

## Free-Volume Model of the Amorphous Phase: Glass Transition

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## Free-Volume Model of the Amorphous Phase: Glass Transition

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(Received August 1, 1960)

Free volume  $v_f$  is defined as that part of the thermal expansion, or excess volume  $\Delta\bar{v}$  which can be redistributed without energy change. Assuming a Lennard-Jones potential function for a molecule within its cage in the condensed phase, it can be shown that at small  $\Delta\bar{v}$  considerable energy is required to redistribute the excess volume; however, at  $\Delta\bar{v}$  considerably greater than some value  $\Delta\bar{v}_0$  (corresponding to potentials within the linear region), most of the volume added can be redistributed freely. The transition from glass to liquid may be associated with the introduction of appreciable free volume into the system. Free volume will be distributed at random within the amorphous phase and there is a contribution to the entropy from this randomness which is not present in the entropy of the crystalline phase. According to our model all liquids would become glasses at sufficiently low temperature if crystallization did not intervene. Therefore whether or not a glass forms is determined by the crystallization kinetic constants and the cooling rate of the liquid. The experience on the glass formation is consistent with the generalization: at a given level of cohesive energy the glass-forming tendency of a substance in a particular class is greater the less is the ratio of the energy to the entropy of crystallization.

IN earlier publications<sup>1,2</sup> the authors discussed the glass transition and the factors which determine whether an undercooled liquid will solidify to a glass or to a crystalline body. We concluded, on the basis of a simple free-volume theory<sup>3</sup> of molecular transport, that any liquid, when sufficiently undercooled, would solidify to a glass if crystallization did not intervene.<sup>2</sup> From this it follows that whether or not a liquid forms a glass is determined by the magnitude of the crystallization kinetic constants (i.e., the nucleation frequency and the crystal growth rate) and the rate at which the liquid is cooled. We showed that the experience on glass formation is, on the whole, consistent with the generalizations about the magnitudes of the crystallization kinetic constants.

In the earlier papers we did not explicitly define the free volume in microscopic terms nor did we justify the temperature dependence of the free volume which is necessary to account for the molecular transport behavior. Also we did not specifically relate glass-forming tendency to molecular constitution. We have now partly removed this incompleteness in the earlier treatment by developing further the free volume model. This development, though qualitative, illuminates the concept of free volume and leads to a plausible explanation

for its temperature dependence through the glass transition. A further outcome of the present development is a more general criterion for glass-forming tendency which permits qualitative interpretation of the effect of molecular constitution. A detailed application of this criterion will appear in a forthcoming review article.<sup>4</sup> A more quantitative development of the free-volume model and its use in interpreting the thermodynamic behavior of amorphous phases will be presented in a later paper.

### FREE-VOLUME MODEL OF THE AMORPHOUS PHASE

In molecularly simple substances the "transition" from liquid to glass is manifested by marked changes in viscosity, specific heat, and thermal expansion coefficient within a narrow temperature interval centering about a "glass transition temperature"  $T_g$ . Kauzman<sup>5</sup> has pointed out that the extrapolated specific values of the volume, energy, and entropy of molecularly simple liquids become less than the corresponding values for the crystal at temperatures well below  $T_g$ . Actually the magnitude of these properties always remains larger in the amorphous than in the crystalline phase because of the intervention of the glass transition as illustrated schematically in Fig. 1 for the specific volume. Such behavior suggests, as Gibbs and DiMarzio<sup>6</sup> have pointed out, that there may exist a uniquely defined amorphous state at low temperatures characterized by minimum specific volume-temperature

<sup>1</sup> D. Turnbull and M. H. Cohen, *J. Chem. Phys.* **29**, 1049 (1958).

<sup>2</sup> M. H. Cohen and D. Turnbull, *J. Chem. Phys.* **31**, 1164 (1959).

<sup>3</sup> The first developments of the free volume model of the liquid state are due to Eyring and associates [(a) H. Eyring, *J. Chem. Phys.* **4**, 283 (1936); J. O. Hirschfelder, D. P. Stevenson, and H. Eyring, *J. Chem. Phys.* **5**, 896 (1937)] and to Lennard-Jones and Devonshire (b) J. E. Lennard-Jones and A. F. Devonshire, *Proc. Roy. Soc. (London)* **A163**, 53 (1937); **A169**, 317 (1939)]. The model has been further developed and applied in many subsequent investigations.

