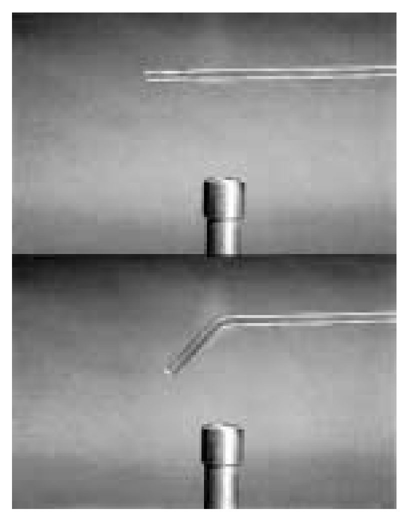

Fig. 16.2.3 - Below its *glass* transition temperature (top), this rod behaves as a solid and responds elastically to forces. But above its *glass* transition temperature (bottom), the rod behaves as a viscous liquid and bends slowly under its own weight.

What is in Glass?

With that introduction to the behavior of *glasses*, it's time to look at what's inside glass. Window glass is mostly silicon dioxide (SiO_2), the chemical found in quartz and quartz sand and commonly called *silica*. Silica is extremely common in nature, making up much of the earth's crust. It's hard and clear and resistant to chemical attack. It's also the best *glass* forming material in existence.

To be a good *glass former*, a material must have trouble nucleating seed crystals and must prevent those seed crystals from growing quickly. Because silica is extraordinarily viscous at its freezing temperature, it's an excellent *glass* former and is easily converted into quartz *glass* or *vitreous quartz*.

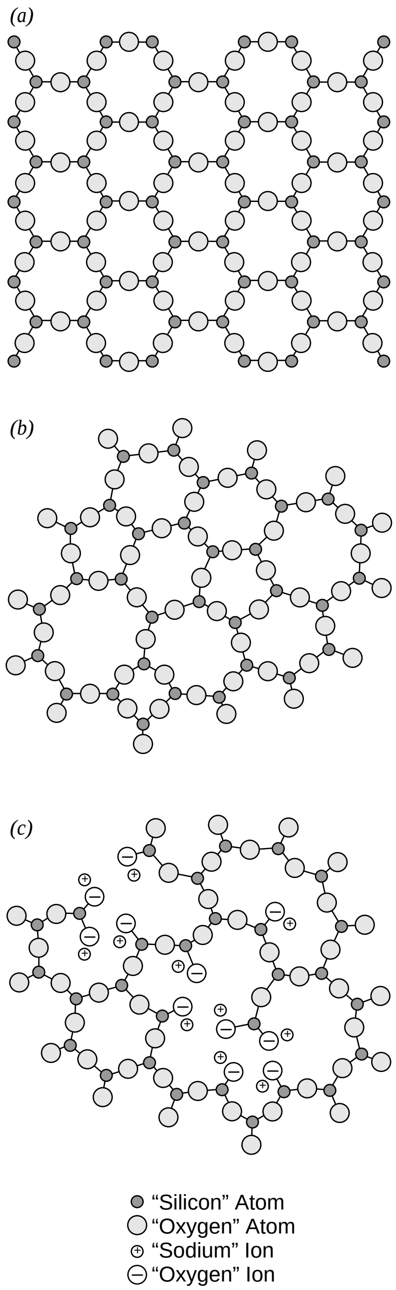

Fig. 16.2.4 - Two-dimensional illustrations of the structures of (*a*) crystalline silica, (*b*) liquid or glassy silica, and (*c*) glassy or vitreous silica containing some sodium oxide.

Silica is held together by covalent bonds, even as a liquid. A **covalent bond** forms between two atoms when they share a pair of electrons. This sharing reduces the electrostatic potential energy of the atoms by placing extra negative charge in between their positive nuclei. It also reduces the kinetic energies of the shared electrons by letting them spread out as waves onto both atoms. Their wavelengths increase as they spread and lengthening an electron's wavelength, like lengthening a photon's wavelength, reduces its energy.

