Chemistry of Glasses

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CHAPTER 1

Glass Formation

1.1 GENERAL ASPECTS

The term *glass* is commonly used to mean the fusion product of inorganic materials which have been cooled to a rigid condition without crystallizing. This generally means the ordinary silicate glasses which are used for making windows and bottle-ware. Literally hundreds of other glasses, each with its characteristic properties and chemical composition, have been made and these do not necessarily consist of inorganic materials. Examples of two familiar glasses made from cane sugar are lollipops and cotton candy; the former are in the shape of a rigid block; and the latter are flexible fibres. Substances of quite diverse chemical composition have been obtained as glasses and it is becoming widely recognized that the property of glass-formation is not, strictly speaking, an atomic or molecular property but rather one of a state of aggregation. Thus the word glass is a generic term and, instead of speaking of 'glass', one should speak of glasses as we speak of crystals, liquids, gases, etc.

Glasses are characterized by certain well-defined properties which are common to all of them and different from those of liquids and crystalline solids. X-ray and electron diffraction studies show that glasses lack long-range periodic order of the constituent atoms. That they resemble liquids and not crystalline solids in their atomic distribution is illustrated in Figure 1.1, in which the radial distribution function of a hypothetical material in the glassy state is compared with that of the gas, liquid and crystalline state of the same composition.

Unlike crystals, glasses do not have a sharp melting point and do not cleave in preferred directions. Like crystalline solids they show elasticity – a glass fibre can be bent almost double in the hand and, when released, springs back to its original shape; like liquids, they flow under a shear stress but only if it is very high, as in the Vickers Hardness Test.* Thus we see that the glassy form of matter combines the 'short-time' rigidity characteristic of the crystalline state with a little of the 'long-time' fluidity of the liquid state. Glasses, like liquids, are isotropic, a property which is of immense value in their use for a variety of purposes.

A glass is generally obtained by cooling a liquid below its freezing point and this has been considered as part of the definition of the glassy state, although as we shall see later it can also be obtained by compressing a liquid. The classical explanation for the formation of a glass is that, when a liquid is cooled, its fluidity

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* There has been widespread misunderstanding of this point in the past, statements having been made that old windows have become thicker at the bottom and that glass tubing bends more and more, with time, when stored in horizontal racks. However, neither has been demonstrated beyond doubt.

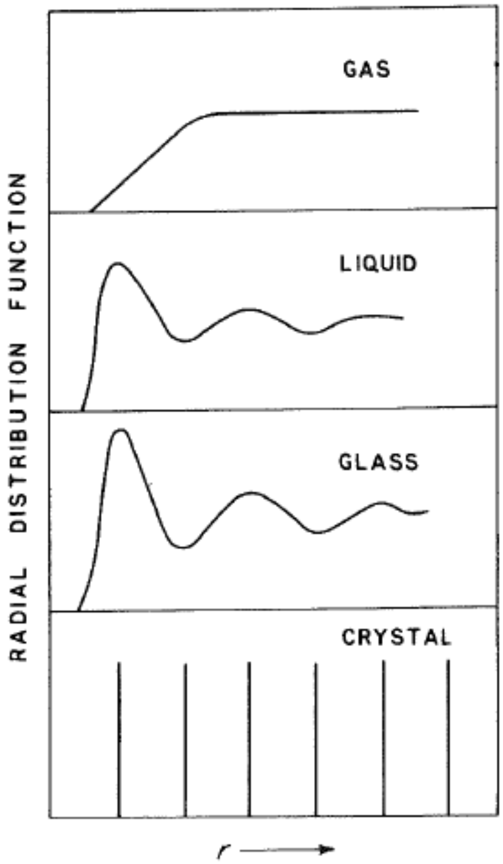

Fig. 1.1 Comparison of the radial distribution function of a glass with that of the gaseous, liquid and crystalline states.

(reciprocal viscosity) decreases and, at a certain temperature below the freezing point, becomes nearly zero. Our liquid becomes 'rigid'.

The relation between crystal, liquid and glass can easily be explained by means of a volume–temperature diagram as shown in Figure 1.2. On cooling a liquid from the initial state A, the volume will decrease steadily along AB. If the rate of cooling is slow, and nuclei are present, crystallization will take place at the freezing temperature T_f. The volume will decrease sharply from B to C; thereafter, the solid will contract with falling temperature along CD.

If the rate of cooling is sufficiently rapid, crystallization does not take place at T_f; the volume of the supercooled liquid decreases along BE, which is a smooth continuation of AB. At a certain temperature T_g, the volume–temperature graph undergoes a significant change in slope and continues almost parallel to the contraction graph CD of the crystalline form. T_g is called the transformation or glass transition temperature. Only below T_g is the material a glass. The location of E, the point corresponding to T_g, varies with the rate of cooling – and thus it is appropriate to call it a transformation *range* rather than a fixed point. At T_g the viscosity of the material is very high – about 10^{13} poise.

