Antique Windowpanes and the Flow of Supercooled Liquids

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If one surveys a group of high school science teachers, or science students, quite a large number of them state that colonial window panes are thicker at the bottom than at the top because the glass is a supercooled liquid that has slowly flowed downward over the hundreds of years since it was installed. It is a delightful idea—textbooks have used it as an illustration, teachers have passed it on,[1] and the Society Committee on Education of the American Chemical Society has included it in a sourcebook (*1*) for physical chemistry teachers. But is it true? This author was skeptical and pursued the matter. It was found that F. M. Ernsberger, an authority in visco–elastic behavior of glass, has taken exception to the stories in a treatise on glass (*2*):

> There is a widespread opinion that glasses are supercooled liquids and therefore have a finite viscosity at ordinary ambient temperatures. Stories are told of glasses flowing under their own weight: of ancient windowpanes that are thicker at the bottom; of glass that has sagged in storage. These observations must find other explanations, because glasses of commercially useful compositions are in fact rigid solids at ordinary temperatures.

But the subject has not been addressed from the point of view of chemical educators.

In trying to find out why ancient windowpanes are thicker at the bottom than the top several illustrations of chemical principles became apparent that could replace the illustration that was being negated. Further, what appears to be the true origin of the effect lies in a process that is of special interest in the history of chemistry.

Consider first the fact that you can bend a piece of an aluminum sheet but not a similar piece of sheet ice lifted from the surface of a pond. The ice will break before it is bent a very little. What chemical variable causes diamonds, glass, and ice to be brittle and difficult to deform and other materials, such as copper wire, to be ductile and easily deformed? The chemical structural effect that is responsible for the ductility of metals was stated clearly by Slater (*3*):

> A metal can be bent and deformed without breaking, much more than most other substances, as for instance ionic crystals. This is particularly striking with the close-packed metals. In a metal, the bonds act quite indiscriminately between any closely neighboring atoms. They do not depend greatly on the exact orientation of the atoms, as the real homopolar valences do. Thus a distortion of the lattice, so long as it does not involve much net change of the interatomic distances, will not greatly change the energy and will not be opposed by a large force.

The bonds joining a copper atom core to its 12 nearest neighbors are in fact much stronger than the hydrogen bonds linking a water molecule to its nearest neighbors in ice, but they are not nearly as directional and difficult to bend. The rigidity of a structure of linked tetrahedra as in ice and diamonds is common knowledge through the architectural innovations of R. Buckminster Fuller.

In quartz crystals or other crystalline forms of SiO_2, or in fused quartz, a glass, each Si is surrounded tetrahedrally by four O atoms. Each O links two neighboring tetrahedra. The differences between the several forms of $SiO_2(s)$ derives from the flexibility of the Si–O–Si bond linking the tetrahedra. The bond angle varies from about 145° in quartz crystals to nearly 180° in the cristobalite structure. All of the structures are bonded in rigid 3D networks; in the glassy form of $SiO_2(s)$ the 3D network contains a wide range of Si–O–Si bond angles, and the periodicity of the crystalline lattices is lost. The glassy state resembles a liquid in having short-range order without long-range order, but it differs in that the entire network is rigid, whereas in the liquid state enough energy is available to break and reform bonds continuously.

There is a laboratory phenomenon called "zero creep" that resembles viscous flow in glasses (*4*). "Zero creep" is not a creep of zero magnitude but a creep of the 0 °C calibration temperatures on 0–400 °C borosilicate (Pyrex) glass thermometers. It may creep upward by as much as 1.4 °C when used intermittently for 20 years over its temperature range and by 1.5 °C in 210 h of heating at 410 °C (*5*). The thermometer bulb changes in size slowly. The explanation illustrates more structural properties of glass.

Most commercial glasses are not pure fused silica. Binary silicate glasses contain, in addition, ionic oxides such as Na_2O and CaO. The added oxides enter the structure as cations and the oxygens add on to the Si. But how can an extra oxygen be attacked to the Si, which already has four bonded to it? By breaking apart the covalent Si–O–Si network, converting a bridging oxygen into two polar groups, i.e., $Si{-}O^{-}\ {}^{-}O{-}Si$. This weakens the 3D network. In borosilicate-type glasses a different network modification occurs. Triangular BO_3 groups substitute for SiO_4 groups.

Now consider the mechanical properties of the lattice. The temperature at which a rigid glass becomes a supercooled liquid is called the glass transition temperature, T_g. When a glass is heated up to T_g enough energy is available to give a measure of flexibility to the lattice structure. It should be clear that the less rigid structures of borosilicate and binary silicate glasses will have lower T_g's than fused silica. One must also ask in considering flexibility of a molecular framework how long one is willing to wait for changes to occur. Two T_g's are appropriate, T_g on a finite laboratory time scale used in ordinary experimental measurements and T_g^0 calculated for the limiting case of infinitely long time periods. The latter, called the ideal glass transition temperature, is based on thermodynamic considerations. The relative values are given in the table.

