THE NATURE OF THE GLASSY STATE AND THE BEHAVIOR OF LIQUIDS AT LOW TEMPERATURES

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When the temperature of a supercooled liquid is brought below approximately two-thirds of the normal freezing point, a rather sudden drop in the specific heat and the thermal expansion coefficient is observed. It is widely agreed that this "glass transformation" is caused by a relaxation effect, through which some process in the amorphous material occurs too slowly at low temperatures to permit thermodynamic equilibrium to be established in all degrees of freedom. It is shown that the molecular movements involved in the relaxation process must resemble closely the movements in viscous flow and dielectric relaxation. Movements of this type permit the liquid structure to change following temperature and pressure changes. Thus it is the contribution of changing liquid structure to the thermodynamic properties which is absent at low temperatures and results in the drop in specific heat and coefficient of expansion.

Accordingly vitrification can always be avoided in principle by making measurements sufficiently slowly. With a view to understanding the "true" thermodynamics of supercooled liquids as observed in such slow experiments the trends in the observed thermodynamic properties of liquids above the glass-transformation temperature are examined. These trends seem to indicate that the entropies and enthalpies, but not the free energies, of many non-vitreous liquids would become less than those of the corresponding crystalline phases at temperatures well above the absolute zero. This paradoxical result would seem to imply that there is a temperature below which a non-vitreous liquid cannot exist, owing to spontaneous crystallization. There are good theoretical reasons for believing in the existence of such a "pseudocritical temperature."

I. INTRODUCTORY SUMMARY

A. The concept of metastability

As is well known, some liquids can be held at temperatures well below their freezing points over very long periods without crystallizing. Liquids in such a state are said to be *supercooled.*

In order to describe this behavior, Ostwald (62) introduced the concept of the *metastable state.* A mechanical system was said to be in a metastable condition if all small displacements of the particles of which it was composed resulted in an increase in the potential energy of the system, while certain large displacements could bring about a decrease in the potential energy. The classic example of this, cited by him, was a marble in a bowl held at some distance above a table. By analogy (and with slight modification of Ostwald's language) we may say that a thermodynamic system at a specified temperature is in a metastable condition or state if all small isothermal changes of its independent thermodynamic variables result in an increase in its free energy, while certain large isothermal changes in these variables can bring about a state with lower free energy. In this sense, then, the supercooled liquid is believed to be in a metastable state with respect to its crystalline phase.

The idea of metastability, by definition, requires that there be states of higher free energy than the metastable state along all possible routes between the metastable and stable states of a thermodynamic system. These intermediate states may be said to give rise to *free energy barriers* impeding the transformation of the metastable into the stable state. A supercooled liquid, in crystallizing, must go through intermediate states having higher free energies than either the liquid or the crystal. Spontaneous crystallization is then interpreted as the result of random accumulations (by thermal fluctuations) of sufficient free energy for the liquid to pass over these barriers.

Conversely, we may say that whenever a free energy barrier exists between two states of a system, we should expect, at least in principle, to be able to distinguish metastable states of that system. The feasibility of studying such metastable states experimentally depends, however, upon two factors: (*a*) the possibility of bringing the system into the metastable state in question, and (*b*) the possibility of keeping the system in that metastable state long enough to make the necessary observations. With supercooled liquids the first factor never presents any difficulty but the second frequently does: most liquids crystallize spontaneously below their freezing points long before we have a chance to measure any of their properties. On the other hand, numerous metastable states of condensed phases and other systems are conceivable (e.g., a hexagonal closepacked sodium chloride crystal, or a wurtzite form of carbon) but cannot be studied experimentally because we do not know how to prepare them, even though it seems likely that, once prepared, they would probably not readily revert back to the more stable forms. The problem of manufacturing diamonds is, of course, entirely of this nature, as are most of the problems of synthetic inorganic and organic chemistry.

Eyring has shown that many physical processes in condensed phases involve passages over free energy barriers. Among these processes are plastic flow, molecular diffusion, and dielectric relaxation. According to the arguments presented above, therefore, we must expect metastable states to occur supported by the free energy barriers involved in these processes. We shall see in this paper that the glassy or vitreous state of liquids is such a metastable state.

B. The nature of the metastability of supercooled liquids

The work of Tammann and others (23, 92, 102) has shown that the crystallization process occurs in two steps: first crystal nuclei must form, and then these nuclei must grow. Depending on the temperature and the substance, either of these two steps may determine the rate of spontaneous crystallization. Therefore, at least two types of free energy barrier may be involved in the metastability of the supercooled liquid. These two types of barrier are believed to be determined as follows: (*1*) The free energy barrier to crystal nucleus formation arises essentially because the melting point of small crystals is lower than that of large ones (see Appendix A). Thus, in any supercooled liquid, crystals smaller than a certain size are unstable, so that in order to form a stable nucleus one must first form crystallites having higher free energies than the same amount of liquid. (*2*) The free energy barrier to crystal growth, on the other hand, is simply that which prevents the movement of a molecule at a crystal–liquid interface from a liquid-like position to a crystal-like position. For temperatures sufficiently below the freezing point, Richards (75) has shown that the molecular movement in crystal growth is essentially a molecular rotation very closely similar to that involved in the orientation of dipoles in an electric field, so that the free energy barrier to crystal growth must be similar to that which gives rise to dielectric relaxation in dipolar liquids.

The practical limitations of the concept of a supercooled liquid as a metastable state are clear: we can study the properties of such a liquid experimentally as long as the necessary measurements can be made rapidly compared with the time required for the liquid to crystallize spontaneously.

The theoretical interpretation of experimental results obtained in this way would appear to be quite simple in principle. One sets up the phase space for the system in question. Certain regions of this phase space will correspond to regular geometrical arrangements of the molecules of the system. Such regions must be assigned to the various possible crystalline forms of the system. Let the volume of phase space enclosing these regions be labelled V_{cryst}. Other regions, much more extensive and of higher energy, will presumably be found which should correspond to the liquid form of the system. Call the volume included in these regions V_{liq}. Then it should be possible to derive the properties of both the supercooled and the normal liquid from the phase integral, or partition function (23, 52)

$$Q_{\text{liq}} = \frac{1}{N!h^{3N}} \int_{V_{\text{liq}}} \cdots \int e^{-H(p_1,\cdots,q_{3N})/kT}\, dp_1 \cdots dq_{3N}$$

$H(p_1, \cdots, q_{3N})$ being the energy at the point $p_1, \cdots, q_{3N}$ in phase space, and the integration being performed only over the volume V_{liq} "defined" above. Similarly, the properties of the crystalline phases may be calculated from

$$Q_{\text{cryst}} = \frac{1}{N!h^{3N}} \int_{V_{\text{cryst}}} \cdots \int e^{-H(p_1,\cdots,q_{3N})/kT} dp_1 \cdots dq_{3N}$$

where the integration is this time over the volume V_{cryst} of phase space.

If this procedure is applied either to the normal liquid above its freezing point (where $Q_{\text{liq}} \gg Q_{\text{cryst}}$) or to the crystal below its melting point (where $Q_{\text{cryst}} \gg Q_{\text{liq}}$), no difficulty should be encountered in specifying V_{liq} or V_{cryst}. In fact, in either case the integration could be carried out over the *entire* volume of phase space and we would expect to arrive at the same answer for all practical purposes. For we know that (except possibly at temperatures immediately above and below the melting points of some substances for which "premelting" and "prefreezing" phenomena have been claimed to occur) the inequalities of Q_{liq} and Q_{cryst} must be overwhelmingly one-sided.[1]

On the other hand, when applying this procedure to the supercooled liquid (for which $Q_{\text{liq}} \ll Q_{\text{cryst}}$), the correct identification of V_{liq} is of the greatest importance and may be quite difficult. We must be very careful to exclude all parts of V_{cryst} from V_{liq}, for even a tiny portion of V_{cryst} might contribute much more to Q_{liq} than the entire integral over the correct V_{liq}. Generally it should not be difficult to avoid such an error, for the crystalline regions of phase space are undoubtedly very easily detected by virtue of their great geometrical regularity. On the other hand, we can expect to encounter regions of phase space which are not obviously either crystalline or liquid-like. We may hope that such regions (which we shall refer to as "ambiguous" regions) either have very high energies, $H(p_1, \cdots, q_{3N})$, and hence very small values of $e^{-H/kT}$, or else have a relatively small extent in phase space; in either instance they should make a negligible contribution to the value of Q_{liq}. The regions of phase space corresponding to states near the tops of the free energy barriers which impede the

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[1] The probability that a sample of ice will turn spontaneously into liquid water is $Q_{\text{liq}}/(Q_{\text{liq}} + Q_{\text{cryst}})$. Now

$$kT \log_e Q_{\text{liq}}/Q_{\text{cryst}} = F_{\text{cryst}} - F_{\text{liq}} \cong (\Delta H_m/T_m)\Delta T$$

where the F's are the free energies of the two forms of the sample, ΔH_m and T_m are the heat of fusion and normal melting temperature, and ΔT is the difference between the temperature of the sample and its normal melting point. For a 1-g. sample of ice at −1°C. it is found that

$$Q_{\text{liq}}/Q_{\text{cryst}} = 10^{-10^{20}}$$

formation of crystal nuclei will, for instance, be in this "ambiguous" region between V_{liq} and V_{cryst}.

In this paper we shall review and interpret the properties of supercooled liquids from this point of view. First we shall consider the rather peculiar "transition" to a "glassy" or "vitreous" state which all such liquids probably pass through when cooled sufficiently. Evidence will be presented to show that, as many workers have suggested, this "transition" is really a relaxation phenomenon arising from the slowness with which molecules change their positions below a certain temperature. As a result of this sluggishness of molecular motion, the liquid is unable to change its structure appreciably during the time required to measure various common liquid properties such as the specific heat, density, and compressibility. Now, a sizeable contribution to many of these properties should arise from the change in the structure of the liquid following a change in temperature or pressure. This contribution of changing liquid structure is, therefore, absent in glasses, and the phenomenon of glass formation provides us with a means of evaluating the contribution of liquid structure changes to the properties of the liquid. A survey of the pertinent data reveals that for many properties these contributions are considerable if not predominant in liquids at low temperatures.

Thus, in the glassy or vitreous state the liquid exhibits a new, more limited kind of metastability as compared with that of the normal supercooled liquid. The energy barriers supporting this metastability are those impeding changes in the positions of molecules in the liquid, and the phase integral of the glass is to be carried out over a volume of phase space, V_{glass}, which not only excludes crystalline configurations but also suppresses many configurations of the liquid which would otherwise become important at lower temperatures. The regions to be included in V_{glass} are even more difficult to specify than those in V_{liq}; in general, they will depend on the temperature at which the glass was formed—which, in turn, depends on the rate at which the liquid was cooled when it vitrified.

In the second part of the paper we shall ask how a liquid would be expected to behave at very low temperatures if experimental measurements were made sufficiently slowly to avoid glass formation—that is, slowly enough to permit the liquid structure always to be in thermodynamic equilibrium with the surroundings (but, of course, not so slowly as to permit spontaneous crystallization). It is reasonable to expect a clue to this behavior from a simple extrapolation to low temperatures of the known properties of supercooled liquids above their glass-transformation temperatures. When such an extrapolation is applied to the observed entropy *vs.* temperature curves of several substances (most strikingly with glucose and lactic acid), a rather startling result is obtained. Not very far below the glass-transformation temperature, but still far above 0°K., the extrapolated entropy of the liquid becomes less than that of the crystalline solid (see figure 4). The extrapolated heat content *vs.* temperature and specific volume *vs.* temperature curves show similar tendencies (see figures 3 and 6): the liquid appears to strive for a lower heat content and a smaller specific volume than the crystal at temperatures well above 0°K.

