

Polymeric, Metallic, and Other Glasses in Introductory Chemistry

Stephen J. Hawkes

Department of Chemistry, Oregon State University, Corvallis, OR 97331; stephen.hawkes@oregonstate.edu

Non-ceramic glasses are not adequately discussed in introductory chemistry (1). Such glasses include polycarbonate, which many corrective lenses are made of, amber, enamel, gelatin, hard candy, coal, refrigerated glycerol, and metallic glasses that have been marketed in recent decades. What is usually discussed in elementary texts is siliceous glass, which is only one example of the state of matter known as glass. This article summarizes published material on glasses at a level appropriate for introductory chemistry. Readers are referred to Johari's article (2) for discussion of siliceous and other ceramic glasses and to the article that follows it by Hicks (3). An excellent treatment aimed at the introductory level is given in the opening chapter of Newton and Davison's *Conservation of Glass* (4), which is an enjoyable book in its own right.

Definition of a Glass

A glass is a rigid solid with less molecular order than a crystal but more than a liquid. This definition is sufficient for most purposes. Parenthetically, glasses are often incorrectly described as amorphous solids having the same disorder as the liquid. Angell (5) has found several minima in the entropy of glasses proving that there is some degree of order so that the glass is not completely amorphous. Indeed, many glasses contain microcrystals. Angell (6) asserted that "glasses form as a weak reflection of a three-dimensional structure, which is so energetically incompetent that it can barely compete with the disordered form."

The meaning of a "weak reflection" is illustrated by two diagrams that are often reproduced in textbooks. They are of a two-dimensional crystal of a hypothetical oxide of a hypothetical element A with the structure A_2O_3 together with another drawing of its glass (7). The structure of the glass is represented as an arrangement of various fused polyhedra, while the crystal structure is represented as a symmetrical arrangement of fused hexagons. Some texts say incorrectly that these diagrams are two-dimensional representations of silica but the author of the diagrams had no such intention and the assertion is incorrect. The diagrams are an illustration of the relation between glass structure and crystal structure, but they are not a representative diagram.

Another definition is offered by Paul (8) as "a state of matter which maintains the energy, volume and atomic arrangement of a liquid, but for which the changes in energy and volume with temperature and pressure are similar in magnitude to those of a crystalline solid." This definition is used below in discussing the formation of a glass, although it is not quite correct because the atomic arrangement is a little more orderly than that of a liquid.

These definitions serve chemists but they do not serve to identify a glass to an observer who does not have equipment to establish the molecular structure of a solid. For such observers, a definition needs to be based on observable properties. For

polymers it is illustrated by this familiar demonstration: a plastic immersed in liquid nitrogen can easily be smashed by a blow. For most of us, this would identify it as a glass. Thus a polymeric glass is a solid polymer that is brittle, unlike a plastic that can be bent or stretched reversibly.

This definition does not work for inorganic glasses. These are indeed brittle, but so are most crystals. An inorganic glass is therefore a rigid brittle non-crystalline solid. This leaves the problem of how to decide whether it is crystalline, and there is no simple solution.

Formation of Glasses

When a liquid crystallizes, its molecules migrate within the liquid and align themselves as a crystal. If the liquid is sufficiently viscous, the molecules move too slowly to form the crystal during any length of time that humans are able to wait. Glycerol behaves in this manner, so that it is almost (but not quite) impossible to make it crystallize. The viscosity of a liquid at the glass transition temperature is about 10^{12} Pa s (10^{13} P) from which it may be calculated, according to Johari, that the molecular jump rate is about 10^{-3} s⁻¹ or about one jump every 25 minutes. Only extraordinarily slow cooling will allow such a system to come to equilibrium.

Glass formation from a plastic is different. Segments of a polymer with 40 or 50 repeating units are able to move, flex, and uncoil. When the plastic is cooled to the glass transition temperature these motions slow. The attractive forces between the molecules then hold the polymer together rigidly, making it a glass. Then only short lengths of the polymer chain of 5 to 10 units can rotate or vibrate. This freezing phenomenon happens more readily if the polymer backbone is rigid, which correlates with greater entropy of a flexible polymer backbone. Polyethylene has a flexible chain as its backbone so it has a low glass transition temperature (much less than 0 °C) whereas that of polycarbonate is 150 °C. Hence the low glass transition temperature of polypropylene (-17 °C). Similarly, the glass transition temperature is higher if there is strong adhesion between the chains, that is, when the enthalpy of adhesion is large. This accounts for the rigidity of polystyrene at room temperature where it is a glass (the glass transition temperature is 100 °C).

