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SPRING COLLEGE ON AMORPHOUS SOLIDS
AND THE LIQUID STATE
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THE GLASS TRANSITION

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1. Definitions and Experimental Characteristics.
2. Kinetics of Nucleation and Crystal Growth.
3. Kinetic (Non-equilibrium) and Thermodynamic (Equilibrium) Aspects of the Glass Transition.
4. Thermodynamics of the Glass Transition.
5. Models of the Glass Transition.

These are preliminary lecture notes, intended only for distribution to participants. Missing or extra copies are available from Room 230.

1. DEFINITIONS AND EXPERIMENTAL CHARACTERISTICS

1.1 Definitions

AMERICAN SOCIETY FOR TESTING MATERIALS (A.S.T.M.):

> "An inorganic product of fusion which has cooled to a rigid condition without crystallizing."

MOREY[1]:

> "A glass is an inorganic substance in a condition which is continuous with, and analogous to, the liquid state but which, as the result of having been cooled from a fused condition, has attained so high a degree of viscosity as to be for all practical purposes rigid."

JONES[2]:

> "A glass, or a substance in the glassy or vitreous state, is a material which has been formed by cooling from the normal liquid state and which has shown no discontinuous change in first order thermodynamic properties such as volume (V), heat content (H) or entropy (S) but has become rigid (i.e. solid) through a progressive increase in its viscosity. Discontinuities are observed, however, in derivative or second order thermodynamic properties such as specific heat capacity and thermal expansivity."

U.S. NATIONAL RESEARCH COUNCIL[3]:

> "Glass is an X-ray amorphous material which exhibits the glass transition, this being defined as that phenomenon in which a solid amorphous phase exhibits with changing temperature a more or less sudden change in the derivative thermodynamic properties, such as heat capacity and expansion coefficient, from crystal-like to liquid-like values."

1.2 Experimental Characteristics

Assume that a liquid has been cooled rapidly enough to prevent crystallization (the kinetics of nucleation and crystal growth are considered in lecture 2). The subsequent behaviour on further cooling is usually represented either in terms of the temperature variation of a first order extensive thermodynamic variable (i.e. volume V, enthalpy H or entropy S), or in terms of the temperature dependence of viscosity. The former emphasizes the thermodynamic (equilibrium) aspects of the glass transition, the latter the kinetic (non-equilibrium) aspects.

The variation of volume with temperature is illustrated in figure 1 for vitreous selenium[4]. This is typical in its general form for all glasses. The experimental characteristics explicit or implicit in figure 1 are as follows:[5]

(i) First order extensive thermodynamic variables, volume V, enthalpy H and entropy S, are continuous with temperature (and pressure) but show a change of slope on the transition liquid → glass. The <u>range</u> of temperature over which this transition takes place is called the glass transition (or transformation) temperature Tg.

(ii) Although first order variables are continuous, there are discontinuities in the second order thermodynamic quantities expansion coefficient α, specific heat C_p and compressibility κ (see bottom right insert to figure 1). For this reason the glass transformation has sometimes been regarded as a second order thermodynamic transition. This is probably not correct, or at best, is a gross oversimplification of the situation, (see lectures 3 and 4).

(iii) It is important to realise that Tg is not an accurately defined temperature. In the first place, the glass transition is not sharp but occurs over a range of temperature. It is sometimes convenient to DEFINE as a specific temperature the point at which the extrapolated liquid and glass lines cross (see top left insert to figure 1). In glass technology this temperature is known as the fictive temperature T_F[2]. It is the temperature at which the glass would be in (metastable) equilibrium if it could be brought to that temperature instantaneously.

(iv) Furthermore, Tg (and hence T_F) depends upon the rate of cooling and subsequent thermal history. In typical silicate glasses, which normally have transformation temperatures in the range

400 to 700^{o}C, Tg can be changed by 100 to 200^{o}C i.e. by 20 to 30% or more[6]. The effect of cooling rate on the glass transition can sometimes be expressed empirically in the form,

$$R = R_o \exp\left[-\frac{1}{C}\left(\frac{1}{T_g} - \frac{1}{T_m}\right)\right] \qquad (1)$$

where R is the cooling rate and R_o and C are constants. Expressed in this way, R_o is the cooling rate at which $T_g = T_m$.

(v) A glass is thermodynamically unstable and if held at a temperature below T_g it will tend to approach the (meta-) stable equilibrium of the supercooled liquid at that temperature. Consider in figure 2a, for example, two glasses prepared by different rates of cooling and, therefore, with different T_g's - T_{g1} (slow cooling) and T_{g3} (fast cooling). If they are both held at a temperature T', the volumes of both will tend towards that of the supercooled liquid at that temperature, i.e. V'. The T_g's will also change, of course. This process is known as 'stabilisation' and the rate at which it occurs will depend very sensitively on temperature. Within a few degress of T_g it will normally take place on a time scale of minutes or hours. Far removed from T_g it will take many years.

(vi) If a glass is re-heated in order to determine T_g by differential thermal analysis measurements for example, anomalies will occur unless the rate of heating is the same as the original rate of cooling. This is illustrated by figure 2[2]. Suppose glass 1 (prepared by slow cooling) with $T_g = T_{g1}$ is re-heated at the (faster) rate corresponding to glass 2 (intermediate rate of cooling). Its volume will tend to undershoot the supercooled liquid line shown by the dotted curve in figure 2) because it is being re-heated too rapidly to come into equilibrium. On the other hand if glass 3 (fast cooling) is re-heated at the intermediate rate its volume will tend to decrease before T_{g3} is reached (dotted curve in figure 2) because its rate of heating is slow enough to allow volume changes (corresponding to stabilisation) to take place at a temperature lower than its own T_g. The derivative curves (α, C_p) will be as shown in figure 2b, and if we were using these experiments to determine T_g, say, the measured value would be closer to T_{g2} rather than the values corresponding to the original rates of cooling.

(vii) It is possible to define and observe a glass transformation pressure P_g[6]. The derivative (dV/dP) is negative, of course, and shows a change of slope but no discontinuity at P_g. The experimental V-P-T relationship for vitreous selenium is shown in figure 3. It is worth noting from this figure that T_g increases with pressure.

(viii) In polymeric materials, which would include Se and possibly other chalcogenide glasses, a glass transformation molecular weight M_g can also be defined[7]. The three quantities T_g, P_g and M_g are empirically related:

$$T_g = T_g^{\infty}(0) - \left(\frac{\partial T_g}{\partial (1/M)}\right)\frac{1}{M_g} + \left(\frac{\partial T_g}{\partial p}\right) P_g$$

where $T_g^{\infty}(0) = T_g$ at P = 0 and M = ∞. In polymeric liquids like Se the average molecular weight and distribution is a function of temperature. Thus in addition to the parameters mentioned earlier one might also expect the T_g of a glass cooled from a polymeric melt to depend upon the thermal history of the liquid above T_m as well as on rate of cooling etc. below T_m.

The temperature dependence of the inverse of viscosity (i.e. of fluidity, ϕ) is illustrated in figure 4, in which the fluidity (in poise^{-1}) is plotted against a reduced temperature (T_m/T) (T_m is the thermodynamic melting point)[8]. In figure 4 the curve labelled "simple liquids" corresponds to liquids such as the intermediate alcohols and glycols which are well known organic glass-forming materials. The curve labelled "complex liquids" corresponds to materials such as fused silica, silicates and borates. The points to note about figure 4 are as follows:

(a) Glass-forming liquids show a smooth decrease in fluidity (increase in viscosity). As also illustrated in figure 4, a liquid which crystallizes has a marked discontinuity in fluidity at its melting point.

(b) The fluidity $\phi \simeq 10^{-13.5}$ poise^{-1} is traditionally taken as the boundary between the supercooled liquid and the (solid) glass.

At that value of fluidity configurational relaxation times are in the range of a few minutes to a few hours (i.e. in the range of typical experimental times).

(c) For many glass-forming liquids, and over a wide range of temperature, the viscosity follows the equation:

$$\eta = C \exp[\ E_\eta/k(T-T_0)] \qquad (2)$$

where C is a constant, E_η is the activation energy for viscous flow and T_0 is some characteristic temperature which is always less than Tg. Equation (2) is known as the Fulcher or Doolittle equation.

It should be recognised that linking glass formation with a non-equilibrium transport property such as viscosity (fluidity) implies that equilbrium thermodynamics cannot be applicable in a straightforward way.

1.3 References

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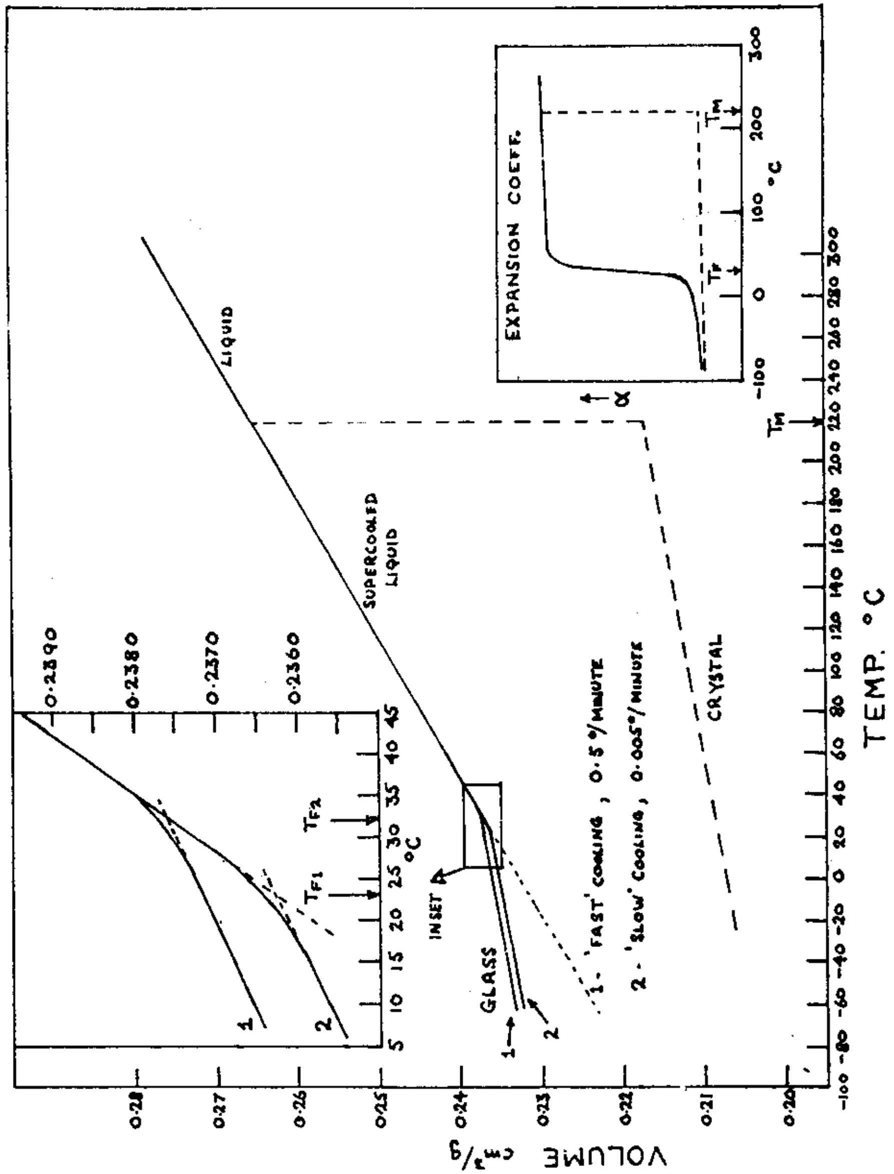
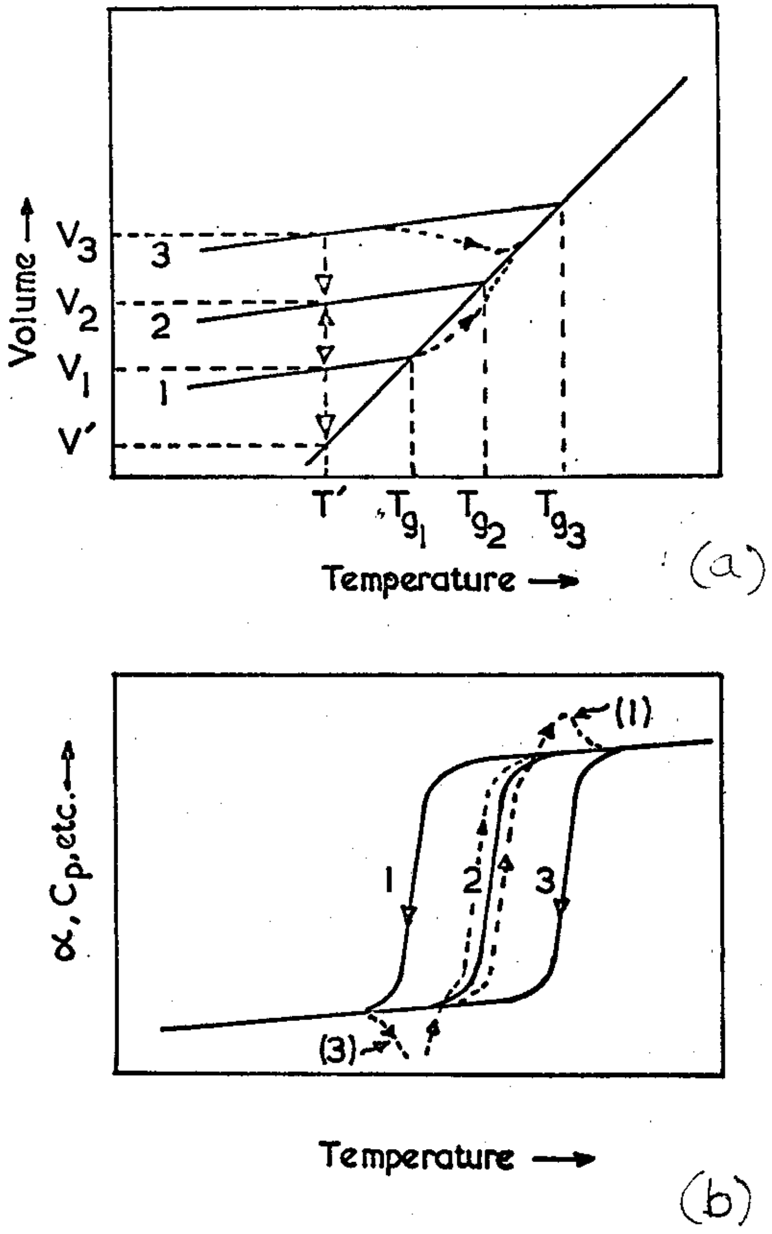


