

Freezing of a Melt to a Vitreous Solid

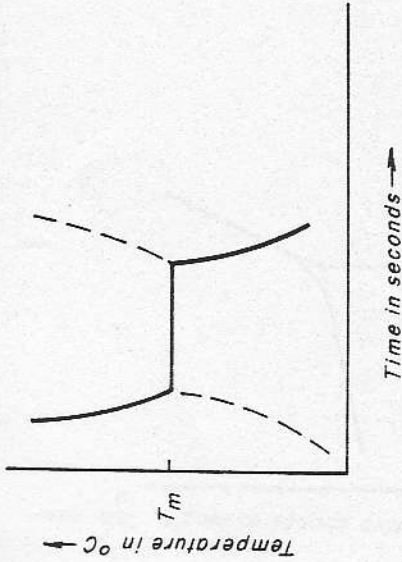


Fig. 2.1. Cooling and melting curves for simple solids.

Fusion and Crystallization. General
 At a certain temperature (the melting point, T_m), vibrating lattice elements of a crystalline solid will no longer return to sites bonded to their neighbors. The crystal lattice collapses and the crystal loses its shape; it changes to the liquid state, i.e., it melts. Unless additional energy is supplied, sufficient to remove all elements from lattice sites, the system maintains equilibrium: As many elements as enter the melt return to the remaining orderly lattice. In this state of equilibrium, a crystal will neither grow nor melt completely.

If, however, additional thermal energy is supplied to the system at the melting point, this energy will be used exclusively to remove further elements from their sites while the temperature remains constant at T_m (Fig. 2.1). The internal energy is increased by what is called the *heat of fusion*. If a liquid freezes, the reverse process takes place. At the melting (or freezing) point T_m , the entire heat of fusion consumed in the melting process is released as heat of crystallization.

The freezing of a melt to a noncrystalline (vitreous, glassy, amorphous) solid represents a deviation from this "normal" (thermodynamically required) freezing process. Only in a special case of solidification is the lowest energy not attained.

Numerous observations suggest that a liquid will solidify to a glass, if the mobility of the elements that should constitute the lattice is sufficiently restricted to hinder their orderly arrangement in the form of nuclei, during the time available in the cooling process.

In silicate glasses, for example, this impediment is caused by the rapid increase in viscosity on cooling, due to the tendency of silicate groups to form 3-dimensional networks. In organic compounds, polymerization and cross-linking induce such increases in polymerization and lack of crystallinity. It is, for instance, difficult to crystallize viscous sugar solutions.

Time plays a decisive role in the formation of criteria of glass formation. The length of time a melt dwells in a temperature range favoring nucleation or growth of crystals is important. For this reason, glass formation depends critically on the rate of cooling. According to the prevailing theories of glass formation, therefore, any material (gaseous or liquid), not just typical "glass-formers," can be frozen to a noncrystalline (vitreous, glassy, amorphous) solid, provided that the material is cooled quickly enough to suppress nucleation and growth of crystals. In fact, the recent attainment of cooling rates of 10^6

$K \cdot s^{-1}$ and more has allowed us to obtain small volumes of wires or ribbons and even fluid metallic melts (metal glasses) in the glassy state.

The first investigations on cooling behavior and glass formation were carried out by Tammann.⁶⁻⁸ According to his now classical investigations, the behavior of the melt (crystallization or glass formation) depends on two parameters: (1) the number of "nuclei" of crystals forming in unit time (nucleation frequency, I), and (2) the linear growth rate in $cm \cdot s^{-1}$ (u) of these nuclei.

Both factors depend on the magnitude of undercooling ($T_m - T$), first increasing under an increasing (thermodynamic) driving force below the melting point and then decreasing at lower temperatures due to kinetic hindrance as the viscosity increases. Plots of I and u vs temperature thus have maxima, and are similar but not equal. Usually the maximum for I occurs at a lower temperature and is broader (Fig. 2.2). Of course, in this case a large separation of the I and u curves favors glass formation, since in the higher T range favoring growth u , not enough nuclei are available to grow. Conversely, for closeness of I and u maxima, easy crystallization is to be expected.

Tammann also recognized that impurity ("inhomogeneous nucleation") may radically affect crystallization. Thus, purified water may be undercooled to $-30^\circ C$.

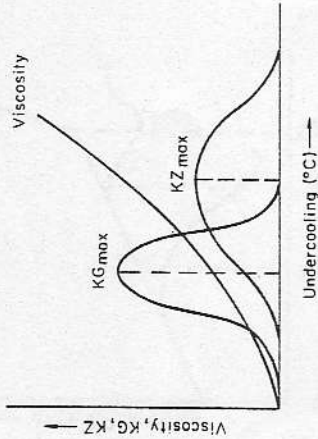


Fig. 2.2. Dependence of nucleation, crystal growth, and viscosity on undercooling of a melt which solidifies to a glass easily. As a rule, the maximum for nucleation is somewhat broader than that for growth.