Covalent bonds are highly directional. Each silicon atom in the silica forms covalent bonds with four oxygen atoms and orients those atoms at roughly the corners of a tetrahedron. Each oxygen atom in the silica forms covalent bonds with two silicon atoms and orients them at roughly two corners of a tetrahedron. The result is an intricate network of silicon and oxygen atoms in which each oxygen atom acts as a bridge between two adjacent silicon atoms. Because of its interlinking structure, silicon dioxide is often called a *network former*.

In crystalline silica, this networking process creates an orderly three-dimensional lattice that's hard to visualize. To help us discuss the basic character of this lattice, let's examine a two-dimensional lattice with similar features (Fig. 16.2.4*a*). The "silicon" atoms in this simplified lattice bind to only three "oxygen" atoms, at the three corners of an equilateral triangle. The "oxygen" atoms bind to two "silicon" atoms, at opposite ends. While this lattice is oversimplified, it illustrates how intricate and orderly a quartz crystal is. If you know the locations of two or three atoms in this lattice, you can predict where all of the other atoms are.

When you melt silica, its atoms remain covalently bound, but they change partners frequently. The orderly crystalline lattice vanishes and is replaced by a tangled network of interconnecting rings (Fig. 16.2.4*b*). While the silicon and oxygen atoms still have the right numbers of neighbors, they often form rings with the wrong numbers of atoms in them.

Once the crystalline order of silica has been destroyed, it's hard to recover. The tangled networks of the liquid are relatively stable and the atoms can't tell which rings have too many or two few members. Moreover liquid silica is still held together by covalent bonds, which constrain the motions of its atoms and make it an extremely viscous fluid. Silica is thus an ideal *glass* former and supercools all the way to a *glass* when you cool it rapidly.

CHECK YOUR UNDERSTANDING #2: Instant Glass
The first test of the atomic bomb near Alamogordo, New Mexico on July 16, 1945, turned the desert sand into glass. Explain what happened.

Soda–Lime–Silica Glass

But pure silica has a serious drawback. Its covalent bonds hold it together so tightly that it doesn't melt until its temperature reaches 1713 °C. That's far above the melting temperatures of most metals, including iron and steel. While pure quartz glass can be made, it's a specialty item and quite expensive. Instead, most common glass contains other chemicals that lower the mixture's melting temperature so that it's easier to work with.

The principal addition to window glass is sodium oxide or *soda* (Na_2O). Although soda contains oxygen atoms, it's held together by ionic rather than covalent bonds. **Ionic bonds** form when the atoms in a material become oppositely charged ions and attract one another. In this case, each oxygen atom in soda removes an electron from two nearby sodium atoms, producing a mixture of negatively charged oxygen ions and positively charged sodium ions.

When soda is added to silica and the two are heated, the mixture melts at a temperature that is below the melting temperature of either material. It's a **eutectic**, a mixture that melts more easily than the materials from which it's made. A mixture containing 25% soda by weight melts at a temperature of only 793 °C. Equally remarkable is the fact that a fine mixture of soda and silica powders can be melted together at temperatures near this value. The soda acts as a flux to melt the silica and the glass manufacturer never has to heat the mixture to silica's normal melting temperature.

The reason for the low melting temperature of this *soda–silica glass* is illustrated in Fig. 16.2.4*c*. The sodium atoms in the mixture donate electrons to the oxygen atoms, leaving the substance full of positively charged sodium ions and negatively charged oxygen ions. In this case, the oxygen atoms have just a single charge. But an oxygen atom with an extra electron only needs to share one electron to complete is electronic shell. As a result, it binds to only one silicon atom and doesn't form a bridge between a pair of silicon atoms.

