

2. Glass transition temperature:

Different operational definitions of the glass transition temperature (T_g) are in use, and several of them are endorsed as accepted scientific standards.

Nevertheless, all definitions are arbitrary, and all yield different numeric results: at best, values of (T_g) for a given substance agree within a few kelvins. One definition refers to the viscosity, fixing (T_g) at a value of 10^{13} poise (or 10^{12} Pa·s). As evidenced experimentally, this value is close to the annealing point of many glasses.

In contrast to viscosity, the thermal expansion, heat capacity, and many other properties of inorganic glasses show a relatively sudden change at the glass transition temperature. Any such step or kink can be used to define (T_g) to make this definition reproducible, the cooling or heating rate must be specified.

The most frequently used definition of (T_g) uses the energy release on heating in differential scanning calorimetry (DSC, see figure).

Typically, the sample is first cooled with 10 K/min and then heated with that same speed.

Yet another definition of (T_g) uses the kink in dilatometry. Here, heating rates of 3-5 K/min are common.

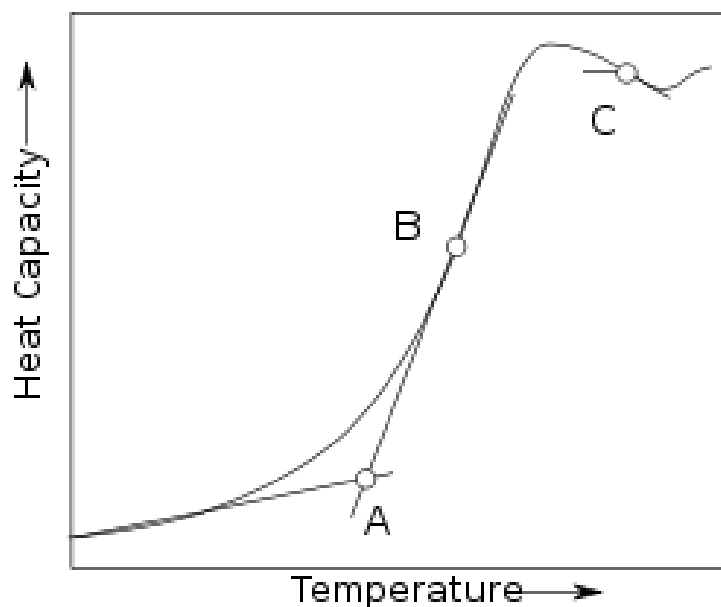


Fig 2.1. Measurement of T_g by differential scanning calorimetry

As a glass-forming liquid is cooled, some of its properties change sharply in a narrow temperature range. In Fig 2.2. the specific volumes of a soda-lime silicate glass and glassy B_2O_3 are shown as a function of a temperature; an abrupt change in the slope of the curve, which is equal to the coefficient of volume expansion, occurs at a certain temperature.

Other properties, such as the heat capacity (see Fig 2.3.) and electrical conductivity, also change abruptly at about the same temperature.

This temperature is called the glass transition or transformation temperature.

It is significant that the viscosity does not show an abrupt change at the glass transition temperature. This result suggests that the viscosity determines the rate at which a property relaxes to some equilibrium value, but may not be related to the magnitude of property changes under different conditions. Therefore a theory for the viscosity probably will not result from consideration of changes in properties of the glass, but only from study of the details of the flow mechanism itself.

Glass transitions occur for many types of glasses. It has been suggested that some amorphous solids do not show a glass transition temperature, but this result has not been established with any certainty.

It is reasonable to associate the glass transition temperature with the slowing down of rearrangements in the glass structure. When these rearrangements occur rapidly during the time of experimental measurements, the glass has the properties of a liquid; when the rearrangements are slow, the glass structure is "frozen" and it behaves like a solid.

In fact, the specific volumes and their temperature dependencies of the glasses shown in Fig 2.2. are quite close to those of the corresponding crystalline solids below the glass transition temperature. The rate of these molecular rearrangements should be closely associated with viscous flow, and indeed the glass transition temperature occurs at a viscosity of about 10^{13} P.

Thus the presence of a glass transition results from the slowing down of viscous relaxation in a liquid.

Estimates of the relaxation time at a viscosity of 10^{13} P are in the range of minutes to a few hours, in reasonable accord with the usual times of experiments.

Since the transition temperatures determined from specific volume and heat capacity are nearly the same, the molecular motions involved in changing these properties with temperature changes are probably similar. Other properties of glasses show changes at the glass transition temperature.

There is some evidence that the elastic modulus of glasses changes sharply at the glass transition temperature, although it is difficult to measure a meaningful value of the modulus much above the glass transition temperature.