If the temperature of the glass is held constant at T, which is a little below T_g, the

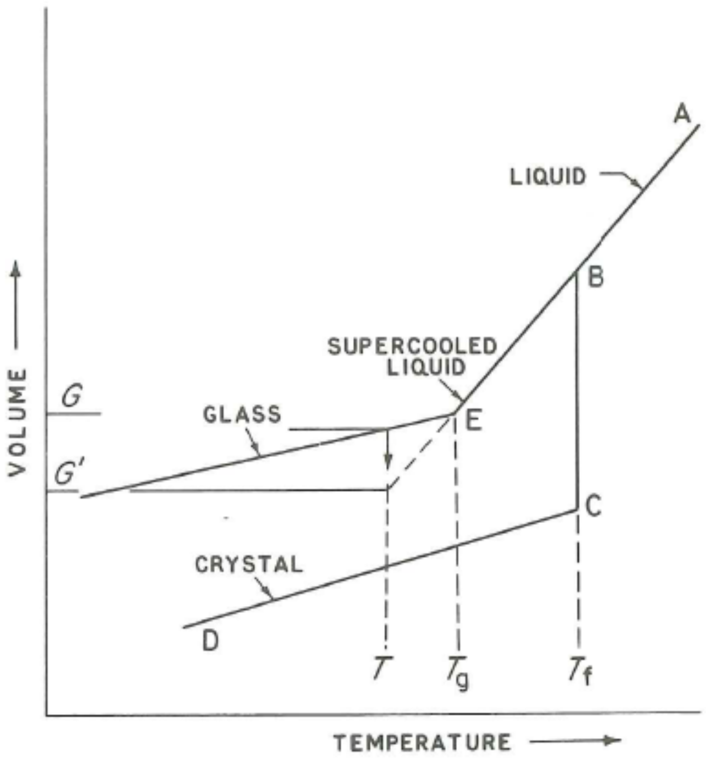

Fig. 1.2 Relationship between the glassy, liquid and solid states.

volume G will continue to decrease slowly. Eventually it reaches the level G' on the dotted line, which is a smooth continuation of the contraction graph BE of the supercooled liquid (undercooled is perhaps a more appropriate word and is used in this book). Other properties of the glass also change with time in the vicinity of T_g. This process by which the glass reaches a more stable condition is known as stabilization. Above T_g no such time-dependence of properties is observed. As a result of the existence of stabilization effects, the properties of a glass depend to a certain extent on the rate at which it has been cooled, particularly through the transformation range.

To understand the glass transition phenomenon let us take an example of a liquid and consider how its different physical properties change on undercooling. Glucose, a familiar substance, is an example of a material which readily undercools to form a glass. It melts at 414 K and, once molten, can be kept below this temperature for a long time without crystallization. The enthalpy, specific heat, specific volume, and thermal expansivity of glucose are shown as functions of temperature in Figure 1.3. We observe that, as the melt is cooled below about 300 K (T_g), its specific heat decreases almost by a factor of two. The specific volume and enthalpy show no analogous change, but they do show a slight discontinuity. There is no volume change or latent heat at this transition but the thermal expansivity decreases by a factor of four. Glucose stays optically transparent and there is no change in refractive index at this temperature, although the temperature coefficient of the refractive index suddenly decreases.