This peculiar result can only mean that somehow the above "reasonable" extrapolation is not permissible. The following resolution of the paradox is proposed: There is reason to believe that as the temperature is lowered the "ambiguous" regions of phase space intermediate between the definitely crystalline and definitely liquid regions begin to be able to contribute significantly to the partition function of the liquid. This means that the free energy barriers between the liquid and the crystal tend to become relatively small at low temperatures. In particular, the barrier to crystal nucleus formation, which tends to be very large just below the melting point, may at low temperatures be reduced to approximately the same height as the free energy barriers which impede molecular reorientations in the liquid and which have been shown to be responsible for glass formation. Under these circumstances crystal nuclei will form and grow at about the same rate as the liquid changes its structure following a change in temperature or pressure. In other words, the time required for the liquid to crystallize becomes of the same order as the time required for it to change its structure following some change in its surroundings. If, then, measurements are to be made on such a liquid before it has had a chance to crystallize, these measurements must also be made before the liquid can bring its structure into equilibrium with its surroundings. But this means, as we have seen, that the liquid will behave as a glass. Thus, as the temperature of a liquid is lowered one is ultimately forced to study it as a glass if one wishes to study it as a liquid at all. A non-vitreous stable liquid cannot exist below a certain temperature, and it is operationally meaningless to extrapolate the entropy, energy, and specific volume curves below that temperature, as we tried to do with such peculiar results.

In order to illustrate these general ideas a simple theory of liquid structure suggested by Mott and Gurney is reviewed. It is shown how, in terms of that theory, one obtains a "pseudocritical point" of the postulated kind between the crystalline and liquid states at low temperatures. The possibility of the existence of such a "pseudocritical point" should furnish an interesting test of the adequacy of any proposed general theory of the liquid state. Many current theories of liquids do not provide for this possibility.

II. THE GLASS TRANSFORMATION

A. Characteristics of the glass transformation

Crystalline glucose melts at 141°C. to an easily supercooled liquid phase whose thermodynamic properties at lower temperatures show an interesting behavior (see figure 1). As the liquid is cooled below room temperature its coefficient of thermal expansion drops rather abruptly by more than a factor of 3 and its specific heat decreases by nearly a factor of 2. These changes occur within a temperature range of about 20°C. The heat content and the specific volume, however, show no analogous abrupt changes; the "transition"—if we wish to call it that—involves no latent heat or volume change.

In table 1 are listed some typical materials which in the supercooled liquid or amorphous form show a similar behavior. Indeed, all supercooled liquids whose

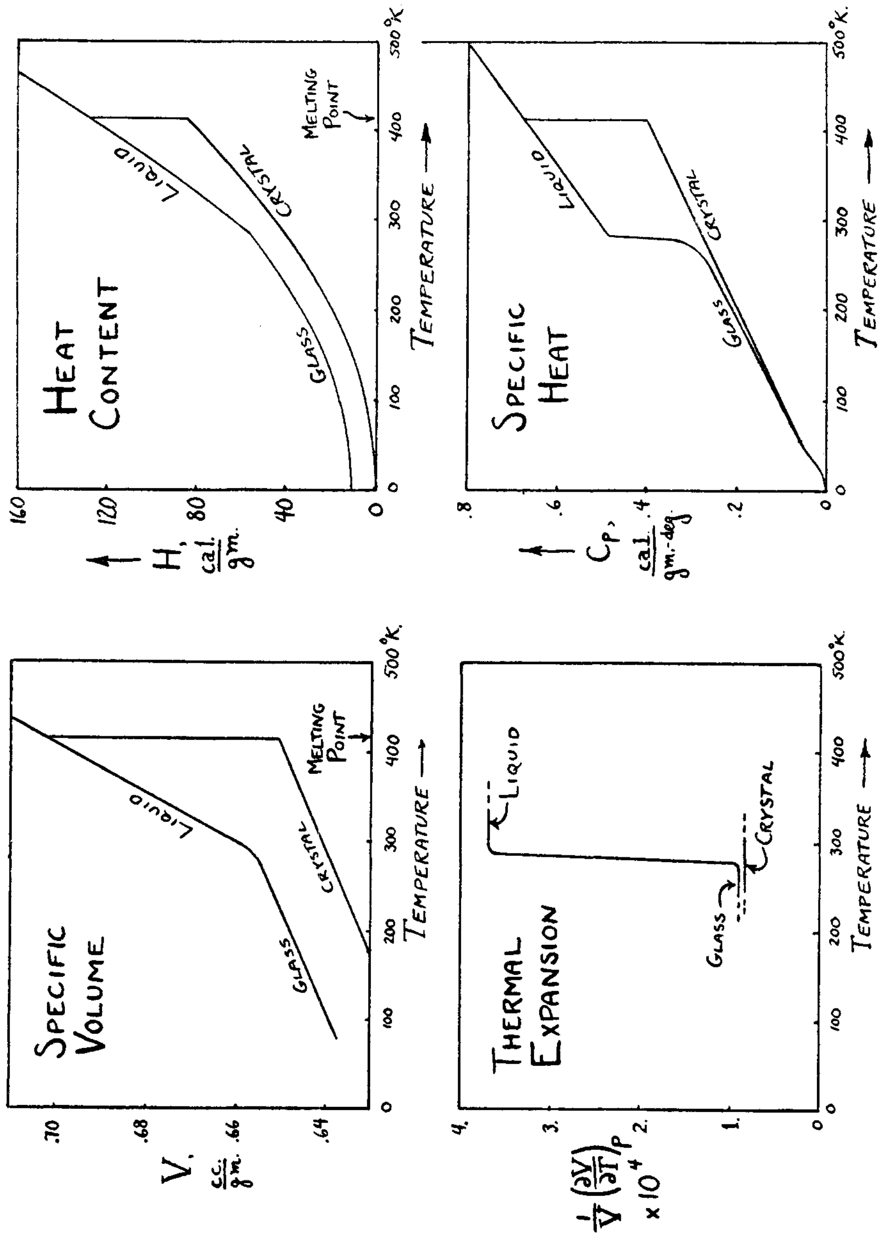

Fig. 1. Thermodynamic properties of glucose. Data from references 61, 67, 69 and 84.

thermal expansions or specific heats have been investigated in the appropriate temperature range seem to undergo a "transition" of this type, as do also practically all other amorphous materials for which no crystalline phase is known. That the occurrence of such a "transition" does not depend upon any very special chemical properties of the liquid is shown by the wide chemical diversity with which it may be associated. In table 1 we find hydrocarbons, strongly hydrogen-bonded liquids, a hydrated ionic compound, linear high polymers, and three-dimensional valence-bonded networks. Thus this behavior is probably a general property of the liquid or non-crystalline state of matter, and we may presume that it would be found for all liquids below their freezing points if the means were at hand to prevent their spontaneous crystallization during the necessary experimental measurements.

TABLE 1

Properties of liquids and glasses at their glass-transformation points

SUBSTANCE	T_g	SPECIFIC HEAT		COEFFICIENT OF EXPANSION × 10^4 (PER °C.)		REFERENCES
		Liquid	Glass	Liquid	Glass	
	°K.	*cal./gram*	*cal./gram*			
3-Methylhexane	80–90	0.397	0.17			(70)
2,3-Dimethylpentane	80–85	0.377	0.20			(70)
Ethanol	90–96	0.417	0.27			(31, 39, 63, 65, 166
1-Propanol	86–100	0.425	0.23			(65, 66)
sec-Butyl alcohol	100–115	0.397	0.20			(1, 70)
Propylene glycol	150–165	0.464	0.25	(6.2)	(2.0)	(65, 66)
Glycerol	180–190	0.456	0.25	4.83	2.4	(27, 65, 66, 79, 84)
d,l-Lactic acid	195–206	0.500	0.26			(70)
$Na_2S_2O_3 \cdot 5H_2O$	231			3.62	2.10	(79)
Sucrose	340			5.02	2.54	(79)
Glucose	280–300	0.51	0.33	3.7	0.90	(61, 67, 69, 84)
Boron trioxide	470–530	0.436	0.30	6.1	0.5	(79, 87, 88, 100)
Silicon dioxide	1500–2000	0.35?	0.30			(103)
Selenium	302–308	0.125	0.080	4.2 1.11	1.7 0.43	(55, 94, 96, 98)
Sulfur	244					(55)
Polyisobutylene	190–200	0.36	0.27	6.0	(0.5)	(19)
Rubber	200	0.39	0.27	6.0	2.0	(5, 6, 77, 81, 104)
Hycar-OR synthetic rubber	245–250	0.44	0.31			(7)
Polystyrene	353–363	0.44	0.30	5.9 4.5	2.1 2.7–2.8	(14, 71, 89)
Colophony	300	0.40	0.27	7.43 5.71 6.1	2.57 3.62 3.8	(79, 94, 96, 98)

The only crystalline substance for which a "transition" of this type has been observed seems to be one of the crystalline forms of cyclohexanol (40).

A non-crystalline material below the temperature at which such a "transition" takes place is said to be in the *glassy* or *vitreous state*. The material in that state is called a *glass*, and the temperature of the change is called the *glass-transformation point*. This temperature is frequently denoted by T_g. There is actually no sharply defined glass-transformation temperature, but rather a range of temperatures over which these changes occur; it would probably be better to use the term "glass-transformation interval." Ordinary window glass is the most common example of this state, but many other common materials, particularly among the natural and synthetic resins, are also normally used as glasses.

It is found that the values of the specific heat and coefficient of expansion of a glass are much closer to those of the crystalline form of the substance (where this is known) than to those of the parent liquid. This is well-illustrated by the data for glucose shown in figure 1. On the other hand, the structure of silicate glasses as revealed by x-ray diffraction studies (13, 74) is closely similar to typical liquid structures. Furthermore, the heat content and specific volume of the glass are continuous with the heat content and specific volume of the liquid. Apparently, then, the glassy state is a form of matter which maintains the structure, energy, and volume of a liquid, but for which the *changes* in energy and volume with temperature are similar in magnitude to those of a crystalline solid. That is, a glass is a liquid in which certain degrees of freedom characteristic of liquids are "frozen in" and can no longer contribute to the specific heat and thermal expansion. The problem presented to us by the glassy state is simply to determine what these degrees of freedom are and to explain how they are frozen in at the glass-transformation point, T_g.

B. Equilibrium and dynamic mechanisms in the glass transformation

This freezing-in of the liquid degrees of freedom in glass formation might be caused by either of two entirely different mechanisms. These are best explained by means of examples.

Equilibrium or *thermodynamic freezing-in* of a degree of freedom in some temperature range may be illustrated by the decrease in the specific heat of hydrogen gas between 300°K. and 50°K. owing to the disappearance of the contribution of the rotational degrees of freedom of the hydrogen molecule. Another illustration might be the well-known transition in ammonium chloride crystals at about 245°K., in which the rotation of the ammonium ion is believed to cease below the transition temperature (72). Here, however, the rotational degrees of freedom are presumably replaced by vibrational degrees of freedom, so that the specific heat below the transition region is not markedly lower than that at higher temperatures.

Dynamic or *relaxation freezing-in* of a degree of freedom may be illustrated by the behavior with decreasing temperature of the dielectric constant of a dipolar liquid (e.g., glycerol) as measured by an oscillating electric field of some specified frequency. The rotational degrees of freedom of the dipoles make their maximum contribution to the dielectric constant only if the dipoles are able to change their positions more rapidly than the oscillating field changes its direction. As the temperature is lowered, however, the rate of change of position of the dipoles rapidly decreases because of the increasing viscosity of the liquid. Ultimately a range of temperatures is reached in which the rotation rate becomes equal to and then much slower than the frequency of the applied field. Over this temperature range the dielectric constant loses the contribution of the rotational degrees of freedom of the dipoles, finally assuming its "optical" value at low temperatures.