Glass Transition Temperatures[a]

Glass	T_g (°C) (measured)	T_g^0 (°C) (calculated)
Silica glass	~1200	—
Pyrex	550	350
Window glass	550	270

[a] From West, A. R. *Solid State Chemistry and Its Applications;* Wiley: New York, 1984; p 601.

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[1] Robert Brill, of the Corning Museum, has records of the stories dating as far back as a high school chemistry class in 1947.

In the "zero-creep" phenomenon the thermometer bulbs are heated above the glass transition temperature and the lattice slowly adjusts to the equilibrium (supercooled) liquid structure stable at that elevated temperature.

Another observable phenomenon, called "anelasticity", also resembles viscous liquid flow. Holloway's volume (*6*) on *The Physical Properties of Glass* in the British Wykeham Science series, specifically written for science teachers, contains an especially clear description of the experiments. If a glass rod at room temperature is twisted, the torsional stress produces an immediate elastic strain. If the stress is removed, the rod returns to its original shape. However, if the stress is applied and maintained for an extended period of time, the rod gradually twists further. Upon removing the stress, the immediate elastic strain is relieved, but the rod does not return to its original untwisted state. It retains the distortion produced during the extended time period over which the stress was applied. Is this small deformation a result of viscous flow? No, because, surprisingly, if one then waits a long time, the rod gradually returns to its original zero-twist state. The delayed elastic recovery effect is associated with the slow diffusion of cations in the structure. Under prolonged stress, the sodium ions are slowly squeezed out of elastically compressed sites in the 3D silicate network to elastically expanded sites and back again when the elastic strain is removed.

Those who are convinced that glass flows like a viscous liquid under its own weight at room temperature sometimes cite the Corning Glass Co. instructions printed on boxes of tubing, "Lay flat, do not stand on end." They note that glass tubing is frequently bowed by detectable amounts, as though the tubing has sagged during storage. However, there is a residual bow in tubing as manufactured. Tubing produced by the Vello process may be bowed by as much as 0.150 in. in a 4-ft length. The reason for the instructions on the boxes is to avoid shipping damage to the ends of the tubing, not to keep it from sagging.[2]

If glass at room temperature has the mechanical properties of a rigid disordered solid rather than of a supercooled very viscous liquid, why are panes of antique window glass thicker at the bottom than the top? There really are observable variations in thickness, although there seem to have been no statistical studies that document the frequency and magnitudes of such variations. This author believes that the correct explanation lies in the process by which window panes were manufactured at that time: the Crown glass process.[3] The process is described vividly in an 1860 chemistry textbook (*7*) by Sheridan Muspratt (founder of the College of Chemistry, Liverpool), drawing considerably from a paper presented by an artisan, Henry Chance (*8*), to the Society of Arts, London. About 9 lb (±1 or 2 oz) of molten glass was collected in a lump as in Figure 1A, rolled, and blown to the shape of a Florence flask (Fig. 1B), and an iron cup was attached as in Figure 2 to keep the shape centered. The flask was then expanded and flattened to the shape of an enormous decanter as in Figure 1C. Next an iron punty was attached and the blow pipe removed (leaving a hole) as in Figure 1D. Finally the shape was spun in a flashing furnace, as in Figure 3, and, to quote,

> The action of heat and centrifugal force combined is soon visible. The nose of the piece, or hole caused by the removal of the blowing pipe, enlarges, the parts around cannot resist the tenden-

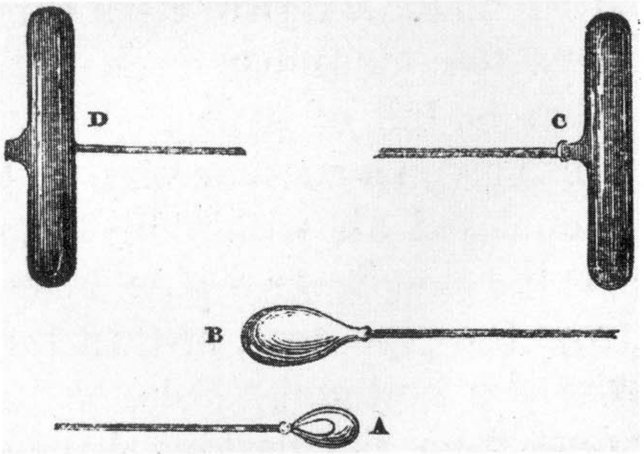

Figure 1. The shapes of the 9 lb of molten glass: A, when gathered; B, blown; C, blown larger and flattened; and D, attached to the "ponty" (known as a punty now) and the blow pipe removed before it was spun to the large disk shape in the flashing furnace. (From ref *7*.)