V–T RELATIONSHIP IN Se.

FIG. 1



(a)

(b)

FIG. 2

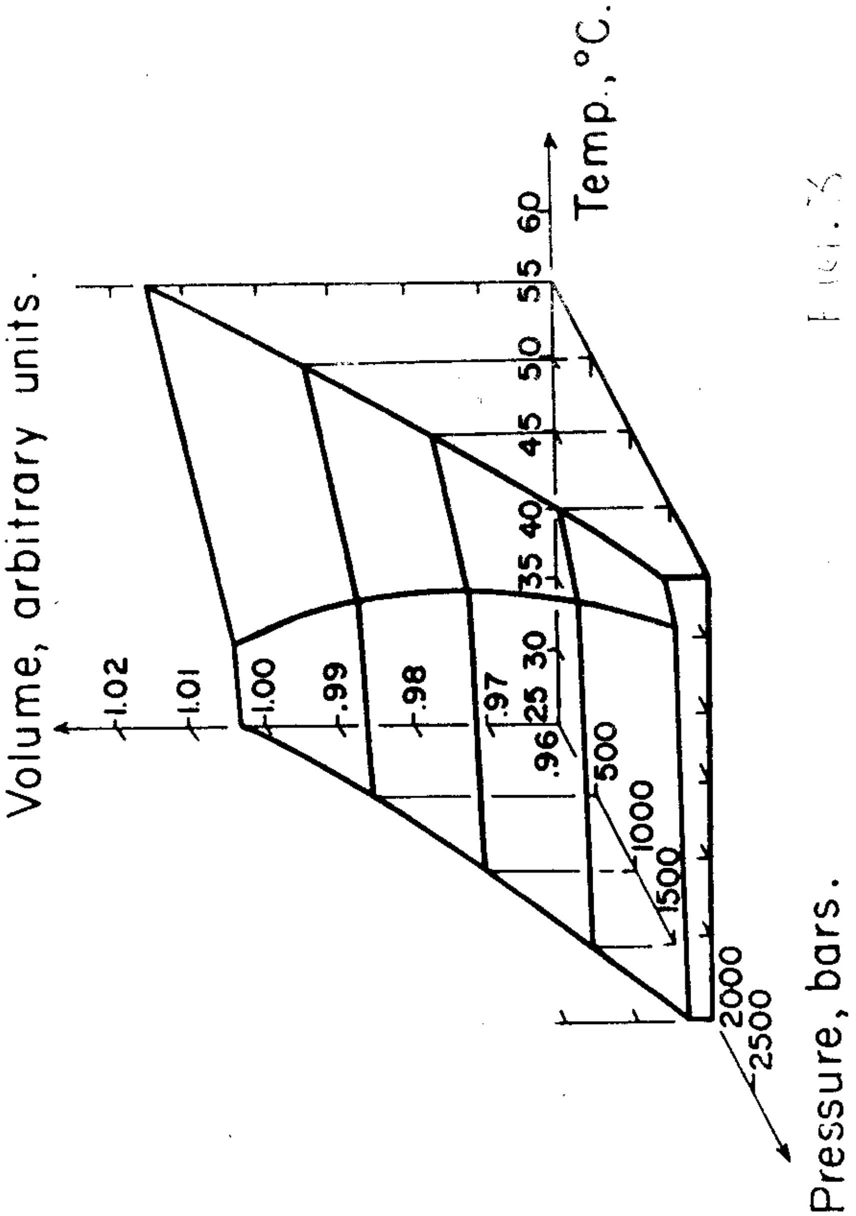

Volume, arbitrary units.
Temp., °C.
Pressure, bars.
1.02
1.01
1.00
.99
.98
.97
.96
25
30
35
40
45
50
55
60
500
1000
1500
2000
2500

FIG. 3

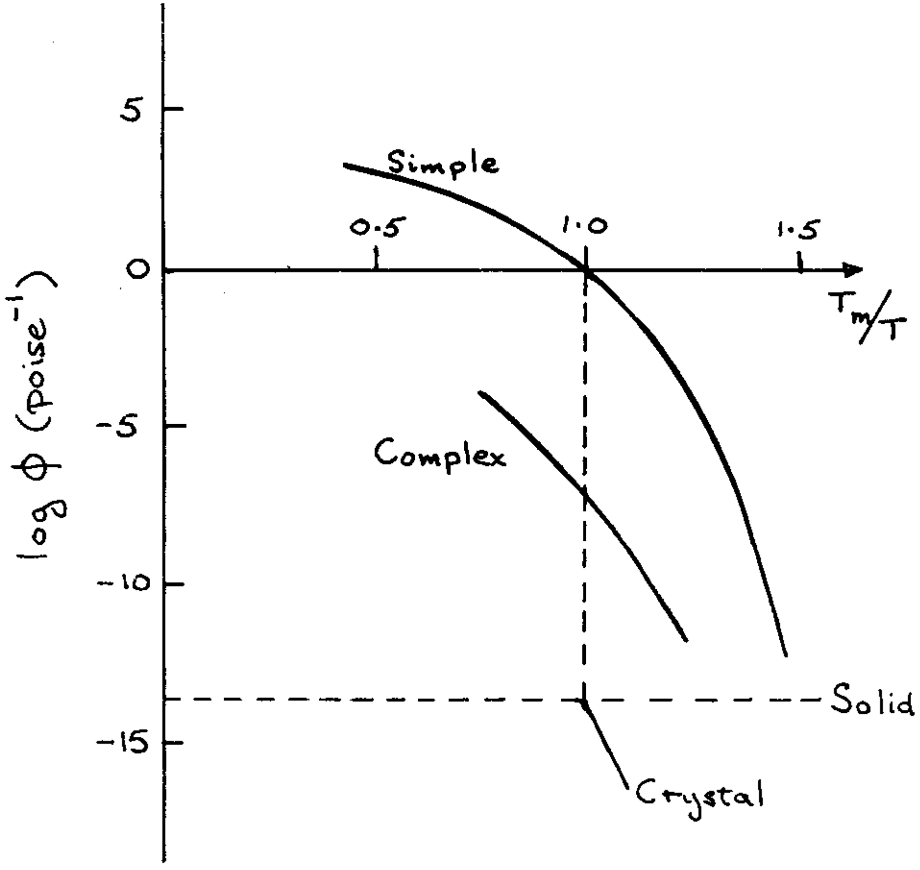

log Φ (poise^{-1})
T_m/T
5
0
-5
-10
-15
0.5
1.0
1.5
Simple
Complex
Solid
Crystal

FIG. 4

2. KINETICS OF NUCLEATION AND CRYSTAL GROWTH

2.1 Introduction

It follows from lecture 1 that the first requirement for glass formation is to avoid the nucleation and growth of crystals as a liquid is supercooled. In this sense at least, the glass transition is clearly a KINETIC (non-equilibrium) phenomenon.

2.2 Formation of Critical Nuclei - Descriptive Account

A liquid has a disordered structure best represented by a radial distribution function (RDF); since a glass is structurally continuous with the liquid from which it is formed (lecture 1) it has a similar structure. Typical RDFs are illustrated in figure 1 for vitreous (glassy) As_2Se_3 (figure 1a), for amorphous Ge (figure 1b) and for liquid Cs at three different temperatures (figure 1c). Note that in figure 1c the RDF becomes sharper as the temperature decreases, i.e. the local (near-neighbour) configuration becomes more ordered. But the RDF represents a time and space average; the distribution (structure) about any particular atom changes rapidly with time. At some times the local order is more pronounced than at others, i.e. the configuration about any given atom is sometimes more like that in a crystalline solid, sometimes more like that in a gas. Near the melting point larger ordered groupings are potential nuclei for the start of crystallisation.

The free energy change for the isothermal formation of a spherical nucleus of radius r is the sum of two terms - one term proportional to its volume, the other proportional to surface area, i.e.

$$\Delta G = f(T)r^3 + g(T)r^2 \qquad (1)$$

Or, at a particular temperature

$$\Delta G = ar^3 + br^2 \qquad (2)$$

where a and b are constant. The form of the two terms and the net ΔG is illustrated schematically in figure 2 for four temperatures, $T > T_m$ (figure 2a), $T = T_m$ (figure 2b), $T \lesssim T_m$ (figure 2c) and $T < T_m$ (figure 2c). The surface term (br^2) is always positive; the volume term is positive for $T > T_m$, zero for $T = T_m$ and negative for $T < T_m$. Thus the net ΔG goes through a

maximum for any $T < T_m$ at a critical radius $r = r_c$. A nucleus with $r < r_c$ will tend to disappear (ΔG decreases spontaneously) while a nucleus with $r > r_c$ will grow (ΔG also decreases). As the temperature decreases below T_m, r_c also decreases; at $T = T_m$, $r_c = \infty$. In the range of temperature where potential nuclei actually grow r_c is usually about 10 atomic diameters. At a temperature just below T_m, r_c is still sufficiently large that suitable nuclei are rarely formed by thermal motion; the rate of nucleation, and hence of crystallisation, is therefore small. As the temperature is lowered r_c decreases and the rate of nucleation (and crystallization) increases rapidly. At still lower temperatures r_c does not become very much smaller and thermal motion also decreases - HENCE THE RATE OF NUCLEATION (AND CRYSTALLIZATION) GOES THROUGH A MAXIMUM.

2.3 Elementary Theory of Nucleation and Crystal Growth[1,2,3]

Suppose a spherical crystal nucleus containing i atoms is formed in a supercooled liquid. The free energy involved is

$$\Delta G_i = Ai^{2/3} - Bi \qquad (3)$$

where the constant A is determined by the interfacial (surface) free energy and B by the excess of the bulk free energy of the supercooled liquid over the crystalline solid. ΔG_i is a maximum when

$$i = i^* = \left(\frac{2A}{3B}\right)^3 \qquad (4)$$

$$\text{i.e.} \quad G_{i^*} = \frac{4A^3}{27B^2} \qquad (5)$$

Thus, if a nucleus reaches the critical size i* it can grow spontaneously. The rate of homogeneous nucleation is the rate at which critically sized nuclei are formed and probability of their formation is

$$\text{proportional to: } \exp-(\Delta G_{i^*}/kT)$$

But for a nucleus to grow, atoms or molecules must be added to it and this will also be a process involving an activation energy e.g. diffusion, re-orientation etc. If ΔG_D is the activation energy associated with the growth process, then the rate of formation and growth of critically sized nuclei is -

$$\chi = C\ \exp-(\Delta G_D/kT)\exp-(\Delta G_{i*}/kT) \qquad (6)$$

Evaluation of the constants A and B (in equation (4)) and C gives -

$$\chi = \frac{nkT}{h}\ \exp-\left(\frac{\Delta G_D}{kT}\right)\exp-\left(\frac{16\pi\sigma^3 T_m^{\ 2}}{3\lambda^2 \Delta T^2 kT}\right) \qquad (7)$$

n = total number of atoms (or molecules)
h = Planck's constant
σ = interfacial free energy of nucleus (per unit area)
ΔT = (T_m-T), i.e. the supercooling

and $\lambda = (\Delta H_f/V_m)$, where ΔH_f is the latent heat of fusion and V_m is the molar volume.

