26

Processing Glass and Glass-Ceramics

CHAPTER PREVIEW

Glass has changed the world more than any other material. In Chapter 21 we described some of the different types of glass and their properties. In this chapter we will look at the main methods used to fabricate glass products. In terms of the volume of glass that is produced each year, glass processing could be said to be the most important processing method for ceramics. The largest segments of the market are

- Flat glass for windows
- Containers (including bottles, jars, and tableware)

These products are formed using essentially two methods [one is recent (in glass terms) the other has its roots in antiquity]:

- The float glass process
- Blowing

We will also look at some processes that are used to modify glass for specific uses such as the application of thin-film coatings for solar radiation control and tempering and laminating for safety glass. In the last section of this chapter we will examine how glass-ceramics are produced.

This chapter does not cover the processing of some special glass products. For example, the processing of optical fibers is described in Chapter 32, but we introduce the important ideas here. Optical fibers must meet stringent quality requirements. We must understand these requirements to understand why the elaborate processing methods are necessary.

This chapter covers three closely related topics:

- Processing as dictated by applications
- Shaping
- Treating

26.1 THE MARKET FOR GLASS AND GLASS PRODUCTS

More than half of the total worldwide ceramics market is glass products, accounting for over $50 billion/year. Figure 26.1 shows the distribution of glass sales. The market for manufactured glass products emphasizes three main types of glass:

- Hollow glass (bottles, drinking glasses, lamp bulbs, glass containers) 35%
- Flat glass (mirrors, windows) 30%
- Fiberglass (includes glass fiber) 17%

Hollow glass includes most of the container glass and tableware we use (i.e., consumer glassware). Table 26.1 lists examples of the applications for these product categories.

26.2 PROCESSING BULK GLASSES

Glass production starts with a mixture of raw materials, which for glass manufacture often contain a high proportion of naturally occurring minerals (for example, sand and limestone). However, some industrial chemicals such as sodium carbonate (Na_2CO_3) and alumina (Al_2O_3) are also used. The mixture containing the raw materials in the

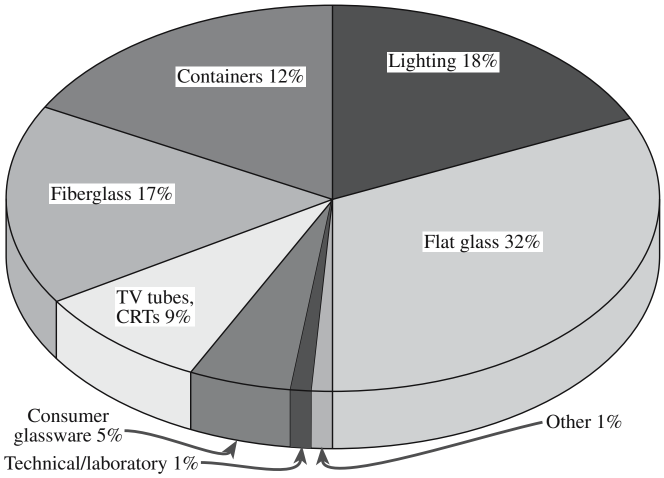

FIGURE 26.1 Percent distribution of glass sales; total: $48,260 million.

TABLE 26.1 Glass Product Types and Applications

Glass product type	*Applications*
Flat glass	Automotive: cars and trucks
	Architectural: commercial buildings, storefronts
	Residential: windows, doors, sunrooms, skylights
	Patterned glass: shower doors, privacy glass
	Blanks for microscopes and telescopes
Containers/tableware	Beverage
	Liquor, beer, wine
	Food
	Pharmaceutical, drugs
	Glasses, plates, cups, bowls, serving dishes
Fiberglass and glass fiber	Wool: insulation, filters
	Textile: plastic or rubber tire reinforcements, fabrics, roof shingle and roll goods reinforcement
	Optical communications
Specialty glass	Artware, stained glass, lead and lead crystal, lighting
	TV picture tubes and flat-panel displays, ovenware and stovetop
	Ophthalmics, aviation, tubing, foamed glass, marbles

appropriate amounts is known as the *batch*. The batch contains a mixture of glass formers, modifiers, and intermediates; the amount of each component depends on the application of the final glass product. In Table 26.2 we link the different ways of giving a batch composition and the sources of some of the raw materials.

FLAT GLASS RAW MATERIALS

- Limestone, $CaCO_3$
- Silica sand, SiO_2
- Soda ash, Na_2CO_3
- Alumina hydrate, $Al_2O_3{\cdot}3H_2O$
- Burnt dolomite, $CaO{\cdot}MgO$

Batch melting depends on the source of energy, the refractory used to contain the glass, details of the batch, processes occurring during melting, and fining (see Section 26.3).

We must also consider the possibility of oxidation and/or reduction of the glass, homogenization processes, and defect in the glass.

By far the greatest amount of flat glass is soda-lime silicate glass. You must be familiar with the terminology used in the glassmaking industry: soda is sodium oxide (Na_2O) and lime is calcium oxide (CaO), so soda-lime silicate glass consists mainly of Na_2O, CaO, and SiO_2. Glass manufacturers often use the common names for these oxides, which are not always the generally recognized scientific name. If you are unsure of the composition of a particular mineral then you need to look at its formula.

All manufacturers of flat glass use basically the same formula, but they never actually use the compounds Na_2O or CaO. Values of the components are usually given in weight percent (wt%). Typical values are 72 wt% SiO_2, 14 wt% Na_2O, wt% CaO, 4 wt% MgO, and 1 wt% Al_2O_3. The molecular formula for a glass of this composition can be calculated as follows.

Step 1: Divide the wt% of each component in the batch by its molecular weight.

Oxide	*wt (g)*	*Molecular weight (g/mol)*	*wt%/molecular weight (mol)*	*Ratio*
SiO_2	72	60.1	1.20	120
Na_2O	14	62.0	0.23	23
CaO	9	56.1	0.16	16
MgO	4	40.3	0.10	10
Al_2O_3	1	102.1	0.01	1

Step 2: Divide each ratio by the smallest ratio in column 4. This gives the number in column 5.

Step 3: Write out the molecular formula for the glass. The molecular formula of our flat glass is then $Al_2O_3{\cdot}10MgO{\cdot}16CaO{\cdot}23Na_2O{\cdot}120SiO_2$.

To make the batch it would not be economical to use only synthesized or pure ingredients. For most glasses a large proportion of the batch is made up of naturally occurring minerals that have been through a beneficiation process. Table 26.3 (top) shows the typical batch constituents used to make the $Al_2O_3{\cdot}10MgO{\cdot}16CaO{\cdot}23Na_2O{\cdot}120SiO_2$ glass. To determine how much of the raw material we need to add to the batch to obtain the desired amount of oxide in the final glass, we need to know the fraction of that oxide in the raw material. For the principal raw materials used in glass making this fraction is given in column 5 in Table 26.2. For example, during melting limestone will decompose as follows:

TABLE 26.2 Principal Raw Materials Used in Glassmaking

Material	*Alternative name*	*Theoretical formula*	*Oxides*	*Fraction*	*Batch*	*Purpose*
Alumina	Calcined alumina	Al_2O_3	Al_2O_3	1.000	1.000	
Aluminum hyd.	Hydrated alumina	$Al_2O_3 \cdot 3H_2O$	Al_2O_3	0.654	1.531	
Aplite (typical	—	—	Al_2O_3	0.240	4.167	Source of Al_2O_3
composition)	—	—	$Na_2(K_2)O$	0.100	—	
	—	—	SiO_2	0.600	—	
	—	—	CaO	0.060	—	
Feldspar	Microcline (composition	$K_2O \cdot Al_2O_3 \cdot 6SiO_2$	Al_2O_3	0.180	5.556	Source of Al_2O_3
	of commercial spar)	—	$K_2(Na_2)O$	0.130	—	
			SiO_2	0.680	—	
Nepheline syenite	—	—	Al_2O_3	0.250	4.000	Source of Al_2O_3
(typical composition)	—	—	$Na_2(K_2)O$	0.150	—	
	—	—	SiO_2	0.600	—	
Calumite	Calcium-aluminum	$2CaO \cdot MgO \cdot 2SiO_2$	SiO_2	0.380		
	silicate	$2CaO \cdot Al_2O_3 \cdot SiO_2$	Al_2O_3	0.117		
		$2(CaO \cdot SiO_2)$	CaO	0.400		
			MgO	0.080		
Kyanite (90%	—	$Al_2O_3 \cdot SiO_2$	Al_2O_3	0.567	1.763	
concentrate)	—	—	SiO_2	0.433	—	
Kaolin	China clay	$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$	Al_2O_3	0.395	2.57	
	—		SiO_2	0.465	—	
Cryolite	Kryolith	Na_3AlF_6	—	—	—	Flux and opacifier in opal glasses
Antimony oxide	—	Sb_2O_3	Sb_2O_3	1.000	1.000	
Arsenious oxide	White arsenic	As_2O_5	As_2O_5	1.160	0.860	Fining and decolorizing
Barium carbonate	—	$BaCO_3$	BaO	0.777	1.288	Source of BaO
Barium oxide	Baryta	BaO	BaO	1.000	1.000	
Barium sulfate	Barytes	$BaSO_4$	BaO	0.657	1.523	Flux and fining
Boric acid	Boracic acid	$B_2O_3 \cdot 3H_2O$	B_2O_3	0.563	1.776	Source of B_2O_3
Borax	—	$Na_2O \cdot 2B_2O_3 \cdot 10H_2O$	B_2O_3	0.365	2.738	Source of B_2O_3
	—		Na_2O	0.163	6.135	
Anhydrous borax	(“Pyrobor”)	$Na_2O \cdot 2B_2O_3$	B_2O_3	0.692	1.445	Source of B_2O_3
	—	—	Na_2O	0.308	3.245	
Lime, burnt	Quick lime	CaO	CaO	1.000	1.000	
Lime, hydrated	Calcium hydrate	$CaO \cdot H_2O$	CaO	0.757	1.322	
Limestone	Calcium carbonate	$CaCO_3$	CaO	0.560	1.786	Source of CaO
Calcium carbonate	Whiting	$CaCO_3$	CaO	0.560	1.786	Source of CaO
Lime, dolomitic	Burnt dolomite	$CaO \cdot MgO$	CaO	0.582	1.720	Source of CaO
	—	—	MgO	0.418	2.390	and MgO
Dolomite	Raw limestone	$CaO \cdot MgO \cdot 2CO_2$	CaO	0.304	3.290	Source of CaO
	(dolomitic)		MgO	0.218	4.580	and MgO
Lime, hydrated, dolomitic	Finishing lime	$CaO \cdot MgO \cdot 2H_2O$	CaO	0.423	2.363	Source of CaO
	—		MgO	0.304	3.290	and MgO
Litharge	Lead oxide, yellow	PbO	PbO	1.000	1.000	
Red lead	Minium	Pb_3O_4	PbO	0.977	1.024	Source of PbO
Bone ash	Calcium	$3CaO \cdot 2P_2O_5 + xCaCO_2$	CaO	0.372	2.700	
	phosphate		P_2O_5	0.628	1.592	
Iron oxide, red	Rouge	Fe_2O_3	Fe_2O_3	1.000	1.000	Color
Potassium hydroxide	Caustic potash	KOH	K_2O	0.838	1.194	Source of K_2O
Potassium nitrate	Saltpeter	KNO_3	K_2O	0.465	2.151	Source of K_2O
Potassium carbonate.	Calcined potash	K_2CO_3	K_2O	0.681	1.469	Source of K_2O
Glassmaker’s potash	Potassium carbonate, hydrated	$K_2CO_3 \cdot \frac{3}{2}H_2O$	K_2O	0.570	1.754	Source of K_2O
Sand	Glass sand, quartz	SiO_2	SiO_2	1.000	1.000	
Soda ash	Sodium carbonate coml.	Na_2CO_3	Na_2O	0.585	1.709	Source of Na_2O
Sodium nitrate	Saltpeter chili	$NaNO_2$	Na_2O	0.365	2.741	Oxidizing and fining
Salt cake	Sodium sulfate	Na_2SO_4	Na_2O	0.437	2.290	Oxidizing and fining
Zinc oxide	—	ZnO	ZnO	1.000	1.000	

TABLE 26.3 Batch Composition and Sources in the United States

Raw material	*Oxides supplied*	*Fraction of oxide*	*Weight of oxide required (g)*	*Weight of raw material in batch (g)*
Limestone	CaO	0.560	90	61
Silica sand	SiO_2	1.000	720	720
Soda ash	Na_2O	0.585	140	239
Alumina hydrate	Al_2O_3	0.654	10	15
Burnt dolomite	CaO	0.582	90	96
	MgO	0.418	40	

Source		*U.S.A. location*
Silica sand	Bank sand	Jersey shore
	Sandstone	Allegheny mountains
Soda ash	Trona deposits	Wyoming
Limestone	Dolomite	All over, e.g., Alabama
Feldspars	In pegmatites	North Carolina
B_2O_3	Borax	California

$$CaCO_3\ (s) \rightarrow CaO\ (s) + CO_2\ (g) \qquad (26.1)$$

The fraction of CaO (molecular weight: 56.1 g/mol) in $CaCO_3$ (molecular weight: 100.1 g/mol) is 0.560, or 56%. Hence, for each kilogram of limestone added to the batch the melt will contain only 0.56 kg of CaO. So using the raw materials listed above, and by bearing in mind the fraction of each oxide provided by each mineral, we can determine the batch composition for a 1 kg melt of flat glass. These are the numbers given in Table 26.3 (top). Note that the lime comes from both burnt dolomite and limestone. A batch weighing 2 t can be measured to an accuracy of 0.1%.

Table 26.3 (bottom) shows where we might actually have to go to obtain these raw materials. [If we are making bottles and jars the batch will likely contain cullet, recycled glass; see Section 37.7.]

After the batch has been thoroughly mixed, it is melted at high temperature to form a homogeneous liquid melt. For small-scale melting of glass the batch will be placed in a crucible. For glass-melting experiments in the laboratory it is common to use Pt, or a Pt alloy such as Pt-5% Au or Pt-20% Rh crucibles.

These crucibles are very expensive, but they can withstand high temperatures, they do not contaminate the glass melt, and they can be easily cleaned and reused. Other crucible materials, usually used for larger batch sizes, include silica, alumina, and mullite.

Large-scale industrial production of glass is carried out in continuous furnaces called tanks. Glass-melting tanks are the second largest industrial furnaces, the largest being the blast furnaces used in making iron and steel. Figure 26.2 shows the inside of a glass-melting tank and Figure 26.3 shows a schematic of a glass-melting tank for producing glass containers. The tanks are typically 10–40 m long, 3–6 m wide, and 1–1.5 m deep and contain over 2 kt of molten glass. (The largest glass-melting furnaces are 100 m long and 13 m wide.) The furnace is constructed of alumina/zirconia refractories that can withstand the high temperature and corrosive environment of the melt (see Chapter 9). The life of a tank furnace is about 8 years.

With reference to Figure 26.3: The batch is loaded into the hopper (1). In industry, the batch-loading compartment is referred to as the "doghouse." In region (3) the batch begins to melt. The surface temperature of the melt peaks in region (4). During the melting process it is important to control the homogeneity of the mixture and the oxidation state of the components. Region (5), the throat, divides the furnace into two parts—the melting end and the conditioning, or working, region to the right. In the working region the melt is cooled down to about 1300°C and the glass viscosity increases. The glass travels through narrow tunnels called the forehearth (7), where the temperature is further lowered to 1000–1100°C, and on to the forming

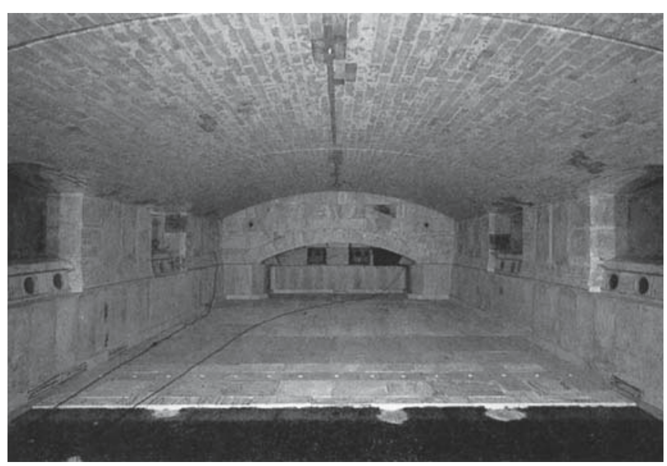

FIGURE 26.2 Inside a typical glass melting tank.

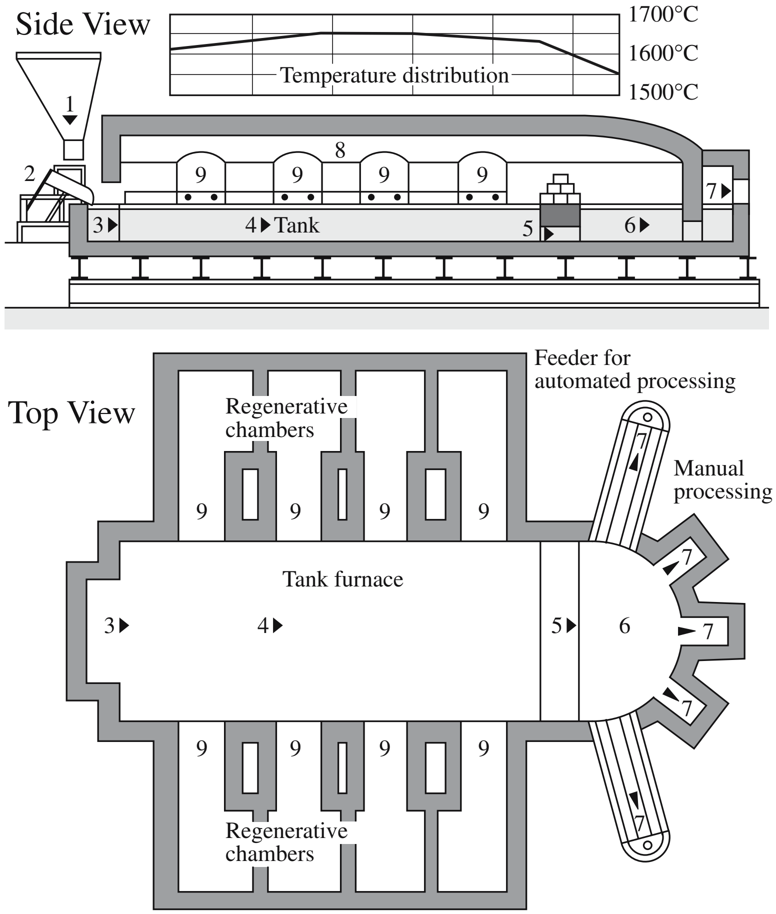

FIGURE 26.3 Schematics of a glass melting tank for producing containers.

machines. Depending upon the requirements of the forming machines, the glass may be delivered in the form of a continuous stream (as shown in Figure 26.4) or in discrete amounts, called gobs. The viscosity of glass at the working point is 10^4 dPa-s (see Chapter 21). The regenerative chambers, region (9), are used to preheat the fuel gases and air to increase the combustion efficiency of the furnace.