<sup>4</sup> D. Turnbull and M. H. Cohen in *Modern Aspects of the Vitreous State*, edited by J. D. Mackenzie (Butterworths Scientific Publications, Ltd., London, 1960).

<sup>5</sup> W. Kauzman, *Chem. Rev.* **43**, 219 (1948).

<sup>6</sup> J. H. Gibbs and E. A. DiMarzio, *J. Chem. Phys.* **28**, 373 (1958).

and specific energy-temperature relations which still lie above the corresponding relations for the crystal. This state should be realized, when the liquid is cooled very slowly and constrained so as not to crystallize, at some temperature well above the absolute zero. Gibbs and DiMarzio have presented a statistical mechanical justification of these concepts as applied to polymer systems.

Our previous discussion of the glass transition<sup>1,2</sup> has implicitly identified the glassy state with this uniquely defined amorphous state. Because no structure change appears to accompany the glass transition and because the transition occurs over a range of temperature, we have supposed that the liquid and glass belong to a single thermodynamic phase.<sup>2</sup> If the glass transition is not a thermodynamic phase change, then what is it?

We believe the answer lies in the hypothesis advanced by Fox and Flory<sup>7</sup> that this transition results from the decrease of the free volume of the amorphous phase below some small characteristic value. With this hypothesis Williams, Landel, and Ferry<sup>8</sup> were able to show that the dependence of fluidity  $\phi$  on temperature in the glass transition region is satisfactorily described by the Doolittle<sup>9</sup> equation

$$\phi = A \exp[-(qv_0/v_f)], \quad (1)$$

where  $q$  is a constant of order unity,  $v_0$  is the volume of a molecule,  $\bar{v}$  is the specific volume, and the free volume  $v_f$  is defined as

$$v_f = \bar{v} - v_0. \quad (1a)$$

(We expect  $v_0$  to be pressure dependent, though at large free volume this dependence may be, for most purposes, negligible.)

The authors<sup>2</sup> have derived an expression for the self-diffusion coefficient of a liquid having the same form as the Doolittle equation. Our derivation was based on the assumptions:

(1) Molecular transport may occur only when voids having a volume greater than some critical value  $v^*$  form by the redistribution of the free volume.

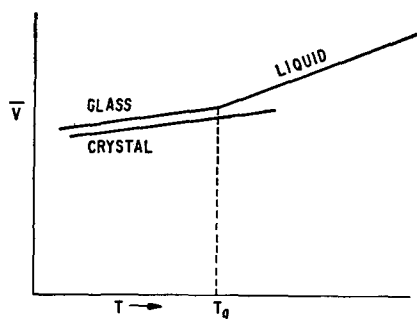


FIG. 1. Schematic specific volume ( $\bar{v}$ )-temperature relations for amorphous and crystalline phases of a substance.

<sup>7</sup> T. G. Fox and P. J. Flory, *J. Appl. Phys.* **21**, 581 (1950); *J. Phys. Chem.* **55**, 221 (1951); *J. Polymer Sci.* **14**, 315 (1954).

<sup>8</sup> M. F. Williams, R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.* **77**, 3701 (1955).

<sup>9</sup> A. K. Doolittle, *J. Appl. Phys.* **22**, 1471 (1951).

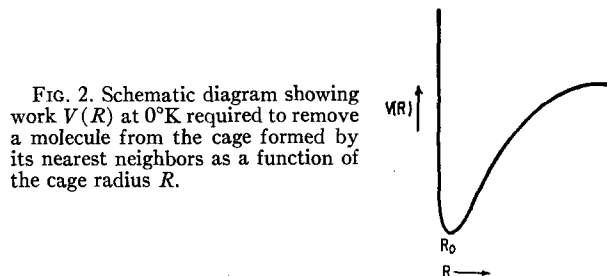


FIG. 2. Schematic diagram showing work  $V(R)$  at  $0^\circ\text{K}$  required to remove a molecule from the cage formed by its nearest neighbors as a function of the cage radius  $R$ .