From equation (7), χ rises very rapidly as T decreases, goes through a maximum and then decreases (NB at T = 0 K, χ = 0). By differentiation -

$$\text{if } \Delta G_D = 0,\ \chi = \chi_{MAX} \text{ when } T = \frac{T_m}{3}$$

As ΔG_D increases, the temperature of χ_{MAX} is displaced towards T_m.

THUS, IF A LIQUID HAS A SUFFICIENTLY HIGH ΔG_D TO ENABLE IT TO BE COOLED BELOW THE TEMPERATURE AT WHICH $\chi = \chi_{MAX}$ WITHOUT CRYSTALLIZING, THEN CRYSTALLIZATION IS <u>LESS</u> LIKELY TO OCCUR ON FURTHER COOLING - THESE ARE THE CIRCUMSTANCES WHICH FAVOUR GLASS FORMATION.

For a wide range of glasses, organic and inorganic, prepared in quantities of at least several grams, and by normal quenching from the melt it is found experimentally that[4]

$$Tg \simeq \frac{2}{3}\ T_m$$

For χ_{MAX} to occur at $T = \frac{2}{3}\ T_m$

$$\left(\frac{\Delta G_D}{kT}\right) \text{ must be} \sim 40$$

and if T = 300 K

$$\Delta G_D \text{ must be} \sim 24 \text{ kcal/mole.}$$

Compare this with E_η, the activation energy for viscous flow:

	E_η (kcale/mole)
Water	5.1 at T_m
Propyl alcohol	20 at Tg
Glucose	125 at Tg
Boric oxide	75 at Tg
Silicate glasses	150 at Tg

2.4 The Critical Cooling Rate

A necessary and sufficient condition for glass formation is that the liquid should be cooled rapidly enough so that detectable nucleation and crystal growth cannot occur.

It is possible to make rough estimates of the cooling rate which must be exceeded (the critical cooling rate, R_c) in order to encourage glass formation in particular liquids; it will obviously be a function of diffusion and flow processes in the liquid. Sarjeant and Roy[5] made an empirical estimate of R_c by first measuring the velocity of crystallisation in a small melt of NaCl subjected to very rapid cooling (10^4 - 10^5 deg/s). They then assumed that for NaCl the spontaneous nucleation and growth rates become extremely low at 10^0 of supercooling and that the minimum detectable crystalline ordering occurs when the crystallite size is ~ 10^{-7} cm. Thus, R_c is the rate which will not allow the growth of a crystallite of that size in a 10^0 interval. For NaCl Sarjeant and Roy find this is to be 1.2 x 10^9 deg/s. They further suggest that R_c can be written

$$R_c = Z\ \frac{T_m}{\tau} \qquad (8)$$

where Z is a constant, T_m the thermodynamic melting point and τ the appropriate jump rate of "structural units" which, for NaCl, is equated with the Restrahlen frequency. Hence, from known parameters, Z ~ 2.0 x 10^{-6}.
To relate R_c to viscosity η, the simplest general relationship is assumed, viz

$$\tau = \frac{V\eta}{NkT_m} \qquad (9)$$

where V is the molar volume and N, Avogadros number. Thus,

$$R_c = 2.0 \times 10^{-6} \frac{T_m^2 R}{V\eta} \qquad (10)$$

where R is the gas constant. This relationship is shown schematically in figure 4, with T_m as a parameter, and it is roughly in accord with experience.

A more quantitative evaluation of R_c has been derived by Davis[6]. From an extension of the theory of nucleation and crystal growth theory described in para. 2.3, he showed that the time t (in seconds) required to form a small volume fraction X of crystal is given by

$$t \simeq \frac{9.3\eta}{kT}\left[\frac{a_o^{\,9}X}{f^3\overline{N}_v}\{\exp(1.07/T_r^{\,3}\Delta T_r^{\,2})\}\{1-\exp(-\Delta H_m\Delta T_r/RT)^{-3}\right]^{\frac{1}{4}} \qquad (11)$$

where a_o is the average atomic diameter, f is the fraction of sites at the crystal/liquid interface where growth can occur, $\overline{N}_v$ is the average volume concentration of atoms, T_r is the reduced temperature (T/T_m) and ΔT_r is the reduced supercooling $[(T_m-T)/T_m]$.
If the temperature dependence of η below T_m is known then equation (11) can be plotted in the form of a time-temperature-transformation (T-T-T) curve expressing the time required for a just detectable volume fraction X of crystal to grow, as a function of temperature. An example, for $X = 10^{-6}$, is shown in figure 5 for the elements Ge and Te[6]. The critical cooling rate R_c is then given approximately by the linear cooling curve required to just miss the nose of the T-T-T curve and is given by

$$R_c \simeq \frac{T_m - T_n}{t_n}. \qquad (12)$$

where T_n and t_n are the temperature and time, respectively, corresponding to the nose. The value obtained for Te is 10^8 K/s and for Ge is 10^6 K/s. The latter is about two orders of magnitude less than the value estimated experimentally.

2.5 Universality of Glass Formation

To exceed the critical cooling rate R_c is a necessary and sufficient condition for glass formation. It is also a minimum condition, i.e. any cooling rate in excess of R_c will result in a liquid solidifying as a glass. In principle, therefore, it should be possible to quench any liquid into a glassy (vitreous) state and glasses are known to form from liquids in which the bonding is basically covalent, ionic, metallic, hydrogen-bonded or van der Waals-bonded. Some materials, notably pure metals and simple ionic compounds such as NaCl, have not been prepared in a glassy form but so far as is known this must be a practical limitation of the cooling technique. The range of cooling rates available in a variety of techniques is listed in the table below.

Annealing	(Large telescope mirrors	10^{-5} deg/s
	(Optical glasses	$\sim 3 \times 10^{-4}$ deg/s
	(Ordinary glasses	$10^{-3} - 10^{-2}$ deg/s
Air quenching - typical experimental batches (10's of grams)		1 - 10 deg/s
Small drops (1-100 mgm) into liq. Hg.		$10^2 - 10^3$ deg/s
Strip furnace (mgm batches)		$10^3 - 10^4$ deg/s
Splat cooling		$10^5 - 10^7$ deg/s
Evaporation, sputtering		?

2.6 References

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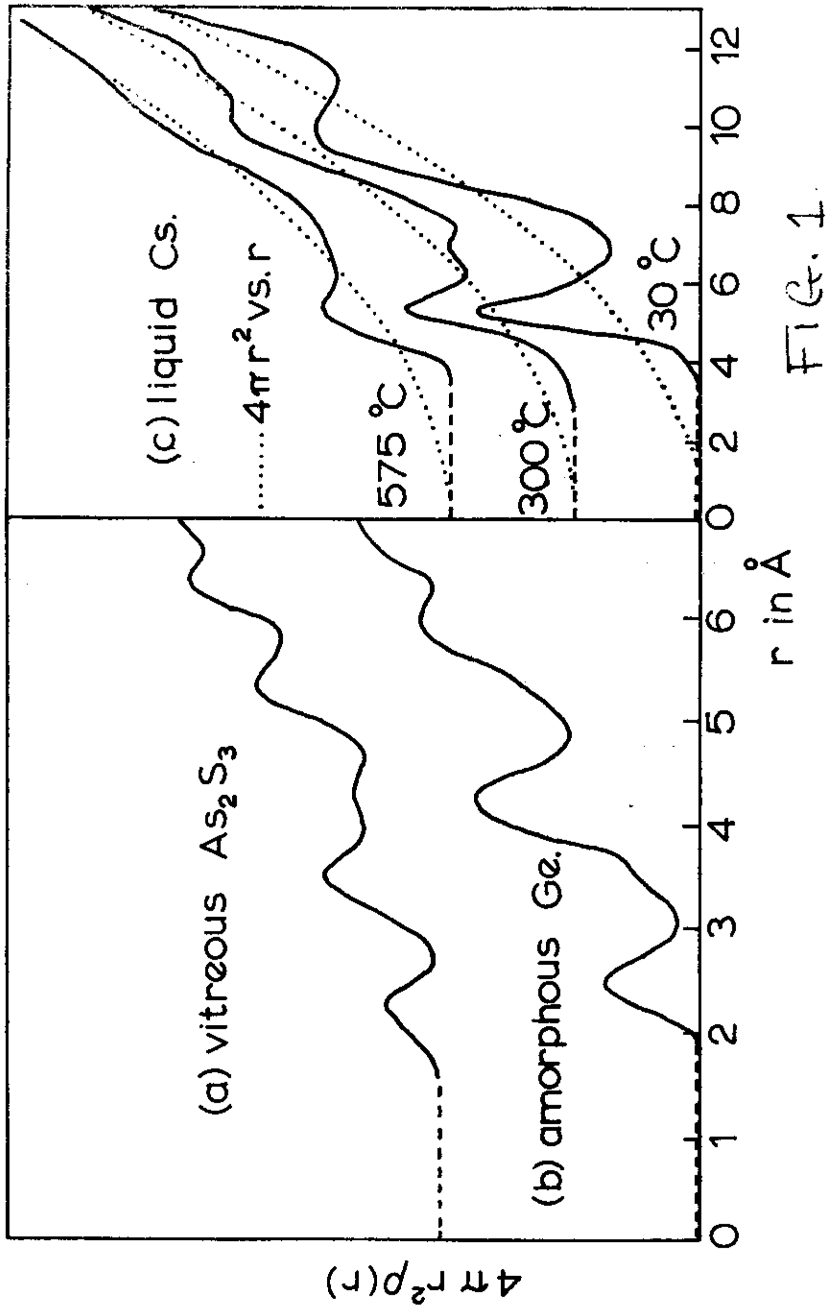


FIG. 1

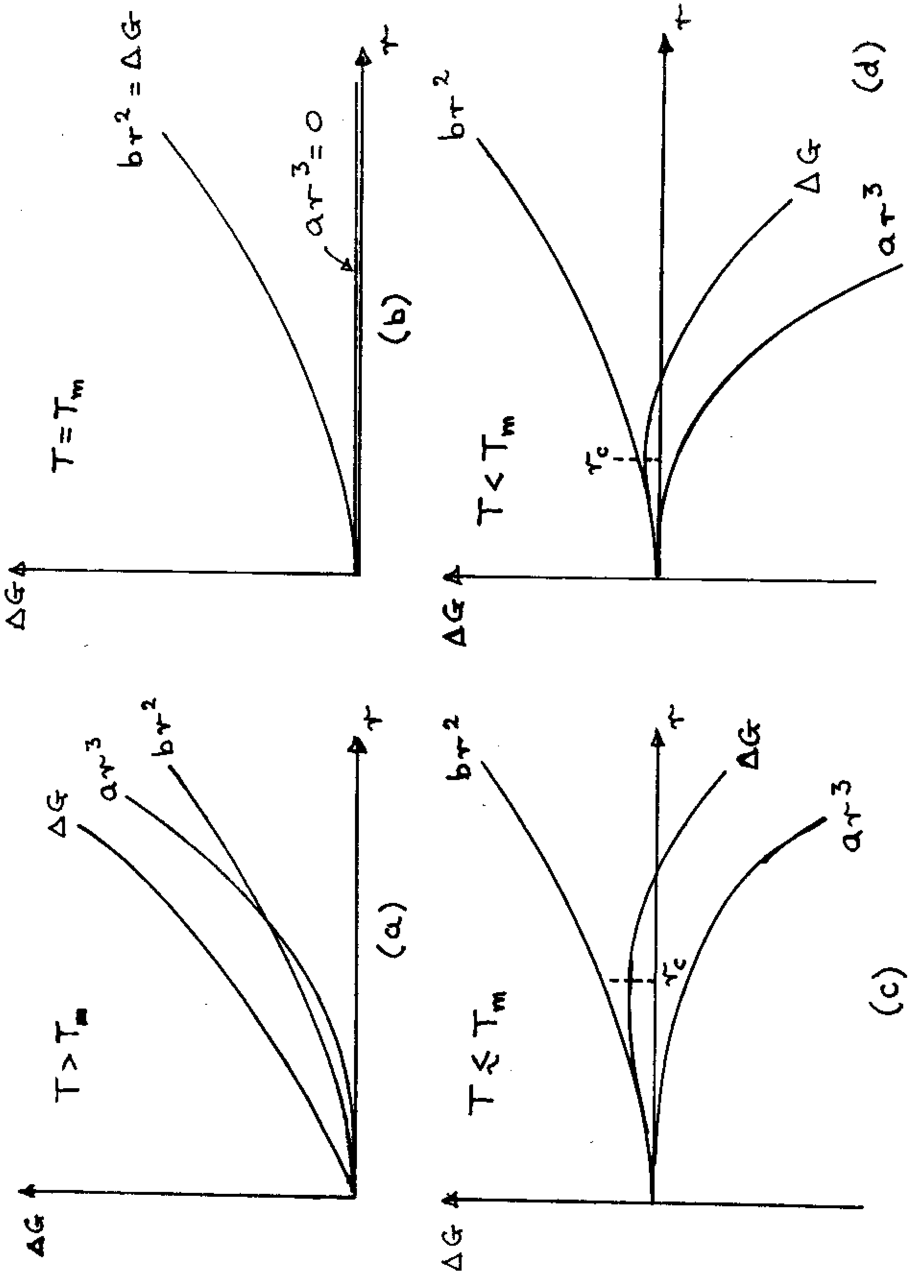

T = T_m
br² = ΔG
ar³ = 0
(b)
r
ΔG
T < T_m
br²
ΔG
ar³
r_c
(d)
T > T_m
ΔG
ar³
br²
(a)
T ≤ T_m
br²
ΔG
ar³
r_c
(c)

FIG. 2.