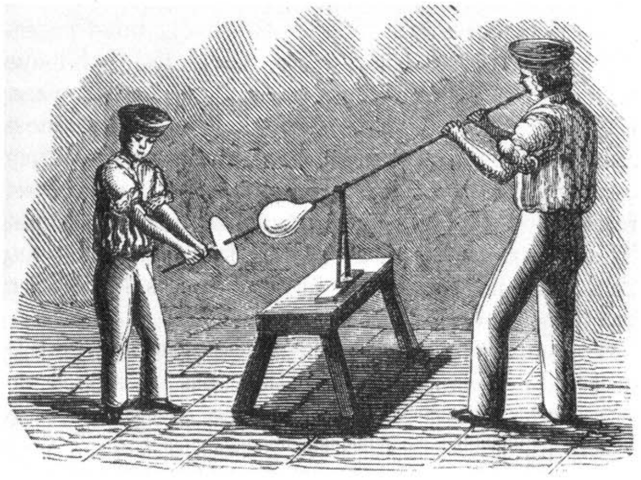

Figure 2. The glass blower enlarging the glass flask, assisted by his helper in keeping the mass of molten glass centered. (From ref *7*.)

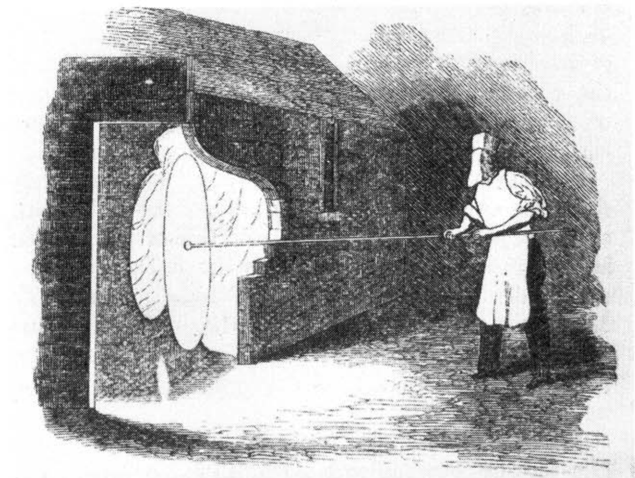

Figure 3. Expanding the open decanter shape to a 60-in.-diameter disk in the flashing furnace. (From ref *7*.)

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[2] R. Lemker, Operations Manager, Fallbrook Plant, Corning Glass, Corning, NY, personal communication, 1988.

[3] The Architectural Conservator at Old Williamsburg, Thomas Taylor, and David Colglazier, Conservator at Old Sturbridge Village, only heard of the flowing supercooled liquid stories recently and were skeptical, having believed for many years that the observed irregularities came from the glass manufacturing process.

> cy, the opening grows larger and larger; for a moment is caught a glimpse of a circle with a double rim; the next moment, before the eyes of the astonished spectator, is whirling a thin transparent circular plate of glass which, but a few minutes before, was lying in the glass-pot, an indistinguishable portion of the molten mass. The sound of the final opening of the piece has been compared to that produced by quickly expanding a wet umbrella. In this way a flat circular disc, nearly sixty inches in diameter, or sometimes more, is produced, of almost uniform thickness, except at the point of attachment to the ponty, where there is a swelling called, as already stated, the bull's-eye. The glass at the edge of the disc is also in some cases a little thickened. Still whirling, the *table*, as it is now called, is carried off, laid flat upon a support called a whimsey, detached by shears, or otherwise, from the ponty, lifted into the annealing kiln upon a fork and piled upon its edge against the preceding table.

The glass was amazingly flat and uniform in thickness for a hand-fabricated disk 5 ft in diameter, but not in comparison to sheet glass drawing processes of recent years and float glass processes widely used now. Anyone who has attempted any glass blowing will recognize the difficulties inherent in the process pictured.

After the tables were cooled, panes were cut. Quoting Muspratt further,

> The cutting of a circle into rectangular sheets, must necessarily be attended with waste, while the bull's-eye confines those sheets to comparatively small sizes. Uniformity of thickness also, except by the most skillful manipulation, is difficult of attainment.... The splitter carefully examines each table before splitting it, and turns it round till he has brought it into the position in which he may split it to the best advantage, announcing at the same time its quality. The first quality is called *best*—the next, seconds—then thirds—fourths—CC—CCC or Irish—and tables containing any very glaring defects, come under the denomination of *coarse*.... No wonder that tables of the best quality are few and far between, in some manufacturies a forlorn hope never to be realized.

The variations in thickness were apparently of less concern than other defects such as vesicles, blisters, dust, lines, curves, and scratches. However, the quality was apparently lower in earlier years.

> A table of crown glass of to-day would scarcely recognise as of kindred origin a table of the earlier part of the present century. The principle of the process in each case was the same; it is the improvement of minute details that produces so different a result. To Mr. Hartley and Mr. Chance who, during the years 1832 to 1836, gave to the manufacture of this glass their constant attention, is owing, in a great measure, its present status.

The explanation being put forward here as to why antique window panes are thicker at the bottom than the top is not yet complete. Why at the bottom rather than at the top? A window glazier's instruction book of the period, if one could be found, might contain the answer. It would certainly make good sense to install the glass with the thick edge down!

Acknowledgment

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