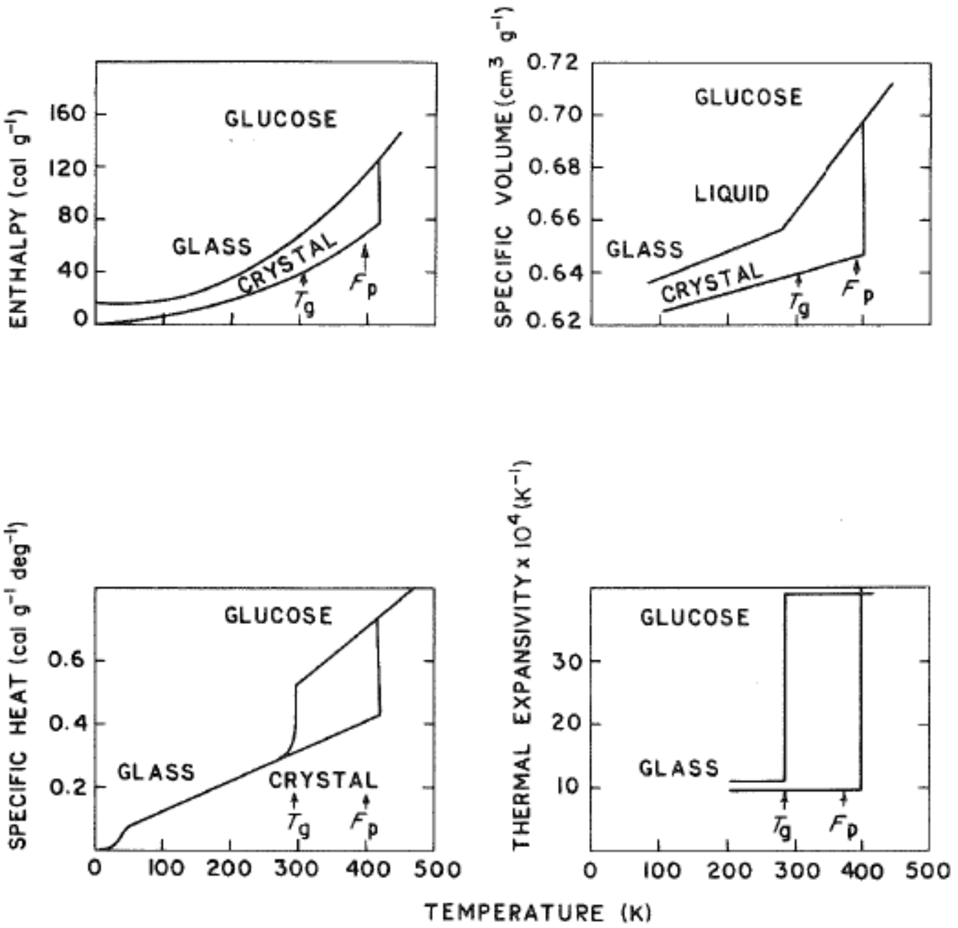

Fig. 1.3 The enthalpy, specific heat, specific volume and thermal expansivity of glucose as a function of temperature.

Liquids can also be transformed into the glassy state by the application of pressure. The melting point of selenium under one atmosphere pressure is 493 K. The volume of selenium at 313 K changes non-linearly with pressure; near 11 kbar there is a discontinuity in the curve which is similar to that seen at E on cooling in Figure 1.2. The compressibility, obtained from the slope of the curve, decreases by about 40 per cent at 11 kbar, in very nearly the same way as the thermal expansivity. At higher pressures the compressibility of liquid selenium is very close to that of the crystalline phase. The pressure at which there is a sudden decrease in compressibility is known as the pressure of glass transition, P_g, and selenium at a pressure above 11 kbar is in the glassy state.

We see from the above that we can now have a phenomenological rather than a generic definition of the glassy state: a glass is 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.

As is evident from Figure 1.3, at the glass transition the liquid and glass differ in the second derivative of the free energy, G, with respect to temperature, T, and pressure, P, but not in the free energies themselves, or in their first derivatives. In Figure 1.3 the specific volume of glucose, given by

$$V=\left(\frac{\partial G}{\partial P}\right)_T$$

is unchanged at the transition, but the thermal expansivity

$$\alpha=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P=\frac{1}{V}\left(\frac{\partial^2 G}{\partial P\,\partial T}\right)$$

and the compressibility

$$\beta=-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T=-\frac{1}{V}\left(\frac{\partial^2 G}{\partial P^2}\right)_T$$

undergo an abrupt change. Analogously, the enthalpy

$$H=G-T\left(\frac{\partial G}{\partial T}\right)_P$$

does not change, but the heat capacity

$$C_{\mathrm{p}}=\left(\frac{\partial H}{\partial T}\right)_P=-T\left(\frac{\partial^2 G}{\partial T^2}\right)_P$$

changes at the transition. These considerations indicate that the glass transition has more or less the characteristics specified for a second-order thermodynamic transition. Whether or not it is a true thermodynamic transition is a question that has not yet been satisfactorily answered.

1.2 GLASS-FORMERS

The ability of a substance to form a glass does not depend upon any particular chemical or physical property. It is now generally agreed that almost any substance, if cooled sufficiently fast, could be obtained in the glassy state–although in practice crystallization intervenes in many substances.

Table 1.1
Maximum undercooling of pure liquids*

Substance	(T_m) *Melting point* (*K*)	(ΔT) *Extent of supercooling* (*K*)	$\Delta T/T_m$
Mercury	234	77	0.33
Tin	506	105	0.21
Platinum	2043	370	0.18
Carbon tetrachloride	250	50	0.20
Benzene	278	70	0.25

* After Staveley [14].

Most common liquids, when pure and in the form of a small drop, can be undercooled before spontaneous crystallization. Some typical examples are shown in Table 1.1.