(2) No energy is required for free volume redistribution.

The resulting expression is as follows:

$$D = ga^*u \exp[-\gamma v^*/v_f], \quad (2)$$

where  $g$  is a geometric factor usually taken to be  $\frac{1}{6}$ ,  $a^*$  is a molecular diameter,  $u$  is the gas kinetic velocity, and  $\gamma$  is an overlap factor which should lie between  $\frac{1}{2}$  and unity.

According to the foregoing arguments, the problem of explaining the glass transition is reduced to that of explaining the temperature dependence of the free volume; however, before we can develop such an explanation we must specify the concept of free volume more precisely.

Consider a molecule in a cage formed by its nearest neighbors. If the potential energy of pairwise molecular interaction is described by the Lennard-Jones potential function, the work  $V(R)$  at  $0^\circ\text{K}$  required to take a molecule from the center of its cage into the vacuum will vary with the cage radius  $R$  as shown schematically in Fig. 2. This function  $V(R)$  has a minimum at  $R_0$  and rises steeply as  $R$  decreases for  $R < R_0$ . At  $R > R_0$  the function rises less steeply and exhibits a linear region, as shown, at  $R$  considerably beyond  $R_0$ .

The potential of the molecule will vary with its position within the cage. This "inner potential,"  $V(r)$  where  $r$  is the displacement of the central molecule from the mean center of the cage, has been evaluated for various pairwise interaction laws. For example, Fowler and Guggenheim<sup>10</sup> have presented the potential as calculated from the Lennard-Jones interaction law for different volumes corresponding to various cage radii. For  $R$  near  $R_0$ ,  $V(r)$  is parabolic at small  $r$  with a minimum at  $r=0$ . At larger  $R$  the minimum region of  $V(r)$  is shallower and broader. The potential level at the minimum corresponds to  $V(R)$  and thus increases with  $R$ . A volume  $\omega$ , which we call the "central volume," is available to the center of the molecule. In the innermost part of this volume the potential difference  $\Delta V(r) = V(r) - V(0)$  is small relative to  $kT$  and the molecule will move freely with its gas kinetic velocity. However in the peripheral part of the central volume  $V(r)$  rises steeply and here the motion of the molecule will be vibrational.

<sup>10</sup> R. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, New York, 1952), p. 340.

The average  $\bar{R}$  of the cage radii will increase with increasing temperature. For  $\bar{R}$  not much greater than  $R_0$  the total expansion  $\Delta\bar{v}/v_0$  is proportional to  $\bar{R} - R_0$ , thus

$$(\bar{v} - v_0)/v_0 = \Delta\bar{v}/v_0 = A(\bar{R} - R_0). \quad (3)$$

Let us consider how this "excess volume"  $\Delta\bar{v}$  is distributed among the different cages. From the form of  $V(R)$  it is apparent that for  $\bar{R}$  near  $R_0$  the potential energy of the system will be least when the excess volume is distributed uniformly among the cages. Let  $\Delta\epsilon$  be the increase in potential energy required to redistribute the excess volume nonuniformly. This redistribution energy is very large at  $\bar{R} \approx R_0$  and would approach  $\infty$  for a hard sphere repulsive potential. As  $\bar{R}$  increases beyond  $R_0$ ,  $\Delta\epsilon$  decreases and, for redistribution within certain limits, approaches zero when  $\bar{R}$  reaches values in the linear region of  $V(R)$ . We shall call that part of the excess volume which may be redistributed with no increase in energy the "free volume"  $v_f$ . Thus we may write

$$\Delta\bar{v} = v_f + \Delta v_c. \quad (4)$$

The result that a part of the excess volume can be redistributed with no accompanying energy change was assumed in the authors' earlier treatment of molecular transport in amorphous phases<sup>2</sup> but we then neglected  $\Delta v_c$  and set  $\Delta\bar{v} = v_f$ .

