CHAPTER 1

Introduction

The presence of glasses in our everyday environment is so common that we rarely notice their existence. Our current casual attitude toward the family of materials known as glasses has not always existed. Early Egyptians considered glasses as precious materials, as evidenced by the glass beads found in the tombs and golden death masks of ancient Pharaohs. The cave-dwellers of even earlier times relied on chipped pieces of obsidian, a natural volcanic glass, for tools and weapons, *i.e.*, scrapers, knives, axes, and heads for spears and arrows.

Humans have been producing glasses by melting of raw materials for thousands of years. Egyptian glasses date from at least 7000 B.C. How did the first production of artificial glasses occur? One scenario suggests that the combination of sea salt (NaCl) and perhaps bones (CaO) present in the embers of a fire built on the sands (SiO_2) at the edge of a saltwater sea (the Mediterranean?), sufficiently reduced the melting point of the sand to a temperature where crude, low quality glass could form. At some later time, some other nomad found these lumps of glass in the sand and recognized their unusual nature. Eventually, some genius of ancient times realized that the glass found in the remains of such fires might be produced deliberately, and discovered the combination of materials which lead to the formation of the first commercial glasses.

The first crude man-made glasses were used to produce beads, or to shape into tools requiring sharp edges. Eventually, methods for production of controlled shapes were developed. Bottles were produced by winding glass ribbons around a mold of compacted sand. After cooling the glass, the sand was scraped from inside the bottle, leaving a hollow container with rough, translucent walls and usually lopsided shape. Eventually, the concept of molding and pressing jars and bottles replaced the earlier methods and the quality of the glassware improved.

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It began to be possible to produce glasses which were reasonably transparent, although usually still filled with bubbles and other flaws.

The invention of glass blowing around the first century B.C. generated a greatly expanded range of applications for glasses. The quality of glass jars and bottles improved dramatically, glass drinking vessels became popular, and the first clear sheet glasses became available; which eventually allowed the construction of buildings with enclosed windows. Colored glasses came into common use, with techniques for production of many colors regarded as family secrets, to be passed on from generation to generation of artisans. The method for producing red glasses by inclusion of gold in the melt, for example, was discovered and then lost, only to be rediscovered hundreds of years later. The combination of the discovery of many new colorants with the invention of glass blowing eventually lead to the magnificent stained glass windows of so many of the great cathedrals of Europe and the Near East.

The advent of the age of technology created many new opportunities for the application of glasses. The evolution of chemistry from the secretive practices of alchemists searching for the philosopher's stone, to a profession involving millions of workers worldwide was strongly influenced by the invention of chemically-resistant borosilicate glasses. Modern electronics became a reality with the invention of glass vacuum tubes, which evolved into the monitors for our computers and the televisions we watch every day. Recently, the development of glass optical fibers has revolutionized the telecommunications industry, with fibers replacing copper wires and radically expanding our ability to transmit flaw-free data throughout the world.

Unlike many other materials, glasses are also esthetically pleasing to an extent which far transcends their mundane applications as drinking vessels and ashtrays, windows and beer bottles, and many other everyday uses. Why are we so delighted with a lead crystal chandelier or a fine crystal goblet? Why do we find glass sculptures in so many art museums? Why are the stained glass windows of the great cathedrals so entrancing? What aspects of objects made of glass make them so desirable for their beauty, as well as their more pragmatic uses?

The answers to these questions may lie in the ability of glasses to transmit light. Very few materials exist in nature which are transparent to visible light. Metals are opaque, as are virtually all natural organic materials. Many liquids are transparent, but they are transient in nature, without the enduring qualities we desire in our possessions. A list of the few transparent natural solids includes diamonds, emeralds, rubies, and many other precious and semi-precious stones. It is difficult

to think of a naturally transparent solid which is not highly valued for its transparency and brilliance. Our heritage as humans would seem to provide a bias toward placing a high value on such objects. We are still fascinated by "bright, shiny objects."

1 DEFINITION OF A GLASS

What is a "glass"? The glasses used by mankind throughout most of our history have been based on silica. Is silica a required component of a glass? Since we can form an almost limitless number of inorganic glasses which do not contain silica, the answer is obviously, "No, silica is not a required component of a glass." Glasses are traditionally formed by cooling from a melt. Is melting a requirement for glass formation? No, we can form glasses by vapor deposition, by *sol-gel* processing of solutions, and by neutron irradiation of crystalline materials. Most traditional glasses are inorganic and non-metallic. We currently use a vast number of organic glasses. Metallic glasses are becoming more common with every passing year. Obviously the chemical nature of the material cannot be used to define a glass.

What, then, is required in the definition of a glass? All glasses found to date share two common characteristics. First, no glass has a long range, periodic atomic arrangement. And even more importantly, every glass exhibits time-dependent *glass transformation* behavior. This behavior occurs over a temperature range known as the glass transformation region. A glass can thus be defined as "an amorphous solid completely lacking in long range, periodic atomic structure, and exhibiting a region of glass transformation behavior." Any material, inorganic, organic, or metallic, formed by any technique, which exhibits glass transformation behavior is a glass.