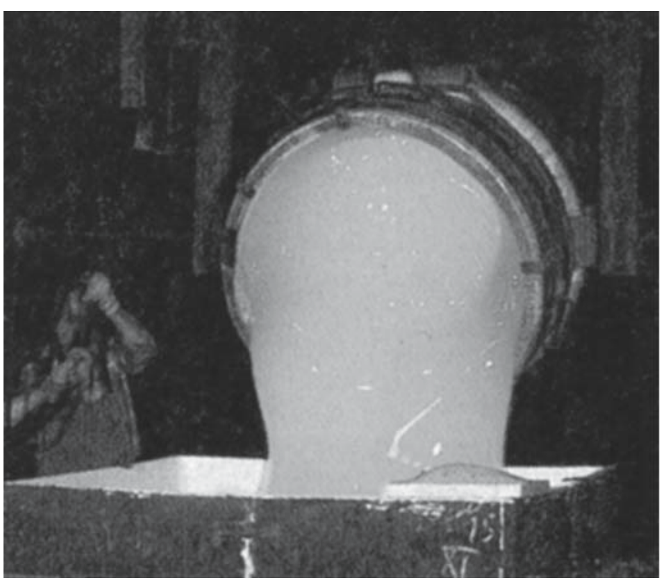

FIGURE 26.4 Pouring molten glass into a mold.

26.3 BUBBLES

The temperature required to form a glass melt varies with the composition of the batch. Typically melting temperatures are in the range 1300–1600°C. At this stage of the process the melt may contain many gas bubbles, mainly CO_2 and SO_2, from the dissociation of carbonates and sulfates. Bubbles also come from reactions between the glass melt and the refractories. Gas bubbles (which are known as seeds or blisters if the size is >0.5 mm) are usually undesirable in the final product because they affect its appearance. Bubbles are eliminated during melting by a process known as fining.

Fining can be achieved by increasing the temperature of the molten glass by about 150°C to reduce its viscosity. From Stokes' law (or by comparing the rise of bubbles in Cola versus liquid soap) we know that the drift velocity

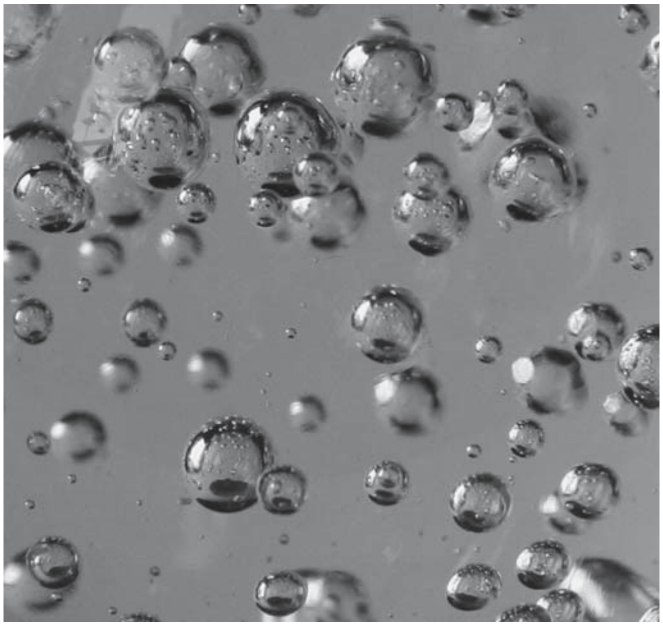

FIGURE 26.5 Example of a bubble deliberately blown in glass.

of the bubbles toward the surface of the melt is increased as the viscosity of the melt is decreased.

Fining is also traditionally achieved by adding fining agents, such as Na_2SO_4 or NaCl, to the melt at the end of the melting process. The fining agent decomposes as shown in Eq. 26.2 to produce a large quantity of gas bubbles, which coalesce with existing bubbles, increasing their volume and hence taking them to the surface faster.

$$Na_2SO_4\ (s) \rightarrow Na_2O\ (l) + SO_2\ (g) + 1/2O_2\ (g) \quad (26.2)$$

Arsenic oxide, As_2O_3, is another fining agent (giving a mixed-valence effect), but it is not so widely used today because it is toxic. The reaction involving arsenic oxide is a little more complicated than that shown for Na_2SO_4, but the effect is the same. Fining will occur toward the end of region (4) in Figure 26.3. Modern systems will also use mechanical bubblers.

In some studio glass and tableware, bubbles are introduced intentionally as illustrated in Figure 26.5.

DEFECTS IN GLASS MELTS

Stones: opaque particles of rock or batch material embedded in the glass
Cords: thin string of inhomogeneity
Seed or blister: elongated bubble (~0.5 mm)

26.4 FLAT GLASS

Flat glass is not necessarily flat but is generally flatish! Historically, glass windows were not made in the way they are now. There are three basic methods for producing flat glass:

- Rolling
- Drawing
- The float process

The float process is so important to the glass industry that we will discuss it separately in the next section. In this section we will discuss the formation of flat glass by rolling and drawing**.** Figure 26.6 shows an example of a method for producing flat glass by rolling. The molten glass flows from the tank furnace over a refractory lip and between a set of water-cooled rollers where it solidifies into a continuous ribbon. The glass ribbon is transported over rollers into a tunnel-like annealing furnace (called a lehr in the glassmaking industry). Inside the lehr, the glass is first reheated to between 600 and 800°C. On the way through the lehr the temperature decreases slowly in a carefully controlled manner to minimize the development of internal stresses within the glass.

The glass thickness is controlled by a combination of factors:

- The rotational speed of the rollers
- Their spacing
- The glass pull rate

Typical pull rates are 0.5–5 m/min producing sheets 3–15 mm thick and up to 3.6 m wide.

A drawing process can also be used to produce flat glass. A solid metal plate is dipped into a bath of molten glass and then slowly withdrawn from the melt. This process would present no problems if we were interested in producing a glass rod (Figure 26.7). Producing a planar sheet is problematic because the sheet would neck down to a narrow ribbon. This difficulty is overcome by cooling the sheet as it is drawn; it is passed between two coolers as shown in Figure

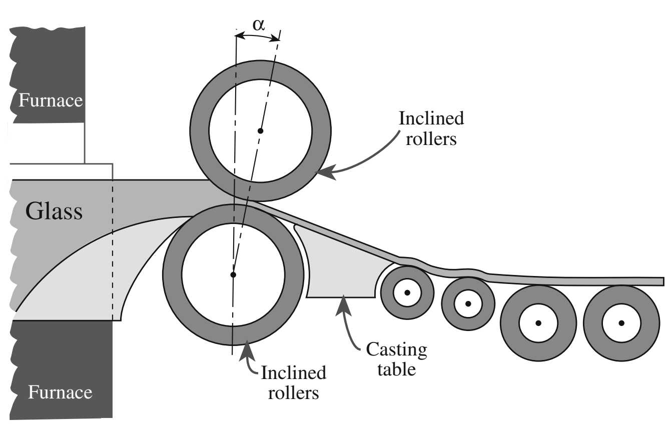

FIGURE 26.6 Continuous casting of flat glass.

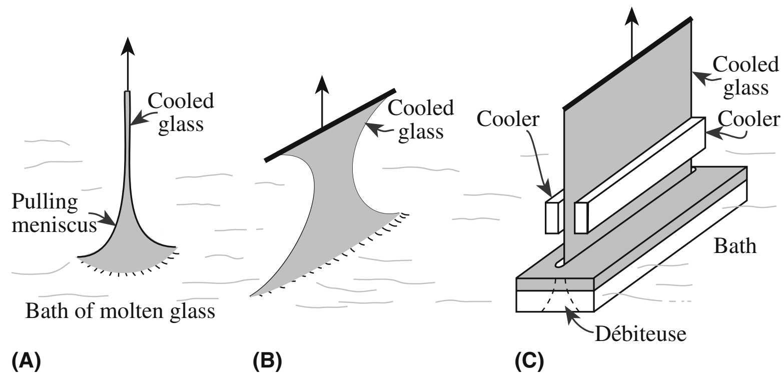

FIGURE 26.7 Principle of drawing from molten glass: (a) a circular rod; (b) problem of pulling a planar sheet; (c) use of a débiteuse and cooling to allow the formation of a sheet of constant width.

26.7c. These coolers solidify the glass and produce a sheet of fixed width. (We will see a similar process used in crystal growth in Section 29.6.)

There are several variations on the drawing process and these are illustrated schematically in Figure 26.8, which gives a different view of Figure 26.7.

In the Fourcault process the glass is drawn through a slot in a clay block (called the debiteuse or draw bar). The glass sheet is pulled upward through a system of steel rollers about 7 m high. The sheet at the mouth of the debiteuse is cooled at its edges in order to retain the width. As the glass travels upward it is annealed in a vertical lehr. After annealing and cooling the glass can then be cut into sections.

In the Pittsburgh process, the draw bar is completely submerged where it lowers the temperature of the glass below the meniscus. This modification allows increased drawing rates.