We may now distinguish two regimes in the thermal expansion of an amorphous phase. In the first regime which occurs at the lowest temperatures all of the thermal expansion arises from the anharmonicity of the vibrational part of the motion of the molecule. The redistribution energy is large and the volume added in expansion will thus tend to be uniformly distributed among the cages. Hence  $v_f \approx 0$  and

$$\Delta\bar{v} \approx \Delta v_c. \quad (5)$$

In this regime the increase in entropy due to the volume change alone will be very small. The magnitude of the thermal expansion will be of the order of that for the crystalline solid.

As the temperature of the amorphous phase is increased in the low temperature regime the thermal expansion increases and reaches some value  $\Delta\bar{v}_0$  corresponding to  $\bar{R}$  near the linear range of  $V(R)$ . For  $\Delta\bar{v}$  greater than  $\Delta\bar{v}_0$  a second regime will predominate in the thermal expansion in which most of volume added is "free" for redistribution. The free energy of the amorphous phase should be a minimum when this free volume is distributed at random. *Such a random distribution of free volume can occur in the amorphous but not in the crystalline phase.* Hence at  $\Delta\bar{v}$  somewhat greater than  $\Delta\bar{v}_0$  the amorphous phase should be more stable than a crystalline phase having the same volume. This comes about because of the positive configurational entropy which arises from the randomization of the free volume. This entropy term may constitute a sub-

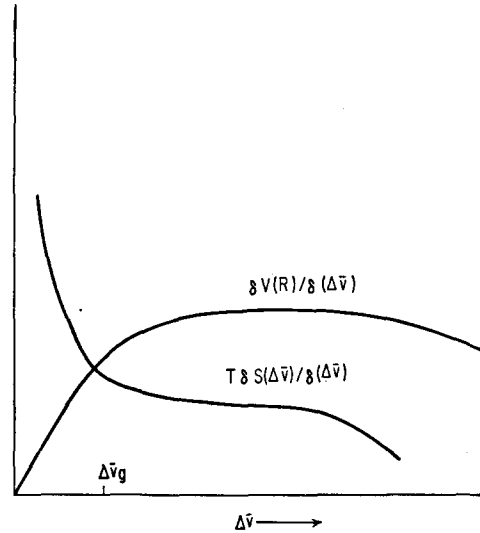


FIG. 3. Schematic diagram showing the derivatives of the potential and entropy functions for an amorphous phase as a function of the excess volume  $\Delta\bar{v}$ . The volume added starts to become redistributed freely at  $\Delta\bar{v} \geq \Delta\bar{v}_0$ . This results in a smaller rate of decrease in the entropy derivative.

stantial part of the entropy of fusion and an evaluation of it will be described in a forthcoming paper. Even without a quantitative calculation of the randomization entropy certain important inferences of a qualitative nature can be drawn about the transition from glass to liquid. Again we shall take the point of view that the transition results from the appearance of considerable amounts of free volume in the system. Then in the low temperature thermal expansion regime the amorphous phase will be a glass since, according to our arguments, virtually none of the volume added will appear as free volume until  $\Delta\bar{v}$  reaches the value  $\Delta\bar{v}_0$ . In the temperature range in which the total thermal expansion is of the order of  $\Delta\bar{v}_0$  free volume will begin to appear and according to the arguments advanced in our earlier paper<sup>2</sup> the fluidity will increase very rapidly to values characteristic of liquidlike behavior. Also the randomization entropy will begin to appear and the increase in entropy with volume,  $\delta S(\Delta\bar{v})/\delta\bar{v}$ , of the amorphous phase will be much greater than it would otherwise have been. That is, the rapid fall of  $\delta S(\Delta\bar{v})/\delta\bar{v}$  from the high value characteristic of a nearly harmonic solid,  $3Nk\gamma/\bar{v}$  for a monatomic solid ( $\gamma$  = average logarithmic volume derivative of the vibration frequencies), toward the low value characteristic of a nearly perfect gas  $Nk/\bar{v}$  is slowed by the appearance of the entropy of randomization.<sup>10a</sup> The expected form of the entropy derivative and its comparison with the corresponding  $V(R)$  derivative are shown in Fig. 3. The intersection of  $\delta V(R)/\delta\Delta\bar{v}$  with  $T\delta S(\Delta\bar{v})/\delta\Delta\bar{v}$  determines the equilibrium excess volume  $\Delta\bar{v}_0$  at the