Soda–silica glass is full of *non-bridging oxygen atoms* that end the network rather than extending it. Their presence weakens the glass and lowers its melting temperature. While this ease of melting is important for glass manufacturing, soda–silica glass is less robust in almost every way than pure silica glass. It's softer and weaker than silica glass so it scratches and breaks more easily. It has more internal friction so it wastes energy in bending and emits a dull tone when struck. It's also much less chemically resistant than quartz *glass*. In fact, it's water-soluble.

Sodium ions are so water soluble that they allow water to enter the glass's molecular network and chop it to pieces. As a result, soda–silica glass can be dissolved in water and painted onto surfaces. It's called *water glass* and is used to seal the outsides of eggs so that they don't dry out. It's also included in laundry detergent, where it protects the washer from corrosion.

Soda–silica glass can be made much less water-soluble by adding calcium oxide or *lime* (CaO) to it. Calcium oxide is an ionic solid, but it's not soluble in water and makes the glass much more durable. *Soda–lime–silica glass* is almost insoluble in water and is the principal commercial glass. Windows, bottles, and jars are all made of soda–lime–silica glass.

In each of these glasses, silica is the *glass* or network former and soda and lime are modifiers. The *glass* former's job is to create the tangled network that gives the liquefied material its high viscosity and allows it to supercool all the way to the *glass* transition temperature. A modifier's job is to ease the path to the *glass* transition and to alter the properties of the glass that's produced. Most importantly, modifiers help to ensure that the *glass* former doesn't crystallize during cooling, a serious problem called *devitrification*.

CHECK YOUR UNDERSTANDING #3: Low Temperature Liquids

A mixture of soda and silica melts at a temperature below the melting point of either material. How does this resemble a mixture of ice and salt?

Other Glasses

There are many other compounds and mixtures that can form *glasses*. Most of these systems involve oxygen atoms, which are excellent bridging atoms and good at producing covalent networks. But there are some *glasses* that don't contain oxygen and there are even *glasses* that contain only metal atoms (see ❐). Because these exotic *glasses* are rarely used in windows, we'll focus instead on the more common oxygen-containing glasses (Table 17.2.1).

❐ Amorphous or *glassy* metals are made by ultrafast cooling of liquid metals. In "splat" cooling, a thin stream of molten metal pours onto a spinning refrigerated wheel. The liquid cools and solidifies in millionths of a second to produce a paper-thin ribbon of metallic *glass*. However, even when cooled incredibly quickly, only special alloys form metallic *glasses*. Such *glasses* are much harder than normal metals because they have no crystalline structure and can't undergo slip.

Table 17.2.1 - The approximate compositions and uses of various common forms of glass.

Type of Glass	*Composition (by weight)*	*Uses*
Soda–Lime–Silica	73% silica, 14% soda, 9% lime, 3.7% magnesia, and 0.3% alumina	Glass Windows, Bottles, and Jars
Borosilicate	81% silica, 12% boron oxide, 4% soda, and 3% alumina	Pyrex Cookware and Laboratory Glassware
Lead (Crystal)	57% silica, 31% lead oxide, and 12% potassium oxide.	Lead Crystal Tableware
Aluminosilicate	64.5% silica, 24.5% alumina, 10.5% magnesia, 0.5% soda.	Fiberglass Insulation and Halogen Bulbs

Silica isn't the only *glass* forming chemical. Other materials that create tangled networks and form *glasses* during rapid cooling include phosphorus pentoxide (P_2O_5), germanium oxide (GeO_2), and boron oxide (B_2O_3). Of these, only boron oxide is commercially important and then only when mixed with silica.

The problem with pure boron oxide glass is that it's not very durable and dissolves easily in hot water. However, boron oxide-silica glasses are quite stable and play important roles in laboratories and kitchens under trade names such as Pyrex and Kimax. These *borosilicate glasses* tolerate temperature changes much better than soda–lime–silica glasses.