These liquids can be cooled to within 20 per cent of their melting temperature before spontaneously returning to the thermodynamically stable crystalline form. A few liquids, on the other hand, can be undercooled so much that they fail to crystallize and eventually become glass. These glass-forming liquids are often, although not without exception, liquids which are very viscous at the melting point; liquids which do not form glasses have much lower viscosities. Some typical results are shown in Table 1.2.

Table 1.2
Viscosity of various liquids at their melting temperatures*

Substance	*Melting temp. (°C)*	*Viscosity (poise)*
H_2O	0	0.02
LiCl	613	0.02
$CdBr_2$	567	0.03
Na	98	0.01
Zn	420	0.03
Fe	1535	0.07
As_2O_3	309	10^6
B_2O_3	450	10^5
GeO_2	1115	10^7
SiO_2	1710	10^7
BeF_2	540	10^6

* After Mackenzie [15].

However, a high viscosity at the freezing point is not a necessary or sufficient condition for the formation of a glass. Figure 1.4 shows the viscosity at the freezing point of aqueous sucrose solutions. No glasses are formed in this system with less than about 60 wt % sucrose. Although the viscosity of the solution containing 50 wt % sucrose is the same as that with about 80 wt % sucrose, the latter forms a glass and the former does not.

The viscosity in the system TeO_2–PbO at the liquidus temperature is below 1 poise, but it forms a glass; this is to be compared with ordinary silicate glasses where the viscosity at the liquidus temperature is around 10^5 poise. Figure 1.5 shows part of the phase equilibrium diagram for the system TeO_2–PbO; here glass formation appears to cease at the composition $4TeO_2.PbO$. It is to be noted that the primary phase of crystallization also changes from TeO_2 to $4TeO_2$ PbO at this composition ratio. Thus it may tentatively be suggested that the ability of this material to form a glass is in some way related to the fact that there must be difficulty in forming TeO_2 crystals from the liquid, while the formation of $4TeO_2{:}PbO$ is relatively easy. It is important to note that the difficulty in forming crystals may be due to a high viscosity of the melt as in Table 1.2 and to

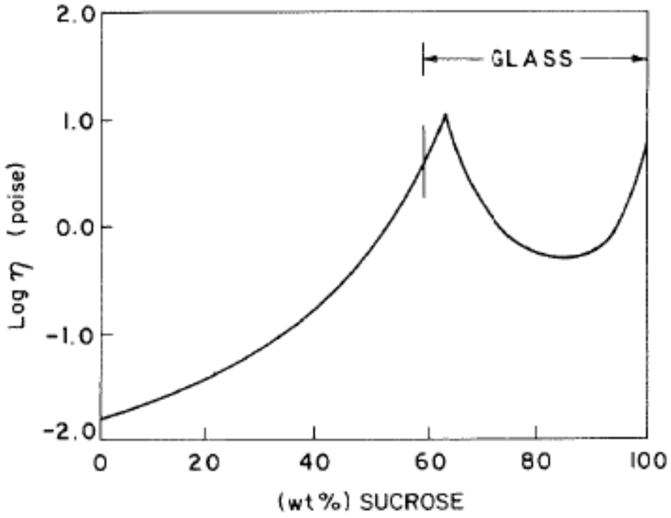

Fig. 1.4 Viscosity at the liquidus temperature in the sucrose–water system.

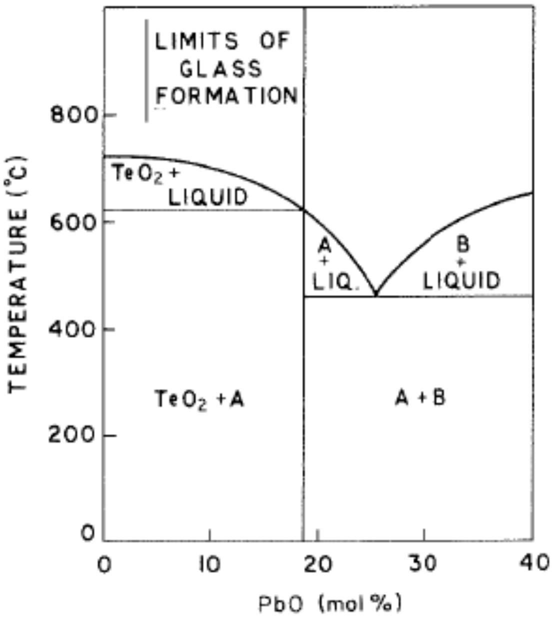

Fig. 1.5 Phase equilibrium diagram for the TeO_2–PbO system showing limits of glass formation.
Probable compositions: A – $4TeO_2$:PbO
B – $3TeO_2$:2PbO

the amount of rearrangement of the atoms (change in configurational entropy) that is necessary in order that the particular crystals may be formed when cooled at a typical rate.

