

CHEMISTRY of GLASSES

A. PAUL

SECOND EDITION



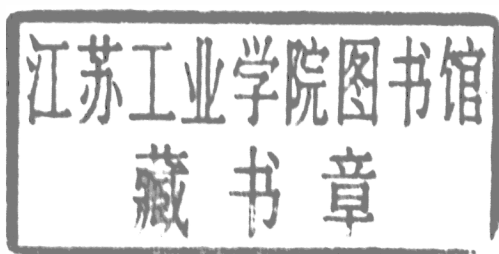
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Chemistry of Glasses

Second edition

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Chemistry of Glasses

*To my teachers
Professor D. Lahiri and Professor R.W. Douglas
who introduced me to glass science*

Preface to the second edition

It is encouraging to note that the first edition of the book was well received by the students and teachers – whom the book is primarily meant for. Two important topics related to chemistry of glasses were missing from the first edition: the chemistry of glass batch reactions, and the sol–gel method of glass making. The present author does not have adequate experience of these two topics. Dr Pavel Hrma of Case Western Reserve University, a well known expert in his field, has kindly volunteered to write on the chemistry of glass batch reactions which is included as Chapter 5 in the present edition; we hope the readers find it interesting and helpful. Dr I. Strawbridge has contributed a new chapter dealing with the sol–gel method. Dr A. K. Varshneya of New York State College of Ceramics, Alfred University has written the section ‘Strength of Glasses’ – which undoubtedly will increase the usefulness of the present edition.

Finally, the author would like to express his sincere thanks and gratitude to all the reviewers of the first edition of the book for their kind and valuable comments.

Amal Paul
Indian Institute of Technology
Kharagpur

Preface

‘The preface . . . either serves for the explanation of the purpose of the book, or for justification and as an answer to critics’.

Lermontov

This book is based mainly on the lectures on the Chemistry of Glasses which I gave at the University of Sheffield to the final year honours and postgraduate students of Glass Technology and Materials Science. Most books reflect the interests and enthusiasm of their authors, and the present one is no exception.

The chemistry of glass is a rapidly developing field because the frontiers of advanced chemistry and advanced physics are merging together and consequently this book will soon require considerable amplification and modification. However, my experience in teaching the chemistry of glasses for more than a decade has shown me that there is much need for a good text-book on the subject. This book is therefore intended to be a stop-gap which, until it receives that new revision, may serve as a useful reference work for students and research workers alike.

I gratefully acknowledge the influence on my thinking of many of those colleagues at Sheffield with whom I have been in contact during the past twenty years or so. In addition to these personal influences, other published works have had considerable influence in modifying my approach, especially Cotton and Wilkinson’s *Advanced Inorganic Chemistry*. Dr Peter James helped me in writing Chapter 2, and Professor Peter McMillan not only read the whole manuscript but also made a number of most helpful suggestions.

Finally, I wish to thank Professor Roy Newton, ex-Director of the British Glass Industry Research Association, for his encouragement and those valuable suggestions which helped this book to be less parochial than it would otherwise have been.

Amal Paul

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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

* 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.

GLASS FORMATION

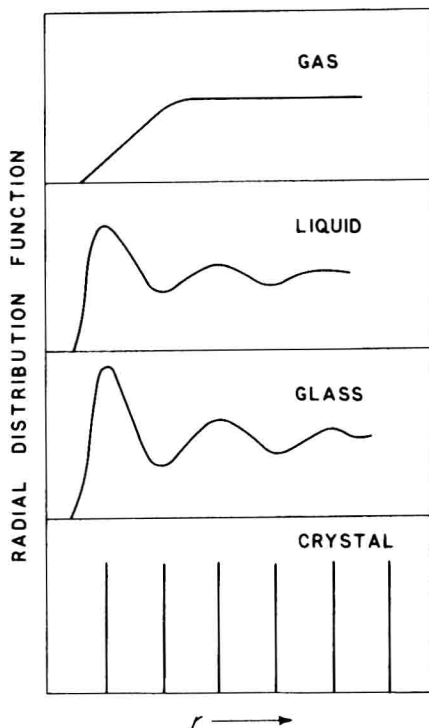


Fig. 1.1 Comparison of the radial distribution function of a glass with that of the gaseous, liquid and crystalline states.

(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

GENERAL ASPECTS

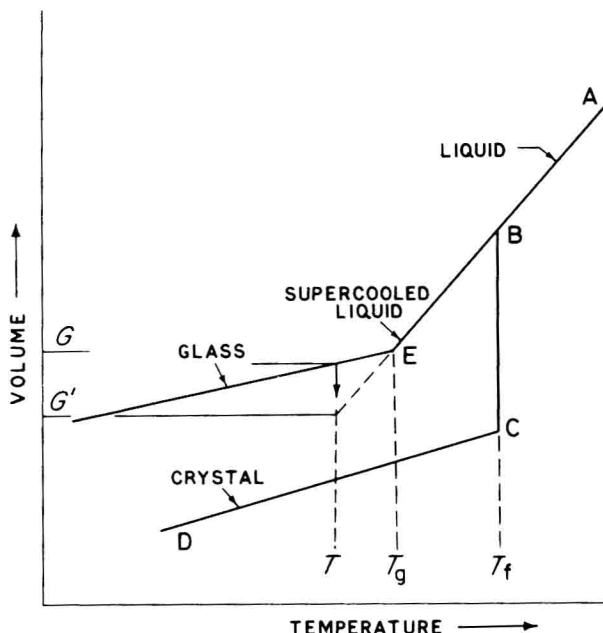


Fig. 1.2 Relationship between the glassy, liquid and solid states.