Another example of relaxation freezing of degrees of freedom is in the measurement of the specific heats of gases by determination of the velocity of sound in the gas. If sound waves of too high a frequency are employed, certain of the vibrational degrees of freedom of the gas molecules may not have sufficient time to come into equilibrium with the fluctuating temperatures in the sound wave. They will then not be able to contribute to the effective specific heat, which will therefore seem to have a lower value than that found with slower methods of measurement.

These two mechanisms are fundamentally distinct. The thermodynamic mechanism arises from a structural change in the system or from the quantum-mechanical discreteness of its energy levels; it is an equilibrium phenomenon. The relaxation mechanism, on the other hand, is a consequence of a deficiency in the experimental procedure: it results from changing the external forces acting on a system and then making measurements before the system has had time to reëstablish complete thermodynamic equilibrium with its changed surroundings.

Experimentally we can in principle distinguish between the two mechanisms very simply: If some degree of freedom seems not to be contributing to a property of a system when a certain time is allowed for equilibrium to be reached, we merely prolong the equilibration time more and more and seek the limiting value of the property as the equilibration is extended for an indefinitely long time. If this limiting value is less than that expected from the full participation of all of the degrees of freedom of the system, then the thermodynamic mechanism must be operating. Otherwise we are dealing with a relaxation effect.

Such tests have been applied to a number of the substances listed in table 1. The results seem to indicate that glass formation is a relaxation effect, a view which is now widely held and which we shall assume to be correct (see Simon (85), Littleton (50), Richards (75), Jenckel (33), Morey (56), Kuhn (45), Ueberreitter (101), Alfrey, Goldfinger, and Mark (2), Simha (83), and Spencer and Boyer (89)). It must be admitted, however, that because of the enormous temperature coefficient of the relaxation rate leading to glass formation, the test is not always or even usually easy to apply unequivocally, so that, strictly speaking, there is a remote possibility that some of the substances listed in table 1 may really show a thermodynamic transition into a glass-like state.

It has been pointed out, especially by Boyer and Spencer (11) (see also Gee (25)), that the glass transformation has more or less the characteristics specified by Ehrenfest for a second-order transition. That is, the two "phases" involved differ in the second derivatives of the free energy, F, with respect to temperature and pressure, but not in the free energies themselves or in their first derivatives.

Thus the volume $V = (\partial F/\partial p)_T$ is unchanged in the transition but the coefficient of expansion

$$\alpha = \frac{1}{V}(\partial V/\partial T)_p = \frac{1}{V}(\partial^2 F/\partial p\,\partial T)$$

does undergo a rather sudden change; similarly the enthalpy

$$H = F - T(\partial F/\partial T)_p$$

is unchanged but the heat capacity

$$C_p = (\partial H/\partial T)_p = -T(\partial^2 F/\partial T^2)_p$$

undergoes a rather sudden change. Since, however, these considerations apply only to systems in thermodynamic equilibrium, it does not seem desirable to refer to the glass transformation as a second-order transition, unless it is intended to imply that a thermodynamic mechanism for the freezing-in of degrees of freedom is involved in the sense discussed above.

Similarly it might be desirable to restrict the term "glassy or vitreous transformation" to those changes in liquids in which relaxation effects are predominant. Thus we may define a glass as an amorphous or non-crystalline material in which certain internal degrees of freedom characteristic of the liquid state have not had time to come into thermodynamic equilibrium with their surroundings. The glass-transformation temperature, T_g, could then be "defined" in a very general way as the temperature below which the relaxation time for some degree of freedom is long compared with the duration of an experiment. Obviously, according to this "definition" the value of T_g might depend in an essential way on *(1)* the property or properties studied in the experiment, *(2)* the duration of the experiment, and *(3)* what we mean by a long time. With regard to the first of these factors, it is clear that we have *a priori* no reason to expect that, for instance, the relaxation rates of a liquid will be exactly the same for thermal expansion as for dielectric polarization or mechanical deformation. Surely the detailed molecular processes resulting in an increase in the volume of a liquid following an increase in its temperature are not quite, if at all, the same as those occurring on application of an electric field or a mechanical force. Therefore, we may expect the relaxation rates, and hence the value of T_g, to depend on the property being measured.

We see that any attempt at a precise definition of T_g requires the entirely arbitrary specification of conditions which are never mentioned or even implied in the definition of, say, a thermodynamic melting point. It does not seem desirable to attempt such a precise definition of T_g. Instead, we shall proceed to define it on more convenient though admittedly somewhat arbitrary lines.

We have seen that it is both convenient and customary to detect the occurrence of a glass transformation by means of specific heat and thermal expansion measurements. Therefore it is natural to define the glass-transformation temperature in terms of these two properties alone. Furthermore, the conventional measurements of specific heats and coefficients of thermal expansion generally allow times of the order of several minutes to 1 hr. for equilibrium to be established. Thus in a more limited but more convenient and conventional sense we may define the glass-transformation point of a liquid as *that temperature at which the specific heat or the thermal expansion coefficient of the liquid shows a more or less sudden change due to relaxation effects in experiments allowing something like 10 min. to 1 hr. for equilibrium to be reached.*

C. Identification of the molecular motions involved in the glass-relaxation process

Insofar as we are justified in regarding glass formation as a relaxation process, the problem of the nature of the glassy state may be stated in the form of two questions: (*1*) What are the molecular movements which are so slow in glasses? (*2*) How do these motions contribute to the specific heat, thermal expansion, and other properties which differ in glasses and liquids?

The key to the answer to the first of these questions is to be found in the four following facts: (*a*) T_g as determined by specific heat measurements is always very nearly the same as T_g from coefficients of expansion. (*b*) The temperature coefficient of the relaxation rate in glass formation is very large. (*c*) At T_g the relaxation time for dielectric polarization is of the order of several minutes to an hour. (*d*) Liquids at their T_g have viscosities of about 10^{13} poises.

(*a*) *The near identity of the* T_g*'s from specific heats and expansion coefficients* is illustrated by the data for glucose shown in figure 1 and is implied in the manner of presentation of the data of table 1. This fact is significant even though it may not be too surprising, since there is no reason in principle why the relaxation rates for changes in heat content and volume should be related. *Apparently the molecular motions involved in the readjustment of the liquid energy and of the liquid volume following a change in temperature are closely similar.*

(*b*) *The rapid change in the relaxation rate with temperature* is illustrated by some results of Jenckel (33), who found that the half-time for the equilibration of the density of amorphous selenium following a change in the temperature varies from 5 min. at 35°C. to 130 min. at 30°C. Spencer and Boyer (89) have made a similar study on polystyrene and found half-times to vary from 25 min. at 90°C. to 13.6 hr. at 30°C.

Indeed, the strong dependence of the relaxation rate on the temperature is the cause of the apparent abruptness in the change in the specific heat and coefficient of expansion around T_g which has led some workers to believe that the glass transformation is thermodynamic in nature. The range of temperatures over which these changes occur is determined by the difference between the temperature at which the relaxation process just becomes noticeable during a measurement and the temperature at which this relaxation becomes negligible in the same time. Let us assume that the change in any property, P, with time, t, following some change in external conditions obeys a unimolecular law, $P_e - P = \Delta P \exp(-kt)$, where P_e is the final equilibrium value of P, k is a rate constant, and ΔP is a constant. (As will be discussed further below, the observed glass relaxation usually does not follow such a unimolecular law very well.) If we more or less arbitrarily say that the relaxation process is negligible at the end of a time t at temperature T_1 when $(P_e - P)/\Delta P = 0.9$ (corresponding to $k_1t = 0.105$), and is essentially completed in the same time at another, higher temperature T_2 when $(P_e - P)/\Delta P = 0.1$ (corresponding to $k_2t = 2.30$), then $k_2/k_1 = 21.9$. That is, between T_1 and T_2 the relaxation rates change by something of the order of twentyfold. For glycerol this change requires a temperature interval of about 10°C.

It is clear that the relaxation rate undoubtedly depends exponentially on the temperature. Therefore, by well-known arguments we may conclude that *the relaxation process involves the passage of the relaxing unit over a potential energy barrier very considerably higher than the mean thermal energy.*

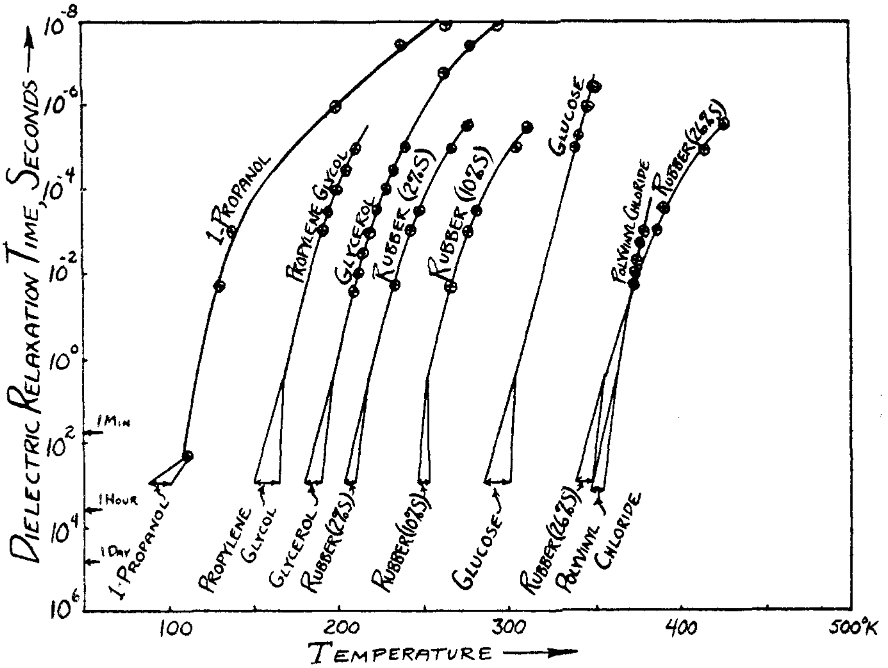

FIG. 2. Relationship between dielectric relaxation times and glass-transformation temperatures. Horizontal arrows indicate the range of the observed T_g. Data from table 2 and reference 36.

(c) The close relationship between dielectric relaxation and the glass transformation is indicated in figure 2, where the temperature dependence of the dielectric relaxation times of a number of glass-forming liquids is shown, along with an indication of the temperature range in which the glass transformation is observed to take place. In all examples except possibly 1-propanol a reasonable extrapolation yields dielectric relaxation times of the order of a few minutes to an hour at the glass-transformation point. This result means that *the relaxation process leading to glass formation involves molecular motions closely related to those performed by dipoles (and by inference then also by any molecules) when they jump from one equilibrium orientation to another owing to thermal agitation.*

(*d*) It has been widely noticed that *liquids at the glass-transformation point have viscosities near* 10^{13} *poises* (19a, 32, 64, 68, 78, 95). The significance of this fact becomes clear when considered from the point of view of Eyring's theory of viscous flow (18). According to this theory the viscosity, η, of a liquid whose flow is Newtonian can be given in terms of the rate, k_0, at which its molecules jump from one equilibrium "lattice position" in the liquid to another by

$$\frac{1}{\eta} = \frac{\lambda^2 A}{lkT} k_0$$

where k is Boltzmann's constant, T is the absolute temperature, λ and l are lengths of the order of molecular dimensions, and A is of the order of such dimensions squared, so that $\lambda^2 A/l \cong V/N$, where V is the mole volume and N is Avogadro's number. Thus we can obtain an approximate expression for the molecular jump rate k_0 in terms of the viscosity:

$$k_0 \cong RT/V\eta$$

If V is 30 cc., T is 300°K., and η is 10^{13} poises, k_0 turns out to be about one jump every 3 hr., which, considering the approximations we have made, is about the same as the expected relaxation rate at T_g.[2]

Evidently the relaxation processes in glass formation have close similarity to the molecular processes in viscous flow. Furthermore, in the light of Eyring's theory of viscosity, these processes probably involve jumps of molecular units of flow between different positions of equilibrium in the liquid's quasicrystalline lattice.