1.2.1 Glass-forming elements

Of all the elements in the Periodic Table, only a few in Groups V and VI can form a glass on their own:

Phosphorus: White phosphorus when heated at 250°C under a pressure of more than 7 kbar produces a glass. The same material can also be prepared by heating white phosphorus with mercury (catalyst) in an evacuated sealed tube at 380°C.

Oxygen: Oxygen has been claimed to be prepared in the glassy form by cooling liquid oxygen, but this is controversial, since the material may be the cubic γ-phase of crystalline oxygen.

Sulphur and selenium: Sulphur and selenium form glasses easily with different ring and chain equilibria.

Tellurium: On the basis of irregular volume changes when molten tellurium solidifies, it has been suggested that tellurium may form a glass, however this has not yet been proved beyond doubt.

1.2.2 Glass-forming oxides

B_2O_3, SiO_2, GeO_2 and P_2O_5 readily form glasses on their own and are commonly known as 'glass-formers' for they provide the backbone in other mixed-oxide glasses. As_2O_3 and Sb_2O_3 also produce glass when cooled very rapidly. TeO_2, SeO_2, MoO_3, WO_3, Bi_2O_3, Al_2O_3, Ga_2O_3 and V_2O_5 will not form glass on their own, but each will do so when melted with a suitable quantity of a second oxide. TeO_2, as discussed before, will not form a glass, but a melt of composition $9TeO_2$:PbO will produce on cooling a glass even though PbO is not a glass-former either. Figure 1.6 shows a section of the periodic table, the ringed elements having simple glass-forming oxides and the boxed elements having the second type of oxides, 'conditional glass-formers' according to Rawson (1).

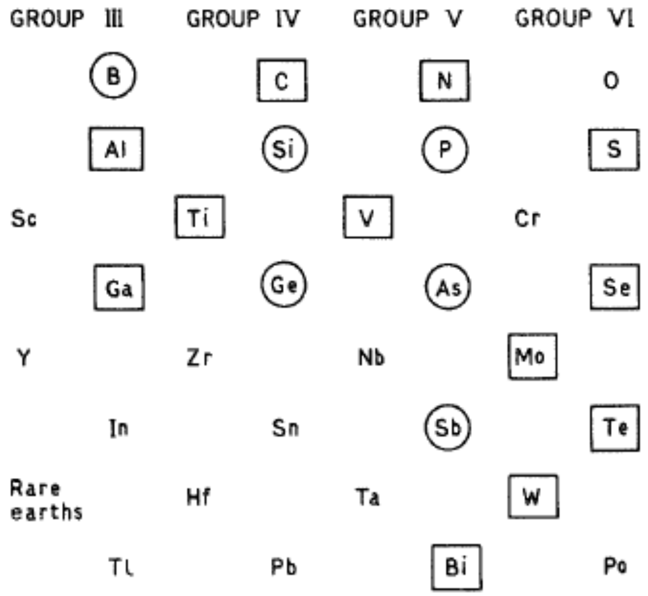

Fig. 1.6 Elements, the oxides of which are either glass-formers or conditional glass-

Table 1.3
Ranges of glass formation in binary systems
(after Imaoka [13])

Metal oxide	*Mol %*			
	B_2O_3[a]	SiO_2[b]	GeO_2[c]	P_2O_5[d]
Li_2O	100–57.3	100–64.5	100–76.2	100–40
Na_2O	100–62.0 33.5–28.5	100–42.2	100–62	100–40
K_2O	100–62.3	100–45.5	100–40.5	100–53
Tl_2O	100–55.5	–	100–52.5	100–50
MgO	57.0–55.8	*100–57.5	–	100–40
CaO	72.9–58.9	*100–43.3	84.5–64.5	100–46
SrO	75.8–57.0	*100–60	86–61	100–46
BaO	83.0–60.2	*100–60	100–90 82.5–70.4	100–42
ZnO	56.0–36.4		100–52	100–36
CdO	60.9–45.0			100–43
PbO	80.0–23.5		100–43	100–38
Bi_2O_3	78.0–37.0		100–66	

[a] 1–3 g material melted in Pt crucible and allowed to cool freely in air.
[b] 1–2 g material – as above.
[c] 1–3 g melt – as above.
[d] 1–3 g melt – as above.
* Involves extensive liquid–liquid phase separation.

The regions of glass formation in some simple binary systems are given in Table 1.3.