Soda and lime aren't the only modifiers used in commercial glasses. All of the alkali oxides and alkaline earth oxides act as modifiers when mixed with silica or other *glass* formers. Changing the modifiers in soda–lime–silica glasses produces subtle alterations in the mechanical, chemical, and optical properties of the glass. The most common alternative modifiers are potassium oxide (K_2O), which is substituted for soda, and magnesium oxide or *magnesia* (MgO), which is substituted for lime. Barium oxide (BaO) and strontium oxide (SrO) are frequently substituted for lime in glass that must block X-rays, such as that on the front of a television picture tube.

There are also some chemical compounds that are intermediate between *glass* formers and modifiers. While these compounds don't form *glasses* on their own, they participate in the tangled networks initiated by other compounds such as silica. The most important intermediate compounds are aluminum oxide or *alumina* (Al_2O_3) and lead oxide (PbO). *Aluminosilicate glasses* tolerate high temperatures better than soda–lime–silica glasses and are used in halogen lamps, furnaces, and fiberglass insulation. A small amount of alumina is included in most glasses to help them tolerate weather better.

Lead oxide is included in special optical glasses to increase their indices of refraction. It also makes them dense, hard, and X-ray absorbing. The *lead crystal* used in decorative glassware and windows isn't crystalline at all. Instead, it's a *glass* consisting mostly of soda, lead oxide, and silica. This soda–lead oxide-silica glass refracts light strongly and disperses its colors. Because its networks are more complete than those in soda–lime–silica glass, lead crystal is stronger and it has less internal friction. Lead crystal rings beautifully when you strike it gently with a hard object.

One other important variation in window glass is color. The pure glasses that we've considered up until now are colorless because they have no way of absorbing photons of visible light. But impurities and imperfections can give these glasses colors. Many of the colored glasses that appear in stained glass windows are that way because they contain metal ions such iron, cobalt, or copper. The electrons in these ions have many empty orbitals to which they can move and they absorb photons of visible light. Just which colors these ions absorb depend on their structures and on how many electrons they're missing.

Because iron ions that are missing three electrons appear green, iron impurities in common window glass make it appear slightly green. Copper and cobalt ions that are missing two electrons appear blue (blue bottle glass). Manganese ions that are missing three electrons appear purple. Chromium ions that are missing three electrons appear green (green bottle glass). Vanadium ions that are missing four electrons appear red. And so it goes. There is also special ruby glass that contains tiny particles of gold metal and appears red because these metal particles absorb green and blue light.

Most well mixed glasses are completely uniform throughout and have no internal variations in refractive index to scatter and reflect light. But there are also *opal* or *milk glasses* that are not uniform and scatter light like a cloud. These translucent glasses are used in privacy windows and are produced when particles of one type of glass precipitate out of solution in another type of glass during cooling. Materials in which crystalline particles precipitate out of solution in a glass during cooling are called *glass-ceramics* and are generally translucent rather than transparent.

CHECK YOUR UNDERSTANDING #4: Play It, Sam
How can you distinguish a lead crystal wine glass from one made of soda–lime–silica glass?

Making Glass Windows

Making glass is relatively easy compared to making steel. In principle, all you have to do is mix the raw materials, melt them together into a liquid, and form the liquid into a finished product as it cools. As long as you cool it quickly through the temperature range at which seed crystals can nucleate and grow, it will turn into glass. Nonetheless, there are some interesting procedures involved in creating glass and its products, particularly windows.

The raw materials in soda–lime–silica glass are commonly occurring minerals. Silica (SiO_2) is obtained from quartz sand and sandstone. Soda ash (Na_2CO_3), which decomposes into soda (Na_2O) and carbon dioxide (CO_2) when heated, is a naturally occurring mineral called trona and can also be produced by reactions between limestone and salt. Limestone ($CaCO_3$), which decomposes into lime (CaO) and carbon dioxide (CO_2) when heated, is a ubiquitous sedimentary rock.

These three minerals are heated together in a large ceramic chamber to a temperature of roughly 1500 °C. At this temperature, the soda acts as a flux and helps the other two minerals to melt. Soon the entire mixture is liquid. Because it contains several different compounds, the liquid glass is carefully stirred to ensure that it's uniform throughout.