From these four facts we must conclude that the relaxation processes in glass formation are of a rather general type. Their similarity to the molecular processes in dielectric relaxation and viscous flow is particularly interesting, since a good deal of information is available concerning the mechanisms of these proc-

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[2] We may also in this connection make use of Einstein's theory of rotational Brownian motions (17), according to which the mean time required for a molecule to change its orientation by an angle of θ radians is

$$\tau_\theta \approx \frac{\theta^2}{2} \cdot \frac{4\pi\eta r^3}{kT}$$

where r is the radius of the molecule (assumed to be spherical) and η is the viscosity of the surrounding medium (assumed to be the macroscopically observed viscosity). If we write $V/N = 4\pi r^3/3$ = molecular volume as before, we find

$$\tau_\theta \approx \frac{3\theta^2 V\eta}{2RT}$$

or for the rate of relaxation

$$k_\theta \approx \frac{2}{3\theta^2} \frac{RT}{V\eta}$$

Except for the factor $2/3\theta^2$ this is similar to the result from Eyring's theory. Presumably a rotation of a molecule by about one radian is, according to the Einstein theory, about as frequent an occurrence as a jump by a molecule from one equilibrium position to another in the liquid according to the Eyring theory.

esses. It would appear that, particularly in liquids far below their boiling points, there exists a considerable amount of short-range quasicrystalline order. Because of this the positions and relative orientations of neighboring molecules are rather rigidly fixed, so that a change in the position of any one molecule requires simultaneous relatively drastic changes in the positions of all of its neighbors. As a result, molecular motions of any kind in such liquids lead to a considerable temporary local disruption of the liquid structure. This accounts for the very large positive entropies of activation which are observed for viscous flow and dielectric relaxation in many amorphous substances at low temperatures (36). It also accounts for the following rather remarkable fact.

A number of very different kinds of molecular motions may occur in liquids: Molecules may rotate about some axis as in dielectric relaxation, they may move to new lattice sites as in diffusion, and they may move past one another in local shearing motions as in viscous flow. These movements are quite dissimilar, and yet they all seem to occur at about the same frequency. We can account for this by supposing that in order for *any* kind of molecular movement to occur in a liquid, a definite amount of temporary disruption of the liquid structure must occur in the neighborhood of the moving molecules. Once this disruption has occurred, one kind of movement is about as easy to perform as any other. It is, therefore, not too surprising that the molecular movements involved in glass formation have turned out to belong in this same general class.

D. Identification of the degrees of freedom involved in the glass transformation

Having answered the first of the two questions concerning the nature of the glassy state, we must now consider the second: How do these molecular motions influence those physical properties which differ in glasses and liquids? What are the degrees of freedom which do not contribute to the thermodynamic properties of vitreous liquids and how do they involve the ability of molecules to change their positions?

It is often suggested that the degrees of freedom in question are the momenta associated with the changing positions of the molecules. By this it is implied that, for instance, the drop in the specific heat below T_g may be due to the cessation of the "free rotation" of molecules and of parts of molecules. This cannot possibly be the case. At temperatures just above the glass-transformation point we have seen that the dielectric relaxation times of polar liquids are of the order of seconds. This can be interpreted to mean either that the molecules rotate extremely slowly or, better, that at any instant only very few freely rotating molecules are present. From either point of view the kinetic energy associated with the freely rotating molecules must be extremely small and their contribution to the specific heat must be entirely negligible.

That the mere ability to make relatively infrequent changes in equilibrium position during an experimental measurement does not by itself lead to any appreciable contribution to the specific heat or thermal expansion is clearly shown as follows: The self-diffusion of lead atoms in solid lead at a temperature T is known to be given by a diffusion constant (4):

$$D = 5.1 \times 10^{-6110/T} \text{ cm.}^2\text{/sec.}$$

It is easily shown (82) that the diffusion constant can be expressed in terms of k_0, the number of jumps per second of atoms between lattice points, and λ, the distance between those points, by $D = k_0\lambda^2$. If λ is 3 Å., then $\log_{10} k_0 = 15.8^{-6110/T}$, and it is found that k_0 for lead atoms is one jump per second at 114°C. and one jump per day at 23°C. Thus if simply the ability of atoms to jump several times during an experiment could give rise to a contribution to the specific heat or the thermal expansion, lead would show a glass-like transformation somewhere between 20° and 120°C. Of course, no such transformation is observed. Similarly, Murphy (60) observed that the dielectric relaxation time of ice becomes of the order of hours at 130°K., but Giauque and Stout (26) found no significant glass-like transformation in ice between 15°K. and 273°K.

A clear distinction exists, therefore, between liquids and crystalline solids in this respect. The reason for this distinction was first pointed out by Simon (85). When the temperature of a simple crystal is changed, only the amplitudes of the very nearly harmonic oscillations of the atoms and molecules making up the lattice are affected. No changes in the crystal structure occur requiring that the molecules be reshuffled among their lattice positions. Therefore the inability of the molecules to move about in the lattice of a crystal during an experiment has no effect on the thermodynamic properties of the crystal. On the other hand, as the temperature of a liquid is changed, the liquid structure changes in a relatively drastic way. Thus the average coördination number and the extent of the short-range order both decrease as the temperature is raised (8, 8a, 57, 73). But the coördination number of any particular molecule in a liquid can change only by whole numbers, and the short-range order in any particular microscopic region must vary by similarly discrete steps. Each such change must require a relatively drastic rearrangement in the positions of, say, a dozen or so molecules relative to one another. Such rearrangements can only occur if molecules are free to move from one equilibrium position to another—i.e., if molecules are capable of making movements of just the sort which we have already shown to be involved in the glass transformation.

Accompanying these structural changes in the liquid there are energy and volume changes which, since they occur continuously as the temperature is changed, appear as contributions to the specific heat and thermal expansion. It must be these contributions which disappear below the glass-transformation point. The degrees of freedom which are ineffective in glasses are therefore undoubtedly exclusively configurational and do not involve momenta at all; glass formation probably affects the potential energy term of the Hamiltonian of the liquid, not the kinetic energy term.

E. Interpretation according to the hole theory of liquids

Any further discussion of the degrees of freedom involved in glass formation must be in terms of some particular theory of liquid structure. It is interesting to try to interpret the phenomena at T_g in terms of the hole theory of liquids.[3]

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[3] The possible rôle of holes in glass formation was suggested by T. Alfrey, G. Goldfinger, and H. Mark (2).

According to one form of this theory, a liquid is a quasicrystal with some of the lattice points occupied by molecules and others not occupied at all—that is, they are occupied by holes. The best evidence for this theory is probably the law of Cailletet and Mathias, according to which the mean densities of the liquid and vapor of many substances are independent of the temperature when these two phases are in equilibrium with each other. This was interpreted by Eyring (18) to mean that as the temperature is raised and molecules go from the liquid into the vapor, the space in the liquid formerly occupied by the vaporized molecules is not taken up by other molecules but remains as holes of size equal to that of a vaporized molecule. The observed decrease in density of the liquid with increasing temperature is thus largely due to the introduction of holes into the liquid and only slightly due to increased amplitudes of molecular oscillations such as cause the thermal expansion of crystals. The energy required to form such a hole is of course the latent heat of vaporization. As the temperature is raised and holes are introduced energy must be supplied, so that there is a contribution of the holes to the specific heat of the liquid.

Now the introduction of holes must require a considerable rearrangement of molecules among new equilibrium positions. If these rearrangements cannot occur during the duration of an experiment, the contribution of the holes to the specific heat and thermal expansion cannot be made.[4] Then, according to the hole theory of liquid structure, the drop in specific heat and thermal expansion at T_g is equal to the contribution of holes to these properties at that temperature. Let ΔC_p be the change in the specific heat (in units of calories per gram per degree) at T_g, and let $\Delta\alpha$ be the change in the coefficient of expansion (in units of cubic centimeters per cubic centimeter per degree). Then the volume of holes introduced into 1 cc. of the normal liquid above T_g by a change of temperature ΔT is $\Delta\alpha\Delta T$ cubic centimeters. The energy required to form this volume of holes is $\rho\Delta C_p\Delta T$ cal., where ρ is the density of the liquid. The energy required to form 1 cc. of holes is thus $\rho\Delta C_p/\Delta\alpha$. On the other hand, as a consequence of Eyring's arguments, the product of the heat of vaporization per gram and the density, $\rho\Delta H_{\text{vap}}$, is the energy required to form 1 cc. of holes having the sizes and shapes of the molecules of which the liquid is composed—that is, holes of the type known to occur at temperatures for which the Matthias–Cailletet law is valid. Clearly, if the holes which exist in supercooled liquids are of the same type as those occurring near the critical point, $\Delta C_p/\Delta\alpha$ should be approximately equal to ΔH_{vap}.

Values of $\Delta C_p/\Delta\alpha$ and estimated values of ΔH_{vap} are given in table 2 for all

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[4] Alfrey, Goldfinger, and Mark speak of the holes as diffusing into the sample from its surface. If this diffusion is to be interpreted as occurring in the same way as ordinary molecular diffusion, with the hole moving only between adjacent lattice sites, then the rate of volume change following a change in temperature—and hence the value of T_g—will depend on the size and shape of the specimen. This seems unlikely. On the other hand, it is quite possible that holes can appear directly at any point in the liquid, resulting in a corresponding expansion of the liquid as a whole. In a sense the hole has still "diffused" in from the surface, but the mechanism is altogether different from that ordinarily associated with diffusion.

liquids for which the necessary data exist. Apparently several times as much energy is required to form a given volume of holes around T_g as to form the same volume of holes each having the same size and shape as a molecule. This could be interpreted to mean that the holes at these low temperatures are much smaller than entire molecules, since it would be expected that considerably more energy would be required to form, say, four quarter-sized holes than one full-sized one because of the larger surface which is involved. Such an interpretation is, however, incompatible with the usual and attractive concept of holes as empty lattice sites, and we are led to suspect that the hole theory may not be very useful when applied to liquids at very low temperatures.

TABLE 2

Comparison of the heat of vaporization with the energy required to introduce holes into liquids at low temperatures

SUBSTANCE	ΔC_p	$\Delta\alpha \times 10^4$/DEGREE	$\Delta C/\Delta\alpha$	ΔH_{vap}*
	cal./degree/gram			*cal./gram*
Glycerol	0.27	2.4	1100	250
Propylene glycol	0.26	4.3	600	250
Glucose	0.18	2.8	640	200
Selenium	0.045	0.68–2.5	180–660	390
Rubber	0.12	4.0	300	100
Polyisobutylene	0.11	5.5	200	100
Polystyrene	0.14	1.8–3.8	370–780	90

* Estimated from heats of vaporization of volatile materials of similar structure, using Trouton's rule if necessary.