1.3 ATOMISTIC HYPOTHESES OF GLASS FORMATION

Glass formation is a kinetic phenomenon; any liquid, in principle, can be transformed into glass if cooled sufficiently quickly and brought below the transformation range. A good glass-forming material is then one for which the rate of crystallization is very slow in relation to the rate of cooling. As discussed in the earlier section, with conventional rates of cooling, some melts produce glass more easily than others. These facts lead many workers to postulate different atomistic hypotheses correlating the nature of the chemical bond, and the geometrical shape of the groups involved, with the ease of glass formation. It should be pointed out that, although these empirical hypotheses explain glass formation in some allied liquid systems, a unified hypothesis capable of explaining the phenomenon of glass formation in all the known systems has yet to be developed.

1.3.1 Goldschmidt's radius ratio criterion for glass formation

According to Goldschmidt [2] for a simple oxide of the general formula A_mO_n, there is a correlation between the ability to form glass and the relative sizes of the

Table 1.4
Limiting radius ratios for various coordination polyhedra

Polyhedron	*Coordination number*	*Minimum radius ratio*
Equilateral triangle	3	0.155
Tetrahedron	4	0.225
Trigonal bipyramid	5	0.414
Square pyramid	5	0.414
Octahedron	6	0.414
Cube	8	0.732

oxygen and A atoms. Glass-forming oxides are those for which the ratio of ionic radii R_A/R_O lies in the range 0.2 to 0.4. For ionic compounds the coordination number is often dictated by the radius ratio rule. From simple geometrical considerations of the maximum number of spherical anions packed around a cation maintaining anion–cation contact, the results set out in Table 1.4 can be calculated. Thus according to Goldschmidt, a tetrahedral configuration of the oxide is a prerequisite of glass formation. However, it should be pointed out that in glass-forming oxides the anion–cation bonding is far from purely ionic. Besides, as discussed earlier in the case of $9TeO_2$:PbO the coordination number of Te is six and not four. BeO with $R_{Be}/R_O \sim 0.221$ does not form glass.

1.3.2 Zachariasen's random network hypothesis

Since the mechanical properties and density of an oxide glass are similar to those of the corresponding crystal, the interatomic distances and interatomic forces must also be similar. Zachariasen [3] postulated that, as in crystals, the atoms in glass must form extended three-dimensional networks. But the diffuseness of the X-ray diffraction patterns show that the network in glass is not symmetrical and periodic as in crystals. For example, in the case of SiO_2 the only difference between the crystalline and glassy forms is that in vitreous silica the relative orientation of adjacent silicon–oxygen tetrahedra is variable whereas in the crystalline form it is constant throughout the structure. Such a difference is shown pictorially in Figure 1.7 for an imaginary two-dimensional oxide (A_2O_3) in both crystalline (a) and vitreous (b) forms.

Zachariasen proposed a set of empirical rules which an oxide must satisfy if it is to be a glass-former:

(1) No oxygen atom may be linked to more than two atoms of A.
(2) The number of oxygen atoms surrounding A must be small (probably 3 or 4).
(3) The oxygen polyhedra share corners with each other, not edges or faces.

If it is further required that the network be three-dimensional, a fourth rule must be added:

(4) At least three corners of each polyhedron must be shared.

Zachariasen's hypothesis has been more or less universally accepted; however, the

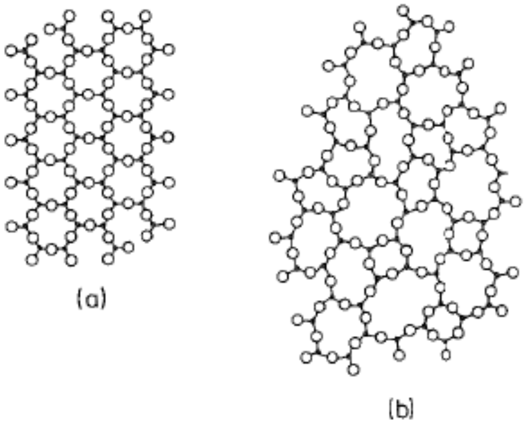

Fig. 1.7 Schematic two-dimensional representation of the structure of (a) a hypothetical crystalline compound A_2O_3 and (b) the glassy form of the same compound.

following limitations are pertinent and should be pointed out here.

(1) Although in most of the oxide glasses the coordination number of oxygen is two, Bray [4] has reported that in binary Tl_2O–B_2O_3 glasses with low Tl_2O content, the coordination number of oxygen may be three.

(2) The coordination numbers of silicon, phosphorus and boron in glass are 4, 4 and 3 or 4 respectively. However, as described earlier, the coordination number of tellurium in PbO–TeO_2 glasses is 6 with respect to oxygen. Alkali–phosphate glasses containing more than 50 mol % alkali oxide contain two-dimensional chains of various sizes, thus a three-dimensional network need not be a prerequisite for glass formation.