As the plastic is cooled the molecules vibrate less, so the free volume is reduced. Consequently, the density increases as more of the volume of the plastic is occupied by the molecules and less by nearly empty space. At the glass transition temperature and below, the volume of the polymer contracts more slowly as temperature decreases and in fact decreases at almost the same rate as a crystal. At this point, using Paul's definition (8), it is a glass.

Liquids behave similarly. A liquid develops a high viscosity as it approaches the glass temperature, so that the molecules can rearrange only slowly or imperceptibly. As they cool, the

free volume decreases, as shown by an increase in the density, until the glass transition temperature is approached and it then shrinks more slowly. The rate at which it shrinks becomes almost the same as for a crystal. This again defines it as a glass.

Rigidity

Why does a plastic or an elastomer become a glass when immersed in liquid nitrogen? Why does the glass shatter when struck? A plastic usually consists of a crystalline part and an elastomeric part. When a plastic is bent or struck or stretched, the long molecules of the elastomeric part move apart or their coiled structure unravels. When the stress ceases, they spring back together in nearly the same arrangement as before the stress was applied. The energy of the stress is absorbed and can be detected as an increase in temperature of the stretched polymer. When a glass is similarly stressed, the molecules are tightly held together so they cannot move significantly or uncoil. So the energy is dissipated by breaking the chemical bonds in the molecules creating a fracture and breaking the glass.

Why are the molecules more tightly held? This is not clear. There is much that is not understood about the glass transition, as is discussed in a recent article "The Mysterious Glass Transition" (9) that discusses the present state of knowledge of the transition and the research that is now in progress. Sperling (10) describes the various theories of the glass transition but it would be unwise to include any explanation in introductory chemistry until the transition is better understood. As an example of what is not understood, the change from a liquid to a glass takes place over a surprisingly short temperature range, typically about 5 °C. There are various explanations for the short temperature range (11) that may become obsolete in a few more years with further research.

Glass Transition Temperature

The IUPAC definition (12, 13) of the glass transition temperature is that at which the viscosity is 10^{13} dPa s (that is 10^{13} P). In the case of a plastic a different definition is used. Consider two plots of the specific volume against the temperature (or of any other property that is linear with temperature). One of the plots is for the substance in the glassy state and the other plot for the substance at temperatures well above the glass transition. The result is two straight lines of different slopes. As the temperature of the glass transition is approached, these two straight lines change to curves that meet each other forming one continuous line with a change in the slope around the glass transition temperature. When the straight portions of the lines are extrapolated, their point of intersection is considered to be the glass transition temperature. This and other definitions are discussed in the *Polymer Handbook* (14).

The glass transition temperature increases slightly with increasing pressure (from 0.005 to 0.03 K atm⁻¹ but usually around 0.02 K atm⁻¹). This illustrates that the glass transition temperature increases as the molecules are squeezed together so that the glass is more easily formed. It follows that the glass transition is related to how close the molecules are to each other. The effect is otherwise unimportant at the introductory level.

For a series of polymers of the same monomer, the glass transition temperature usually increases with the molecular

mass up to some limiting value, but there are exceptions that are discussed in the *Polymer Handbook* (14). A teacher should be aware of this, but will probably not need to discuss the exceptions with beginning students.

The above description of glass formation assumes that the substance is cooled slowly. When it is cooled quickly, there is not enough time for changes to take place. At the first approach to the glass transition, the density becomes a little greater than in the liquid or elastomer. If the cooling is slow, then further increase in the density occurs at the next incremental reduction in temperature. However, if the cooling is fast, there is not enough time for the molecules to reorganize, so the first arrangement is frozen and remains that way as the fast cooling prevents further change. The initial temperature at which the glass forms when the cooling is fast is by definition the glass transition temperature for fast cooling. Quantitatively, the glass transition temperature varies nearly¹ linearly with the rate of cooling (15).

The glass that is formed then slowly adopts the equilibrium glassy structure that it would have if it were cooled slowly. The movement of the molecules in the glass is slow, so this re-equilibration is also slow, often geologically slow, depending on the temperature at which the glass is stored. The time that is required for polystyrene to reach 1/e (that is 0.37) of the volume contraction that would be expected after a very long time² is tabulated by Marvin and McKinney (16): stored at the glass transition temperature, the time is 5 minutes; stored at 12 °C below the transition temperature it takes 1 year; and at 40 °C below it takes 10¹² years. Other glasses may be presumed to approach their equilibrium condition similarly, so that most glasses never approach the equilibrium condition even in geological time.

The Nature of a Glass

A glass is a solid with molecules held together so strongly that it is rigid, but in which the arrangement of the molecules may be nearly as random as in a liquid, having a structure that is only a weak reflection of the structure of a crystal. Hydroxylic monomeric compounds form rings and strings of hydrogen-bonded molecules even in the liquid state. Some elementary texts show such arrangements in liquid water. These become more complex and stable as the temperature of the liquid is reduced, resulting in a dramatic increase in viscosity in the glass transition region of temperature. These arrangements persist in the glassy state. The same is true of ceramic glasses such as window glass.