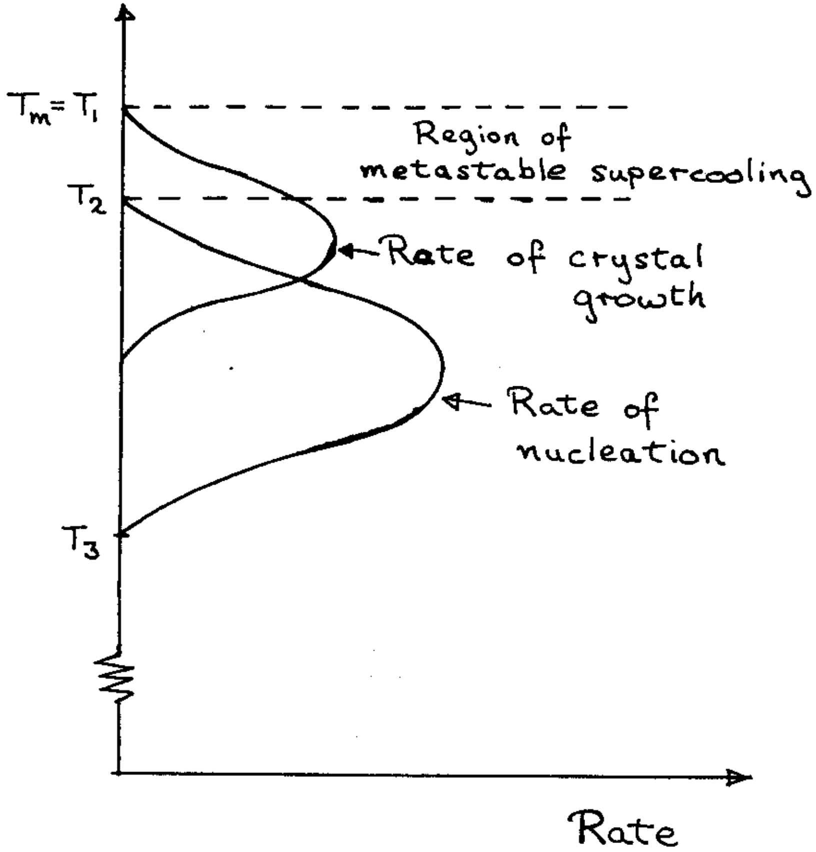
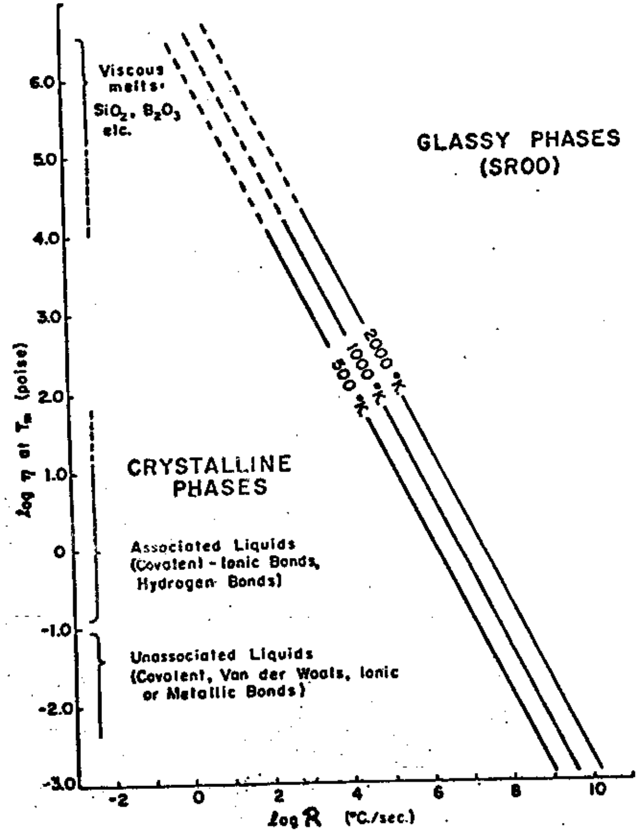

T_m = T_1
T_2
T_3
Region of metastable supercooling
Rate of crystal growth
Rate of nucleation
Rate

FIG. 3



Plot of the Logarithm of Melt Viscosity vs. Logarithm of Critical Cooling Rate at Various Melting Temperatures

FIG. 4.

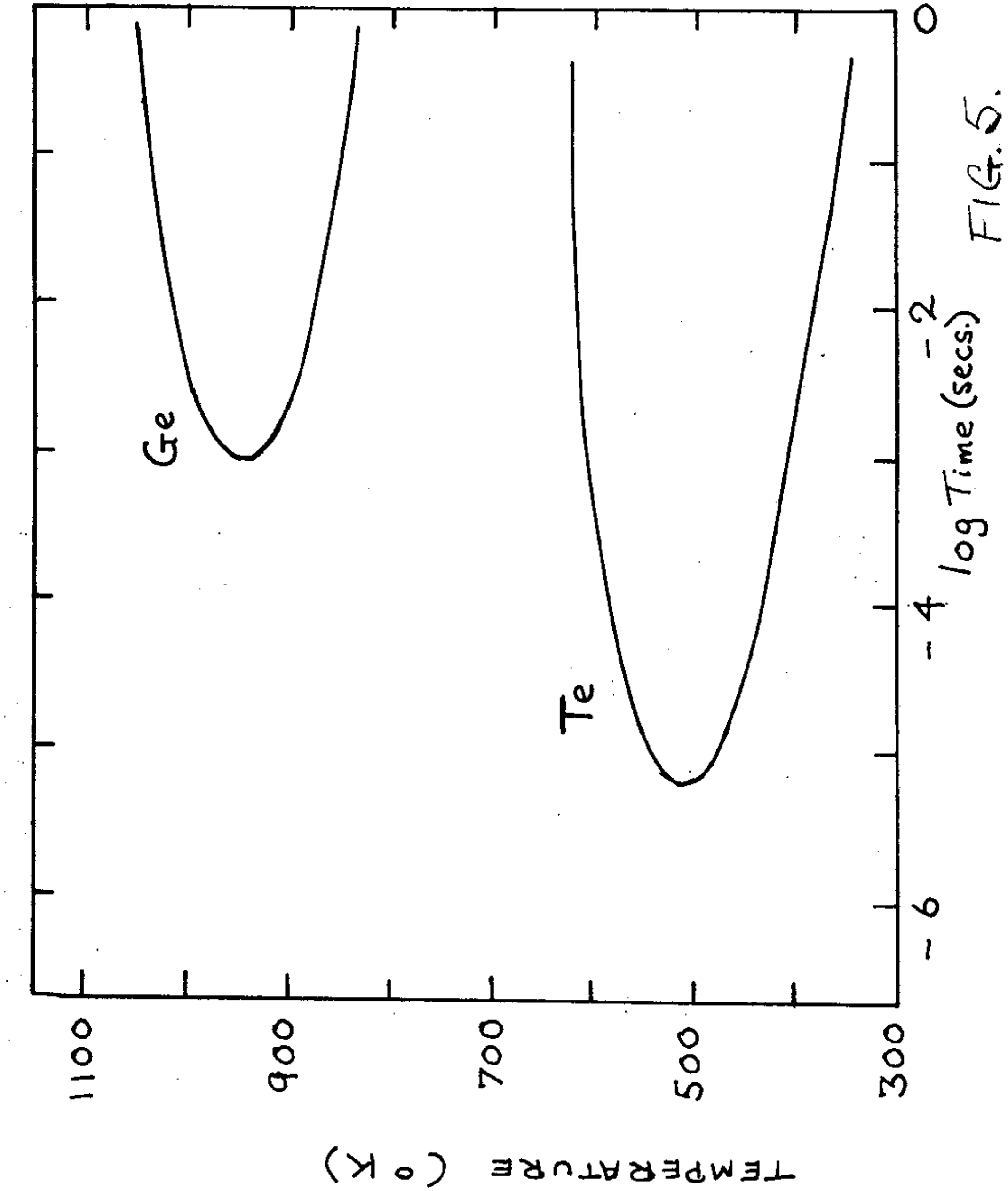


FIG. 5.

3. KINETIC (NON-EQUILIBRIUM) AND THERMODYNAMIC (EQUILIBRIUM) ASPECTS OF THE GLASS TRANSITION

3.1 Liquid Supercooling

As explained in lecture 2 a prerequisite for glass formation is the prevention of nucleation and crystal growth as a liquid is cooled below its melting (freezing) point. Once the temperature has been reduced below that at which the rate of crystal growth is a maximum then further supercooling makes it more and more likely that the liquid will solidify to form a glass. The ease, or otherwise, of glass formation is therefore very sensitive to the dynamics of flow and diffusion processes in liquids and to the rate of cooling. In this sense glass formation is clearly a kinetic process but this says nothing about what happens when, having avoided crystallisation, the supercooled liquid solidifies to a glass, i.e. the phenomenon associated with the glass transition temperature Tg, described in lecture 1. Is this an equilibrium thermodynamic transition or a non-equilibrium kinetic (or relaxational, or dynamic) process? The two possibilities are fundamentally distinct. A thermodynamic mechanism arises from a structural or configurational change in the system (or from quantum mechanical discreteness of energy levels) at some definable equilibrium temperature. A relaxational mechanism is a consequence of a deficiency in the experimental procedure; it results from changing the external forces acting on the system and making measurements before the system has had time to re-establish thermodynamic equilibrium.

Thermodynamic and relaxational mechanisms can in principle be distinguished experimentally. If some degree of freedom seems not to be contributing to a property of a system when a certain time has been allowed for equilibrium to be reached, the equilibriation time is simply prolonged more and more to determine the limiting value of the property in question[1,2]. If the limiting value is less than that expected for full participation of all degrees of freedom of the system then a thermodynamic change must have taken place. Such tests have been applied to some organic glasses which can be studied at relatively low temperatures e.g. glycol and glycerol and the results always seem to indicate that the glass transition is a relaxational phenomenon. For example, as illustrated schematically in figure 1, in stabilisation experiments on glasses with different Tgs, the limiting equilibrium V (or H, or S) of the meta-stable supercooled liquid can be approached from both sides[1,2].