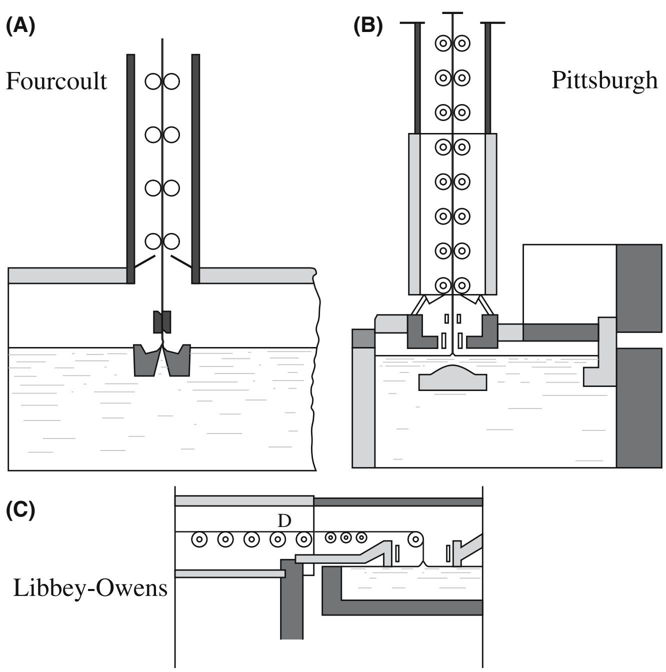

FIGURE 26.8 Drawing processes for window glass. (a) Fourcault, (b) Pittsburgh, and (c) Libbey-Ownes.

In the Libbey–Owens or Colburn–Libbey–Owens process the drawn glass sheet is bent through 90°, ~1 m above the surface of the bath, on a polished chrome-nickel alloy roll; there is no debiteuse. The glass then travels into a horizontal lehr for annealing.

By the mid 1900s these three processes were responsible for the world's entire production of flat glass, with 72% being made by the Fourcault process, 20% by the Colburn–Libbey–Owens process, and 8% by the Pittsburgh process. These processes have now been replaced almost entirely by the float process.

Plate glass is flat glass that has been ground and polished to produce two perfectly plane and parallel faces with a high quality optical finish. The surface of a flat glass sheet is flattened by grinding it between two cast-iron wheels with sand abrasive and water lubricant. As the grinding progresses, the particle size of the abrasive is decreased producing a very fine satin surface. The operation is completed by polishing the sheet with a suspension of iron oxide on felt pads; this abrasive is known as rouge because of its color (see Chapter 36). The processing of plate glass can be entirely mechanized with continuous simultaneous grinding and polishing on both faces. However, the float-glass process has almost entirely ended this older method of manufacturing plate glass. The quality of float-glass may not be quite as high as that of plate glass, but the cost is considerably lower because of the elimination of the mechanical grinding and polishing operations.

26.5 FLOAT-GLASS

The float process was developed in 1959 by Pilkington in the UK and revolutionized the flat-glass industry. It has been hailed as one of the major inventions on the twentieth century. Worldwide, there are only ~170 float-glass plants, but these have a combined output of 3000 miles of flat glass, 4–8 feet wide, each day. Annually these plants produce the equivalent of a ribbon of glass over one million miles long. Over 90% of the world's window glass is produced using the float process.

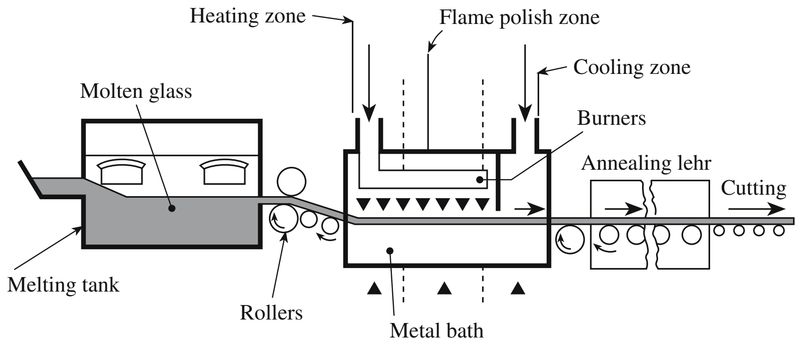

FIGURE 26.9 Schematic diagram of the float glass process.

A schematic of the float process is shown in Figure 26.9. Molten glass is fed from the furnace between two rollers onto a bath containing molten tin at about 1000°C (the melting temperature of tin is 232°C). The tin bath is 4–8 m wide and up to 60 m long. Equilibrium between gravitational forces and surface tension produces a sheet of uniform thickness. The equilibrium thickness, h_e, can be calculated using an equation derived by Langmuir:

$$h_e = \left\{ \frac{(\gamma_{Gv} + \gamma_{Gt} + \gamma_{tv})2\rho_t}{g\rho_G(\rho_t - \rho_G)} \right\}^{1/2} \quad (26.3)$$

There are three interfacial energy (γ) terms between the different phases glass (G), air (v), and tin (t); g is the acceleration due to gravity, which has a value of $9.806\ m/s^2$, ρ_G and ρ_t are the density of the glass and tin, respectively.

In practice, it is possible to produce glass thicknesses between about 2 mm and 20 mm using the float process, depending upon the glass viscosity and the drawing speed. At the exit, the temperature of the glass is decreased to ~600°C, at which point the tin is still fluid, but the glass can be removed in a “rigid” condition. The glass ribbon leaves the bath and enters the lehr for annealing. The glass leaves the lehr at ~200°C, is cooled to room temperature, and is cut to size. The main advantage of the float process is the production of planar glass sheets with a high optical quality—the planarity approaches that of plate glass without the need for polishing. Moreover, the output rate is 5–10 times higher than the drawing rate for window glass. About 25 t of finished glass can be produced per hour by the float process.

On the negative side, the equipment requires careful control of the atmosphere above the bath, which must be neutral or slightly reducing to avoid oxidation of the bath and the maintenance of constant surface tension, which controls the thickness of the sheet. The atmosphere is approximately 90% N and 10% H. The hydrogen ensures that there is an oxygen-free environment: molten tin is easily oxidized. The glass can, itself, be affected adversely by the presence of oxygen, which can make the surface appear hazy. Purity and reliability are therefore critical factors in float-glass manufacture. Approximately $5\ m^3$ of hydrogen is required for each ton of glass produced.

GLASS THICKNESS

It is instructive to estimate the value of h_e. A reasonable value for the glass/Sn interfacial energy is $\sim 1\ J/m^2$, the surface free energy of molten tin is $0.68\ J/m^2$, the density of Sn is $7.5\ g/cm^3$, the surface free energy of a molten soda-lime-silicate glass is $0.35\ J/m^2$, and the density for a silicate glass is $2.5\ g/cm^3$, hence h_e is ~9 mm. This calculated value is actually slightly higher than the actual equilibrium thickness, ~7 mm. Remember that we are using only an estimate for the energy of the glass/Sn interface.

26.6 GLASSBLOWING

The classic glassblowing pipes are made from iron tubes about 100–150 cm in length with an opening about 1 cm in diameter. At one end the tube had a mouthpiece and at the other end it has a button-like extension. The glassmaker gathers a gob of molten glass on one end then blows through the mouthpiece to form a hollow shape as demonstrated in Figure 26.10. This process was important historically because by blowing glass with a pipe it was possible not only to produce simple round shapes but also other thin-walled objects. By blowing the glass into a wooden mold it became possible to produce items with a standard reproducible shape. The glassblowing pipe was also the first step in making flat glass. The glass was blown into a large cylindrical body, cut along its length, and “ironed” flat while it was still hot and soft. This is known as muffle glass and is still used today to make traditional stained glass.

Today the glassworker’s blowpipe is very similar to the original design and works in the same way. The original blowing technique is used now mainly for specialty glass applications such as glass ornaments and studio-art glass.

FIGURE 26.10 Demonstration of blowing glass into a mold. Note the worker's bench, the annealing burners, and the box of frit.

To produce hollow glassware for bottles and jars the original blowing technique has been mechanized. The process starts by forming a blank or preform (called a parison) by blowing into or pressing a gob of glass as illustrated in Figure 26.11. (The hole into the furnace is called the parison hole; traditionally, the glassblower would gather a glob, or gob, of glass on the blowpipe and roll it to make the parison.) After the initial shaping process, the parison is blown by compressed air to the final shape. With today's automated techniques, from parison to final product can take less than 10 seconds.

- The blow-and-blow process is used to make narrow-neck containers (Figure 26.11a).
- The press-and-blow process is used to make wide-mouth jars (Figure 26.11b).