F. Effect of vitrification on properties other than the thermal expansion and the specific heat

The *compressibility* would be expected to decrease in the same way as the thermal coefficient of expansion at T_g, since the structural contribution to the volume should depend on the pressure as well as on the temperature. The only available information on the compressibilities of non-polymeric glasses above and below T_g is due to Tammann and Jellinghaus (96), who found increases in the compressibility of 60 per cent for salicylin glass, of 33 per cent for selenium glass, and of 68 per cent for colophony glass on going above the respective glass-transformation temperatures. Scott (81) found similar changes for rubber at its transformation point. Tammann and Jenckel (97) found that if materials which form glasses are cooled under pressure from above the glass-transformation point, they maintain an abnormally high density when the pressure is released. Thus, they were able to prepare samples of boron trioxide glass having densities of from 5 per cent to more than 7 per cent above normal by subjecting boron trioxide to a pressure of 5700 kg./cm.^{2} above 250°C. and cooling under this pressure to room temperature. These strikingly large density increases disappeared on raising the temperature close to T_g under normal pressure. Clearly in these experiments the abnormal density is due to forcing holes or other structural features tending to lower the density out of the sample at a temperature at which the molecules are still mobile, and then only releasing the pressure at temperatures so low that the density-lowering structures cannot be reformed in the material.

There is evidence from both Scott's and Tammann's results that increasing the pressure increases T_g. Similarly, Kobeko and Shushkin (44) have reported that the glass-transformation temperature of a mixture of phenolphthalein and salol can be raised 50°C. by applying 6000 atm. of pressure. Since increasing pressures would be expected to slow down the relaxation processes at a given temperature, this effect is in the expected direction according to our view. Such an effect on the viscosity is well known, and Danforth (15) found that the dielectric relaxation time of glycerol was increased by high pressures. On the other hand, it should be mentioned that Gee (25), considering the glass-like transformation in rubber as a true thermodynamic transition of the second order, has been able to show that the observed effect of pressure on the transition temperature in rubber is of the order of magnitude expected from Keesom's equation (38) for the effect of pressure on the temperature of a second-order transition,

$$(\partial T/\partial p) = TV\Delta\alpha/\Delta C_p$$

where T is the transition temperature, V is the specific volume, and $\Delta\alpha$ and ΔC_p are the changes in the expansion coefficient and specific heat at the transition.

The *thermal conductivity* of a condensed phase is determined by the anharmonicity of the intermolecular potential and by the regularity of the arrangements of the molecules (9), so it should not depend very much on the ability of the liquid to change its structure. Therefore, no significant change in this property is to be expected at T_g. This is essentially confirmed for glucose by Green and Parks (28) and for rosin and phenolphthalein by Kuvshinski (46). On the other hand, Schallamach (80) has obtained some very strange results for the thermal conductivity of rubber in the vicinity of its T_g. In agreement with Green, Parks, and Kuvshinski, he was able to cool rubber as much as 100°C. below T_g without noticing any discontinuity in the temperature dependence of the thermal conductivity. At sufficiently low temperatures, however, there was a sudden drop in the conductivity accompanied by a "clicking noise." On reheating the conductivity remained low up to T_g, where it increased rapidly to its normal value. It is questionable if this behavior has any significant bearing on the glass transformation, however.

According to Roseveare, Powell, and Eyring (76) the *viscosity* of a liquid should depend in part on how many holes are present in the liquid, being lower the greater the number of holes present. We should, according to this view, expect the viscosity–temperature curve to show some effects of the freezing-in of an excess number of holes below T_g. Such an effect is indeed observed in the silicate glasses (48, 49, 91) and in glucose glass (68), the viscosity below T_g being abnormally low as compared with the values expected from the extrapolation of data taken above T_g. The viscosity just below T_g is also observed to increase with the passage of time by as much as a factor of 10 or more, presumably because the holes, etc., gradually seep out of the specimen on standing.

All liquids have *elastic rigidity moduli*, but it is only when their viscosities are high that it becomes possible to measure them by the usual techniques. Such a modulus should certainly depend in part on the change in liquid structure under external stress for the same reason that the compressibility depends in part on this property. Therefore the modulus, if measured by the usual "slow" methods, should change around T_g. Parks and Reagh (68) found a rapid decrease in the torsion modulus of supercooled glucose threads above T_g. The high-temperature value of the modulus was only about one-twentieth of that found below T_g. Taylor (99) was able to observe a time-dependent portion of the elastic moduli of several silicate glasses in a limited temperature range near T_g. Kobeko, Kuvshinski, and Gurevich (42) made detailed studies of the time dependence of the elastic deformation of rosin, phenolphthalein glass, and rubber as a function of the temperature near the glass-transformation point and found a time-dependent decrease in the modulus near T_g. For phenolphthalein and rosin there is a difference of about tenfold between the "slow" (temperature above T_g) and "fast" (temperature below T_g) moduli.

Although a very considerable change in elastic properties of the simple glasses thus usually takes place at T_g, the long-chain polymeric glasses show even greater changes. This, of course, is because of the possibility of long-range elasticity in polymers, a phenomenon which is entirely dependent on the ability of the polymer to change its molecular configuration during the course of the experiment. Thus the results of Meyer and Ferri (53) show that the onset of long-range elasticity in rubber containing 8 per cent sulfur as the temperature is raised occurs at approximately the glass-transformation point, as observed by Kimura and Namikawa (41) for rubber containing this amount of sulfur. Even more clear are the results of Alexandrov and Lazurkin (1), who measured the elasticity of rubber and other polymers when subjected to periodic stresses of frequencies varying between 1 min.$^{-1}$ and 1000 min.$^{-1}$ If their results on rubber are extrapolated to frequencies of 1/10 min.$^{-1}$ to 1/100 min.$^{-1}$ (equivalent to experiments lasting from several minutes to an hour or so; *cf.* the treatment in figure 2 for dielectric relaxation), it is found that the elasticity undergoes a large increase (equivalent to the onset of long-range elasticity) at approximately the same temperature as T_g.

G. The kinetics of vitrification

One might expect that the relaxation processes in glass formation would follow an exponential decay law such as was set forth earlier in this paper. This is often found not to be the case. Jenckel (33) found that the change in volume following a change in temperature is exponential in the square root of the time. Boyer and Spencer (10) propose a hyperbolic tangent law based upon Eyring's equation for non-Newtonian flow. Lillie (49) found that the viscosity changes with time according to the relation

$$d\eta/dt = k(\eta_0 - \eta)/\eta$$

where k is a constant and η_0 is the viscosity reached at equilibrium. Taylor (99), on the other hand, finds a simple exponential law to be adequate for the time-dependent portion of the elastic deformation of silicate glass, and Boyer and Spencer (10) found the same for the volume change of polystyrene.

The situation would seem to be very similar to that in dielectric relaxation, where it is also found that the unimolecular decay law is not followed. In the case of dielectric relaxation the reason for this seems to be that there is no single relaxation time, but rather a whole distribution of them (24). This may include rates which differ by many powers of 10, so causing the relaxation to be spread out in time much more than would be expected according to the unimolecular law. This spreading-out of the relaxation process is characteristic of all of the empirical expressions referred to above, so there is good reason to believe that a similar complication exists here. Indeed, according to the explanation which has been offered for the distribution of dielectric relaxation times (36), it would be surprising if such a distribution did not occur in glass formation.

Although we have been stressing the similarity between the various relaxation processes involved in glasses, it is worth pointing out that these similarities probably do not extend to complete identity. Thus the details of the kinetics of the change in volume following a change in temperature will probably not be found to be identical with the elastic relaxation following a change in stress or the change in dielectric polarization following a change in the applied electric field. A detailed study of these differences might prove quite interesting.

H. Usefulness of glasses in theoretical investigations of the liquid state

We have seen that the glass transformation provides us with the means of separating the effects of changing liquid structure on various properties from the other factors involved in these properties. This separation is only possible at those temperatures at which the relaxation times are of the same order as the duration of the experiment. It would be desirable, however, to study the change in this contribution as the temperature is altered. This can be done, as we have seen, by changing the duration of the experiment, but for many properties we are not free to change equilibration times by a very large amount. This is unfortunately especially true of calorimetric measurements. Measurements of thermal expansion can be made over indefinitely long times but cannot be made with equilibration times shorter than 1 or 2 min. It is in this connection, however, that measurements using sound would be particularly useful (75). Depending on the experimental arrangement, the velocity of sound waves will depend on the shear modulus or on the compressibility of the medium through which they pass, so that from the measured velocity of such waves the shear modulus and the compressibility could be found. Just as the contributions of rotating dipoles to the dielectric constant can be separated from the contributions of atomic and electronic polarization by comparing dielectric constants obtained with electromagnetic waves of very low and very high frequencies, so the contribution of changing liquid structure to the compressibility and to the shear modulus could be separated from the contributions of the other factors by studying the sound velocity over a wide range of frequencies. Thus, sonic and ultrasonic methods coupled with extended static experiments might make possible the analysis of the elastic properties of liquids into their two components over a fairly considerable range of temperatures.[5] Important steps in this direction are being made by Mason (51).

When a substance can be prepared in both crystalline and supercooled forms, however, a much simpler means of separating the two contributions is open to us over a limited range of temperatures. We have seen that certain properties of glasses have values very close to those of the crystalline solid. Therefore, we have merely to measure the property for the crystal and for the supercooled liquid, subtract the one from the other, and obtain very closely the contribution of the changing liquid structure to that property. This procedure should work well for the specific heat, coefficient of expansion, and compressibility at all temperatures between the melting point and T_g.

I. Concept of torpid states of matter

The glassy state of liquids is only a single example of a more widespread condition in which matter has been compelled to change its state too rapidly for its structure to remain in normal equilibrium. Because a certain sluggishness is implied in such behavior, matter in such a condition might be said to be in a *torpid state.* For example, when metals and other crystalline solids are plastically deformed at relatively low temperatures, their structures change because the applied stress makes possible movements of atoms which under equilibrium conditions would practically never be tolerated. After severe plastic deformation of such crystals their x-ray diffraction patterns are markedly altered and their lattice energies and plastic properties are changed ("work hardening"). If the same amount of deformation were permitted to take place sufficiently slowly, on the other hand, the crystal would presumably be able to retain its normal structure and other properties. Crystals in this so-called "work-hardened" condition, like glasses, are in a torpid state.

(1) A limitation of the Eyring relation for plastic flow

It seems likely that whenever in plastic deformation the external forces compel the molecular units of flow to move much more rapidly than they normally would under the influence of thermal fluctuations, some kind of temporary or permanent changes in the plastic properties can be expected. This is easily seen in terms of Eyring's expression for the rate of shear as a function of the applied stress. According to Eyring (18)

$$\text{Rate of shear} = K[\exp(af) - \exp(-af)] = 2K \sinh af$$

where K is a constant and af is the ratio to the mean thermal energy, kT, of the work done by the external stress, f, in pushing the flow units into the activated state. The first exponential in this expression arises because the external forces do work in *lowering* the activation energy barrier for molecular shear processes tending to relieve these forces. The second exponential arises because the

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[5] A change in equilibration times by a factor of 10^9 could easily be accomplished in this way.

external forces do work in *raising* the activation energy barrier for the molecular processes in the opposite direction. When af is small, that is, when the activation energy is supplied chiefly by thermal fluctuations, sinh $af \cong af$ and we have ordinary Newtonian flow. When, on the other hand, most of the activation energy is supplied by the external forces, so that $af \gg 1$, the second exponential in the hyperbolic sine becomes negligible and sinh $af \cong 1/2 \exp(af)$. Flow according to this law is observed in the creep of metals (16, 35), textile fibers (29, 30), and other materials. Evidently in this type of flow those particular molecular motions which result in a change of shape of the specimen tending to relieve the applied stresses will be very much more frequent than other types of molecular motion. Furthermore, any "backtracking," represented by the second term in the hyperbolic sine expression, will be definitely discouraged. Now among the former "forward" types of motions, it may happen that some lead to a situation analogous to a "blind alley" or to a "traffic jam." That is, certain types of motion of the units of flow may result in entanglements such that further forward movements of these flow units become impossible. In order for the entanglements to become unsnarled we might expect that the flow units may under some conditions first have to "backtrack." If this is the case, then the suppression of the backtracking movements by the external forces will lead to a work hardening of the material which will make the Eyring expression inapplicable without some modification.