3.2 Kinetic or Relaxational (Non-Equilibrium) View of the Glass Transition

Probably all experimental observations on the glass transformation are at least qualitatively consistent with the view that the phenomenon occurs becuase as the temperature is reduced certain 'configurational' changes associated with changes in the volume of the supercooled liquid become so slow that they can no longer take place on the time scale of the experiment. Below the glass transition any further changes of V (or H or S) with temperature are associated with the temperature dependence of the (anharmonic) vibrational and rotational modes of the atoms or molecules. The expansion coefficient of the glass is, therefore, practically identical with that of the cyrstalline form of the material (as shown in the insert to figure 1 of lecture 1). If X represents the extensive variables of a liquid (V, H or S) then

$$\left(\frac{dX}{dT}\right)_{\text{liquid}} = \left(\frac{\delta X}{\delta T}\right)_{\substack{\text{vib.,}\\ \text{rot.,}\\ \text{etc.}}} + \left(\frac{\delta X}{\delta T}\right)_{\text{config}} \qquad (1)$$

and it is the second term which is ineffective ("frozen-in") in the glass. Equivalent statements could be made about the effects of pressure and its derivative properties. It is very difficult, however, to quantify the kinetics of the process. Indeed the very nature of the configurational changes which are supposed to be "frozen-in" at the glass transformation are ill-understood but some indication of the processes contributing to the configurational relaxation (or prevented from contributing in the case of glass) is given by four experimental observations, three of which are generally true for a wide variety of glasses:

(i) The transformation temperature Tg determined from measurements of α and C_p are very nearly the same[1,2]. There is no a priori reason for supposing that the relaxation rates for changes in heat content and volume should be related. The fact that they are apparently the same in the liquid ↔ glass transition suggests that the molecular or atomic motions involved in the readjustment of energy and volume following a change in temperature, are very similar.

(ii) The temperature coefficient for the relaxation rate in the glass transformation region is very large (e.g. for volume changes in experiments such as those illustrated in figure 1). This is a crucial factor but it is not easy to get quantitative information. Douglas[3] pointed out, however, that for stabilised glasses, at least, the stress relaxation is a simple linear phenomenon obeying the superposition principle. This allows a viscosity to be calculated from the stress relaxation modulus and for stabilised oxide glasses, at any rate, the activation energy for this viscosity is very high e.g. ~ 7 eV. Jones[2] has also emphasised that viscosity activation energies in the transformation range are large and can be double the relevant bond energy. Thus, the relaxation cannot represent an atomic or simple molecular diffusion process.

(iii) At Tg most glasses have viscosities of about $10^{13.5}$ poise. From simple rate theory of viscous flow this implies a 'jump' rate of perhaps one every few minutes. This is about the same as the expected relaxation rate at Tg since, according to the kinetic view, the transformation occurs when the relaxation rate is the inverse of the experimental observation time which will normally be a few minutes or more[1,4]. Hence, the relaxation processes in glass formation probably have a close similarity with the mechanisms of viscous flow. It must be recalled however (previous para.) that the activation energies for viscous flow in the transformation range of typical oxide glasses are very large.

(iv) There is sometimes a close relationship between dielectric relaxation and the glass transformation, i.e. the dielectric relaxation time is about one minute to one hour at Tg[5]. This observation has only been made, however, in certain organic glasses.

The inference from the above observations is that at the glass ↔ liquid transition, atomic or molecular motions associated with the phenomena as diverse as

the redistribution of energy and volume,

viscous flow and diffusion processes, and

dipole reorinetation,

all occur at about the same frequency. One can account for this by assuming that for any type of molecular motion to occur a temporary disruption of rearrangement of the liquid configuration is required in the neighbourhood of the atom or molecule. Once this rearrangement has taken place any type of molecular motion is equally likely. In a sense, therefore, the process is cooperative, probably involving a large number of atoms or molecules. The very large activation energies for relaxation in the transformation region are particularly relevant to this point. When the temperature is reduced below Tg the configurational degrees of freedom are ineffective and it is obvious that Tg will depend upon the relaxation rate and the duration of the 'experiment' (i.e. rate of cooling).

The situation can be aptly summed up by the use of a dimensionless number familiar in rheology, viz. the Deborah Number, D.N.:[6]

$$\text{D.N.} = \frac{\text{Time of relaxation, } \tau}{\text{Time of observation}}$$

The difference between 'solids' and fluids is then defined by differences in D.N. If the time of observation is large, or τ is small, D.N. is small and the consequences of the relaxation process (whatever they may be, e.g. plastic flow) can be observed. On the other hand if D.N. is large the material behaves as a solid. Consider this in terms of the V-T diagram for a glass (e.g. figure 1 of lecture 1) and the relaxation time for the structure to adapt to a change in temperature. In the liquid, the relaxation time will be perhaps 10^{-18} - 10^{-13} sec. (depending on the type of liquid) and hence D.N. is very large for normal experimental times. As the temperature is reduced to Tg the relaxation time approaches a few minutes, i.e. Tg is defined as the temperature where D.N. = 1. In the glassy state ($T < Tg$)τ decreases rapidly with T, the structure cannot change to its appropriate equilibrium configuration and D.N. becomes very small. In a normal glass formation experiment the time of observation is kept fixed, and D.N. is changed by varying τ through its temperature dependence. An analogous experiment, however, would be to change D.N. by keeping the temperature, and hence τ, fixed and varying the time of observation. This would be most conveniently done by making measurements as a function of frequency, e.g. to measure the specific heat C_p or compressibility κ, of a liquid, by ultrasonic absorption[7]. The expected results of such an experiment are shown schematically in figure 2. At low frequencies, the time of observation ($= 1/2\pi f$) is long compared with τ and D.N. is very small. When $\tau = (1/2\pi f)$, D.N. = 1 and if the frequency is increased further a typical sigmoid-type relaxation curve is obtained. At high frequencies D.N. becomes very large. The particular temperature at which the experiment is performed could be regarded as a glass transformation temperature corresponding to the observation time ($1/2\pi f_{mid}$) where f_{mid} is the frequency of the mid-point in the relaxation curve. This is completely consistent with the kinetic view of the liquid ↔ glass transition. As in all relaxation processes, the sharp decrease in κ or C_p as the frequency increases through f_{mid} is caused by the inability of the system to respond to the external stimulus. In this siutation, however, the liquid is at all times in internal thermal equilibrium, i.e. the 'glassy' state corresponding to $f > f_{mid}$ is an equilibrium glass[7]. It should also be realised that several different mechanical and electrical relaxation processes are possible in liquids and glasses[3,7,8]; only when the relaxation involves configurational or structural changes is it realistic to equate it with a glass transformation. In organic polymers, there are often structural relaxation processes connected with, for example, side groups; these processes usually freeze-in at temperatures below the main glass transformation and are referred to as secondary glass transitions.

3.3 Limitation of the Relaxational Approach

Although the available experimental evidence favours the relaxational model, the enormous temperature coefficients of relaxation make tests such as that illustrated in figure 1 almost impossible to apply unequivocally[1,2]. It is difficult to eliminate the possibility that there is a real thermodynamic transition to a glassy state at temperatures below normally attainable Tgs.

Kauzmann[5] posed the question - what behaviour would liquids show at low temperatures if enough time could always be allowed to avoid vitrification (glass formation)? Would it be found that a "non-vitreous" liquid could exist in some kind of meta-stable equilibrium close to 0^oK?

Figure 3 compares the trends in temperature dependence of some crystals and supercooled melts above Tg and extrapolated to lower temperature[5]. Note that for glucose, S for the liquid phase rapidly approaches that of the crystal (similarly for H and V). This is even more marked for lactic acid but less so for glycerol and probably not at all for boric oxide (B_2O_3), although the latter becomes glassy at relatively high temperatures. It seems unlikely that S_{liq} could every become less than $S_{cryst.}$ but it could be argued that these results do suggest that the supercooled liquid may pass continuously into the crystalline state (analogous to the liquefaction of gases at the critical pressure). There seems little justification for this however as the S-curves do not approach the absicca at the same temperature as the H-curves, and the free energies of the two phases show no tendency to approach each other down to Tg[5].

How therefore can the curves in figure 3 be extrapolated below Tg? Probably the "non-vitreous" liquid curves of ΔS vs. T [Δ ≡ (liquid - crystal)] must become horizontal not far below Tg and since

$$\frac{\delta \Delta H}{\delta T} = T\,\frac{\delta \Delta S}{\delta T} \qquad (2)$$

this would imply a similar change in slope of ΔH vs. T. In turn, this means that

$$\Delta Cp = 0$$

$$\text{i.e. } (Cp)_{liquid} = (Cp)_{crystal}.$$

But this is exactly what happens at the glass transition which has been interpreted as a relaxation process unconnected with equilibrium thermodynamics! Is this a coincidence or might the glass transition be a thermodynamic phenomenon, at least in some circumstances?

3.4 References

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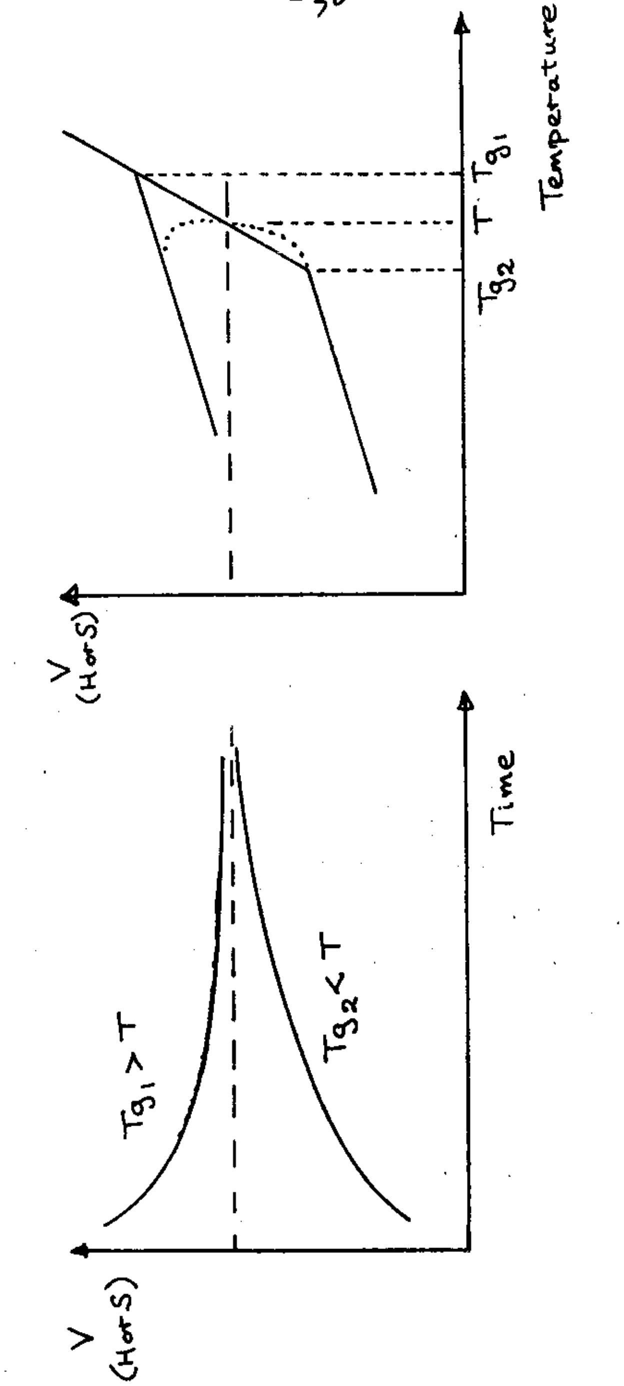

FIG. 1.

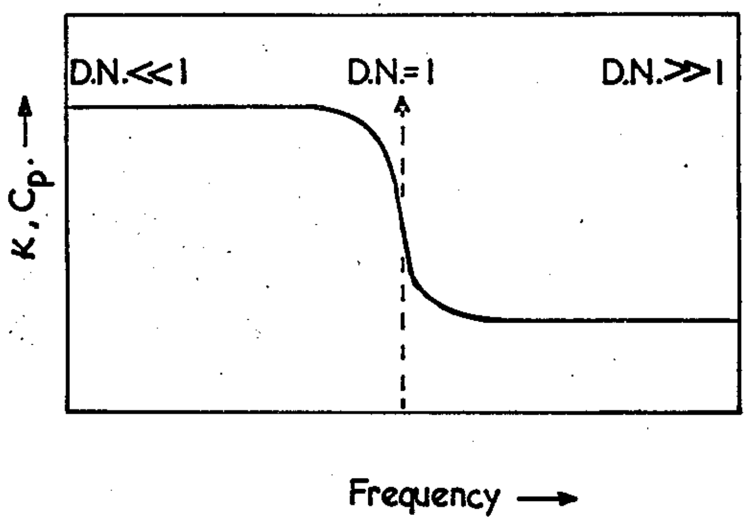
D.N.<<1
D.N.=1
D.N.>>1
κ, C_p →
Frequency →

FIG. 2.