Gases released from the minerals, particularly carbon dioxide, water vapor, and trapped air, cause the liquid to froth. One of the hardest tasks in glass making is eliminating the bubbles. This process, called *fining*, involves waiting for the bubbles to float to the surface and adding small quantities of additional chemicals—often arsenic and antimony compounds—to help the bubbles escape.

Finally, the glass is cooled to a working temperature of about 800 °C, passing quickly through the temperature range in which it can crystallize. As it cools, the liquid's viscosity increases dramatically. In the melting region of the chamber, its viscosity is about 10 Pa·s or 1000 times that of water. At 800 °C, its viscosity has risen to 1,000 Pa·s or 100,000 times that of water. It flows like a thick syrup and is ready for use in making bottles or windows.

Glass bottles are formed by injecting gobs of glass into molds and then blowing air into them to create their hollow interiors. The injection step creates the neck of the bottle, attached to a carefully shaped but uninflated glass bubble. The blowing step inflates that bubble to create the bottle's storage region. The

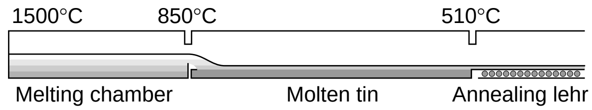

Fig. 16.2.5 - Float glass is made by pouring liquid glass onto the surface of liquid tin. As the ribbon of liquid glass flows away from the melting chamber, it cools and hardens. Finally, it's annealed in a long tunnel-shaped lehr before being cut into sheets.

glass is then cooled slowly through its glass transition temperature to produce a finished bottle.

Windowpanes are produced by pouring liquid glass onto a pool of molten tin (Fig. 16.2.5). This "float" method was developed in 1959 and revolutionized window making. The biggest problem in window making has always been producing perfectly flat surfaces on both sides (Fig. 16.2.6). The top surface of liquid glass is naturally flat but the bottom surface conforms to whatever it's lying on. When the glass is poured onto a liquid metal, its bottom surface is supported by another perfectly flat surface. The finished plate of float glass is thus perfect on both sides.

That this process works is a wonderful confluence of behaviors. First, tin melts at the relatively low temperature of 232 °C but doesn't boil until 2260 °C. This range allows the liquid glass to harden while the tin remains liquid. Second, liquid tin is far denser than liquid glass so the glass floats easily on top, supported by the buoyant force. Third, tin and glass are immiscible—tin is held together by metallic bonds while glass is bound by covalent and ionic bonds. The two liquids don't bind strongly to one another so they keep to themselves. The glass remains chemically unaffected by the liquid tin below it.

As the hot glass flows out onto the tin, it naturally spreads until it's about 6 mm thick. A glassmaker can produce thicker windowpanes by corralling the spreading liquid so that it remains relatively thick. To produce thinner sheets, the glassmaker stretches the liquid to spread it more thinly. The float technique can produce extremely flat glass in thicknesses ranging from less than a millimeter to several centimeters. (As shown in Fig. 16.2.7, glass's tolerance of stretching also makes it possible to fabricate incredibly thin glass fibers and tubes).

The soda–lime–silica mixture used for float glass has a *glass* transition temperature of about 540 °C. When the glass leaves the liquid tin, it's already slightly below that temperature. However, its rapid change in temperature on the tin surface has caused it to shrink and this shrinkage creates stresses in the glass. If the glass were simply cooled to room temperature at this point, the stresses would remain trapped forever and would weaken the glass. Stresses also make the glass birefringent, which can distort the light passing through it.