Such a possibility is especially evident in the flow of linear polymers. Here it seems very likely from Flory's work (20, 37) that the flow takes place by the successive movements of relatively short segments of the entire molecule. Many of these motions, however, undoubtedly result in severe entanglements of different chains very similar to the knots and interpenetrating loops which occur in a badly snarled mass of string which one has tried to disentangle by merely pulling on a few loose ends. These entanglements are probably most easily undone if the segments are given time to retrace their movements at least partially and try again in some other way to get out of each other's way.[6] A similar "entrapment" of flow units probably also occurs in the deformation of crystals and is at least partially responsible for the decrease in creep rate with time usually observed with such materials. It is apparent that wherever the exponential type of flow is encountered, its interpretation in terms of the simple Eyring picture should be made with some caution, since such materials may be in a torpid state in the sense outlined above.

(2) The recrystallization of cold-worked metals

We have seen that in crystalline solids such as metallic lead the inability of the elements of the crystal lattice to rearrange themselves during an experimental measurement does not seem to have any effect on the normal thermodynamic properties. But if the solid has been cold-worked this factor becomes more im-

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[6] It seems likely that such conditions, which will be expected to become more stringent with increasing chain lengths, are responsible for the Flory equation for the melt viscosity as a function of molecular weight: $\eta = \text{const.} \times \exp(b\sqrt{M})$, where b is a positive constant.

portant, since the return of the deformed crystals to their normal equilibrium structure can occur at a finite rate only if the atoms or molecules in the lattice are sufficiently mobile. The *recrystallization temperature* of crystalline solids is thus probably analogous to the glass-transformation temperature of supercooled liquids, and its numerical value presumably depends on factors similar to those which fix T_g.

In table 3 is a comparison of the observed recrystallization temperatures with the "T_g" values estimated from self-diffusion data for various metals in the manner outlined previously in this paper (Section II,D). A rough correlation is seen to exist, but apparently the recrystallization temperature tends to be rather *lower* than the calculated T_g. Now the recrystallization process would be expected to require a great many successive jumps by the various atoms in the crystal, so that we should expect that the recrystallization temperature would be, if anything, *higher* than T_g calculated in this manner. The explanation for this discrepancy is that cold-working markedly increases diffusion rates, as has been found experimentally by Fonda, Walker, and Young (21). The diffusion data used in table 3, on the other hand, were obtained on well-annealed metals, so that we have grossly underestimated the diffusion rate, and hence the jump rate, in the cold-worked condition which characterizes metals showing recrystallization.

TABLE 3

Comparison of recrystallization temperatures of metals and T_g estimated from self-diffusion data

METAL	LOG$_{10}$ k_0*	TEMPERATURE FOR $k_0 = 1$ SEC.$^{-1}$	TEMPERATURE FOR $k_0 = 1$ DAY^{-1}	OBSERVED RECRYSTALLIZATION TEMPERATURE (3)	REFERENCE
		°C.	°C.	°C.	
Lead	$15.7 - 6110/T$	116	35	0	(4)
Zinc					
‖ axis	$14.7 - 4460/T$	130	-28	15	(54)
⊥ axis	$17.0 - 6800/T$	127	49		
Copper	$16.0 - 12550/T$	512	371	200	(4)
Silver	$15.0 - 10100/T$	401	272	200	(34)
Gold	$17.1 - 11200/T$	382	271	200	(4)

* k_0 = jump rate $\cong 10^{15} D$ sec.$^{-1}$, where D is the self-diffusion constant at temperature T in units of cm.^{2}/sec. (see Section II, D).

The well-known observation that recrystallization temperatures are lowered by increasing the amount of cold working is probably also due in part to this effect.

III. THE BEHAVIOR OF NON-VITREOUS LIQUIDS AT LOW TEMPERATURES

The vitreous or glassy state of liquids evidently only exists because experiments performed by mortal beings must of necessity be of limited duration. It is interesting to speculate on the behavior which liquids would show at very low temperatures if enough time could be allowed in thermodynamic measurements to avoid vitrification. Would it be found under these conditions that the non-vitreous liquid could exist in any kind of metastable equilibrium close to the absolute zero?

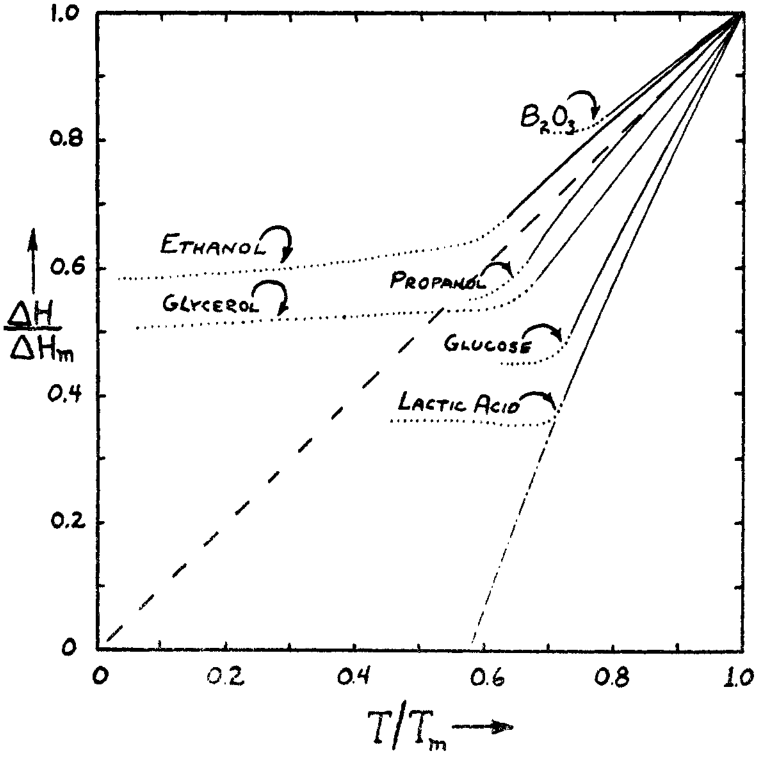

FIG. 3. Differences in heat content between the supercooled liquid and crystalline phases. Abscissa: temperature expressed as fraction of the melting temperature. Ordinate: difference in heat content expressed as fraction of the heat of fusion. ——, normal supercooled liquid; · · · , glassy state; ·—·—·—, presumed behavior of normal supercooled lactic acid below the glass-transformation temperature. See table 1 for references for data.

A. The experimental evidence

In trying to answer this question it is pertinent to compare the trends in the temperature dependence of the thermodynamic properties of crystals and their supercooled melts above the glass-transformation point. These trends can then be extrapolated to lower temperatures in order to throw some light on the above question. The available data are summarized in figures 3 to 6. Their trends are rather startling. It is seen that for glucose, for instance, the entropy of the liquid phase is rapidly approaching equality to the entropy of the crystalline phase when vitrification sets in. The heat contents of liquid and crystalline glucose seem likewise to be approaching equality at temperatures well above absolute zero. The same is true of the specific volume of liquid and crystalline glucose. Lactic acid shows the same behavior to an even more marked degree than does glucose, while glycerol, ethyl alcohol, and propyl alcohol show it to a somewhat lesser degree. Boron trioxide, on the other hand, seems not to show it at all, partly, perhaps, because it becomes a glass at a relatively higher temperature than the other substances mentioned.

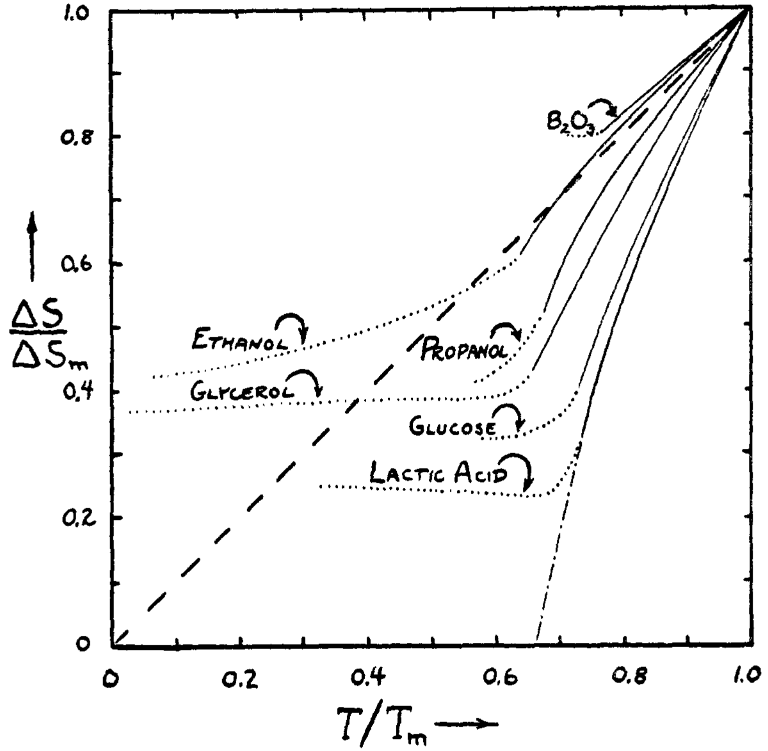

FIG. 4. Differences in entropy between the supercooled liquid and crystalline phases. Abscissa: as in figure 3. Ordinate: difference in entropy expressed as fraction of the entropy of fusion.

B. An apparent paradox

It might be argued that these results show that the non-vitreous liquid can somehow pass continuously over into the crystalline state in a manner analogous to the liquefaction of gases above the critical temperature (see, for example, Simon (85)). There is little justification for such a view, however, since the entropy curves do not seem to approach the abscissa at the same temperatures as the heat content curves. Moreover, the free energies of the two phases show no tendency to approach one another down to T_g (figure 5).

Then how are these curves to be extrapolated below T_g? Certainly it is unthinkable that the entropy of the liquid can ever be very much less than that of the solid.[7] It therefore seems obvious that the "true" or "non-vitreous" curves

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[7] It could conceivably become slightly less at finite temperatures because of a "tighter" binding of the molecule in the highly strained liquid structure, with consequent higher frequencies of vibration and a lower density of vibrational levels.

of $S_{\text{liq}} - S_{\text{cryst}}$ *vs.* temperature must become horizontal below some temperature not very far from T_g. Such a change in the slope of the entropy curves, however, implies a similar change in the slope of the $H_{\text{liq}} - H_{\text{cryst}}$ *vs.* temperature curves, since the two slopes are related by the expression:

$$\left[\frac{\partial(H_{\text{liq}} - H_{\text{cryst}})}{\partial T}\right]_p = T\left[\frac{\partial(S_{\text{liq}} - S_{\text{cryst}})}{\partial T}\right]_p$$

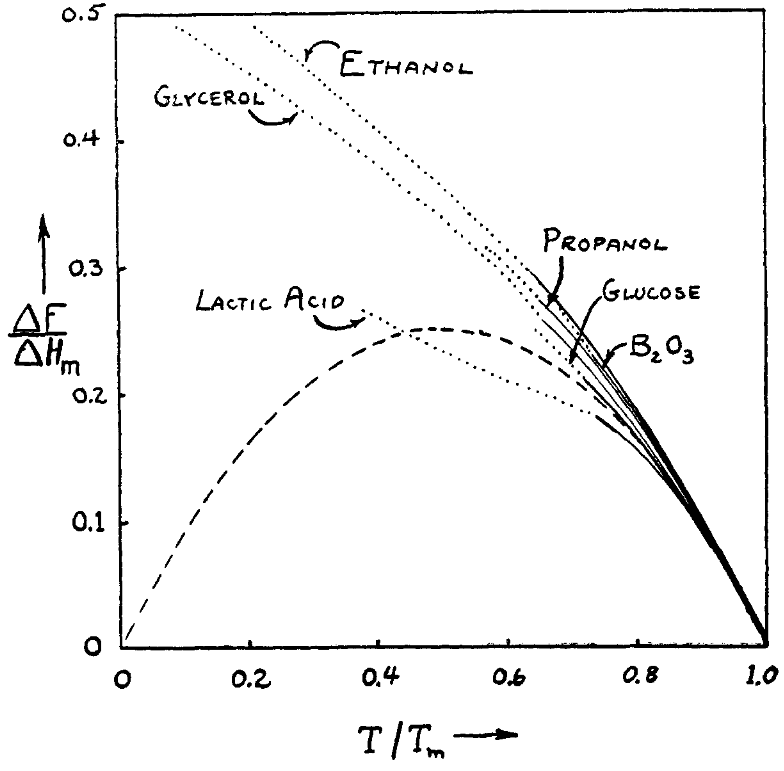

FIG. 5. Differences in free energy between the supercooled liquid and crystalline phases. Abscissa: as in figure 3. Ordinate: difference in free energy expressed as fraction of the heat of fusion.