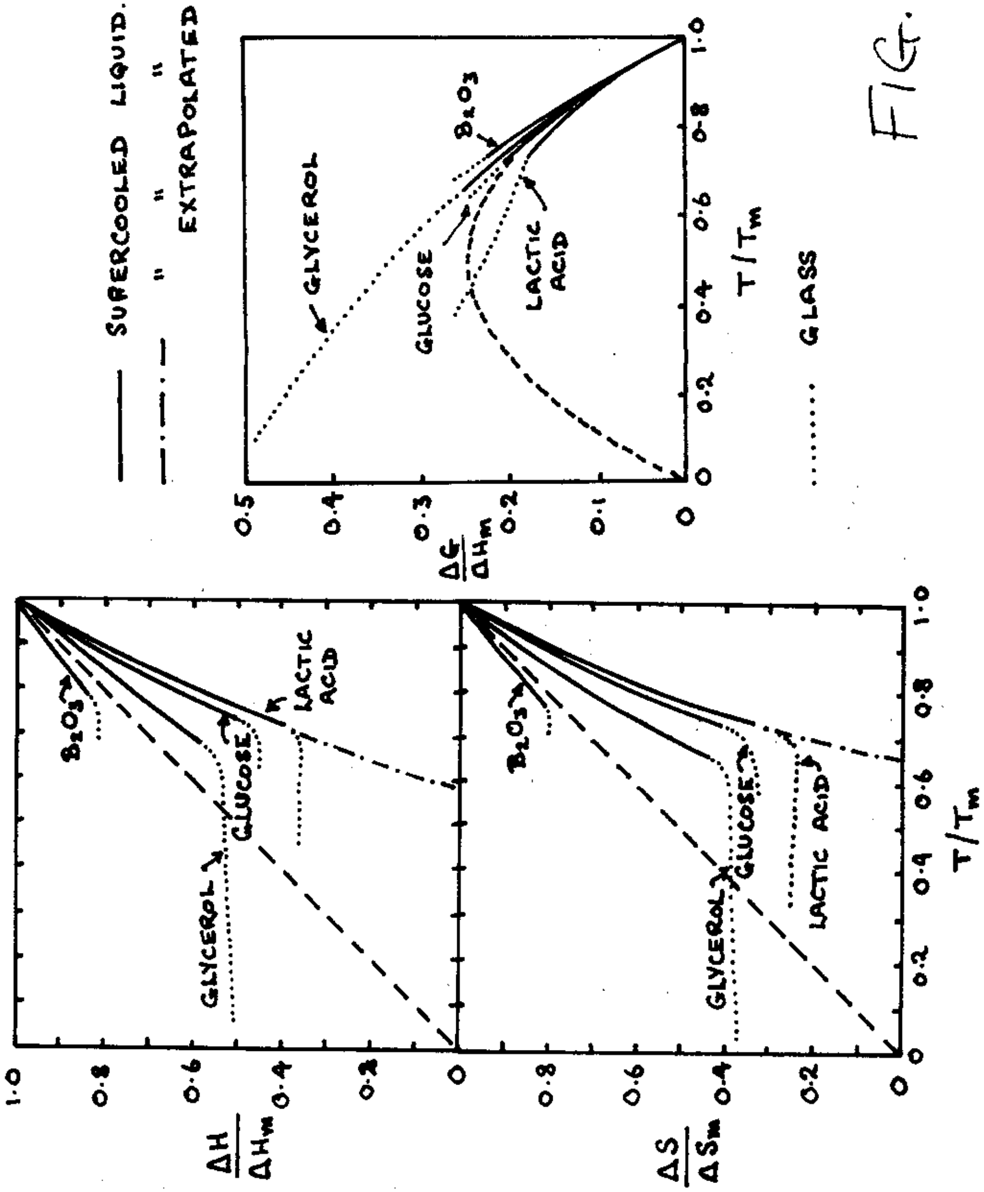
SUPERCOOLED LIQUID.
" "
" EXTRAPOLATED
GLASS
$\frac{\Delta G}{\Delta H_m}$
0.5
0.4
0.3
0.2
0.1
0
T/Tm
0
0.2
0.4
0.6
0.8
1.0
GLYCEROL
GLUCOSE
B_2O_3
LACTIC ACID
$\frac{\Delta H}{\Delta H_m}$
1.0
0.8
0.6
0.4
0.2
0
$\frac{\Delta S}{\Delta S_m}$
0
0.8
0.6
0.4
0.2
0
T/Tm
0
0.2
0.4
0.6
0.8
1.0
B_2O_3
GLUCOSE
GLYCEROL
LACTIC ACID

FIG. 3.

4. THERMODYNAMICS OF THE GLASS TRANSITION

4.1 Introduction

There are two problems involved in the thermodynamics of the glass transition. Firstly, can the non-equilibrium (thermodynamically unstable) glassy state which solidifies at normally attainable Tgs be treated by a thermodynamic formalism? Secondly, does a truly equilibrium transition occur (presumably at lower Tgs) if cooling rates are made slower and slower (i.e. the problem posed in lecture 3), and if so what is its thermodynamic status? The first question is relatively easy to answer.

4.2 Irreversible Thermodynamics of the Non-Equilibrium Glass[1]

The problem is to relate the thermodynamic properties of the *non-equilibrium* glass to those of the *equilibrium* liquid from which it was formed. Two relevant properties are, for example

$$\alpha_l = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \text{the coefficient of expansion}$$

and

$$\kappa_l = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad \text{the compressibility}$$

(The subscript 'l' is used to denote 'liquid'. Later the subscript 'g' will be used to denote 'glass'.) For liquids these definitions are sufficient since V = V(P,T). To describe the glass at least one extra parameter must be introduced and this is denoted z. A necessary property of z is that it shall be constant for a *given* glass (e.g. it will be different along the lines 1, 2 and 3 in figure 2a of lecture 1) and to vary with T (and P) in the liquid.

Thus

$$V = V(P,T,z) \quad \text{for a glass}$$

while,

$$V = V(P,T,z) \quad \text{but } z = z(P,T) \text{ for the liquid.}$$

The physical significance of z is unimportant at the moment but it could be regarded as a measure of, say, the configurational order, or viscosity, or 'free volume'; or we could equate it to the fictive temperature T_F (lecture 1). It is usually referred to simply as an 'ordering parameter'.

The statements made above imply that a single ordering parameter is adequate to define the state of a glass. This further implies that two glasses brought to the same volume and temperature by different routes (e.g. the glass at V_2, Tg_2 in figure 2a of lecture 1) are in the same thermodynamic state with the same H and S as well as V, i.e. a state completely defined by P, T and z.

There are several ways to proceed from here. In the formalism of irreversible thermodynamics developed by de Donder[1,2] three assumptions are made:

1. Thermodynamic properties are all single valued functions of P, T and z.
2. During an irrversible process associated with changing z there is an increase in entropy S given by

   $$TdS_{irr} = dQ + Adz$$

   where A is a thermodynamic state function called the affinity.
3. For all realisable changes Adz > 0.

Irreversibility is allowed for by the introduction of the term Adz and assumption (3) means that in equilibrium A = 0. It should be clear from the preceeding discussions that in the kinetic view the glass transformation is not a unique phenomenon. It is only one type of relaxation process. Others are to be found in visco-elastic behaviour (which is often closely related to the glass transformation), electric polarisation (which may or may not be related to glass transformation), magnetic polarisation, chemical reactions and so on[3]. The approach via irreversible thermodynamics is equally applicable to all.

Applying the above definitions and assumptions to the V = V(P,T,z) relationship leads to

$$\frac{dTg}{dP} = \frac{\Delta\kappa}{\Delta\alpha} \qquad (1)$$

where $\Delta\kappa = (\kappa_l - \kappa_g)$, and $\Delta\alpha = (\alpha_l - \alpha_g)$.
Similarly from the H = H(P,T,z) or S = S(P,T,z) relationships,

$$\frac{dTg}{dP} = \frac{TV\Delta\alpha}{\Delta C_p} \qquad (2)$$

where $\Delta C_p = (C_{pl} - C_{pg})$. Note straight away that both equations predict that Tg increases with pressure, as is observed experimentally (see lecture 1). From equations (1) and (2)

$$\frac{\Delta C_p \Delta\kappa}{TV\Delta\alpha^2} = 1 \qquad (3)$$

Equations analogous to (1), (2) and (3) can also be derived from the usual treatment of an equilibrium second-order thermodynamic transition; in that context they are sometimes called the Ehrenfest equations[4]. Their appearance here should not be construed as meaning that the glass transformation is a true second order thermodynamic transitions - the conditions for that conclusion are much more restrictive. Before considering equations (1) to (3) in more details it is worth mentioning some other results of the thermodynamics.

Instead of using the undefined parameter z, variables more suited to practical problems could be chosen and incorporated in the formalism. In calormetric experiments on glass the most convenient parameters is the fictive temperature T_F (see lecture 1) which in the present terms would be defined by

$$A\ (P,T_F,z) = 0 \text{ with } T_F = T_F(P,z) \qquad (4)$$

Making a linear approximation and using the above definition,

$$\begin{aligned} A(P,T,z) &= A(P,T_F,z) + (T - T_F)\ \left(\frac{\delta A}{\delta T}\right)_{P,z} + \ldots\ldots \\ &= (T - T_F)\ \left(\frac{\delta A}{\delta T}\right)_{P,z} + \ldots\ldots \end{aligned} \qquad (5)$$

With appropriate thermodynamic relationships, e.g.

$$dQ = dE + PdV = TdS_{irr} - Adz$$

a variety of results can be derived. For instance

$$TdS_{irr} = Adz = -V\Delta\alpha\ (T - T_F)dP + \left(\frac{\Delta Cp}{T_F}\right)\ (T - T_F)\ dT_F \qquad (6)$$

At constant pressure this gives

$$dS_{irr} = \Delta C_p\ \left(\frac{1}{T_F} - \frac{1}{T}\right)\ dT_F \qquad (7)$$

From the second law it follows that

$$\frac{dT_F}{dt} \gtrless 0 \text{ according as } (T - T_F) \gtrless 0 \qquad (8)$$

This means that $(dS_{irr}/dT) \to 0$ as $T_F \to T$, <u>in whatever direction</u>. In other words, the approach of a glass to equilibrium is a consequence of the entropy principle just as in any other system, but equilibrium can be approached from temperatures either above or below T_F. This is, in effect, a description of the stabilisation phenomena described in figure 1 of lecture 3. A fictive pressure P_F can also be defined by

$$A(P_F,\ T,z) = 0 \text{ with } P_F = P_F(T,z)$$

Using the same linear approximation, it can be shown that

$$\frac{T - T_F}{P - P_F} = -\ \frac{VT\Delta\alpha}{\Delta\ Cp} = \frac{\Delta\kappa}{\Delta\alpha} \qquad (9)$$

Thus, a sudden isobaric change in temperature δT which leaves T_F unchanged is thermodynamically equivalent to a pressure increment of

$$\delta P = -\ \frac{\Delta Cp}{TV\Delta\alpha}\ \delta T \qquad (10)$$

This can become quite large (thousands of atmospheres) and is effectively the driving force tending to stabilise the glass.

Most of the discussion of the thermodynamics of glass has revolved around the validity or otherwise of equations (1) to (3). The lack of reliable data makes it difficult to establish whether or not equation (3) is valid. Generally, however, the experimental evidence[1] is that

$$\frac{\Delta Cp\Delta\kappa}{TV\Delta\alpha^2} > 1$$

It is in the region of 1.2 to 2.4 in Se, for instance, and approximately 1.6 in a borosilicate glass. Equations (1) to (3) are a direct consequence of the assumption that a single ordering parameter can describe the thermodynamic state of a glass (together with P and T of course). The fact that equation (3) is not obeyed means that a single parameter is not adequate, i.e. that two glasses brought to the same V and T by different routes are <u>not</u> necessarily in the same thermodynamic state. Either of equations (1) or (2) could still be independently valid, however, and a closer consideration of their implications can give some insight into the factor(s) determining the glass transition[5]. They are, as emphasised before, both the result of a one-parameter description using an ordering parameter.