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.

GLASS FORMATION

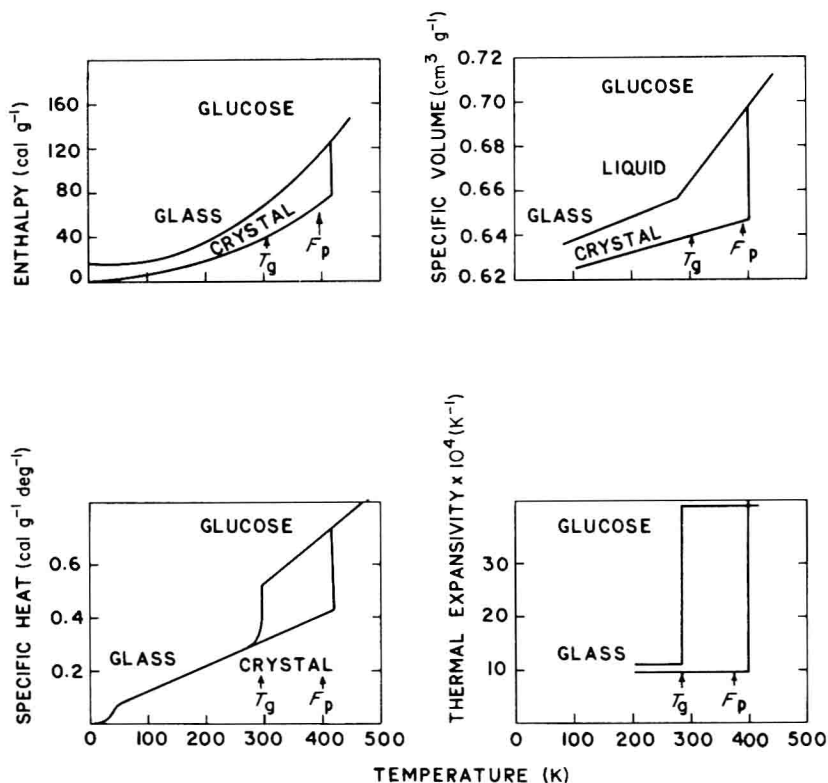


Fig. 1.3 The enthalpy, specific heat, specific volume and thermal expansivity of glucose as a function of temperature. (After Johari [16]).

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

GLASS-FORMERS

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

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

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*

<i>Substance</i>	(T_m) <i>Melting point</i> (K)	(ΔT) <i>Extent of supercooling</i> (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].

GLASS FORMATION

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*

<i>Substance</i>	<i>Melting temp. (°C)</i>	<i>Viscosity (poise)</i>
H ₂ O	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 ₂ O ₃	309	10 ⁶
B ₂ O 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 TeO₂-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 10⁵ poise. Figure 1.5 shows part of the phase equilibrium diagram for the system TeO₂-PbO; here glass formation appears to cease at the composition 4TeO₂.PbO. It is to be noted that the primary phase of crystallization also changes from TeO₂ to 4TeO₂.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 TeO₂ crystals from the liquid, while the formation of 4TeO₂.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

GLASS-FORMERS

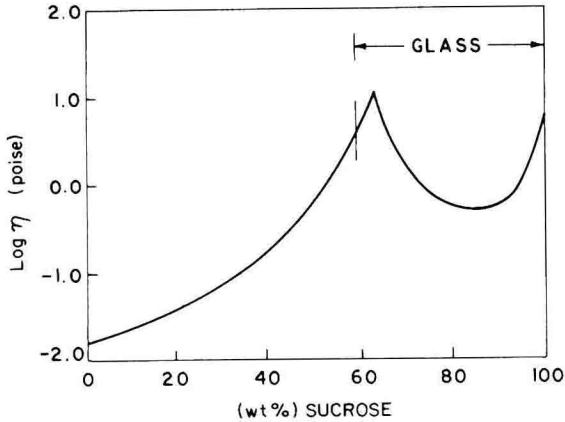


Fig. 1.4 Viscosity at the liquidus temperature in the sucrose–water system.

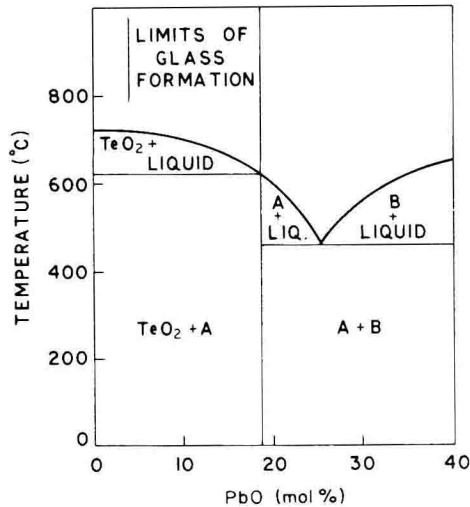


Fig. 1.5 Phase equilibrium diagram for the TeO_2 – PbO system showing limits of glass formation.

Probable compositions: A – $4\text{TeO}_2:\text{PbO}$
B – $3\text{TeO}_2:2\text{PbO}$

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:

GLASS FORMATION

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 9 TeO_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).

GROUP III	GROUP IV	GROUP V	GROUP VI
(B)	[C]	[N]	O
[Al]	(Si)	(P)	[S]
Sc	[Ti]	[V]	Cr
[Ga]	(Ge)	(As)	[Se]
Y	Zr	Nb	[Mo]
In	Sn	(Sb)	[Te]
Rare earths	Hf	Ta	[W]
Tl	Pb	[Bi]	Po

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