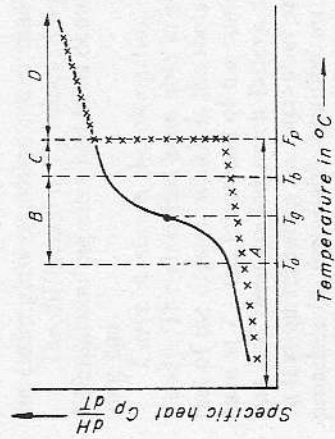


Fig. 2.3. Change of specific heat in the range of high temperatures for crystalline and vitreous solids. F_p = melting point (liquidus) of crystals, T_g = transition temperature, $B(T_g - T_b)$ = softening interval (plastic range), $C(F_p - T_b)$ = undercooled liquid glass melt, A = crystalline solid, D = liquid melt.

Significant Differences between Crystalline and Noncrystalline (Glassy) Solids

Both crystals and glasses are solids; that is, constituent atoms essentially will no longer respond to stress by changing sites. They will just be displaced within their ranges of vibration. The common factor is a viscosity above about 10^{13} Pa.¹ However, there are fundamental differences in their properties and behavior.

If we inspect the change of the specific heat C_p with temperature for crystalline and vitreous solids of equal composition, the features illustrated in Fig. 2.3 are observed. Regardless of whether melts had originated from a crystalline or vitreous solid, above the melting point T_m they are identical and show the identical decrease of C_p with temperature.

If at T_m the melt freezes to a crystal, C_p discontinuously decreases to the much lower value of the crystalline solid. On further cooling, a much less pronounced linear decrease of C_p follows until, near absolute zero temperature, the Debye T^3 relation holds.

If, however, at T_m crystallization is avoided, further cooling first shows a continuation in the decrease of C_p , the melt representing an "undercooled liquid."

However, at a temperature T_b , C_p begins to drop at an increasing slope through an inflection at temperature T_g down to a temperature T_a , where it approaches the value of the crystalline solid. During this interval, the melt solidifies to a glass, attaining a viscosity of about $10^{13.5}$ at T_a . On further cooling, C_p values remain generally near but slightly above those for the crystalline solid, decreasing at a slightly greater rate. This shows clearly that the glass is in a higher energy, metastable state compared to the crystal. The range T_b to T_a represents the glass transition* (the "softening range" of glass technologists). The inflection point is named "glass (transition) temperature," usually designated T_g . Although it will be shown that T_g depends on thermal history, it is widely used in science as well as technology to characterize noncrystalline solids in the same manner as T_m characterizes crystalline solids. This requires standardization and/or disclosure of the heat treatment used. In the glass-transition interval, viscosity increases from about 10^8 to $10^{13.5}$.

*In contrast to the German use of the term "transformation" for this range, American usage limits the term "transformation" to true solid phase changes.

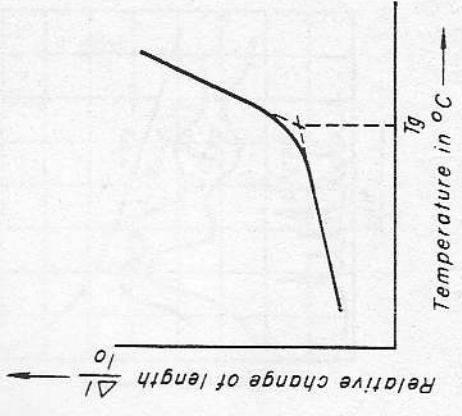


Fig. 2.4. Determination of the transition temperature of a glass by measuring the change of length in temperature dependence.

Similar curves as for C_p (Fig. 2.3) are obtained for other properties such as the coefficient of expansion, ($\alpha = (1/v)(\partial v/\partial T)$), volume, refractive index, electrical resistance, etc. The conventional method for the determination of T_g is the measurement of the change in length of a glass sample at a continuous standardized rate of heating (Fig. 2.4), but various other methods are used as well.

In the transition range, decisive changes in microstructure occur which take increasing amounts of time as the lower temperature limit is approached. For this reason, all glass properties in this range depend on temperature and time, so that different heating and cooling rates, or generally any variations in time and temperature (thermal history), will induce variations in property values. This is the main reason that T_g varies with thermal history. Comparisons can be made only if conditions are standardized. A widely accepted standard required cooling at $1^\circ\text{C}\cdot\text{min}^{-1}$ through the transition interval, followed by heating at $5^\circ\text{C}\cdot\text{min}^{-1}$. Otherwise, the sample should be retreated, or at least, conditions of the experiment reported. From a scientific viewpoint,

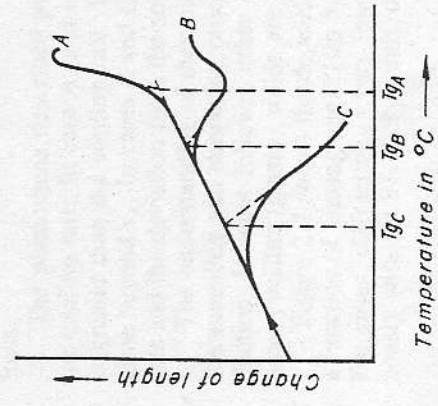


Fig. 2.5. Change in length of a borosilicate glass with increasing temperature (after Salmang (Ref. 10). A = slowly cooled, bulk; B = rapidly cooled, bulk; C = extremely rapidly cooled (6 μm fiber).