Figure 26.12 shows the ribbon machine developed in 1926 by Corning for high-speed production of light bulbs. In this process a stream of molten glass is made into a ribbon by passing it through a pair of rollers. The ribbon

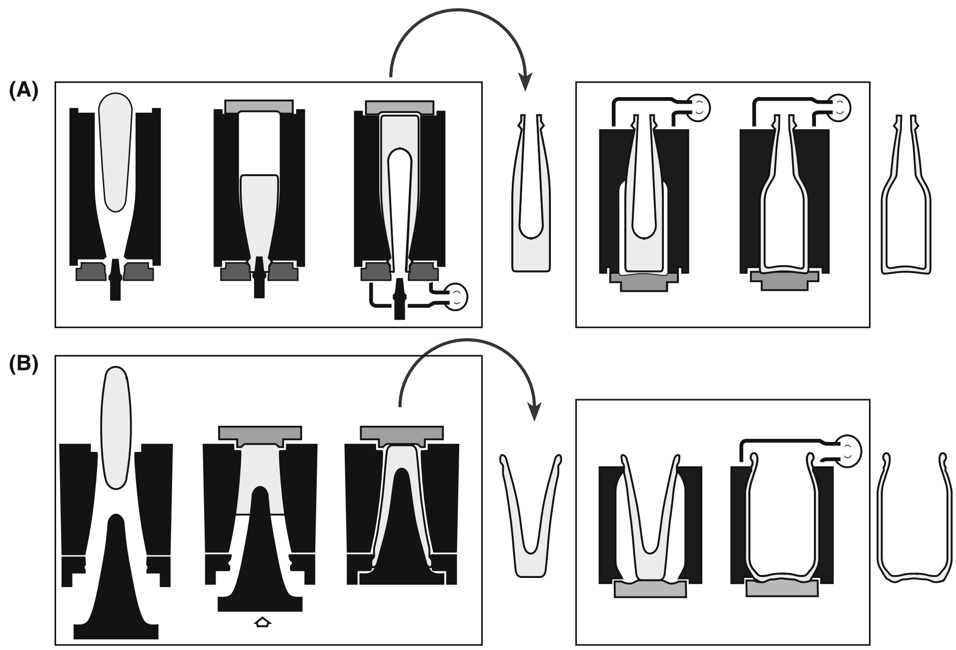

FIGURE 26.11 Automatic fabrication of hollow ware: (a) formation of the blank by blowing followed by blowing in a mold (blow and blow); (b) formation of the blank by pressing followed by blowing (press and blow).

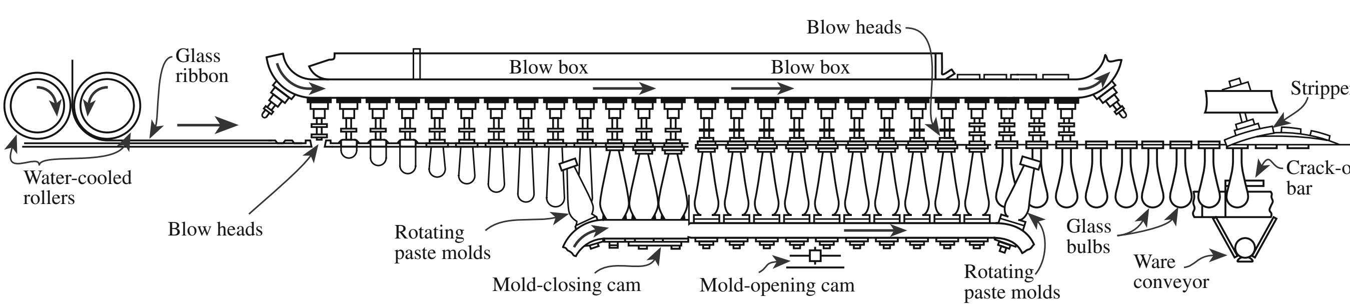

FIGURE 26.12 The Corning ribbon machine for glass lamp bulbs.

passes under a series of blowheads that are attached to a rotating turret (the blowhead turret). Air is puffed into the glass and the glass begins to take the form of a blown shell. The glass shell is then enveloped by a mold mounted on a rotating turret below the blowhead turret. The shells are blown to their final form while in the mold. The finished shells are cracked away from the ribbon, collected, and carried through the annealer. More than 50 light bulb shells (in single molds) can be made per second in one machine!

26.7 COATING GLASS

Coated glass also has a long history. Stained glass used in church windows has long used flashed glass, which is clear glass with a coating of a colored glass. Today we use many other types of coatings, but flashed glass is still used in the glass studio (see Section 26.14).

Normal window glass transmits between 75% and 90% of the incident radiation. We can apply thin coatings to the surface to alter the radiation and heat-transmission characteristics. In architectural applications, coatings on glass are used to reduce the amount of energy needed to heat buildings in the winter and cool them in the summer. One way to do this is by allowing the transmission of visible light while reducing the transmission of infrared (IR) radiation (heat). Such glass would reduce the amount of energy required to air condition a room in the summer.

One conventional way to reduce the transmission of heat is to add a component to the glass batch that strongly absorbs radiation in the IR region. When FeO is added to the glass formulation, the product strongly absorbs radiation in the 0.7–2.5 μm range. Since the absorption sharply increases above 0.6 μm, the transmitted visible light does have a noticeably green tint. But this can be corrected to a certain extent by adding other components (commonly Se and Co). A 6-mm-thick glass window that contains FeO may absorb ~50% of the total incident radiation but only ~25% of the radiation in the visible part of the electromagnetic spectrum.

Thin films are also used to control the light-transmission characteristics of window glass by reflecting a large amount of IR radiation.

Such films allow a higher retention of heat in a room during the winter, thus reducing the energy costs associated with heating. Normal flat glass can be coated with metallic or nonmetallic layers to maintain a high degree of visible light transmission combined with a considerable amount of heat reflection (40–60%). Thin (10–20 nm) metal films of Cu, Ag, and Au are all used commercially; each gives a very high reflectivity. The metal layer is deposited using physical vapor deposition (PVD) techniques such as evaporation and sputtering (see Chapter 28). Metal coatings can also be applied using dipping and spraying techniques, followed by firing to densify the coating (see Chapter 27).

Single-layer and multilayer coatings of oxides are also used to enhance reflectivity in the near IR. These coatings work because of optical interference effects and usually have a thickness about one-quarter of the wavelength of the radiation such that the primary wave reflected off the first interface is 180° out of phase with the secondary wave reflected from the second interface. The result is destructive interference of the two waves. Thin films of TiO_2, Ti_3N_4, CrN_x, and Zn_2SnO_4 are all used commercially for this application.

Figure 26.13 shows a schematic diagram summarizing the principles behind solar radiation control panels. For solar-

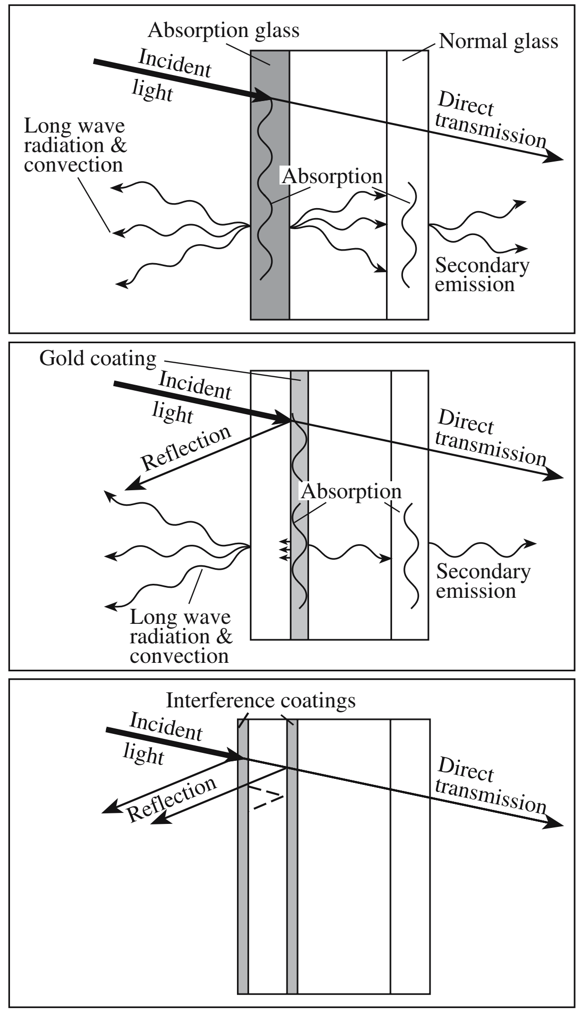

FIGURE 26.13 Illustration of approaches for solar protective double glazing with absorbing and reflecting panes.

MULTILAYER COATING

An example of the effectiveness of a multilayer coating, which works on the interference principle, is the Sb_2S_3/CaF_2 superlattice. For 11 alternating layers of Sb_2S_3 ($n = 2.70$) and CaF_2 ($n = 1.28$), the reflectance is 0.9999 at $\lambda = 1\,\mu m$.

protective double glazing, a coated glass pane is combined with an uncoated pane.

Radiation can also be modified using electrochromism. Electrochromism is the production of color by applying an electrical field. Electrochromic compounds such as WO_3 are coated on the glass using a variety of thin film techniques. The point defect reaction is reversible.

$$WO_3 + xM^+ + xe^- = M_xWO_3 \qquad (26.4)$$

When a direct current (dc) voltage is applied, the optical absorption characteristics of the compound change. The gain/loss of color occurs by the inclusion/elimination of the M^+ ion. In this case, the M^+ ion can be H^+, Li^+, Na^+, or Ag^+. The absorption characteristics of electrochromic materials can thus be tailored for specific applications simply by adjusting the applied voltage.

26.8 SAFETY GLASS

Flat glass often breaks due to impact or to the application of a relatively low applied pressure. At most temperatures, the failure occurs in a brittle manner and results in the production of a number of sharp fragments, which, of course, can cause serious injury. Special treatment of the glass can make it less susceptible to breaking and can thus reduce the chance of injury. Hence the United States and many other countries require the use of safety glass in buildings and vehicles. There are two forms of safety glass:

- Tempered
- Laminated

Tempered glass (or toughened glass as it is also often called) is made by quickly heating flat glass to about 150°C above T_g. (Remember: the viscosity at the T_g is ~10^{13} dPa·s.) For a soda-lime silicate glass $150 + T_g$ is 525–545°C. The glass is then blasted with cold air. The outside of the glass cools much more quickly than the inside. Hence the inside is still contracting after the surface has already solidified. The result is that the outer surface layer is subject to compression and the inside layer is subject to tension. This tempering process changes the behavior of the glass when it breaks. For example, when a sheet of tempered glass breaks, the fragments are small and almost regularly shaped with no sharp edges. The principle used in the tempering process is the same as that used to make crackle glass: the internal stress at the surface is different from that in the bulk.

