

serve to illustrate the difficulty in finding a comprehensive structural theory of glass formation.

#### 18.1.4 Criteria of Sun and Rawson

Other correlations have been proposed between structural features and the glass-forming tendency of simple oxides. Sun suggested that the other element-oxygen bond strength is important. He noted that glass-forming oxides have bond strengths  $\approx 330 \text{ kJ mol}^{-1}$ , whereas modifier ions, which are not part of the network structure, have bond strengths to oxygen that are below this value.

Rawson modified Sun's criterion and related glass-forming tendency to the ratio of bond strength: melting temperature. This ratio accounts for both the bond strength and the thermal energy available to break the bonds, which depends on temperature. It is virtually impossible to crystallize  $\text{B}_2\text{O}_3$  glass and this can be understood from Rawson's criterion, since  $\text{B}_2\text{O}_3$  has a relatively low melting point,  $\sim 400^\circ\text{C}$ . This criterion may also explain why, in binary systems, the glass-forming compositions are often located around the low melting eutectics. A good example is provided by the  $\text{CaO}-\text{Al}_2\text{O}_3$  system: neither  $\text{CaO}$  nor  $\text{Al}_2\text{O}_3$  is itself capable of forming a glass (except perhaps by ultra rapid quenching of thin films) but compositions between  $\text{CaAl}_2\text{O}_4(\text{CA})$  and  $\text{Ca}_3\text{Al}_2\text{O}_6(\text{C}_3\text{A})$  (see Fig. 19.8) readily form glasses. These compositions are in the region of low melting eutectics with liquidus temperatures in the range  $\sim 1400$  to  $1600^\circ\text{C}$ .

An additional factor in binary and more complex glass-forming systems is that the liquid or glass composition may be quite different to that of the related crystalline phases. In order for crystallization to occur on cooling of the liquid it may therefore be necessary for long range diffusion of atoms or ions to occur. Consequently, this leads to a reduction in the rate of crystallization and an increase in the ease of glass formation.

#### 18.2 Thermodynamics of glass formation—behaviour of liquids on cooling

There are two main types of pathway that a liquid may follow on cooling. Either it may crystallize at or below the melting temperature,  $T_m$ , or it may undercool sufficiently, without crystallization, to form a glass. The volume-temperature characteristics for a liquid that follows either of these two pathways are shown in Fig. 18.2. The behaviour of most non-glass-forming liquids is similar to the changes represented by curves *abcd*. Crystallization occurs, *bc*, at temperature  $T_m$ , although for kinetic reasons, the liquid may undercool somewhat before freezing actually occurs. The difference in slope of regions *ab* and *cd* indicates that the coefficient of thermal expansion of liquids is usually greater than that of solids.

The behaviour of glass-forming liquids on cooling is similar to the changes represented by curves *abef* (or *abgh*). In region *be*, the liquid is undercooled but

does not freeze. At each temperature in this region, the liquid rapidly reaches a state of internal equilibrium following a temperature change but is, nevertheless, thermodynamically metastable relative to the crystalline state. With decreasing temperature, however, the liquid viscosity gradually increases until a stage is reached at which the liquid can no longer maintain itself in internal equilibrium. The atomic arrangement that is present in this undercooled liquid then becomes effectively 'frozen in' and on further cooling, the material acquires the rigid, elastic properties of a crystalline solid but without the regular three-dimensional periodicity of a crystal structure. This change in properties or behaviour, from an undercooled liquid to a glass, takes place at a temperature or range of temperatures called the *glass transition temperature*,  $T_g$ .

For any given composition, it is generally possible to prepare glasses with different degrees of stabilization; i.e. with somewhat different  $T_g$  values. With a slow rate of cooling, and provided that crystallization does not occur, the undercooled liquid may be able to maintain itself in internal equilibrium until a somewhat lower temperature than it would if it had been rapidly cooled. Consequently,  $T_g$  is lowered somewhat (compare points *e* and *g* of Fig. 18.2). The glass transition effectively represents the crossover of two timescales: the timescale to measure some property such as viscosity (value  $\sim 10^{13} \text{ P} \leq T_g$ ) and the timescale for internal reorganization of the liquid to occur on changing the temperature. The latter timescale is of the order of a few minutes at  $T_g$  and, in

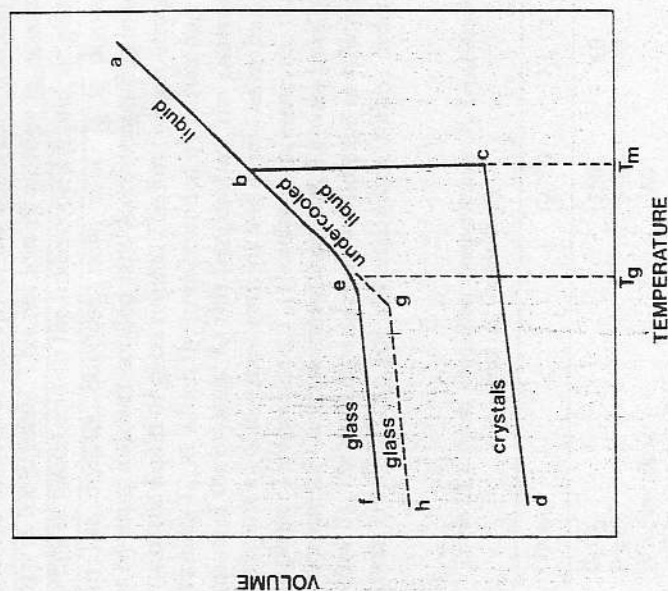


Fig. 18.2 Volume-temperature characteristics (schematic) for crystals, liquid and glass

practice, it is not possible to extend the dashed curve *eg* very far since progressively longer times are required for the liquid to contract and attain internal equilibrium.