To reduce the stresses trapped in the glass, it's carefully annealed in a long tunnel called a *lehr*. It's kept near the glass transition temperature for a long time so that the atoms in the glass can rearrange just enough to relieve the stress. When most of the stress has been eliminated, the finished glass is finally allowed to cool to room temperature. In the optical glass used in lenses and telescopes, the annealing is done much more slowly. In many cases, the glass is cooled through the *glass* transition temperature at a rate of less than 1 °C per hour. The glass disk of the 200-inch telescope mirror at Mt. Palomar was cooled from 500 °C to 300 °C at the phenomenally slow rate of only 1 °C per day.

Fig. 16.2.6 - Early glass windows were made by blowing a large glass sphere on the end of an iron pipe. This sphere was cut off the pipe and attached to a metal rod called a punty. Spinning the punty caused the hot sphere to open up into a large flat disk, like a pizza. When this disk cooled, it was cut into a number of small panes. Because each pane was precious, even the central one was used. The bullseye mark left by the punty is plainly visible in these old windows.

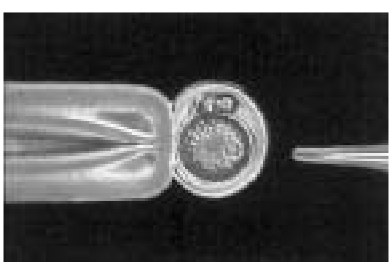

Fig. 16.2.7 - Glass tubing can be heated and stretched to form tubes with microscopic dimensions; miniature copies of the original tubes. Here one glass tube holds a mouse embryo while a much smaller glass tube prepares to inject DNA into it.

CHECK YOUR UNDERSTANDING #5: Glassy Sweets

Many hard sheet candies are smooth and glossy on one side but dull on the other. What causes the difference?

Strengthening Windows

Once it leaves the annealing lehr, the float glass is ready for use. But first it must be cut to size. Cutting glass is a tricky business because it lacks a crystalline structure and its amorphous nature gives it some peculiar properties. To begin with, glass can't undergo any plastic deformation because it can't undergo slip. If you bend glass, it deforms elastically up until the moment it breaks via brittle fracture. When that break finally occurs, a crack propagates uncontrollably through the glass because the glass has no crystalline grains to stop it or change its path.

The crack always begins at the surface of the glass, where a defect weakens the molecular structure. Even the most perfect glass surface has a few defects in it and any one of these can initiate a crack when it's under tensile stress. (For an interesting way to minimize these defects, see ❐.) When you bend a piece of glass, you stretch one surface while compressing the other and create a tensile stress on the stretched surface. If this tensile stress is large enough, a defect there will become a crack and will propagate through the glass so that it shatters.

❐ Fiberglass is made by pulling hot aluminosilicate glass into thin strands. Hot glass is a simple liquid and will stretch without breaking to form fantastically thin fibers. These fibers are so narrow that they have almost no surface area and thus very few surface defects. As a result, glass fibers are difficult to break and are very strong. They are used as structural materials and as thermal insulation.

Simply bending glass and hoping that it will break along a straight line isn't a practical scheme for cutting glass. Instead, you use a diamond scribe to scratch the glass along the intended break. The scratch introduces defects right where you want the cracks to occur. Wetting the scratch helps because water creates defects in glass and weakens it. If you then stress the glass carefully, either mechanically or by a sudden change in temperature, you can usually get it to crack along the scratch. Still, the glass often breaks in an undesired direction and you are left with useless fragments.

Another way to cut glass is with an abrasive saw. Here a rapidly turning disk containing extremely hard crystals chips out tiny fragments from the glass. The chipping exerts only a modest stress on the glass so that it doesn't crack. Although slow, this method is quite reliable. Similar abrasive techniques are used to cut decorative glass.

Once it's been cut to size, the window is finished. It's ready for installation in a house or building. But it's not ready for use in an oven or an automobile. This window would not be able to tolerate the sudden changes in temperature present in an oven and would pose a serious hazard during a collision in an automobile. So the glass must be heat stabilized and strengthened.