CRACKLE GLASS

Crackle glass has been produced for its artistic appearance for over 150 years (perhaps since the sixteenth century in Venice). The glass is heated to ~1000°C and then plunged into water causing cracks to form across the surface; if reheated and blown further the cracks heal on the interior; a similar effect is produced in glazes.

The other form of safety glass is laminated glass, which consists of two or more glass sheets (usually float glass) joined with a layer of an elastomeric polymer such as poly (vinyl butyral) (PVB). The glass layers are bonded to the polymer by a combination of pressure and heating. When laminated glass is broken, the broken pieces of glass are stuck to the polymer and the broken sheet remains transparent. Car windshields are laminated glass in which the two bonded sheets are both tempered glass. If a stone breaks the windshield when the car is moving, the polymer sheet holds the fragments of glass together so that they do not cause injury to the occupants of the car. The side and rear windows of an automobile are routinely made from tempered glass.

The front and rear windows of an automobile are often curved. The flat glass is shaped before the tempering process because the tempered condition would disappear at the bending temperature. One of the advantages of laminated glass over tempered glass is that laminated glass can be processed further; for example, it can be cut and drilled. Bulletproof glass is thick laminated glass (25–60 mm thick) consisting of at least four layers of glass laminated with an elastomeric polymer.

26.9 FOAM GLASS

Because we do not usually want glass to contain large numbers of bubbles, we reduce the number of bubbles in the glass melt using the fining process. The opposite approach is used to make foam glass: additional gases or gas-bearing materials are added to the melt producing a large quantity of bubbles.

One of the major applications of foam glass is in the manufacture of insulating panels for buildings. Insulating panels made from foam glass can be light, rigid, and good thermal insulators. As usual for porous materials, the thermal property is due to the low heat conductivity of the bubbles (i.e., pores).

- Foam glass is the porous ceramic of the glass world.
- Bubbles may be intentionally included in art glass.

26.10 SEALING GLASS

Special glasses have been developed that are used as the “glue” usually between another glass and a metal. The main challenge is engineering α while controlling the chemistry and keeping the sealing temperature reasonable.

Borosilicate (alkaline earth/alumina) glass is used to seal glass to W (lighting applications).
Borosilicate (Na) glass is used to seal glass to Mo.
Borosilicate (K) glass, with a high concentration of B (20% B_2O_3), is used to bond to Kovar (Westinghouse's trade name for the Fe–Ni–Co magnetic alloy that has α close to that of the glass).
Pb glass is used if electrical insulation of a joint is critical.

PHOTOSENSITIVE AND PHOTOCHROMIC
Photosensitive: the glass is sensitive to light.
Photochromic: the color is changed by exposure to light.

26.11 ENAMEL

Ceramic enamel compositions are used for a wide variety of applications, including decorative coatings for glassware and china. In industry they are used in coating baths, stovetops, etc. They are used whenever a metal requires a coating that is more durable than paint. It is also used to form colored borders around glass sheets used as automotive windshields. The reason for the colored borders is to enhance the appearance and to decrease the degradation of the underlying adhesives by ultraviolet (UV) radiation. The enamel compositions consist of a glass frit (a powdered glass), a colorant, and an organic vehicle. The mixture is applied to the required part and then fired to burn off the organic vehicle and to fuse the enamel to the surface of the substrate.

In the art world, enameling is carried out using small furnaces and grams of powdered glass; in industry, square meters of surface can be enameled uniformly. The principle is the same, only the scale differs. A large piece like a cast-iron bath would be shot-blasted to clean it, coated with a ground coat that will bond to the Fe, dried, and heated to nearly 1000°C. It is then sprinkled with dry enamel frit while still hot and brought back to temperature. Five such coatings of enamel would be routine. The composition of the enamel must be chosen so that it is in compression after cooling. The composition would be modified on curved regions to maintain this compression.

Color is produced in ways similar to other glass. (We discussed color in glass in Section 21.8.) As recently as 1999, the French Consumer Safety Committee considered the safety of the use of UO_2 dye to make enamels for the preparation of jewelry and enameled tiles. Old yellow enamels contained up to 9% UO_2 and frits using nondepleted U are certainly more "radioactive" than those of today. The committee noted that having 50% Pb in the frit might help absorb the radiation, but this increased the toxicity of the frit powder! Safety in enameling is therefore always a concern because the technique uses powders.

26.12 PHOTOCHROMIC GLASS

Photosensitive glass is the glass analog of photographic film where Au or Ag atoms (as halide particles) are affected by the action of light. Such glass is used in printing and image reproduction. Heat treating after exposure to light can cause a permanent change in the glass. Photochromic glass (discovered at Corning in the 1960s), darkens when exposed to light but then returns to its original clear state when the light is removed; hence it is used in sunglasses or other ophthalmic lenses. The light affects small (~5 nm or a little larger) $AgCl_xBr_{1-x}$ crystals in the glass. To manufacture photochromic glass the glass must be heated to over 1400°C, shaped, and then annealed again at 550–700°C to allow the small halide crystals to form in the initially homogeneous glass. Large flat glasses are not generally affordable, but the new approach is to use sol-gel processing (Chapter 22) to form a photochromic layer on conventional preformed glass sheets.

The principle is that the near-UV radiation generates electron-hole pairs in the halide particles. The electrons are trapped by the interstitial Ag ions producing Ag colloids on the surface of the halide particle. The activation energy for this process is only 0.06 eV so the Ag ion moves easily in the halide; in addition, a small amount of Cu increases the effect by at least an order of magnitude. This is the same process used in photography and is explained by the same Gurney–Mott theory. The metal particles formed in the process are 1–5 nm in size, but because the halide must be >5 nm to show the effect the second annealing T is critical.

26.13 CERAMMING: CHANGING GLASS TO GLASS-CERAMICS

Worldwide sales of glass-ceramic products exceed $500 million a year. The highest volume is in cookware and tableware consumer items (such as plates and bowls) and domestic ovens (stovetops and stove windows). In this section we will look at how these commercially important ceramics are processed.

Glass-ceramics are formed by controlled crystallization of a glass. They consist of a high density (maybe >95 vol%) of small crystals in a glass matrix. The important feature of the processing of glass-ceramics is that the crystallization must be controlled. As usual, crystallization occurs in two stages:

- First the crystals are nucleated.
- Then the crystals grow.

The rate at which these two processes occur is a function of temperature. We can control the nucleation process by adding a nucleating agent (typically either TiO_2 or ZrO_2) to the glass batch.

Initially the glass batch is heated to form a homogeneous melt. The shape of the desired object is formed from the glass at the working point by the usual processes such as pressing, blowing, rolling, or casting. Remember, the viscosity of the glass is ~10^4 dPa-s at the working point (like honey). After annealing to eliminate internal stresses, the glass object then undergoes a thermal treatment that converts it into a glass-ceramic. The first part of the heat treatment is nucleation. The optimum nucleation temperature generally corresponds to a glass viscosity of 10^{11}–10^{12} dPa·s. During this step, which may last for several hours, an extremely high density (10^{12}–10^{15}/cm^3) of nuclei forms. Following nucleation, T is increased to allow growth to occur. The crystal-growth step, like nucleation, may take several hours. The optimum temperature for crystal growth is selected to allow for the maximum development of the crystalline phase without viscous deformation of the object. Figure 26.14 shows the complete processing cycle for a glass-ceramic.

ION EXCHANGE

Glass can be strengthened by ion exchange in which small ions in the surface layer are replaced by larger ions, which put the surface into compression.

Step 1: Rapid exchange of Na^+ or K^+ with H^+ or H_3O^+ from solution:

$$\text{Si–O–Na}^+ + \text{H}^+ + \text{OH}^- \rightarrow \text{Si–OH}^+ + \text{Na}^+ (\textit{solution}) + \text{OH}^-$$

This step is usually controlled by diffusion and exhibits $t^{-1/2}$ dependence.

Step 2: Loss of soluble silica in the form of $Si(OH)_4$, resulting from breaking of Si–O–Si bonds and the formation of Si–OH (silanols) at the glass solution interface:

$$\text{Si–O–Si} + \text{H}_2\text{O} \rightarrow \text{Si–OH} + \text{OH–Si}$$

This stage is usually reaction controlled and exhibits a $t^{1.0}$ dependence.

Step 3: Condensation and repolymerization of an SiO_2-rich layer on the surface depleted of alkalis and alkaline-earth cations.

Step 4: Migration of Ca^{2+} and PO_4^{3-} groups to the surface through the SiO_2-rich layer forming a CaO–P_2O_5-rich film on top of the SiO_2-rich layer, followed by growth of the amorphous CaO–P_2O_5-rich film by incorporation of soluble calcium and phosphates from solution.

Step 5: Crystallization of the amorphous CaO–P_2O_5 film by incorporation of OH^-, CO_3^{2-}, or F^- anions from solution to form a mixed hydroxyl, carbonate, fluorapatite layer.

The glass-ceramic process uses the same rapid forming techniques employed in glassworking, permitting the economical production of objects with complex shapes or thin walls that are difficult or impossible to produce with other, more traditional, ceramic-forming techniques.