(3) Hagg [5] pointed out that an infinite three-dimensional network may not be a necessary condition for glass formation. He concluded: 'it seems as if a melt contains atomic groups which are kept together with strong forces, and if these groups are so large and irregular that their direct addition to the crystal lattice is difficult, such a melt will show a tendency to supercooling and glass formation'.

1.3.3 Smekal's mixed bonding hypothesis

According to Smekal [6] pure covalent bonds have sharply defined bond-lengths and bond-angles and these are incompatible with the random arrangement of the atoms in glass. On the other hand, purely ionic or metallic bonds completely lack any directional characteristics. Thus the presence of 'mixed' chemical bonding in a material is necessary for glass formation. According to Smekal, glass-forming substances with mixed bonding may be divided into three classes as follows:

(a) Inorganic compounds, e.g. SiO_2, B_2O_3, where the A–O bonds are partly covalent and partly ionic.

(b) Elements, e.g. S, Se having chain structures with covalent bonds within the chain and Van der Waals' forces between the chains.

(c) Organic compounds containing large molecules with covalent bonds within the molecule and Van der Waals' forces between them.

1.3.4 Sun's bond-strength criterion for glass formation

Since the process of atomic rearrangement which takes place during the crystallization of a material may involve the breaking and reforming of interatomic bonds, it may be reasonable to expect a correlation between the strength of these bonds and the ability of the material to form a glass. The stronger the bonds, the more sluggish will be the rearrangement process and hence the more readily will a glass be formed. This suggestion was first put forward by Sun [7], who showed that the bond strengths in glass-forming oxides are in fact particularly high. Some typical values from Sun's calculations are given in Table 1.5. It will be seen that the glass-forming oxides have single bond strengths greater than 90 kcal mol^{-1} and the modifiers have bond strengths less than 60 kcal mol^{-1}.

Table 1.5
Calculated single bond strengths of some oxides

Metal	*Dissociation energy (E_d) (kcal mol^{-1})*	*Coordination number (N)*	*Single bond strength (E_d/N) (kcal mol^{-1})*
B	356	3	119
		4	89
Si	424	4	106
Ge	431(?)	4	108
P	442	4	111
V	449	4	112
As	349	4	87
Sb	339	4	85
Zr	485	6	81
Zn	114	'2'	72
Pb	145	'2'	73
Al	317–402	6	53–67
Na	120	6	20
K	115	9	13
Ca	257	8	32

Sun himself pointed out that, although the bond strengths V–O, As–O and Sb–O are relatively high, the oxides are not good glass-formers. In fact V_2O_5 will not form a glass when melted alone. Sun suggested that 'small ring formation' may occur in the melts of these materials, which would result in easy crystallization.

A few other hypotheses, like Winter's p-electron criterion [8], Rawson's modification of Sun's hypothesis [9] etc., have been put forward from time to time. But none of these hypotheses are really capable of explaining glass formation to a more satisfactory extent than already described and will not be discussed further in this book.

1.4 KINETIC APPROACH TO GLASS FORMATION

Whether or not a given liquid will crystallize during cooling before T_g is reached is strictly a kinetic problem involving the rate of nucleation and crystal growth on the one hand and, on the other, the rate at which thermal energy can be extracted from the cooling liquid. In recent decades there have been several treatments of the conditions of glass formation, based on considerations of crystallization kinetics, and a good review is contained in the article *Under what conditions can a glass be formed*? by Turnbull [10]. This author pointed out that there are at least some glass-formers in every category of material, based on bond type (covalent, ionic, metallic, Van der Waals, and hydrogen). Cooling rate, density of nuclei and various material properties like crystal–liquid surface tension, and entropy of fusion etc. were suggested as significant factors which affect the tendency of different liquids to form glasses. This approach naturally raises the question *not* whether a liquid will form a glass on cooling, but rather *how fast* must a given liquid be cooled in order to avoid any detectable crystallization?

Uhlmann [11], developing Turnbull's idea, has provided some useful guidelines for glass formation by using theoretical time–temperature–% transformation (T–T–T) curves to specify critical cooling rates in terms of material constants. In the case of single-component materials or congruently melting compounds, if the nucleation frequency and rate of crystal growth are constant with time, then the volume fraction X crystallized in a time t may be expressed as:

$$X \sim \tfrac{1}{3}\pi I_v u^3 t^4 \text{ (for small values of } X\text{)} \tag{1.1}$$

where I_v is the nucleation frequency per unit volume, and u is the rate of advance of the crystal–liquid interfaces per unit area of the interfaces (This is dealt with in more detail in Chapter 2). Both nucleation frequency I_v and rate of advance u are inversely proportional to the viscosity of the liquid.