<sup>10a</sup> The entropy of randomization may be regarded as equivalent to, but perhaps more precisely defined than, the communal entropy discussed by other authors.<sup>3a, 15</sup>

given temperature;  $d(\Delta\bar{v}_0)/\bar{v}dT$  is the coefficient of thermal expansion  $\alpha$ . If  $\delta S(\Delta\bar{v})/\delta(\Delta\bar{v})$  is temperature independent,  $\alpha$  must increase rapidly in the transition region, in which the  $V(R)$  derivative falls away from its initial linear course, to a value much larger than that characteristic of the low temperature regime. This type of volumetric behavior actually is observed in the glass transition (see Fig. 1). Thus the glass transition temperature  $T_g$  may be considered to be approximately the temperature at which the excess volume attains the value  $\Delta\bar{v}_0$  and at which free volume begins to appear. From the principle of corresponding states, which will be discussed later, it is expected that  $V(R/R_0)/h_v$ , where  $h_v$  is the heat of vaporization, will be the same for all liquids in a given class. It follows, therefore, that for such liquids  $T_g$  should be proportional to  $h_v$  as is observed.

According to the simple model just developed the glass transition at  $T_g > 0^\circ\text{K}$  should be a universal characteristic of liquid behavior and would always occur if crystallization did not intervene. Whether or not crystallization intervenes will be determined by the magnitude of the crystallization kinetic constants (the nucleation frequency  $I$ , and the crystal growth rate  $u$ ) and the cooling rate.<sup>10b</sup>

#### EFFECT OF GLASS TRANSITION ON MOLECULAR TRANSPORT PROPERTIES

The molecular transport properties of interest to us are the fluidity  $\phi$ , the self diffusion constant  $D$ , and the kinetic constant for crystal growth  $D_u$ . From the limited information available there has emerged some simple semiempirical relations between these properties for amorphous phases. Thus the self-diffusion coefficient and the fluidity are related by

$$D = BT\phi, \quad (6)$$

where the magnitude of the constant  $B$  usually is near the Stokes-Einstein value

$$B = k/3\pi a_0, \quad (6a)$$

where  $a_0$  is the molecular diameter. This relation seems to hold well into the glass transition range but the data for this range are very limited.

The velocity of growth of crystals into an undercooled amorphous phase at constant composition may be expressed<sup>11</sup> as

$$u = (fD_u/a_0)[1 - \exp(\Delta g/kT)], \quad (7)$$

where  $\Delta g$  is the free energy of crystallization per molecule and  $f$  is the fraction of crystal surface sites to which

molecules can be attached. If it is assumed that the kinetic constant for growth  $D_u$  is equal to the coefficient of diffusion in the amorphous phase, the crystal growth rate and fluidity may be related as follows:

$$u = (fBT\phi/a_0)[1 - \exp(\Delta g/kT)]. \quad (8)$$

This relation seems to describe the velocity of crystal growth into very viscous undercooled liquids quite well with reasonable values for  $f$ .<sup>11,4</sup> From it we calculate that the velocity of crystal growth at a fluidity of  $10^{-13}$  poise<sup>-1</sup> is of the order of 1 Å per day. Thus a glass once formed should persist for a very long period even though the crystal is the more stable phase.

It is known<sup>12-15</sup> that the equilibrium properties of simple liquids may be correlated by means of a principle of corresponding states. According to this principle the property of the liquid is some universal function of a reduced temperature  $\tau$ . For our purposes the reduced temperature may be defined somewhat loosely as follows:

$$\tau = kT/h_v, \quad (9)$$

where  $h_v$  is the molecular heat of vaporization. There is considerable evidence that the molecular transport properties of liquids also may be correlated by means of the principle of corresponding states. Thus Cino-Castagnoli *et al.*<sup>16</sup> have shown<sup>16a</sup> that the fluidity of some molecularly simple substances are in approximate accord with the principle.