The most important and useful glass-ceramic system is the Li_2O–Al_2O_3–SiO_2 (LAS) family that was first developed at the Corning Company by Stookey. One commercial LAS glass-ceramic is Pyroceram®, which has β-spodumene (LiAl[Si_2O_6]; α = ~10^{-6}/°C) as the major crystalline phase. The low α, together with excellent high temperature stability and insensitivity to thermal shock, means that these materials find applications as cookware, benchtops, hot-plate tops, ball bearings, and matrices for fiber-reinforced composites.

If the crystallization temperature is kept ≤900°C the crystalline phase that is formed in LAS glass-ceramics is β-quartz. The β-quartz crystals are <0.1 μm in diameter. Crystal sizes below the wavelength of visible light (λ = 0.7–0.4 μm), a good match in refractive index between the glass and the crystal phase, coupled with a low birefringence result in high transparency. Table 26.4 lists the compositions and applications of some commercial transparent LAS glass-ceramics based on β-quartz.

Application 1: Machinable glass-ceramics are derived from the K_2O–MgO–Al_2O_3–SiO_2 system containing some fluorine. In Macor® the crystalline phase is potassium fluorophlogopite [$KMg_3(AlSi_3O_{10}F_2)$]. Phlogopite is a mica mineral and the plate-like mica crystals are randomly oriented in the glass phase as shown in Figure 18.23. Macor® can be machined to precise tolerances (±0.01 mm) and into intricate shapes using conventional steel tools: they can be drilled, cut, or turned on a lathe.

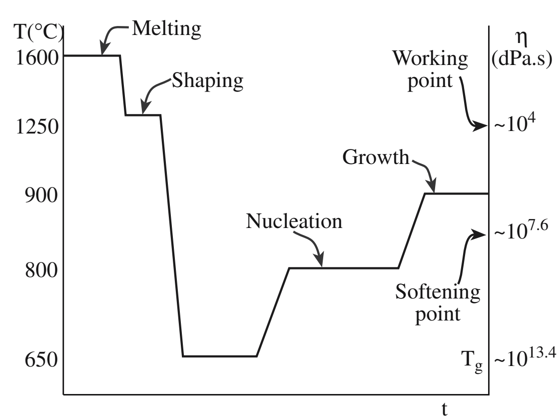

FIGURE 26.14 Processing cycle for a glass-ceramic.

TABLE 26.4 Base Compositions and Applications of Transparent Glass-Ceramics Based on Quartz Solid Solutions

	Composition, wt%														
Material	*SiO_2*	*Al_2O_3*	*MgO*	*Na_2O*	*K_2O*	*ZnO*	*Fe_2O_3*	*Li_2O*	*BaO*	*P_2O_5*	*F*	*TiO_2*	*ZrO_2*	*As_2O_3*	*Commercial application*
Vision	68.8	19.2	1.8	0.2	0.1	1.0	0.1	2.7	0.8	—	—	2.7	1.8	0.8	Transparent cookware
Zerodur	55.5	25.3	1.0	0.5	—	1.4	0.03	3.7	—	7.9	—	2.3	1.9	0.5	Telescope mirrors
Ceran	63.4	22.7	u	0.7	u	1.3	u	3.3	2.2	u	u	2.7	1.5	u	Black infrared transmission cooktop
Narumi	65.1	22.6	0.5	0.6	0.3	—	0.03	4.2	—	1.2	0.1	2.0	2.3	1.1	Rangetops; stove windows

u = unknown

Application 2: Another commercial fluoromica glass-ceramic called Dicor® has been developed for dental restorations. Dicor has better chemical durability and translucency than Macor. It is based on the tetrasilicic mica, $KMg_{2.5}Si_4O_{10}F_2$, which forms fine-grained (~1 μm) anisotropic flakes. Dicor dental restorations are very similar to natural teeth both in hardness and appearance. They are easy to cast using conventional dental laboratory methods and offer significant advantages over traditional metal–ceramic systems.

Application 3: Calcium phosphate, $Ca_3(PO_4)_2$, glasses can be made into glass-ceramics to form a material resembling the mineral part of bone. Since bone is porous, the first step is to produce a foam glass. This is achieved by decomposing carbonate in the glass melt. The foam glass simultaneously undergoes a controlled crystallization, transforming it into a porous glass-ceramic. The dimensions of the interconnections between the pores must be sufficient to allow the ingrowth of living bone tissue, which ensures a permanent joint with the surface of the prosthesis.

In principle, any glass can be converted to a glass-ceramic by finding a suitable nucleation agent and the appropriate heat treatment. In practice, a number of technical factors (among which is the production of the base glass) limit the choice.

We can use the phenomenon of photosensitivity to make a machinable glass! For example, we could use CorningWare ($Li_2O \cdot Al_2O_3 \cdot SiO_2$) as the starting material and then add <1 wt% Cu, Ag, or Au. The idea behind the technique is similar to the photochromic glass, but we then leach out the Li_2SiO_3 crystals to leave a high density of small voids in the glass.

1. Irradiate the glass with UV (Figure 26.15).
2. Anneal Au^0 agglomerates (small particles); nuclei for crystalline ceramic Li_2SiO_3 ($2SiO_2 \cdot Li_2O$).
3. Place the glass in dilute HF to dissolve the Li_2SiO_3 (dissolution is 10× faster than for the glass). This method can produce densities of 3.6×10^4 holes/square inch.
4. Reexpose the glass to UV (no mask) and anneal; all is then polycrystalline, e.g., with 0.001% Au, 0.001–0.03% AgCl, or 0.001–1.00% Cu_2O.

Before leaving the topic we should mention that this is not the only way to prepare glass-ceramics. Another group of these materials used for dentistry go by the label In-Ceram®. The material is prepared as a porous crystalline ceramic (alumina, spinel, and zirconia have all been used) and then infiltrated with an La-rich glass. The resulting glass-infiltrated ceramic can be quite translucent, can be colored to match other teeth, and is mechanically tough (for a ceramic). It can be coated with porcelains for improved appearance.

26.14 GLASS FOR ART AND SCULPTURE

Today, the glass art world is very active with more abstract pieces by Chihuly and others being hung in many public buildings (e.g., the Victoria and Albert Museum in London; Figure 26.16). Exhibitions travel round the United States and the world. The field is actually much wider than you might imagine.

The glass harp produces the "sound of the universe" according to Goethe. The musician Gluck gave an entire concert using the glass harp in London in 1746. Sound is

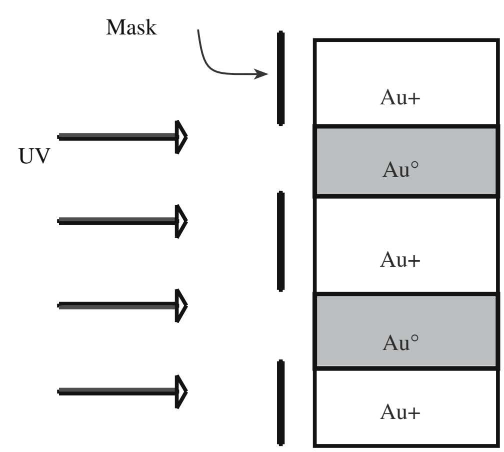

FIGURE 26.15 Process for making porous glass.

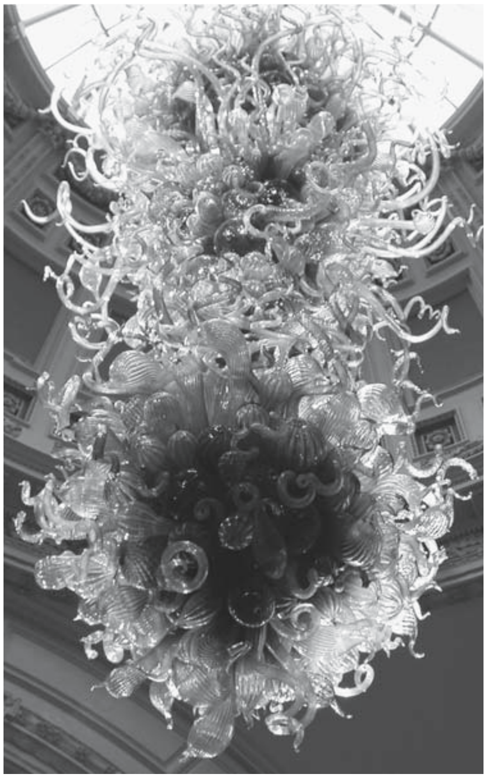

FIGURE 26.16 Chihuly installation at the Victoria and Albert Museum in London.