Angell (1970) has shown that, thermodynamically, there is a theoretical lower temperature limit at which the glass transition can occur and which he has termed the *ideal glass transition temperature*,  $T_0$ . The explanation for this is found by considering the relative heat capacities and entropies of liquid and crystalline phases of the same composition. The entropy,  $S$ , of a substance is related to its heat capacity,  $C_p$ , by

$$S = \int_0^T \frac{C_p}{T} dT = \int_0^T C_p d(\ln T) \quad (18.1)$$

From a graph of  $C_p$  versus  $\ln T$ , the entropy at a particular temperature is given by the area under the curve up to that temperature, as shown in Fig. 18.3 for temperature  $T_1$ . In cases where a phase change has occurred below the temperature of interest, it is necessary to add the entropy of the transition to that derived from the heat capacity curve. For instance, in Fig. 18.3, at temperature  $T_m$ ,

$$S(\text{crystals}) = \int_0^{T_m} C_p d(\ln T) \quad (18.2)$$

but

$$S(\text{liquid}) = \int_0^{T_m} C_p d(\ln T) + \Delta S(\text{melting}) \quad (18.3)$$

Let us now compare the relative entropies of an undercooled liquid and crystals, both of which are at the same temperature. At a temperature between  $T_g$  and  $T_m$

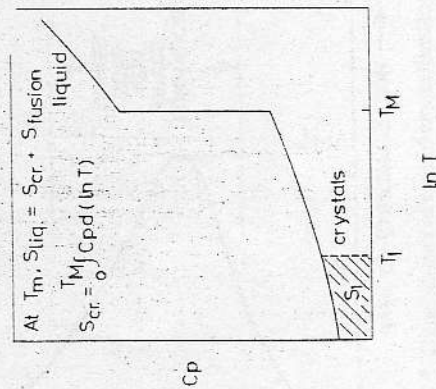


Fig. 18.3 Heat capacity and entropy as a function of temperature

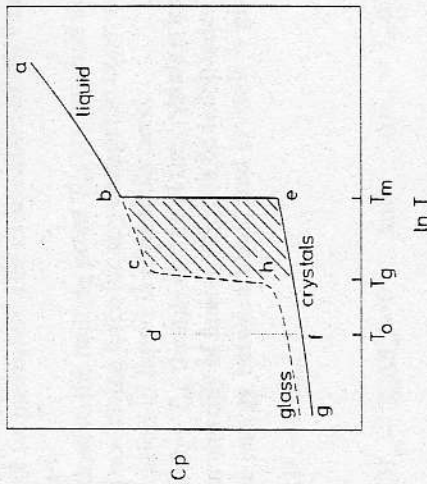


Fig. 18.4 Estimation of ideal glass transition temperature,  $T_0$

(Fig. 18.4), an undercooled liquid, curve *bc*, has a higher heat capacity than the corresponding crystalline phase, curve *eg*. Therefore, on cooling below  $T_m$ , a liquid loses entropy more rapidly than does the crystalline phase that is cooled by the same amount. At the glass transition temperature,  $T_g$ , the shaded area corresponds to the net loss of entropy of the undercooled liquid relative to the loss of entropy of the crystals. This net loss of entropy is, nevertheless, smaller than the entropy of fusion and so the undercooled liquid, or glass, has a higher entropy than the crystals. Suppose, now, that  $T_g$  is displaced to lower temperatures by using a slower cooling rate. A corresponding increase in the net loss of entropy of the liquid or glass results. The limiting situation arises at some lower temperature,  $T_0$ , at which the area bounded by curves *bd/e* is equal to the entropy of fusion of the crystals. At this temperature, the undercooled liquid or glass would have lost all of its excess entropy and would have the same entropy as the crystalline phase. Temperature,  $T_0$ , therefore represents the theoretical lower limiting temperature for the glass transition since, if it were possible to supercool a liquid to below  $T_0$ , the unlikely situation would exist in which an amorphous phase had lower entropy than the corresponding stable, ordered, crystalline phase.

Table 18.1 Glass transition temperatures  $T_g$  (measured) and  $T_0$  (calculated)

Glass	$T_g$ (°C)	$T_0$ (°C)
B <sub>2</sub> O <sub>3</sub>	250	60
Pyrex	550	350
Window glass (Na <sub>2</sub> O, CaO, SiO <sub>2</sub> )	550	270
Lead crystal (PbO, SiO <sub>2</sub> )	440	150
Ca(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	-50	-70

measured. Most liquids freeze very rapidly at or just below  $T_m$  and their rate of crystallization cannot be measured. The explanation of the behaviour shown in Fig. 18.5 is as follows.