To make an oven window more tolerant of thermal shocks, its chemical composition must be changed. Because soda–lime–silica glass has a large coefficient of volume expansion, it expands considerably as its temperature rises and this expansion can produce huge stresses in the glass. If one half the oven window is suddenly heated, it will expand and try to stretch the other half. If the resulting tensile stress is large enough, that window will crack and break. However, the oven window is made out of a borosilicate glass such as Pyrex. Borosilicate glasses have coefficients of volume expansion that are about a third those of soda–lime–silica glasses. Thus it takes a much larger thermal shock to break a Pyrex window or container. For that reason, most cookware and laboratory glassware is made out of borosilicate glass.

To strengthen a car window, its mechanical structure must be changed. Glass breaks when its surface begins to tear apart. If you modify the glass so that its surface is normally under compressive stress, it will be much harder to get a tear started and the glass will be stronger.

The best way to put the glass's surface under compressive stress is to **temper** the glass. Tempering is done by heating the glass until it softens and then suddenly cooling its surfaces with air blasts. When the glass's surface cools through the *glass* transition temperature, it becomes solid-like and no longer shrinks rapidly with temperature. However the inside of the glass is still liquid-

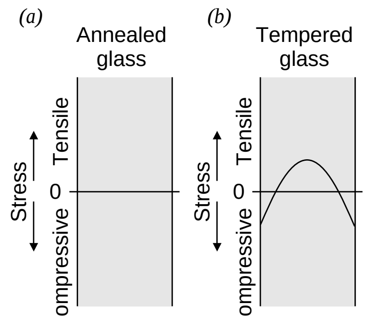

Fig. 16.2.8 - (*a*) Properly annealed glass has no internal stresses. (*b*) Tempered glass is specially heat treated so that its surfaces are under enormous compressive stresses while its body is under substantial tensile stress. Tempered glass is very hard to break.

Fig. 16.2.9 - When a small rock cut through the compressed outer skin of this tempered glass car window, it exposed the tense inner layer. That layer immediately began to tear and the entire window broke into thousands of tiny fragments.

like and continues to shrink rapidly as it cools. As the glass inside shrinks, the surface layers are placed under enormous compressive stresses (Fig. 16.2.8).

This compressive stress makes it difficult to initiate a crack in the outer surface of tempered glass. You must first stretch that outer surface so much that the compressive stress disappears and becomes tensile stress. Breaking tempered glass takes about three times as much force as breaking ordinary glass.

But tempered glass has an interesting complication. When it breaks, it undergoes *dicing fracture*—the glass crumbles completely into tiny pieces less than a centimeter on a side (Fig. 16.2.9). This catastrophic failure is what makes tempered glass safe in automobile windows. Tempered glass windows are hard to break but once they do break, they crumble into little cubes.

Dicing fracture occurs whenever the body of tempered glass becomes the surface. The body is under severe tensile stress so it will crack and tear whenever possible. As long as it's protected by a shell of compressed glass, the body won't crack. But any penetration into the body will cause the whole sheet to self-destruct. For that reason, tempered glass can't be cut in any way once it has been tempered. Car windows are cut to size before they're tempered because they would crumble if you tried to cut them.

Oven windows and refrigerator shelves are also tempered to give them additional resistance to thermal shocks. By tempering the glass, you make it harder for thermal shocks to put the glass surface under tension and cause it to break.However, a car's front windshield is not tempered because it would crumble when struck by road debris. Instead, it's made by laminating a plastic sheet between two sheets of annealed glass. This three-layered *safety glass* sandwich can tolerate minor breaks without falling apart. The plastic keeps the glass together even if it does break and provides a barrier so that a crack in one sheet of glass can't propagate into the other sheet. *Bulletproof glass* is a natural extension of this idea, with many alternating layers of glass and plastic.

CHECK YOUR UNDERSTANDING #6: Bigger Can Be Better

When soda–lime–silica glass is placed in a liquid containing lots of potassium ions, the large potassium ions can replace sodium ions and cause the glass to swell. Since only the surface layer swells, does this effect strengthen or weaken the glass?