Viscosity

When the logarithm of the viscosity of a liquid is plotted against the reciprocal of the temperature, the result is an almost straight line until the glass transition temperature is approached, when it curves showing decreasing slope. This is sometimes drawn with an extrapolation to a new straight line at lower temperatures but the limited experimental and theoretical evidence suggest that the line is not straight. This is illustrated by the viscosities of glass in this temperature range that are shown in ref 17. Extrapolating the presumed straight line over many orders of magnitude has supported the legend that cold antique glass flows, but this is false (18). Medieval windows are *not* thicker at the bottom.

Sugar

When melted sucrose containing a few percent of water (typically less than 10%) is cooled, it forms a glass at a temperature above room temperature, which is hard candy. It can also be spun into fibers as in cotton candy. When less concentrated solutions of sucrose are cooled the result is a mixture of ice and concentrated solution, and at still lower temperatures it produces a mixture of ice and glass. These mixtures are important in the stability and the texture of frozen foods. When certain impurities are present it forms a rubbery state. In particular, evaporated fruit juice becomes "fruit leather". These effects are discussed at length by Simatos et al. (19).

Glasses of Small Molecules

Students should be aware that glass formation is not restricted to some particular class of liquids but is a universal phenomenon of all liquids, though this deserves only a passing mention in an introductory course. When *any* liquid is cooled sufficiently quickly, it will form a glass. For example, the glass transition temperature for water is 136 K (-137 °C) (20). For small-molecule liquids the cooling usually has to be extraordinarily fast (about 10^6 to 10^{12} K s⁻¹; ref 21) to prevent the liquid from crystallizing. Such cooling rates can be achieved only in sophisticated experiments

Metallic Glasses

Pure metals form glasses when cooled at rates around 10^{10} K s⁻¹, which is too rapid for simple experiments. Even in well-designed experiments glasses can usually be formed only with very minute dimensions. However in recent decades alloys have been made that form glasses at much slower rates of cooling, some as slow as 1 K s⁻¹, and have been described by Telford (22). These have several metals in the alloy with a variety of atomic diameters, making it harder to form crystals and therefore slower. Such liquids allow glasses to form at slower rates of cooling than pure metals.

Metallic glasses have practical advantages over pure metals. Pure metals normally freeze as a multitude of crystals. These join each other at planes where the chemical forces are different from the bulk metal. This weakens them because the crystals can be made to slide past each other as the metal is fractured or bent. Corrosion can begin at these fault planes. Metallic glasses have no crystalline structure so they have no fault planes. Consequently, they are harder than regular metals—twice as hard as steel—and more resistant to corrosion and to wear. They are therefore used advantageously in surgical scalpels where they are superior to steel. Metallic glasses are used to coat other metals to give them a surface hardness and resistance to corrosion. Such coatings are more durable than an electroplated layer of chromium. Metallic glasses are more brittle than pure metals but not as brittle as siliceous or other ceramic glasses. Metallic glasses are also more elastic, so they have been made, for example, into golf club heads. They transmit almost all the energy of the stroke efficiently to the ball instead of dissipating energy as heat. By contrast, a titanium golf club head transmits only 70% of the energy to the ball. Metallic glasses are being investigated as a

replacement for uranium in anti-tank missiles, because they are not flattened on impact. Their resistance to wear and corrosion recommends them for surgical implants in humans.

Metallic glasses that are marketed today have film thicknesses much less than a millimeter because of the need for fast cooling. However, glasses have been made in recent decades in thickness up to 10 cm, allowing manufacture of the products mentioned above.

Is There Time To Teach This?

There is time to include discussion of glasses in introductory chemistry if less valuable subjects are eliminated and the curriculum seriously reconsidered (22, 23). Subjects for elimination would include unreliable (24–28) or useless (29) calculations; phenomena that are rare outside the chemistry laboratory (30); models of the chemical bond that introductory students cannot use (31) or that are incorrect (32–34) or use an outdated pedagogy (35–37); quantum numbers; and a derivation of the periodic table that relies (38) on quantum states.

Notes

1. The temperature that has been shown to vary strictly linearly with the rate of cooling is the so-called "fictive" temperature, but the explanation of "fictive" requires too many unfamiliar concepts for introductory courses. Hence the approximation used here.
2. In infinite time the glass would crystallize, but the time involved could be longer than the present age of the universe.