At temperatures close to the melting point  $T_m$ , crystals and liquid have similar free energy. There is no driving force for any changes to occur and, therefore, the net rate of crystallization of liquid is essentially zero.

At temperatures below  $T_m$ , the free energy of the crystals is less than that of the liquid. Assuming the entropy of fusion,  $\Delta S_m$ , to be independent of temperature, the difference in free energy between liquid and crystals is given by

$$\Delta G = \Delta H - T\Delta S_m$$

However, at  $T_m$ :

$$\Delta G = \Delta H_m - T_m\Delta S_m = 0 \quad \text{and} \quad \Delta H_m = T_m\Delta S_m$$

Therefore,

$$\Delta G = \Delta S_m(T_m - T) \quad \text{for} \quad T < T_m \quad (18.4)$$

The increase in the rate of crystallization below  $T_m$  (Fig. 18.5) therefore corresponds to an increasing difference in free energy between crystals and liquid and hence is associated with a greater driving force for crystallization.

At lower temperatures, especially for glass-forming liquids, an additional factor, the viscosity of the undercooled liquid, becomes increasingly important. With increasing viscosity, the diffusion of atoms or ions through the liquid to the surface of the growing crystal becomes increasingly difficult and the rate of crystallization tends to decrease accordingly.

With decreasing temperature, there are therefore two competing effects. The increased difference in free energy between crystals and liquid favours crystallization whereas the increased viscosity of the undercooled liquid reduces the tendency to crystallization. The peak in the rate of crystallization (Fig. 18.5) corresponds to the situation where these two competing effects have equal weight. On the low temperature side of the peak, the viscosity effect dominates whereas on the high temperature side it is the difference in free energy between crystals and liquid that predominates.

In considering the crystallization of undercooled liquids (Fig. 18.5) and their ability to form a glass, there is a 'danger zone' for glass formation that corresponds to the maximum in the crystallization rates. If it is possible to undercool a liquid through this danger zone, it should be relatively safe from subsequent crystallization (or devitrification) and form a kinetically stable glass.

The above discussion refers to the kinetics of crystal growth and assumes that nucleation has either already taken place or is relatively easy. Two nucleation mechanisms—heterogeneous and homogeneous—may be distinguished. If heterogeneous nuclei, such as foreign particles, are not present in the undercooled liquid, spontaneous homogeneous nucleation may occur. This takes place throughout the bulk of the liquid, without the necessity of artificial nucleation sites. For example, water usually freezes at or just below  $0^\circ\text{C}$ , because

In practice, it is found that always  $T_g > T_0$ ; i.e. the glass transition occurs, on cooling, well before the limiting temperature,  $T_0$ , is reached. Infinitely slow cooling rates would be needed for the glass transition to occur at temperatures approaching  $T_0$ . Glass transition temperatures  $T_g$  and  $T_0$  are given for a selection of glasses in Table 18.1.

### 18.3 Kinetics of crystallization and glass formation

In order for a glass to form, the rate of crystallization of the undercooled liquid must be sufficiently slow that crystallization does not occur during cooling. It is possible, therefore, to treat glass formation in terms of kinetic criteria as well as the structural and thermodynamic criteria referred to above.

Crystallization of an undercooled liquid is a two-stage process that involves (a) the formation of crystal nuclei followed by (b) their subsequent growth. A kinetic condition for glass formation is that the rate of nucleation and/or the rate of crystal growth should be slow. In some undercooled liquids, nucleation is easy because there are plenty of nucleation sites available: foreign particles, container surfaces, etc. The rate of crystallization is then largely controlled by the rate of growth, which varies with temperature in a manner shown in Fig. 18.5. The rate is zero at the melting point, increases to a maximum at a certain degree of undercooling and then falls to zero again at still lower temperatures.

The general form of Fig. 18.5 can be observed experimentally in undercooled liquids which crystallize sufficiently slowly that their crystallization rates can be

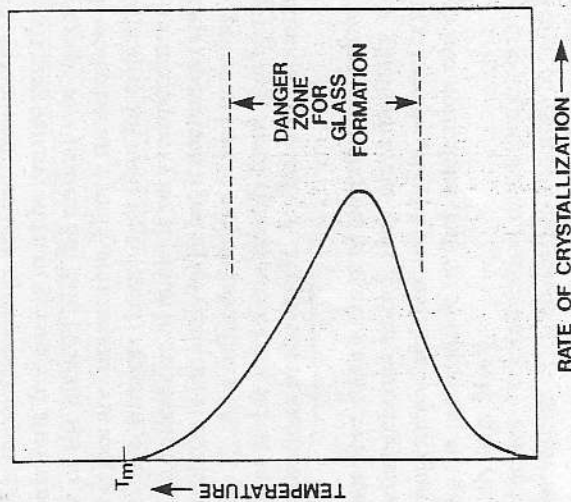


Fig. 18.5 Dependence of rate of crystallization of an undercooled liquid on temperature. (After Tammann)