Also the existence of a single fluidity-reduced temperature relation for substances in a given class can be justified crudely on the basis of the free volume model. Thus from the preceding considerations and those of the preceding section we expect that

$$v_f/v_0 \sim (v_f/v_0)(h_v/kT). \quad (10)$$

And since, as shown in our earlier paper,<sup>2</sup>  $\phi\beta$  is a function of  $v_f/v_0$  it follows that

$$\phi\beta \sim \phi(kT/h_v) \sim \phi(\tau), \quad (11)$$

where

$$\beta = (mT)^{1/3}/\bar{v}^{1/3}. \quad (11a)$$

Figure 4 shows that this relation is approximately valid in the fluid range for liquids (hereafter called "simple liquids") composed of molecules which are not highly asymmetric in shape and which are bound together only by van der Waals forces. We have found few data on fluidities in the glass transition range. However, the reduced glass transition temperatures reported for substances in this class all fall close to the same value, namely,  $\tau_g \sim 0.023$ . Therefore we suggest

<sup>10b</sup> In the quantum fluids He<sub>3</sub> and He<sub>4</sub>, crystallization does not intervene, the amorphous phase being stable at low temperatures and pressures. What is equivalent in these substances to the entropy of randomization disappears gradually in He<sub>3</sub> and via a phase transformation in He<sub>4</sub>; however, the amorphous phase remains fluid down to the lowest temperatures because the structures are blown up by zero point kinetic-energy so that no redistribution of free volume is required for flow.

<sup>11</sup> W. B. Hillig and D. Turnbull, *J. Chem. Phys.* **24**, 914 (1956).

<sup>12</sup> K. S. Pitzer, *J. Chem. Phys.* **7**, 583 (1939).

<sup>13</sup> E. A. Guggenheim, *J. Chem. Phys.* **13**, 253 (1945).

<sup>14</sup> J. DeBoer, *Physica* **14**, 139 (1948).

<sup>15</sup> I. Prigogine, *The Molecular Theory of Solutions* (North-Holland Publishing Company, Amsterdam, 1957).

<sup>16</sup> G. Cino-Castagnoli, G. Pizzella, and F. P. Ricci, *Nuovo cimento* **11**, 466 (1959).

<sup>16a</sup> See also G. Thomaes and J. Van Itterbeek, *Mol. Phys.* **2**, 372 (1959).

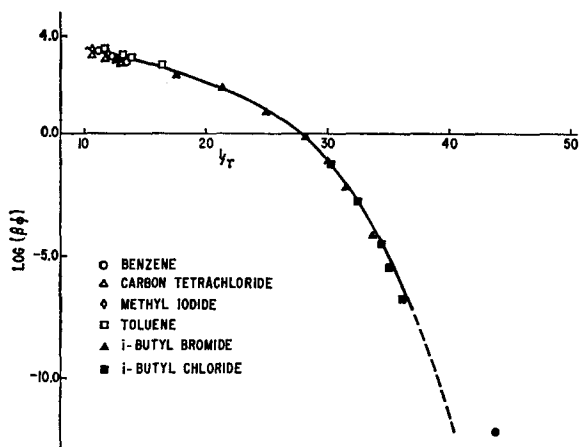


FIG. 4. Relation between fluidity function  $\beta\phi$ , and reduced temperature  $\tau$ , for various simple molecular liquids. The solid circle represents the estimated fluidity function at the glass transition for several simple molecular substances.

that Eq. (11) may hold approximately over the entire fluidity range for substances in a given class.

The fluidities of substances composed of short linear molecules fall close to the Fig. 4 curve at relatively high reduced temperatures but are considerably above this curve at lower temperatures. Also the glass transition temperatures of these substances seem to be well below  $\tau=0.023$ .

The  $\phi=\phi(\tau)$  relations for three types of substances are compared in Fig. 5. In making this comparison the factor  $\beta$  was ignored. This factor does not vary markedly from one compound to another though its inclusion significantly improves the accord between the data and the reduced temperature relation. It is seen that the  $\phi(\tau)$  relation for the polyalcohols is only a little below that for the simple liquids and gives  $\tau_g \sim 0.025$ ; however, it is evident that the form of  $\phi(\tau)$  for boron oxide is very different from that for the simpler liquids.