But if $\partial(H_{\text{liq}} - H_{\text{cryst}})/\partial T$ drops to zero, then the specific heat of the liquid must of course become equal to the specific heat of the crystal. This, however, is exactly what happens in the glass transformation, which we have interpreted as a relaxation phenomenon having little to do with the "true" equilibrium thermodynamics of liquids. Is this a coincidence? Or might the glass transformation, at least in some if not all instances, really be a thermodynamic phenomenon?

C. A resolution of the paradox

Without a much more detailed experimental study of the glass transformation, particularly in glucose and lactic acid, no definite answers can be given to these questions. Perhaps in some instances a thermodynamic "freezing-in" of degrees of freedom does take place as a desperate result of the liquid's excessive generosity with its limited supply of entropy and energy as its temperature is lowered below the melting point. This would imply the existence of some kind of state of high order for the liquid at low temperature which differs from the normal crystalline state. A plausible structure for such a state seems, however, difficult to conceive, and we believe that the paradox is better resolved in another way, involving a closer inspection of exactly what one means by the metastability of liquids and glasses at low temperatures.

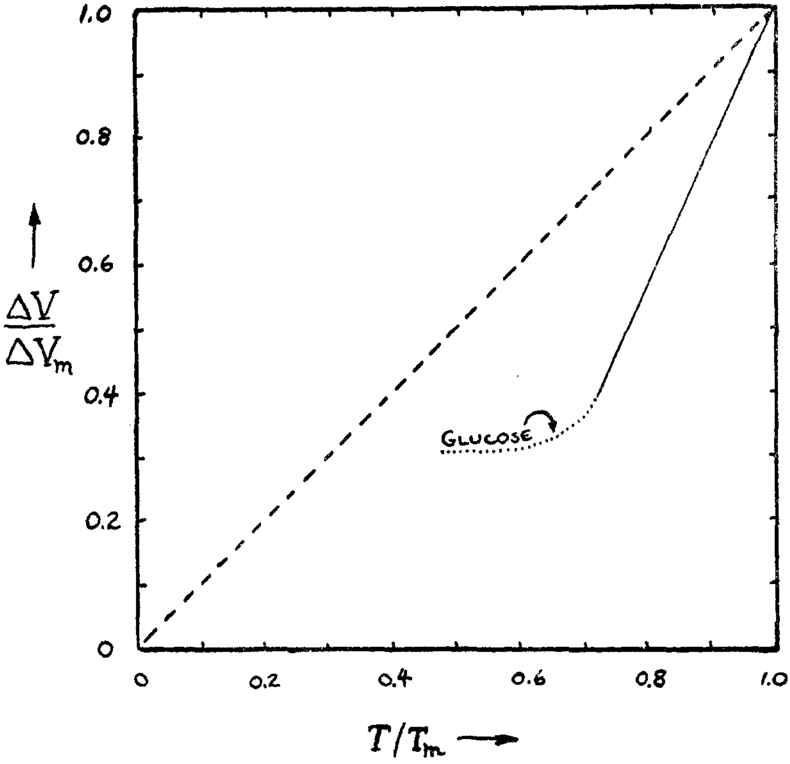

FIG. 6. Difference in specific volume between the supercooled liquid and crystalline phases of glucose. Abscissa: as in figure 3. Ordinate: difference in specific volume expressed as fraction of the change in volume on fusion.

Throughout this discussion we have been making implicit use of the idea that there are two kinds of metastability possible in liquids: *viz.*, that shown by a normal supercooled liquid with respect to the crystal, and that shown by a glass with respect to the normal supercooled liquid. Now metastability implies the existence of a free energy barrier between the metastable state and the normal state. In this case the first kind of metastability arises chiefly from the free energy barrier preventing the formation of crystal nuclei (23, 92, 102), while we have shown that the second kind of metastability is made possible by the free energy barriers which impede the motions of molecules from one equilibrium position in the liquid to another. As the temperature is decreased the height of the first kind of barrier generally decreases very markedly (see Appendix B) while the height of the second kind increases (see table 4). Suppose that when the temperature is lowered a point is eventually reached at which the free energy barrier to crystal nucleation becomes reduced to the same height as the barriers to the simpler motions. (This assumption is shown to be plausible in Appendix B and in Section III,E, below.) At such temperatures the liquid would be expected to crystallize just as rapidly as it changed its typically liquid structure to conform to a temperature or pressure change in its surroundings. It would then become operationally meaningless to speak of a metastable non-vitreous liquid as distinguished from a glass; the two kinds of metastability would merge.

Furthermore, we have mentioned in the introduction to this paper that in order for the distinction between the supercooled liquid and the crystal to have theoretical significance there must be a reasonably clear-cut boundary between the regions in phase space corresponding to the two states. If the free energy barriers between the two states become too low this boundary becomes indefinite, and it is meaningless theoretically as well as experimentally to speak of a non-vitreous liquid.

TABLE 4

Temperature dependence of the free energy of activation for dipole rotation in glycerol ($\Delta F\ddagger = RT \log kT\tau/h$, where τ is the dielectric relaxation time; see reference 36)

TEMPERATURE	LOG$_{10}$ DIELECTRIC RELAXATION TIME*	$\Delta F\ddagger$
°K.		*cal./mole*
186	2.275	12,700
208	−1.477	10,700
228	−4.00	9,070
244	−5.00	8,580
266	−6.78	7,220
290	−7.99	6,250
326	−8.72	5,950

* Time in seconds. Data from references 43 and 58.

Let us denote by T_k the temperature at which the two kinds of barriers become equal. T_k may be above or below the glass-transformation point, T_g, as defined in terms of the "conventional" duration of an experiment. If T_k is *above* T_g it will be impossible for the liquid to be studied as a liquid at temperatures between T_k and T_g other than by experiments of much shorter duration than the "conventional" one, since it will crystallize spontaneously during any experiments requiring more time than the average time between simple molecular jumps. According to the concepts presented in the previous part of this paper, adequate measurements under these circumstances would result in glass-like properties for the liquid. On the other hand, if T_k is *below* T_g it is still possible to distinguish between a glassy state and a true metastable liquid between T_g and T_k.

But below T_k no such distinction is possible; the glass is then the only experimentally attainable form of the liquid as well as the only form of the liquid whose phase integral has theoretical significance. Accordingly, provided the free energy barriers vary with the temperature in the way that we have postulated, it is not permissible to extrapolate the curves in figures 3 to 6 indefinitely below T_g and to infer thereby the existence of a "thermodynamic" glass-like transition.

In the past there has been a considerable amount of speculation concerning the existence of a critical point between crystalline and liquid states analogous to the critical point between liquids and gases. No experimental evidence for or against such a critical point has ever been found (86), though there is reason to believe that none is possible (Bernal (8); but see Frenkel (22) and page 155 of reference 23). It is apparent, however, that the behavior with which we are here concerned has a certain similarity to the behavior at a critical point in that here, as at a true critical point, the free energy barrier between the crystal and the liquid disappears. On the other hand, there is a fundamental difference in that the two states do not really merge and their free energies are decidedly different (see figure 5), so that one cannot go reversibly from the one state to the other without a normal phase change. It therefore seems appropriate to refer to the temperature T_k as a "pseudocritical point." T_k might also be called a "lower metastable limit," although this term is already used in a slightly different, more operational sense (page 7 of Volmer (102)).

D. Comparison of the rates of entropy loss in hydrogen-bonded and non-hydrogen-bonded liquids

It is probably significant that all of the substances in figures 3 and 4 which show the marked tendency for the properties of the liquid and solid to approach one another are strongly hydrogen-bonded. Unfortunately similar data are not available for other types of compounds—except for boron trioxide, which, however, becomes a glass too close to its melting point to give any useful comparative information. It is interesting in this connection to compare the rates of entropy change with temperature for the crystalline and liquid forms of various types of substances near their melting points. Consider the derivative of the quantity $(\Delta S/\Delta S_m)$ with respect to T/T_m, where ΔS is the difference in entropy between the liquid and the solid at a temperature T, and ΔS_m is this difference at the melting point, T_m. If this derivative has the value unity at the melting point, then the initial part of a plot such as is given in figure 4 will fall on the 45° diagonal line of that figure. If its value is greater than unity at the melting point, a behavior similar to that of glucose or lactic acid will be found. If its value is less than unity we may expect either a behavior like that of ethyl alcohol, with a delayed downward plunge of the curve, or there may be no downward plunge at all, and hence no tendency for the entropies of the two phases to become equal above absolute zero. Now

$$\frac{\mathrm{d}\,\dfrac{\Delta S}{\Delta S_m}}{\mathrm{d}\,\dfrac{T}{T_m}} = \frac{T_m}{\Delta S_m}\,\frac{\mathrm{d}\Delta S}{\mathrm{d}T} = (\text{at}\quad T = T_m)\,\frac{\Delta C_{pm}}{\Delta S_m}$$

where ΔC_{pm} is the difference in the specific heats of the solid and liquid at the melting point. Values of the slopes at T_m calculated in this way for various types of materials are given in table 5. Evidently hydrogen-bonded liquids tend to lose their entropies relatively much more rapidly than other kinds of liquids, and the behavior with which we have been concerned is for most other types of substances either delayed over a considerable temperature interval below the melting point, or does not occur at all. It should be noted, though, that the specific heats of solids almost always decrease with decreasing temperature much more rapidly near the melting point than do those of liquids. If this tendency persists very far below the melting point, the entropy of the liquid must ultimately approach that of the solid very rapidly at some temperature above absolute zero.

TABLE 5

Relative rates of loss of entropy with temperature by liquids and crystals at their melting points

(Data from Landolt-Börnstein (47))

SUBSTANCE	$(\Delta C_p)_m/(\Delta S_m)$	SUBSTANCE	$(\Delta C_p)_m/(\Delta S_m)$
Mercury	0.000	Naphthalene	0.15
Bismuth	0.068	Biphenyl	0.66
Cadmium	0.080	Triphenylmethane	0.90
Copper	0.029	Pentacosane	0.37
		Tritriacontane	0.16
Nitrogen	0.71	Mannitol	1.60
Carbon monoxide	0.55	Erythritol	1.10
Nitrous oxide	0.53	Water	1.79

E. Interpretation in terms of a simple liquid model

In the above discussion we have proposed that at low temperatures the free energy barrier to the formation of a stable crystal nucleus will decrease until it becomes of the same order as the barrier for simple molecular rotation or flow. This assumption is made plausible by a consideration of a theory of the microcrystalline structure of liquids proposed by Mott and Gurney (59). Although this theory is undoubtedly rather poor in the neighborhood of the melting point, it should become increasingly satisfactory as the liquid is supercooled.