Literature Cited

1. Hawkes, S. J. *J. Chem. Educ.* **2005**, *82*, 1615–1616.
2. Johari, G. P. *J. Chem. Educ.* **1974**, *51*, 23–27.
3. Hicks, J. F. G. *J. Chem. Educ.* **1974**, *51*, 28–31.
4. Newton, R.; Davison, S. *Conservation of Glass*; Butterworth Heinemann: Oxford, 1996.
5. Angell, C. A. *Science* **1995**, *267*, 1925.
6. Angell, C. A. *J. Phys. Chem. Solids* **1988**, *49*, 863–871.
7. Zachariasen, W. H. *J. Amer. Chem. Soc.* **1932**, *54*, 3841–3851.
8. Paul, A. *Chemistry of Glasses*; Chapman and Hall: New York, 1990; p 4.
9. Langer, J. *Physics Today* **2007**, *60* (2), 8–9.
10. Sperling, L. H. *Introduction to Physical Polymer Science*; Wiley: New York, 2006; pp 381–397.
11. Haward, R. N. *The Physics of Glassy Polymers*; Wiley: New York, 1973; pp 158–159.
12. McNaught, A. D.; Wilkinson, A. *Compendium of Chemical Terminology: IUPAC Recommendations*, 2nd ed.; Blackwell science: Oxford, 1997; p 173.
13. Clark, J. B.; Hastie, J. W.; Kihlborg, L. H. E.; Metselaar, R.; Thackeray, M. M. *Pure and Applied Chemistry* **1994**, *66*, 583.
14. *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1989; pp VI 210–212.
15. Safell, J. R. Analysis of DSC Thermal Curves for Assigning a Characteristic Glass Transition Temperature. In *Assignment of the Glass Transition*; Seyler, R. J., Ed.; ASTM: Philadelphia, 1994; p 142.
16. Marvin, R. S.; McKinney, J. E. In *Physical Acoustics*; Mason, W. P., Ed.; Academic Press: New York, 1965; p 218.

17. *Encyclopedia of Materials Science and Engineering*; Bever, M. B., Ed.; Vol. 7; MIT: Cambridge, MA, 1986; pp 5253–5255.
18. Hawkes, S. J. *J. Chem. Educ.* **2000**, *77*, 846–848.
19. Simatos, D.; Blond, G.; Martin, F. Influence of Macromolecules on the Glass transition in Frozen Systems. In *Food Macromolecules and Colloids*; Dickinson, E., Lorient, D., Eds.; Royal Society of Chemistry: Cambridge, 1995; pp 520–532.
20. Kohl, I.; Bachman, L.; Hallbrucker, A.; Mayer, E.; Loerting, T. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3210.
21. *McGraw-Hill Encyclopedia of Science and Technology*, 9th ed.; McGraw-Hill: New York, 2002; Vol. 8, p 148.
22. Telford, M. *Materials Today* **2004**, *7*, 36–43.
23. Hawkes, S. J. *J. Chem. Educ.* **2005**, *82*, 1615.
24. Hawkes, S. J. *J. Chem. Educ.* **1998**, *75*, 1179.
25. Hawkes, S. J. *Chem 13 News* **1996**, *250*, 1.
26. Hawkes, S. J. *J. Chem. Educ.* **1995**, *72*, 799.
27. Hawkes, S. J. *J. Chem. Educ.* **1994**, *71*, 747.
28. Hawkes, S. J. *J. Chem. Educ.* **1999**, *76*, 1099.
29. Hawkes, S. J. *J. Chem. Educ.* **2008**, *85*, 498.
30. Hawkes, S. J. *J. Chem. Educ.* **2003**, *80*, 1381.
31. Hawkes, S. J. *Khimiya*. **2007**, *16*, 90.
32. Reed, A. E.; Weinhold, F. *J. Amer. Chem. Soc.* **1986**, *108*, 3586–3593.
33. Malm, J. G.; Selig, H.; Jortner, J.; Rice, S. A. *Chem. Rev.* **1965**, *65*, 199–236.
34. Straub, D. K. *J. Chem. Educ.* **1995**, *72*, 889.
35. Gillespie, R. J.; Spencer, J. N.; Moog, R. S. *J. Chem. Educ.* **1996**, *73*, 622–627.
36. Spencer, J. N.; Moog, R. S.; Gillespie, R. J. *J. Chem. Educ.* **1996**, *73*, 627–631.
37. Spencer, J. N.; Moog, R. S.; Gillespie, R. J. *J. Chem. Educ.* **1996**, *73*, 631–636.
38. Gillespie, R. J.; Spencer, J. N.; Moog, R. S. *J. Chem. Educ.* **1996**, *73*, 617–622.

Supporting JCE Online Material

<http://www.jce.divched.org/Journal/Issues/2008/Oct/abs1377.html>

Abstract and keywords

Full text (PDF) with links to cited *JCE* articles