An alternative description of glass formation is to introduce an 'excess function' which is a function of temperature and pressure, and to suppose that the liquid ↔ glass transformation occurs when the excess function goes to zero, or becomes constant. For instance, the notion of unoccupied, or 'free', or excess volume, V_e has featured prominently in many discussions of the glass transformation, especially in polymers. The glass transition is then equated with the condition $V_e \rightarrow 0$ or constant. Thus, if we write[5]

$$dV_e = dV_g + dV_e$$

$$= V\,\alpha_g dT - V\kappa_g dP + V\Delta\alpha dT - V\Delta\kappa dP, \qquad (11)$$

in a glass (i.e. a 'fast' experiment; D.N. >> 1) only the first two terms contribute to dV_e. One could equally well postulate, however, that at the glass transformation an excess entropy $S_e \rightarrow 0$ (or constant). The question of the adequacy of a single ordering parameter then becomes equivalent to asking if the excess thermodynamic variables are functions of a single parameter only, i.e.

$$V_e = V_e\,(z),\ S_e = S_e\,(z),\ H_e = H_e\,(z);\quad z = z(P,T)$$

Put in this way z is a redundant variable since constant V_e, S_e and H_e implies constant z, and vice versa. Thus, V_e say could be adopted as an independent variable to characterise the glass and the sufficiency of a single ordering parameter is then equivalent to the conditions

$$H_e = H_e\,(V_e),\ S_e = S_e\,(V_e),\ V_e = V_e\,(P,T)$$

If P and T are changed so as to keep V_e constant then

$$dV_e = \left(\frac{\delta V_e}{\delta T}\right) dT + \left(\frac{\delta V_e}{\delta P}\right) dP$$

$$= V\Delta\alpha\ dT - V\Delta\kappa dP$$

$$= 0 \text{ at constant } V_e$$

$$\text{Therefore}\quad dP = \left(\frac{\Delta\alpha}{\Delta\kappa}\right) dT$$

Applied to the glass transition this is identical with equation (1)[5]. These arguments imply, therefore, that if V_e determines Tg,

$$\frac{dTg}{dP} = \frac{\Delta\kappa}{\Delta\alpha} \qquad \text{i.e. equation (1)}$$

Similar reasoning shows that:[5]
If S_e or H_e determine Tg

$$\frac{dTg}{dP} = \frac{TV\Delta\alpha}{\Delta Cp} \qquad \text{i.e. equation (2)}$$

Reliable experimental data are again scarce but results on a variety of glasses, including S_e, boric oxide and several vitreous organic polymers, show that the latter equality holds, but not the former[5,6].

One must conclude, therefore, that a one-parameter description is not adequate but that the glass transformation occurs when S_e (or H_e) reaches a critical value, i.e. when excess entropy or enthalpy associated with molecular motion in the liquid becomes 'frozen-in'. It is not possible, by these arguments, to distinguish between the two variables.

It is convenient to conclude this section with brief comments on the thermodynamic status of the glass transition. If either of equations (1) or (2) are valid (but not both), this implies that on the free energy (G) - P - T surface of a liquid, there is an infinite set of points each of which defines a <u>distinct</u> glass[5]. If both (1) and (2) hold, i.e. equation (3) is valid, there are lines of constant V_e, S_e, H_e and z along the G - P - T surface of the liquid, and glasses derived from any point along these lines would be identical. Goldstein[5] points out that only if the lines of constant V_e etc. coincided with lines of constant relaxation time could equation (1) to (3) as applied to glass, be considered as equivalent to the Ehrenfest equations for a true second-order thermodynamic transition. If the time scale of the experiment is altered, however, the location of the transition on the G - P - T surface is changed. One must still conclude therefore that as normally observed the glass transformation is a relaxation process.

4.3 A Finite Limit to Tg

The question of whether a thermodynamically equilibrium transition would occur if the cooling rate were made slower and slower is equivalent to asking if there is a finite limit to Tg,

$$\text{i.e. is there a } Tg/_{\text{limiting}} > 0^{o}K?$$

It is first relevant to observe the trend of configurational (or excess) entropy $S_{config.}$ for a supercooled liquid and glass. Many years ago Simon calculated $S_{config.}$ from calorimetric data (latent and specific heats) for some low-temperature organic glasses and typical data for glycerol are shown in figure 1[7]. Note first that in the glassy state ($T < Tg$) $S_{config.}$ has a constant value of about 5 E.U. and the curve apparently extrapolates down to $0^{o}K$ with little change in $S_{config.}$ This is not a violation of the third law however as the glass is not in thermal equilibrium. The constant $S_{config.}$ of ~ 5 E.U. is the entropy frozen-in to the glass because the relaxation times for configurational re-arrangement exceed experimental times. Thus, much of the configurational disorder (entropy) of the liquid relative to the crystalline solid remains trapped in the glass. This observation implies that there is not an "ideal" glassy state with a unique structure; the structure is whatever the liquid structure happens to be when the glass solidifies at Tg. Anderson[8] and Goldstein[9] have interpreted this in terms of a potential energy V(x) vs. configuration space diagram with a large number of more or less equivalent energy valleys, separated by "mountain passes" whose height is variable within a certain range, but almost all of which become impassable much below Tg - see figure 2.

Of particular significance in the present context is the observation that $S_{config.}$ for the supercooled liquid (operationally, the excess over the crystalline entropy) seems to extrapolate to zero at a finite temperature T_0 at a relatively small temperature difference below the normally attainable Tg (this is simply another way of stating the problem discussed in lecture 3 - para. 3 and figure 3). For many molecular and polymeric glasses ($Tg - T_0$) is only about $40\text{-}60^{o}K$.

It will be recalled from lecture 1 (para. 1.2 (c)) that over a wide range of temperature the viscosity of many glass-forming liquids obeys the empirical equation

$$\eta = C \exp[E_\eta/k(T-T_0)] \qquad (1)$$

In fact, most transport properties of glass-forming liquids - e.g. fluidity (inverse viscosity), diffusion, conductance, dielectric relaxation - seem to follow an equation of identical form so that the characteristic relaxation time τ, associated with a particular property, is given by

$$\tau = \tau_0 \exp[A/(T-T_0)] \qquad (2)$$

Equation (2) seems to be uniquely and universally applicable to glass-forming liquids, and its particular feature is that as $T \rightarrow T_0$ the slope becomes almost infinitely steep so that all physical processes are essentially frozen-out before T_0 is reached. Thus, T_0 is an experimentally inaccessible singularity but it can be estimated by extrapolation of data from higher temperatures. THE STRIKING FACT IS THAT WHERE CALORIMETRIC DATA (i.e. as in figure 1) AND RELAXATIONAL DATA ARE BOTH AVAILABLE, THE TWO T_0s SEEM TO COINCIDE[8,9]. The temperature T_0 has therefore been interpreted as a limiting value of Tg as cooling rates are made slower and slower. It has also been suggested that T_0 is a thermodynamic parameter at which an equilibrium glass transition would presumably occur if it were experimentally attainable[10]. These are very speculative suggestions however and to date no formalised theories have been developed, although the correlation between the calorimetric and the relaxational T_0s appears to be established[8,9,10].

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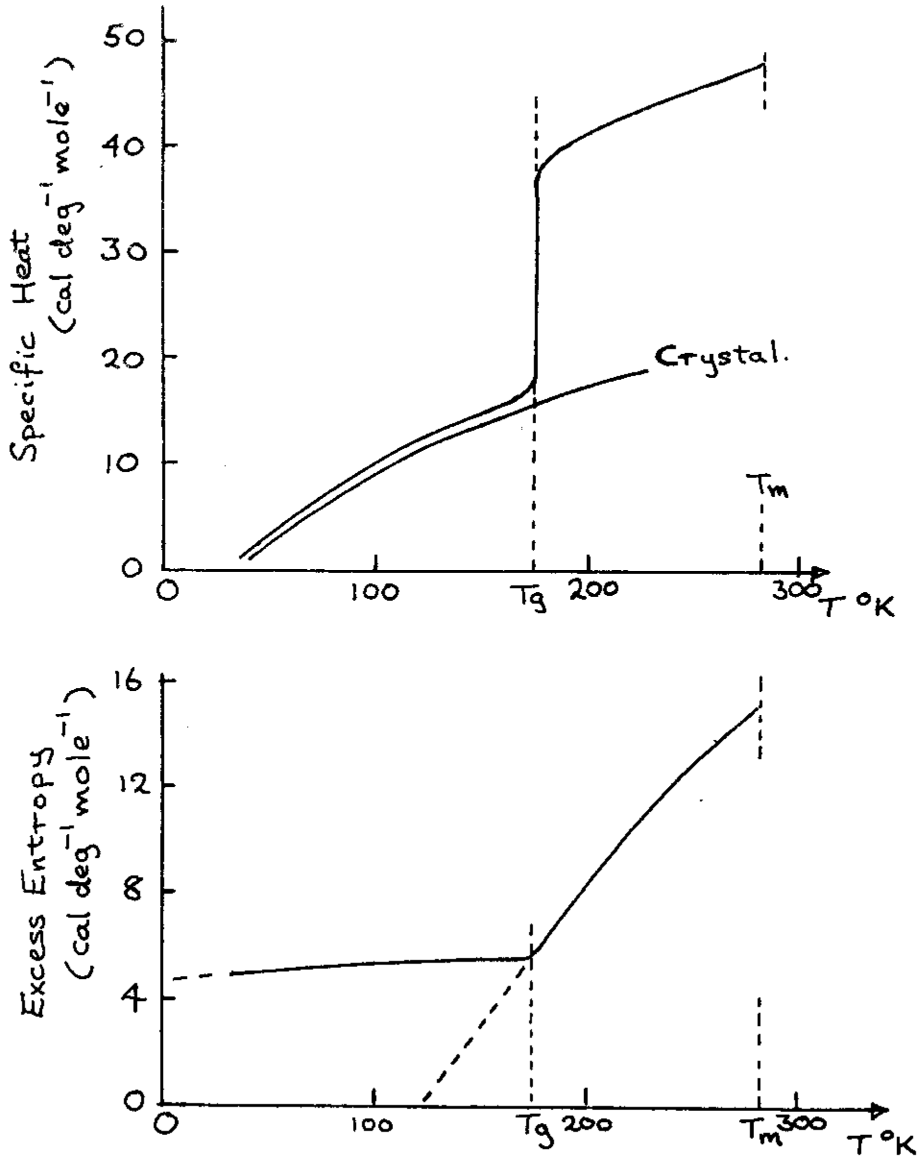

FIG. 1.

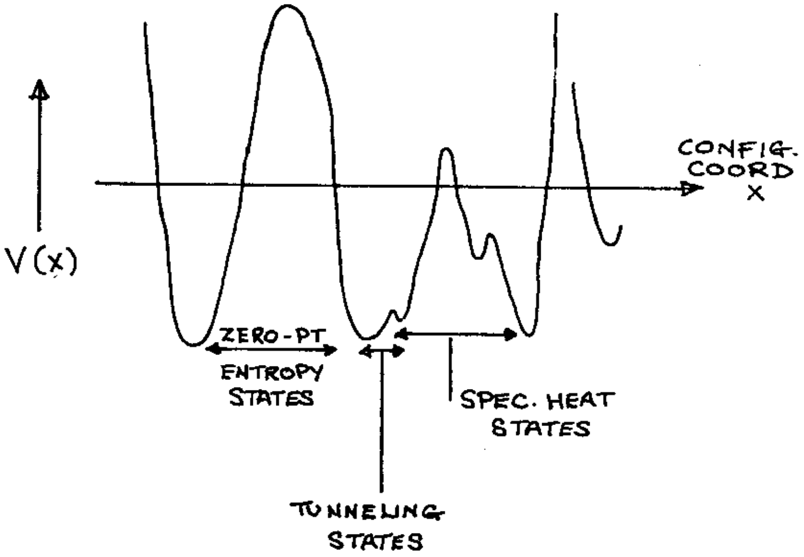

FIG. 2.

5. MODELS OF THE GLASS TRANSITION

5.1 Free Volume

Of various models of the glass transition, those based on the idea of "free volume" have featured most prominently. The first free-volume theories were proposed by Turnbull and Cohen[1,2,3] and they have been developed subsequently by others[4]. A particularly simple approach given by Gee is outlined here[5].

The total volume of a liquid is supposed divided into

(i) a part "occupied" by the molecules (or atoms), and

(ii) a part in which the molecules are free to move.

The contribution (ii) is termed "free volume" and it is assumed to be shared communally by a process in which "holes" of varying size and location are continually moving and being re-distributed. As the liquid is cooled, both occupied and free volumes contract. A glass is then distinguished from a liquid in two ways:

(1) In the glassy state free volume remains constant, independent of temperature.

(2) The re-distribution of free volume no longer occurs; the "holes" remain fixed in the positions they occupied when the glass was formed.

The glass-liquid relationship can then be expressed as follows:

Let α_l = expansion coefficient of the liquid (i.e. of occupied + free volume)

α_g = expansion coefficient of the glass (i.e. of occupied volume only)

$\alpha_l - \alpha_g = \Delta\alpha \equiv$ expansion coefficient of free volume.