From the correlations stated earlier it follows that for any given class of substances,

$$D_u \sim D_u(\tau) \quad (12)$$

to about the same degree of approximation as the  $\phi(\tau)$  relation.

#### GLASS-FORMING TENDENCY AND ITS RELATION TO MOLECULAR CONSTITUTION

As we have seen, the reduced normal boiling temperature  $\tau_b$  and the reduced glass transition temperature  $\tau_g$  seem to be nearly constant for substances in a given class. For example,  $\tau_b \sim 0.095$  and  $\tau_g \sim 0.023$  for the simple liquids. According to the considerations advanced in the preceding section the kinetic constant for crystal growth  $D_u$  should all off from  $\tau_b$  to  $\tau_g$  in the same way as does  $\phi$  (see Fig. 4).

Experience indicates that the other crystallization kinetic constant, the crystal nucleation frequency  $I$ , is a very sharply increasing function of undercooling

and therefore of  $\tau$ . Let  $\tau'$  be the reduced temperature at which the nucleation frequency equals some characteristic measurable value. It is found that,<sup>17</sup> when the reduced thermodynamic melting temperature  $\tau_m$  is far above  $\tau_g$ ,

$$\tau' = \lambda \tau_m, \quad (13)$$

where  $\lambda$  is approximately constant for substances in a given class. For example,  $\lambda$  is about 0.7 to 0.8 for the simple liquids.<sup>17-19</sup>

The values of  $\tau_m$ , in marked contrast with those for  $\tau_b$  and  $\tau_g$ , may vary widely among different substances within a single class. Hence by Eq. (13) the values of  $\tau'$  will do the same. It is evident from these considerations that the over-all crystallization velocity  $\dot{x}$ , which at large undercooling is roughly proportional to  $ID_u^3$ , should be smaller the less is  $\tau'$  or alternatively the less is  $\tau_m$ . Therefore the glass-forming tendency of a substance within a given class will be greater the less is  $\tau_m$  where

$$\tau_m = k \Delta U_m / h \nu \Delta S_m, \quad (14)$$

and  $\Delta U_m$  and  $\Delta S_m$  are, respectively, the energy and entropy of fusion. This generalization about glass-forming tendency can be restated as follows: *The glass forming tendency of a substance in a particular class is greater the less is the energy, at constant cohesive energy, necessary to produce a given amount of disorder.* This statement encompasses the Zacharaisen<sup>20</sup> condition for glass formation as well as the conditions proposed in our 1958 paper.<sup>1</sup>

We can now give a qualitative interpretation of the effect of molecular constitution on glass forming tend-

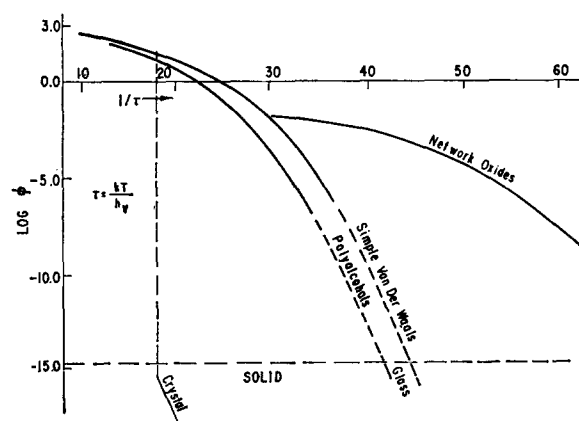


FIG. 5. Relation between fluidity ( $\phi$ ) and reduced temperature ( $\tau$ ) for three classes of substances. The curve for network oxides was constructed entirely from data on  $B_2O_3$  [J. D. MacKenzie, *Trans. Faraday Soc.* **52**, 1564 (1956)].

<sup>17</sup> D. Turnbull, *J. Appl. Phys.* **21**, 1022 (1950).