Mott and Gurney assume that a liquid is really a mass of tiny crystals more or less randomly oriented with respect to each other. Assume that the crystallites are cubes all equal in size and having sides of length a, where a is measured in units of the length of the side of a cubical unit cell. Then the surface area of each crystallite will be $6a^2$. If there are n atoms per unit cell and there are N atoms in the sample of the liquid, the total volume will be N/n times the volume of a unit cell and the total number of crystallites will be N/na^3. The total intercrystalline surface area will then be $3N/na$. If this surface has an interfacial energy of σ ergs per unit cell face, the energy of the liquid will be greater than that of the monocrystalline solid by an amount $E = 3N\sigma/na$.

Each crystallite will only be able to assume a limited number of orientations relative to its neighbors, the stable orientations being those for which its surface pattern matches the patterns of its neighbors. This matching is never perfect (whence the surface energy term), but in general we can expect that the number of stable configurations will increase with the crystallite size according to some power law: Number of configurations = Ja^m. We can expect that the exponent m in the power law will not be very different from 2, since the number of possible matchings should be roughly proportional to the number of unit cell faces on the crystallite surface. Also, when a approaches unity we can expect that the number of configurations will approach unity, so that J will be of the order of unity.

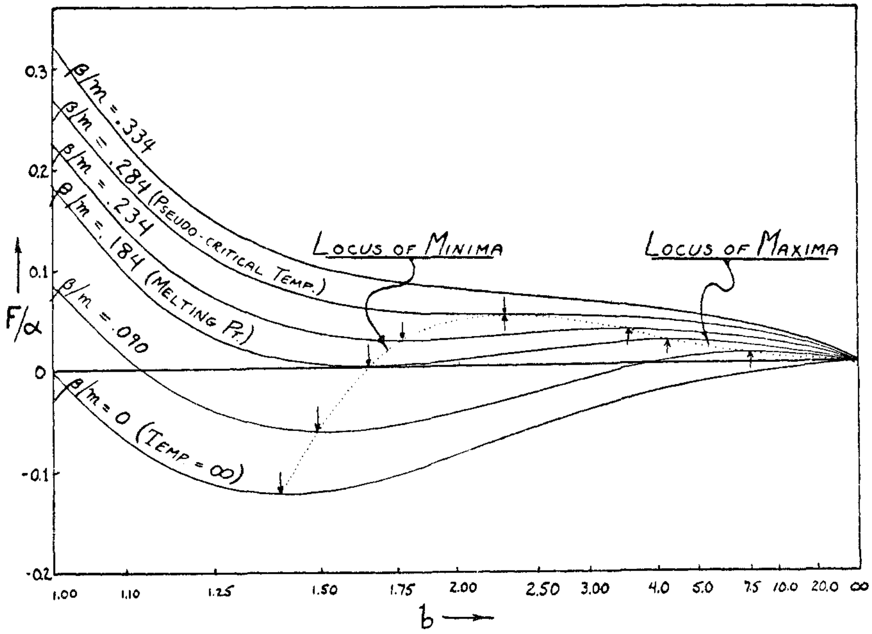

FIG. 7. Dependence of free energy of a liquid on "crystallite size" according to the Mott-Gurney theory of liquids.

The total number of configurations of the N/na^3 crystallites is $(Ja^m)^{N/na^3}$, so that the entropy is

$$S = (Nk/na^3) \log Ja^m$$

Thus we have for the difference in free energy between the liquid and the crystal

$$F = E - TS = 3N\sigma/na - (NkT/na^3) \log Ja^m$$

$$= \alpha\left[\beta/mb - \frac{\log b}{b^3}\right]$$

where $\alpha = mNJ^{3/m}kT/n$, $\beta = 3\sigma/J^{2/m}kT$, and $b = J^{1/m}a \cong a$.

In figure 7 the reduced free energy, $(1/\alpha)F$, is plotted against the reduced crystallite size, b, for various values of β/m. It is found that at infinitely high temperature ($\beta = 0$) there is a free energy minimum at $b = e^{1/3} = 1.395$, this value of b being independent of the values of m, σ, n, and J. As the temperature is decreased the value of b corresponding to the stable liquid decreases slowly until the melting point is reached. Here $F = 0$, giving $b = e^{1/2}$ and $\beta = m/2e$. At the melting point the liquid and the crystal are separated by a free energy barrier having its maximum at $b = 4.25$ and a height $0.303\Delta E_m$, where ΔE_m is the energy of melting for N atoms. As the temperature is lowered below the melting point this barrier decreases in height and occurs at smaller values of b, until at a temperature of 0.65 times the melting temperature the minimum and maximum merge and the barrier vanishes. This temperature would correspond to the "pseudocritical temperature," T_k, mentioned in the previous section. Below it the only barriers to crystallization are those which impede the growth of *stable* crystal nuclei. As Richards (75) has shown, these must be similar to those in dielectric relaxation, and by our earlier arguments these in turn are the barriers involved in glass formation.

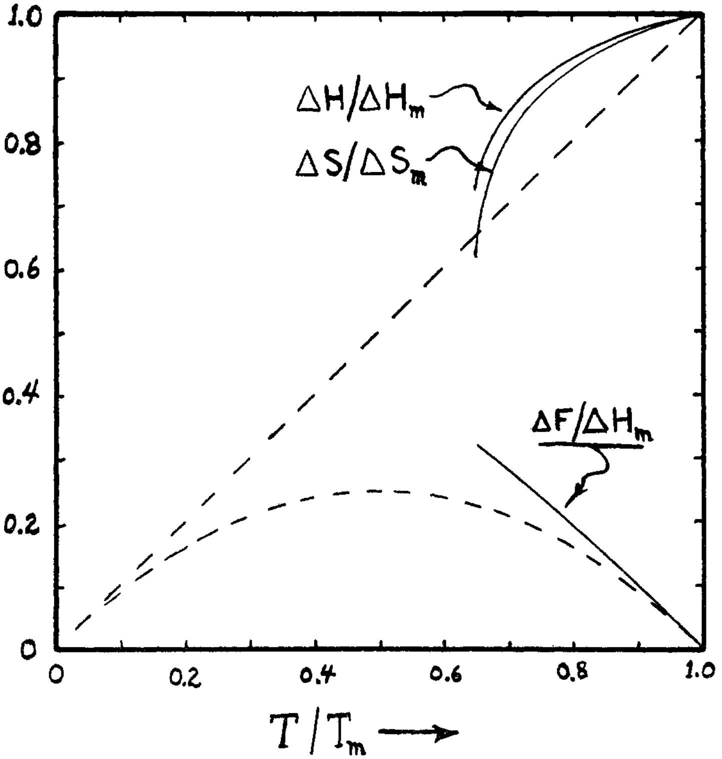

FIG. 8. Difference in the heat content, entropy, and free energy of the supercooled liquid and crystalline phases according to the Mott–Gurney theory of liquids. *Cf.* figures 3 to 5.

In figure 8 is shown the behavior of the energy, entropy, and free energy of the supercooled liquid with temperature according to this theory. The general trends are similar to those in figures 3 to 5, but the heat and entropy curves slope more gradually near the melting point. (We have seen, however, that the substances in figures 3 to 5 are generally abnormal in this respect as compared with simpler liquids.) The tendency for the energy and entropy curves in figure 8 to plunge toward the abscissa just above T_k is particularly striking.

On this crude model the entropy of melting is

$$\Delta S_m = \frac{mJ^{3/m}}{2ne^{3/2}} R = \frac{m}{9n} R \text{ per mole}$$

where R is the gas constant. Now m can hardly be much larger than 2 or 3, and for the face-centered cubic lattice $n = 4$, so ΔS_m is only $R/12$ at most. Observed entropies of melting are of the order of ten times this for such cubic crystals, however, so this model must underestimate the degree of disorder in the liquid very badly, at least in the neighborhood of the melting point.

Thus, although the quantitative aspects of the Mott–Gurney theory are rather unsatisfactory, it offers a simple and possibly essentially correct model for the interpretation of the phenomena in supercooled liquids. A theory of liquids proposed by Bresler (12) employing order–disorder theory with empty lattice sites (holes) also predicts the existence of a "pseudocritical temperature," T_k.

IV. APPENDIX A

Lowering of the melting point due to the finite size of a crystal

If σ is the surface free energy per unit area of the solid–liquid interface, then the free energy of a crystalline cube whose sides are of length r and whose density is ρ will be

$$\rho r^3 \mu_s = 6r^2\sigma + \rho r^3 \mu_{0s}$$

where μ_{0s} is the chemical potential of an infinitely large crystal (i.e., surface effects neglected) and μ_s is the chemical potential with the surface energy included. The chemical potential of the liquid is μ_l. At the true melting point, T_m (corresponding to $r = \infty$),

$$\mu_l(T_m) = \mu_{0s}(T_m)$$

At any other temperature, T,

$$\mu_l - \mu_{0s} \cong \left[\frac{\partial(\mu_l - \mu_{0s})}{\partial T}\right]_{T=T_m} (T - T_m) = -\frac{H}{T_m}(T - T_m)$$

where H is the heat of fusion per unit mass. The melting point of a crystal of size r will occur when $\mu_l = \mu_s$. Thus

$$T_m - T \cong 6\sigma T_m/\rho r H$$

Since σ and H are in all practical cases positive, T is always less than T_m.

The amount of the lowering of the melting point from this source is probably rather small in most cases. Taking $\sigma = 10$ ergs/cm.^{2} and $\rho H = 50$ cal./cc., one finds $(T_m - T)/T_m = 3 \times 10^{-8}/r$, so that r would have to be of the order of 1 micron to give a lowering of 0.1°C. for a substance melting at room temperature.

V. Appendix B

Evaluation of the height of the free energy barrier to crystal nucleus formation

Assume that a cube-shaped crystallite of volume V and surface area $6V^{2/3}$ is immersed in its liquid phase. Let H, S, and T_m be, respectively, the heat of fusion per cubic centimeter, the entropy of fusion per cubic centimeter, and the melting point of an infinitely large crystal ($T_m = H/S$). Let σ be the surface tension of the crystal–liquid interface. Then the free energy of the crystallite at temperature T will be

$$F = (TS - H)V + 6\sigma V^{2/3} = \frac{(T - T_m)}{T_m} HV + 6\sigma V^{2/3}$$

If $T < T_m$, this function goes through a maximum when plotted against V, the maximum being higher and at larger V, the closer T is to T_m. The maximum occurs at

$$V = \frac{64\sigma^3}{H^3}\left(\frac{T_m}{T_m - T}\right)^3$$

giving for the free energy at the top of the barrier:

$$F_{\max} = \frac{32\sigma^3}{H^2}\left(\frac{T_m}{T_m - T}\right)^2$$

Thus the barrier height decreases inversely as the square of the degree of supercooling.

Taking $\sigma = 10$ ergs/cm.^{2} and $H = 50$ cal./cc. as reasonable values, we find

$$\begin{aligned} F_{\max} &= 8 \times 10^{-15}(T_m/T_m - T)^2 \text{ ergs per crystal} \\ &= 120(T_m/T_m - T)^2 \text{ calories per mole} \end{aligned}$$

If $T = 0.75T_m$, this gives $F_m =$ only 1900 cal./mole, which is already much less than the usual free energies of activation for molecular motions in liquids (e.g., *ca.* 10,000 cal./mole for glycerol dipole rotation; see table 4). At this temperature, however, the crystal would only measure

$$V^{1/3} = \frac{4\sigma}{H}\frac{T_m}{T_m - T} = 2 \times 10^{-8}(T_m/T_m - T) \text{ cm.} = 8 \text{ Å}.$$

so the above relation for F_m is undoubtedly a rather crude approximation this far away from the melting point.

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