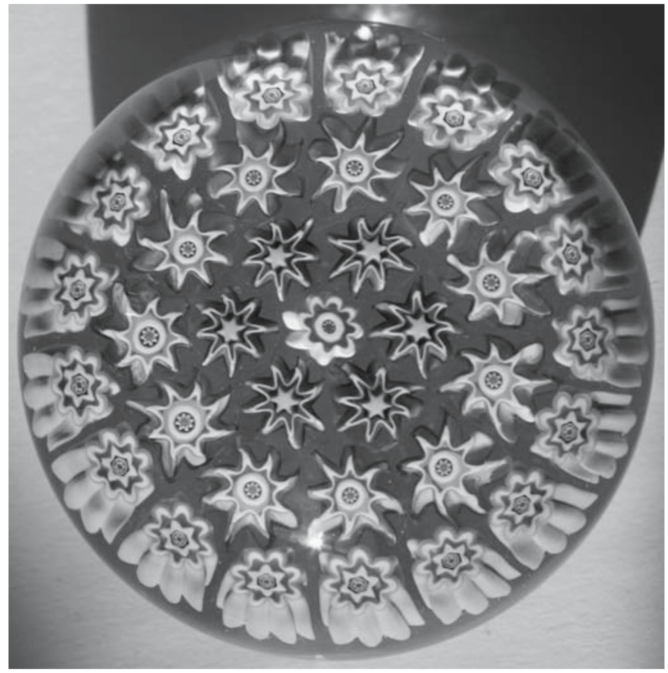

FIGURE 26.17 Millefioré paperweight showing the different glass canes used.

made when a wine glass "sings": run your finger around the rim. The sound is thus produced by making the glass vibrate rather than by making the air in the container vibrate (like blowing over a bottle). Benjamin Franklin made a glass armonica (Mozart wrote music for the armonica): he placed glasses inside one another (not touching) and rotated them on a spindle to make playing easy! Galileo actually explained the resonance phenomenon in 1638. The tone will depend on the mechanical (elastic) properties of the glass.

Murano, a small island near the city of Venice, was the center of glass making for many years. The location was chosen to stop glassworkers from moving away from the vicinity of Venice. It is still famous for its art glass and the glass companies provide free boat taxis from the mainland to encourage customers. The millefiore insets seen in paperweights and glass sculptures, and illustrated in Figure 26.17, are usually associated with Murano. Actually, the technique had already been used in the first century CE.

Paté de verre is an art glass made by sintering pieces of glass, including powder, to make objects with distributions of color that would not be possible if the glass were melted. Essentially, the millefiore glass of Murano is made by this technique but now with larger "particles." It is now being used by industry for the same purpose. The classical sintering technique for processing ceramic powders is thus being used to produce unique glass objects.

MARBLES

Marble King in Virginia makes 10^6 marbles every day.

Art glass, usually in the form of figures and vases, became popular in the 1800s with Lalique, Gallé, Daum Frères, Tiffany, and others as illustrated in Figure 26.18.

Between 1886 and 1936, the father and son team of Leopold and Rudolph Blaschka produced the Harvard glass flowers (shown in Figure 26.19) for use in teaching botany (there are other collections, but this is the best known). Tiffany produced similar specimens for the

FIGURE 26.18 Small vase by Daum Frères.

FIGURE 26.19 Example of a Harvard flower.

art market. The idea is that the color of glass does not change with time and the flowers are three-dimensional. Actually, the Blaschkas used wire, paint (especially in the early years), varnish, and glue to enhance the models at the time. Thus they will not be quite as inert to the atmosphere as hoped, but they are superb examples of lampworking (heating a soda-rich glass and shaping it by pulling and pinching with various tools including tweezers).

In some countries, the best-known form of art glass is the stained-glass window (Figure 26.20). Since it was first developed in the early twelfth century stained glass has been made using several different techniques.

FIGURE 26.20 Example of drawing in stained glass.

Pot-metal glass is bulk glass that has been colored by adding metal oxides in the usual way (Cu for red, Fe for green, Co for blue, etc.). Since the glass must be thick enough for the window, light transmission was often reduced (making the church dark).

Flash glass is produced by dipping a gob of clear glass into a pot of colored glass. When the glass is then blown, the two layers are thin. The colored layer remains only a fraction of the total thickness. If the glass were uniformly colored but not flashed, it would transmit too little light (old church windows make for dark interiors); if the glass were uniformly colored but thin so as not to decrease the light it would have insufficient mechanical strength. The layer can be abraded to produce variations in color on the one piece of glass. Details in the window images can be drawn on the glass using an iron oxide pigment. The drawing is then fired to incorporate it into the glass.

26.15 GLASS FOR SCIENCE AND ENGINEERING

Lenses have been made using glass since microscopes and telescopes were first invented. When visible light is used, this is still generally the case. For transmitted light, the challenge is usually to minimize absorption; some telescopes, such as that on Mount Palomar, use a very wide coated glass reflector. The critical factor is now not transmission but thermal expansion.

Stepper lenses are used in producing very large-scale integration (VLSI) chips using photolithography. The stepper lens is the opposite of an enlarging lens—it shrinks the circuit pattern and prints it onto the semiconductor surface. (The term stepper is used to denote the step-and-repeat exposure system.) In 1997 the line width was 0.25 μm; it is now around 60 nm. The challenge then is to focus light, which has a wavelength much larger than the required resolution.

The Hale Telescope is a 200-inch telescope that was built in ~1949 using a Pyrex blank manufactured by Corning Glass works. Schott Glass has since produced a telescope with a dish that is 8.2 m wide; it is made from Zerodur®, Schott's glass ceramic, using a centrifugal casting process. An interesting link between art and science is the proposal by David Hockney that some of the masters used mirrors and lenses to help compose their paintings. Glass lenses range in size from the end of a fiber used in near-field scanning optical microscopy (NSOM) (see Chapter 10) to the Fresnel plate that was used in lighthouses.

Glass is one of our most important building materials. In 1851, the windows in the Crystal Palace used 300,000 panes, which accounted for 33% of England's annual production of glass. Biosphere 2 (built in the late 1980s) relies entirely on glass to separate the interior from Biosphere 1.

Glass fibers are used in textiles for clothing. The spacesuits used on the Apollo lunar missions were made from glass fiber industrial fabrics.

Glass microspheres are used, for example, in traffic signs and drug delivery. We will describe radiotherapy glasses used in the treatment of unoperable cancers in more detail in Chapter 35. The key process is forming uniform glass spheres. We will also discuss Bioglass in Chapter 35 but not ceramic cremation tiles for after-life applications.

FORMING MICROSPHERES

1. Glass melting
   a. Select chemically pure raw materials (oxides) that do not contain any impurities that would form undesirable radioisotopes during neutron irradiation.
   b. Mix the raw materials.
   c. Melt the raw materials to form homogeneous glass.
2. Spheroidization (microsphere formation):
   a. Crush the glass to particles of the desired size.
   b. Inject particles into a gas-oxygen flame to melt each particle and form a solid glass sphere (flame spray powder).
   c. Collect microspheres in a suitable container.
3. Sizing: screen or separate microspheres into desired size range.

Traffic signs and road marking tape contain spheres that are ~200 μm in diameter and act as microlenses.

In the Ballotini flame drawing process, glass powder is injected into a flame that draws it up a tower until it melts and forms spheres (1–60 μm diameter) dropping outside the flame and cooling under gravity. Filaments used to make the biprism for electron holography are made in the laboratory using a variation on the same principle.

CHAPTER SUMMARY

The production of glass is a multibillion dollar industry. The widespread use of glass products has gone hand-in-hand with developments in glass processing. Arguably the most significant recent development was the float glass process, which allowed high-volume production of very high-quality glass sheets for architectural and transportation applications. Our city skylines certainly are influenced by the use of glass. More recent developments have led to improvements in the energy efficiency of buildings by controlling the transmission and absorption properties of glass. This is part of the "green" revolution in architecture.

Glass processing, which is an industry and art, has its own language. It is necessary to learn that language: in particular, frit, cullet, lehr, fining, gob, and ribbon. The processing terms are from engineering: floating, rolling, drawing, tempering, laminating, and ceramming.

PEOPLE IN HISTORY

Abbe, Ernst (1840–1905) was a professor of optics who worked with Schott, the glassmaker, and Zeiss, the lensmaker, in Jena.

Burne-Jones, Sir Edward Coley (1833–1898) designed stained glass working with William Morris.

Gallé, Émile (1846–1904) was a pioneer in the Art Nouveau movement; he used wheel cutting, acid etching, casing (i.e., layers of various glass), including metallic foils and air bubbles. He called his experiments "marquetry of glass." When you see heavy pieces of deeply colored, nearly opaque glasses, which use several layers of glass and are then carved or etched to form plant motifs, you think of Gallé.

Lalique, René (1860–1945) was one of the creators of Art Nouveau glass. Etched clear glass is a particular trademark.

Littleton, Harvey K. (born 1922 in Corning, New York) was the University of Wisconsin professor who introduced Chihuly, Lipofsky, and others to glass and began the American Glass Movement.

Owens, Michael (1859–1923) invented the automatic bottling machine.

Schott, Otto (1851–1935) see Abbe.

Stookey, S. Donald (another exception to the rule) is one of the greatest scientific creators from Corning Glass.

Trancrede de Dolomieu, Guy S. (1750–1801) was a French professor of mineralogy. The mineral dolomite is named after him.

Zeiss, Carl Friedrich (1816–1888) gave his name to the optics company that was, for many years, based in Jena.

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EXERCISES

26.1 Describe how cords and stones could be removed.

26.2 How much glass in your area is recycled as cullet?

26.3 Why did ancient glass batches contain so much alkali content?

26.4 Why is tin used in the float glass process?

26.5 We process the glass to remove bubbles and thus avoid stresses in the glass. Is this statement true or false? Explain your answer.

26.6 On ceramming a glass, we produce a density of 10^{15}/cm^3 nuclei. How far apart are the nuclei and how does this affect the resulting grain size?

26.7 Why has the art of glass produced so much new interest? Is it new? Discuss.

26.8 Figure 26.1 shows the distribution of glass sales. Using the internet or otherwise, compare these with the figures for Al, steel, and Cu. Discuss your results.

26.9 Estimate the cost of an automobile's windows assuming they are made from tempered glass.

26.10 What are the compositions of some of the common sealing glasses?