The cooling rate required to avoid a given volume fraction crystallized may be estimated from equation (1.1) by the construction of T–T–T curves, an example of which is shown in Figure 1.8 for two different volume fractions crystallized. In constructing these curves, a particular fraction crystallized is selected, the time required for that volume fraction to form at a given temperature is calculated, and the calculations are repeated for other temperatures. The nose in a T–T–T curve, corresponding to the least time for the given volume fraction to crystallize, results from competition between the driving force for crystallization (which increases with decreasing temperature) and the atomic mobility (which decreases with decreasing temperature). The transformation times t_i are relatively long in the vicinity of the melting point as well as at low temperatures. The cooling rate required to avoid a given fraction becoming crystallized can be approximately represented by the relationship:

$$\left[\frac{dT}{dt}\right]_c \sim \frac{\Delta T_N}{\tau_N} \tag{1.2}$$

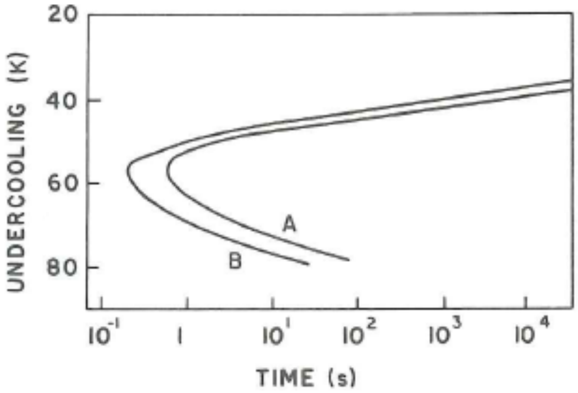

Fig. 1.8 Time–temperature transformation curves for salol corresponding to volume fractions crystallized of (A) 10^{-6} and (B) 10^{-8}.

where $\Delta T_N = T_E - T_N$; T_N is the temperature at the nose of the T–T–T curve; τ_N is time at the nose of the T–T–T curve; and T_E is the melting point. From Figure 1.8 it is apparent that the cooling rate required for glass formation is rather insensitive to the assumed volume fraction crystallized, since the time at any temperature on the T–T–T curve varies only as the one-fourth power of X.

Uhlmann's approach is useful in that it provides a clear basis for the common observation that the most obvious factor which may be correlated with success or failure in undercooling a liquid at some fixed rate is the magnitude of the viscosity at the temperature T_E (the true thermodynamic crystallization temperature). The importance of the value of T_E (for some specified viscosity–temperature relation) in deciding the possibility of obtaining a glass from the liquid is illustrated in Figure 1.9, using T–T–T curves for the molecular substance salol. From that figure it may be noted that, if T_E for Salol were raised by 40°C above the actual value, the critical cooling rate for glass formation would increase four orders of magnitude from $50\,\mathrm{K\,s^{-1}}$ to $10^5\,\mathrm{K\,s^{-1}}$. On the other hand, a lowering of T_E by 40°C would permit glasses to be formed even at cooling rates of $10^{-6}\,\mathrm{K\,s^{-1}}$.

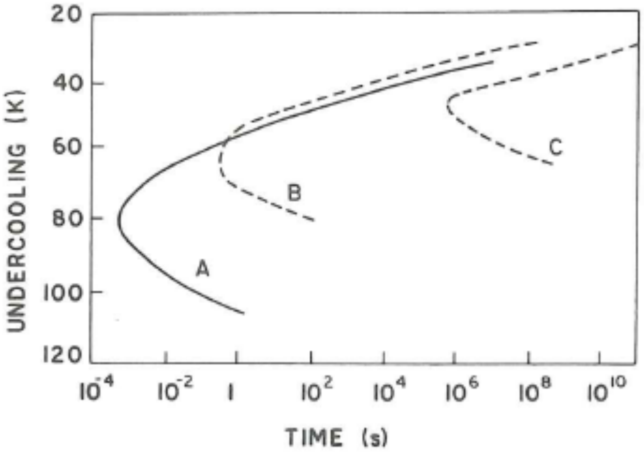

Fig. 1.9 Time–temperature transformation curves for salol-like materials having various melting points. The volume fractions crystallized are 10^{-6} in each case. (A) $T_E = 356.6\,\mathrm{K}$; (B) $T_E = 316.6\,\mathrm{K}$ and (C) $T_E = 276.6\,\mathrm{K}$.

A striking example of the increase in the number of glass-forming substances made possible by manipulating the cooling rate variable is provided by the recent experiments of Nelson *et al.* [12]. These workers have snap-melted powders of various refractory oxides using xenon flash and laser pulse heating techniques. Since the melting points of the substances investigated are very high, cooling by radiant energy loss from the tiny samples is extremely fast. Thus glasses were formed from such unlikely substances as La_2O_3.

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