<sup>18</sup> D. G. Thomas and L. A. K. Stavelly, *J. Chem. Soc.* **1952**, 4569.

<sup>19</sup> H. J. De Nordwall and L. A. K. Stavelly, *J. Chem. Soc.* **1954**, 224.

<sup>20</sup> W. H. Zachariasen, *J. Am. Chem. Soc.* **58**, 3841 (1932).

ency. For example, Zachariassen has pointed out that glass formation in ceramics is strongly favored if the coordination polyhedra make point to point contact in an open structure. In this event only a little energy is needed for small changes in the contact angle of the coordination polyhedra. However, as Zachariassen recognized, the long-range order can be destroyed by such small changes and thus the entropy of amorphization is obtained with the expenditure of only a small amount of energy.

In general the glass-forming tendency of simple organic substances is increased by asymmetrization of the molecule. For example, toluene forms glasses much

more readily than does benzene. The effect of asymmetrization is to increase the entropy of the amorphous phase so that the amorphization energy at the melting temperature is reduced. Also glass formation would be favored by impurity additions which raise the energy of the crystal relative to the amorphous phase at constant composition.

#### ACKNOWLEDGMENTS

We are indebted to Bruno H. Zimm for valuable discussions and for encouragement. Also we are pleased to acknowledge several helpful discussions with L. Guttman and M. B. Webb.

### Vacuum Ultraviolet Absorption Spectrum of Phosgene\*

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(Received July 25, 1960)

The spectrum of phosgene was investigated, for the first time, over the region 2000–600 Å with a dispersion of about 4.15 Å/mm. A number of resolved transitions were found, some with vibrational structure. The vibrational structure was in each case interpreted as a progression in a totally symmetrical frequency. A tentative interpretation of the electronic transitions is given.

#### INTRODUCTION

THE electronic transition of phosgene at longest wavelengths<sup>1</sup> consists of many bands between 3050 and 2380 Å, followed by a continuum which extends into the vacuum ultraviolet region. The present study revealed several transitions of higher intensity at wavelengths shorter than 2000 Å.

Molecules containing the carbonyl group possess a characteristic region of absorption in the near ultraviolet. These molecules also possess transitions in the vacuum ultraviolet which are probably localized in the carbonyl group of the molecule. It is possible to interpret some of the observed transitions of phosgene by analogy with the spectra of other carbonyl compounds. Comparison with the spectra of the chloromethanes is also helpful in the interpretation.

#### EXPERIMENTAL

The absorption spectrum of phosgene was obtained with a 2-m vacuum spectrograph previously described.<sup>2</sup>

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<sup>1</sup> V. Henri and O. R. Howell, Proc. Roy. Soc. (London) **A128**, 178, 192 (1930).

<sup>2</sup> C. R. Zobel and A. B. F. Duncan, J. Am. Chem. Soc. **77**, 2611 (1955).

In the first order the plate factor of this instrument is about 4.15 Å/mm. The background for absorption was provided by the Lyman continuum; Eastman Kodak SWR plates were used.

The emission lines of carbon and silicon which occur in the Lyman continuum were used as wavelength standards.<sup>3</sup> The absorption maxima were read from microphotometer tracings of the plates. The error in measurement was about 10 cm<sup>-1</sup> for vibrational bands and 2–4 Å for the maximum of broad electronic transitions.

The phosgene was obtained from a commercial source and was specified as 99.9% pure. Vapor phase chromatographic and mass spectroscopic analysis showed no detectable impurities. The phosgene was expanded directly into the spectrograph from a calibrated volume to final pressures of 1 to 50 μ Hg. The spectrograph served as a 4-m absorption column.

#### DESCRIPTION OF THE SPECTRUM

The first electronic transition (I) of phosgene in the vacuum ultraviolet region is a broad absorption region with maximum at 1550 Å (64 700 cm<sup>-1</sup>). At 5-μ pressure in 4 m path length the absorption extends over a spectral region of about 160 Å. As the pressure is in-

<sup>3</sup> J. C. Boyce and J. T. Moore, "Provisional wavelength identification tables for the vacuum ultraviolet," M.I.T., 1941.