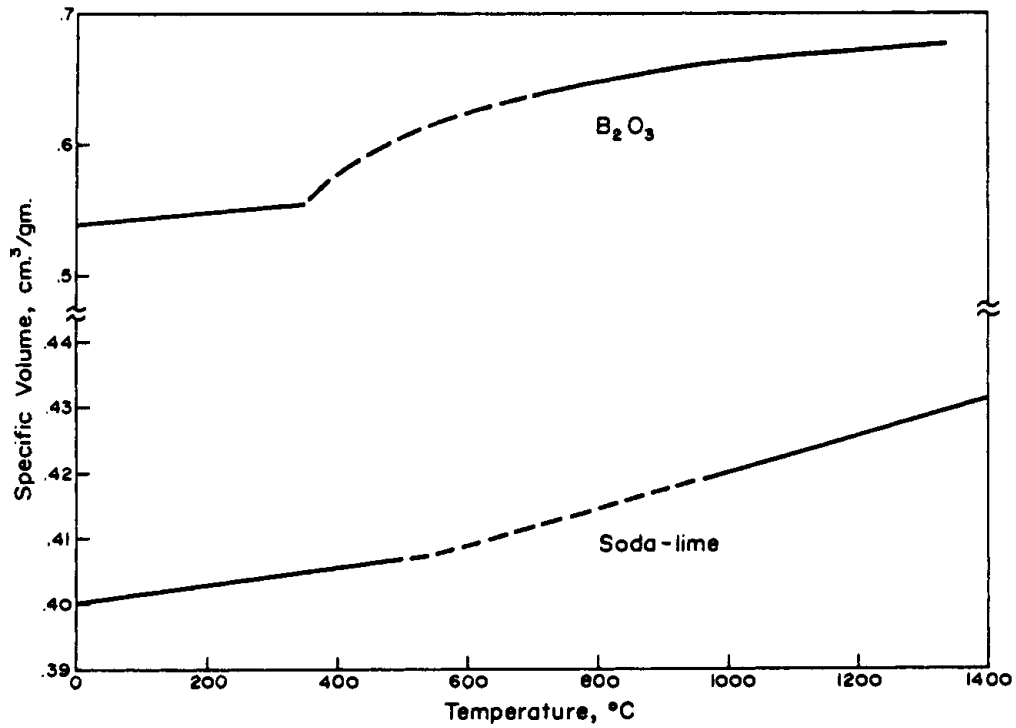


Fig 2.2. Specific volumes of a soda-lime silicate glass (74% SiO₂, 16% Na₂O, and 10% CaO) and glassy B₂O₃ as a function of temperature.

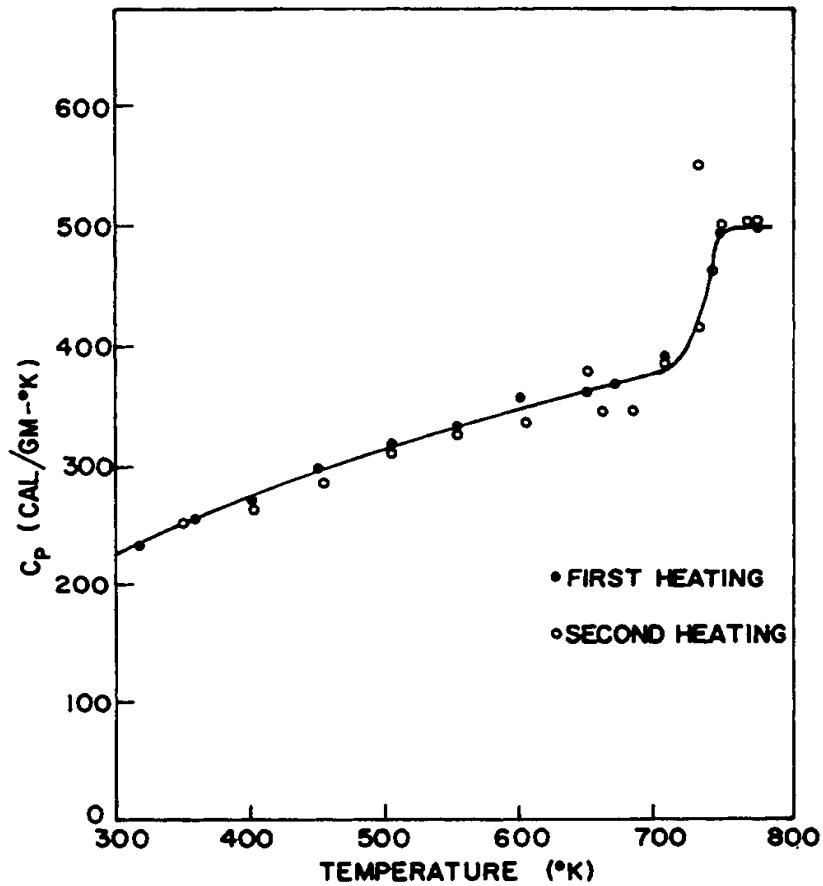


Fig 2.3. Heat capacity of 0.15 Na₂O, 0.85 B₂O₃ glass as a function of temperature.

This change is a manifestation of the increasing ease of molecular motion and consequent change in elasticity with time at a particular temperature. An increase in hydrostatic pressure apparently increases the transition temperature. This result might be expected because of the reduction in relaxation rates with increasing pressure.

It is known that the molecular motions in dielectric relaxation of liquids are related to their viscosities, so a correlation of dielectric relaxation with transition temperature is expected.

It is extrapolated that the entropy of a supercooled liquid of the "fragile" type and found that at some temperature below the glass transition temperature, the entropy of the supercooled liquid becomes less than that of the crystal. Since the liquid is less ordered than the crystal, this result is unexpected and has been called Kauzmann's paradox.

It is concluded that the correct extrapolation of the entropy of the supercooled liquid does not become less than that of the crystal, but only approaches it asymptotically.

Summarized below are (T_g) values characteristic of certain classes of materials.

Material	T_g ($^{\circ}\text{C}$)
Tyre rubber	-70
Polypropylene (atactic)	-20
Poly(vinyl acetate) (PVAc)	30
Polyethylene terephthalate (PET)	70
Poly(vinyl alcohol) (PVA)	85
Poly(vinyl chloride) (PVC)	80
Polystyrene	95
Polypropylene (isotactic)	0
Poly-3-hydroxybutyrate (PHB)	15
Poly(methylmethacrylate) (atactic)	105
Poly(carbonate)	145
Chalcogenide AsGeSeTe	245
ZBLAN glass	235
Tellurium dioxide	280
Polynorbornene	215
Fluoroaluminate	400
Soda-lime glass	520-600
Fused quartz	~1200