The volume-temperature relationships are illustrated schematically in figure 1, and with the <u>total</u> volume V_g at Tg as a reference point, the free volume V_f at $T > T_g$ is given by

$$V_f = V_{fg} + V_g \Delta\alpha (T - Tg) \tag{1}$$

where V_{gf} is the free volume of the glass.

The same arguments can be applied to the effects of pressure and with

$$\Delta\kappa = \kappa_l - \kappa_g \text{ i.e. } \kappa_g \equiv \text{compressibility of occupied volume,}$$

the combined effects of T and P on the <u>free volume of the liquid</u> can be written -

$$V_f = V_{fg} + V_g[\Delta\alpha(T-Tg^o)-P\Delta\kappa] \qquad (2)$$

where Tg^o is the glass transition temperature at P = 0.

If Tg is associated with the temperature at which the free volume of the liquid tends to V_{fg} then it follows that

$$\frac{(Tg-Tg^o)}{P} = \frac{\Delta\kappa}{\Delta\alpha} \qquad (3)$$

Note that this is essentially the same result as equation (1) of lecture 4, i.e.

$$\frac{dTg}{dP} = \frac{\Delta\kappa}{\Delta\alpha}$$

Several arguments have been used to estimate V_{fg}. For example, if the volume obtained by extrapolating the liquid volume to T = 0°K is equated with the occupied volume at T = 0°K then, approximately -

$$V_{occ}(T=0) = V_g(1-\alpha_l Tg) \qquad (4)$$

The total volume of the glass at T = 0°K is

$$V_g(1-\alpha_g Tg)$$

$$\therefore V_{fg} = V_g(1-\alpha_g Tg)-V_g(1-\alpha_l Tg)$$

$$= V_g\Delta\alpha Tg$$

$$\text{i.e. } \frac{V_{fg}}{V_g} = Tg\Delta\alpha \qquad (5)$$

This has been measured for a number of glasses, particularly polymeric glasses, and experimentally TgΔα varies from about 0.08 to 0.13. i.e. AT Tg ~ 11% OF TOTAL VOLUME IS FREE VOLUME.

Note that free volume theories are basically thermodynamic models. The liquid glass transition occurs when an excess function of the liquid - free volume in this case - falls below some critical value and becomes constant (or zero) (see lecture 4, para. 4.2).

5.2 <u>Vibrational Models of the Glass Transition</u>

Glass formation is traditionally discussed by relating glass to its parent liquid phase and this is obviously a natural approach. There have also been attempts to relate the glass transition to vibrational characteristics of the solid. This is a 'solid-state' approach to the problem and it predicts a close correlation between the glass transformation temperature Tg and the Debye temperature <u>of the amorphous solid</u>[6]. It is rationalised on the basis that near θ_D phonon-phonon interactions become dominant and there is a high probability of cooperative phonon interactions generating sufficient local energy to allow 'molecules' to cross the energy barrier preventing their translational motions. The principal experimental evidence is that for a wide variety of glasses (e.g. Se, As_2S_3, As_2Se_3, Au - Ge - Si alloys, various silicates, $ZnCl_2$ etc.) the <u>molar</u> heat capacity approaches the limiting Dulong-Petit value 3nR at Tg[6,7]. Boric oxide (B_2O_3) is an exception; Cp is only ~ 2nR at Tg, indicating $\theta_D > Tg$.

A simpler rationalisation of the Tg ~ θ_D rule for network glasses is to consider the glass transition as a bond-breaking process[8]. For translational motion of nearest neighbours some critical energy E must be supplied to nearest neighbour bonds. The probability of attaining E is small until T reaches values where phonons of sufficient energy become available to cause the population of the higher vibrational levels of nearest neighbour bonds. But this is the temperature θ_D at which ν_D = (kT/h), where ν_D is presumably to be identified with the nearest-neighbour bond frequency[8]. The failure of boric oxide to follow the θ_D ~ Tg rule is explained[7] on the assumption that <u>intra-molecular</u> bonds between the two-dimensional sheets of BO_3 triangles are weak compared with the B-O bonds. In other words, a glass may have several characteristic temperatures associated with various types of bonds and Tg may correspond to the lowest, or one of the lower of these.

The basic premises for this approach are not well-established however, and Schnaus et al[8] point to a notable inconsistency. The two compounds As_2S_3 and As_2Se_3 have the same structure and their Tg's are nearly the same (445 - 462°K for As_2S_3 and 436 - 450°K for As_2Se_3). In both cases $C_p \rightarrow 3nR$ as $T \rightarrow Tg$, but from C_p - T curves Schnaus et al obtain

$$\theta_D = 450 \pm 50^{\circ}K \text{ for } As_2S_3$$

and

$$\theta_D = 350 \pm 50^{\circ}K \text{ for } As_2Se_3.$$

Thus, for As_2Se_3 θ_D is appreciably less than Tg. Schnaus et al also find that the ratio $[\theta_D(As_2S_3)/\theta_D(As_2Se_3)]$ is roughly equal to the ratio of the onset frequencies of As - S and As - Se vibrational bands in the infra-red, and also to the square root of the ratio of reduced masses for the two types of bond. The bond force constants are not, therefore, very different. As Schnaus et al point out, it is probably not surprising that there is no correlation between characteristic vibrational temperatures and the glass transition[8,9]. In this solid-state transition model the glass transition depends primarily on the depth of a potential well E which is related to the transition frequency by

$$\nu = \nu_0 \exp(-E/kT)$$

where ν is a bond vibrational frequency and will usually be 10^{12} - 10^{13} s^{-1}. At the glass transition ν is normally ~ 10^{-2} s^{-1} and is little affected by ν_0. On the other hand characteristic vibrational temperatures are related to ν_0 and this depends strongly on the shape of the potential energy curve near its minimum. The shape and depth of the potential energy well are not necessarily related and hence there is no reason to expect a strong correlation between θ_D and Tg.

5.3 Structural Models

A variety of structural models have been suggested, particularly making use of computer calculations of molecular dynamics[10]. Although not strictly a model of the glass transition, an interesting calculation of the configurational entropy of fused silica has been proposed by Bell and Dean[11]. They constructed a random network of SiO_2 by considering the number of ways in which an SiO_4 tetrahedron could be added to a growing surface. At typical surface sites the number of possibilities tends to be limited e.g. -

(a) because the Si-O-Si angles must be kept in a particular range

(b) one must ensure that further tetrahedra can be added at a later stage

and (c) in particular, the necessity of avoiding configurations which represent overlapping molecules severely restricts the number of possibilities.

On adding a single tetrahedron,

- if it bonds triply to the existing structure, there is one attitude
- if it bonds doubly to the existing structure, one or two attitudes are possible, and
- if it bonds singly to the existing structure, it would be unusual for there to be more than four possible attitudes.

At the most, therefore, the corresponding entropies are kln1, kln2 and kln4. The maximum entropies occur if it is assumed that all possible attitudes are equally likely. To achieve an isotropic network it is necessary to ensure that the number of free bonds per unit area of surface remains roughly constant and it is also assumed therefore that triple, double and single bonding situations occur with relative probabilities:

$(1-\varepsilon)$, $(1-\varepsilon)$ and $(\varepsilon/2)$ where ε is a constant such that $0 < \varepsilon < 1$.

$$\therefore \quad S_{config.} = R\left[\frac{\varepsilon}{2}\ln 1 + (1-\varepsilon)\ln 2 + \frac{\varepsilon}{2}\ln 4\right] \qquad (6)$$

$$= 1.38 \text{ cal.deg}^{-1}\text{mole}^{-1}$$

This result was obtained assuming 1,2 and 4 possible attitudes for triple, double and single bonding situations. These are upper limits and experience suggests that 1, (3/2) and (5/2) would be more realistic estimates.

$$S_{\text{config.}} = R\left[\frac{\varepsilon}{2}\ln 1+(1-\varepsilon)\ln\frac{3}{2} + \frac{\varepsilon}{2}\ln\frac{5}{2}\right] \qquad (7)$$

$$= 0.8 - 0.9 \text{ cal.deg}^{-1}\text{mole}^{-1} \text{ depending on the value of } \varepsilon.$$

Experimental values of the configurational entropy of fused silica are in the range 0.67 to 1.08 $\text{cal.deg}^{-1}\text{mole}^{-1}$.

5.4 Statistical Thermodynamics

Statistical thermodynamic treatments have been developed for polyermic glasses and the first such model was proposed by Gibbs and Di Marzio based on the definition of an equilibrium transition temperature T_o at which the configurational entropy is zero[12]. This temperature can be considered to be the limiting value of Tg as the cooling rate is made slower and slower (see lecture 4, para. 4.3 and figure 1). The configurational entropy S_{config}. is calculated by counting the number of ways in which n_x linear molecules, each x segments long, can be placed on a diamond lattice of coordination number $z = 4$, together with n_o holes. The restrictions imposed on the placing of a molecule on the lattice are incorporated in the hindered rotation which is expressed as the "flex energy" $\Delta\epsilon$, and ϵ_h which is the energy of formation of a hole. The flex energy is the energy difference between the potential energy minimum of the located bond and the potential minima of the remaining (z-2) possible orientations available on the lattice. For polyethylene for example, the *trans* position is considered the most stable and the *cis* positions are the flexed orientations with $\Delta\epsilon$ the energy between the ground (stable) and flexed states. The details vary with the nature of the polymer molecule. The quantity ϵ_h is a measure of the cohesive energy. The configurational entropy is derived from the partition function describing the location of polymer molecules and holes.

As the temperature drops towards T_o the number of available configurational states in the system decreases until at T_o the system possesses only one degree of freedom and this condition leads to[12]:

$$\frac{S_{\text{config.}}(T_o)}{n_x k\, T_o} = 0 = \phi\left(\frac{\epsilon_h}{kT_o}\right) + \lambda\left(\frac{\Delta\epsilon}{kT_o}\right)$$

$$+ \frac{1}{x}\ln\left[\{(z-2)x+2\}\frac{(z-1)}{2}\right] \qquad (8)$$

where $\phi\left(\frac{\epsilon_h}{kT_o}\right) = \ln\left(\frac{\epsilon_h}{S_o}\right)^{[(z/2)-1]} + \frac{f_o}{f_x}\ln\left(\frac{f_o}{S_o}\right)$

and

$$\lambda\left(\frac{\Delta\epsilon}{kT_o}\right) = \frac{x-3}{x}\ln\left[1 + (z-2)\exp(-\Delta\epsilon/kT)\right.$$

$$\left. + (\epsilon/kT)\frac{(z-2)\exp(-\Delta\epsilon/kT)}{1+(z-2)\exp(-\Delta\epsilon/kT)}\right]$$

The fractions of occupied and unoccupied sites are f_x and f_o respectively, and S_o is a function of f_x, f_o and z.

The weaknesses of the Gibbs and Di Marzio theory are

(a) a polymeric molecule of zero stiffness would have a Tg of 0^oK, and

(b) Tg is essentially independent of molecular interactions.

The temperature T_o is calculated to be about 50^oK below normally attainable Tgs and it is not of course an experimentally measurable quantity. In this theory T_o is regarded as a true thermodynamic (equilibrium) second order transition temperature and it is essentially the same T_o as discussed in lecture 4 (para. 4.3).

5.5 References

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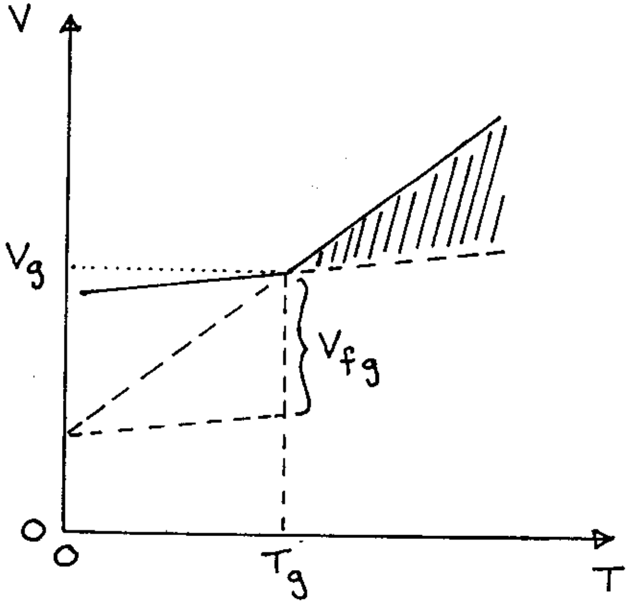

FIG. 1