2 THE ENTHALPY/TEMPERATURE DIAGRAM

We have established that any material which exhibits glass transformation behavior is a glass. What, then, is glass transformation behavior? We traditionally discuss glass transformation behavior on the basis of either enthalpy or volume versus temperature diagrams, such as that shown in Figure 1.1; (this diagram will be discussed in considerably more detail in Chapter 6). Since enthalpy and volume behave in a similar fashion, the choice of the ordinate is somewhat arbitrary. In either case, we can envision a small volume of a liquid at a temperature well above the melting temperature of that substance. As we cool the liquid, the atomic structure of the melt will gradually change and will be

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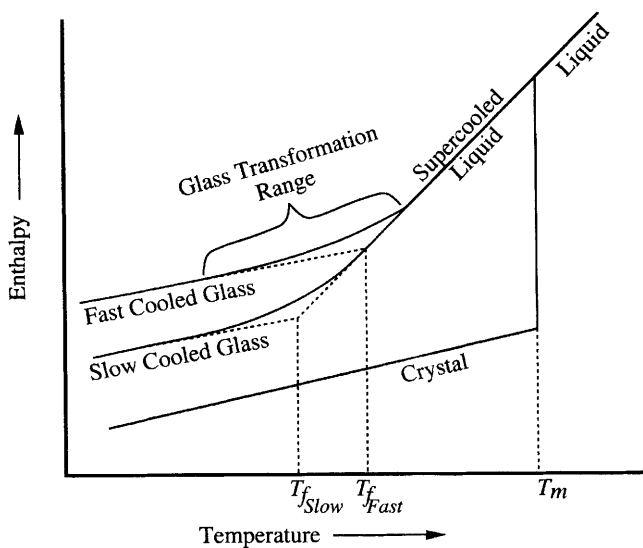
Figure 1.1　*Effect of temperature on the enthalpy of a glass forming melt*

characteristic of the exact temperature at which the melt is held. Cooling to any temperature below the melting temperature of the crystal would normally result in the conversion of the material to the crystalline state, with the formation of a long range, periodic atomic arrangement. If this occurs, the enthalpy will decrease abruptly to the value appropriate for the crystal. Continued cooling of the crystal will result in a further decrease in enthalpy due to the heat capacity of the crystal.

If the liquid can be cooled below the melting temperature of the crystal without crystallization, a supercooled liquid is obtained. The structure of the liquid continues to rearrange as the temperature decreases, but there is no abrupt decrease in enthalpy due to discontinuous structural rearrangement. As the liquid is cooled further, the viscosity increases. This increase in viscosity eventually becomes so great that the atoms can no longer completely rearrange to the equilibrium liquid structure, during the time allowed by the experiment. The structure begins to lag behind that which would be present if sufficient time were allowed to reach equilibrium. The enthalpy begins to deviate from the equilibrium line, following a curve of gradually decreasing slope, until it eventually becomes determined by the heat capacity of the frozen liquid, *i.e.*, the viscosity becomes so great that the structure of the liquid becomes fixed and is no longer temperature-dependent. The temperature region lying between the limits where the enthalpy is that

of the equilibrium liquid and that of the frozen solid, is known as the *glass transformation region*. The frozen liquid is now a glass.

Since the temperature where the enthalpy departs from the equilibrium curve is controlled by the viscosity of the liquid, *i.e.*, by kinetic factors, use of a slower cooling rate will allow the enthalpy to follow the equilibrium curve to a lower temperature. The glass transformation region will shift to lower temperatures and the formation of a completely frozen liquid, or glass, will not occur until a lower temperature. The glass obtained will have a lower enthalpy than that obtained using a faster cooling rate. The atomic arrangement will be that characteristic of the equilibrium liquid at a lower temperature than that of the more rapidly cooled glass.

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

Finally, we need to define a term, which, while commonly used, has only a vague scientific meaning. As indicated above, the glass transformation occurs over a range of temperatures and cannot be characterized by any single temperature. It is, however, convenient to be able to use just such a single temperature as an indication of the onset of the glass transformation region during heating of a glass. This temperature, which is termed either the *glass transformation temperature*, or the *glass transition temperature*, (T_g), is rather vaguely defined by changes in either thermal analysis curves or thermal expansion curves. The values obtained from these two methods, while similar, are not identical. The value obtained for T_g is also a function of the heating rate used to produce these curves. Since T_g is a function of both the experimental method used for the measurement and the heating rate used in that measurement, it cannot be considered to be a true property of the glass. We can, however, think of T_g as a useful indicator of the approximate temperature where the supercooled liquid converts to a solid on cooling, or, conversely, of which the solid begins to behave as a viscoelastic solid