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Free volume theories of the glass transition and the special case of metallic glasses

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Theories based on the concepts of free volume and the existence of holes in liquids are briefly reviewed. Available experimental data on the changes in specific heat and thermal expansion at the glass transition temperature and the temperature dependence of viscosity near transition have been utilized to evaluate the hole formation energy and critical hole size in palladium-, platinum- and gold-based metallic glasses. It has been found that in conformity with theoretical predictions, transport in metallic glasses occurs by the movement of highly ionized atoms. A linear relationship exists between the hole formation energy and glass transition temperature of metallic glasses. It is suggested that a high energy of hole formation is a necessary criterion for easy vitrification of metallic melts. The behaviour of vacancies in crystalline metals is compared with the behaviour of holes in metallic glasses.

1. Introduction

Cohen and Turnbull [1] predicted that liquids of even the simplest structure would go through a glass transition if sufficiently undercooled by very rapid quenching. The growing literature on the production of metallic glasses amply justifies the prediction [2]. The existence of a reversible glass transition in a metallic glass was first established in a classic investigation by Chen and Turnbull [3]. They measured the specific heat of an amorphous $Au_{0.77}Ge_{0.136}Si_{0.094}$ alloy through the glass transition region and detected the anticipated abrupt variation in specific heat over a narrow temperature range. Several such studies have since been conducted by Chen and co-workers [4–9] who have determined the changes in specific heat, thermal expansion coefficients and elastic constants for several palladium- and platinum-based metallic glasses. Cohen and Turnbull's original prediction [1] was based on the concept of free volume.

In a recent study [10], we arrived at the energy for hole formation in metallic glasses from their known viscous behaviour. It was assumed that the free volume in the glass results from the formation of holes as suggested by Eyring and associates [11], who were interested in organic monomers and polymers. The present sequel attempts to show, more generally, that the available data on viscosity, specific heat, thermal expansion coefficients and diffusion coefficients are consistent with Hirai and Eyring's hole theory of the liquid state [12, 13]. Estimates are made of a critical hole size in metallic glasses, that is, the smallest hole size which will permit atomic transport. We contend that the hole and free volume theories which have been so successful in describing the behaviour of polymeric glasses are equally capable of explaining the behaviour of metallic glasses.

2. Free volume and atomic transport in liquids

The transition of an undercooled liquid to glass with decrease in temperature is accompanied by discontinuous changes in thermal expansion, specific heat, compressibility and viscosity. It corresponds to a change in slope in a plot of specific volume as a function of temperature. Batschinski [14] suggested, as early as 1913, that

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*On leave from the Department of Metallurgical Engineering, Banaras Hindu University, Varanasi-5, India the product of shear viscosity, η, and the total thermal expansion of the liquid, $(V - V_0)$, where V is the volume of the material at any temperature T and V_0 its volume at a reference temperature T_0, is a constant;

$$\eta(V - V_0) = K \tag{1}$$

More recently, however, Doolittle [15, 16] showed that the shear viscosities of simple hydrocarbons are better represented by a non-linear expression of the form

$$\eta = A \exp B[V_0/(V - V_0)] \tag{2}$$

where A and B are empirical constants, the latter of the order of unity. V_0 was estimated from either the density or from the thermal expansion characteristics of the liquid, T_0 being equated to zero absolute temperature.

The above-mentioned observations resulted in the rather vaguely defined but operationally very useful concept of *free volume.* The difference between the properties of liquids and solids is generally thought to have its origin in the large free volume of liquids. The term "free volume" has been used in the literature to denote three distinct concepts [17, 18]: (1) The empty volume per mole, which is determined by subtracting the notional volume per mole of a substance, as calculated from the size (van der Waals) of individual molecules, from the measured volume per mole at any given temperature. The van der Waals volume is assumed to be independent of temperature. (2) The excess of measured volume per mole at the temperature of interest over the molar volume of the liquid at zero absolute temperature. This last can be estimated by extrapolation from the variation with temperature of either the density or the thermal expansion of the liquid, as was done by Doolittle [15, 16], with the implied assumption that the liquid is nonassociated and does not undergo any phase changes on cooling to zero absolute temperature. (3) A third estimate involves the calculation of "fluctuation volume" which is the volume swept by the centre of gravity of a molecule in the course of its thermal vibration. In the present paper, the second interpretation listed above, viz. the "expansion volume", is considered to be identical with the free volume and is shown schematically in Fig. 1.

The free volume at any given temperature is often expressed as a fraction of the total volume at zero absolute temperature. Thus, the *relative free volume* $f_T = (V - V_0)/V_0$; Equation 2 can therefore be rewritten as

$$\eta = A \exp(B/f_T) \tag{3}$$

The development of Equation 3, the Doolittle equation, was followed by the observation by

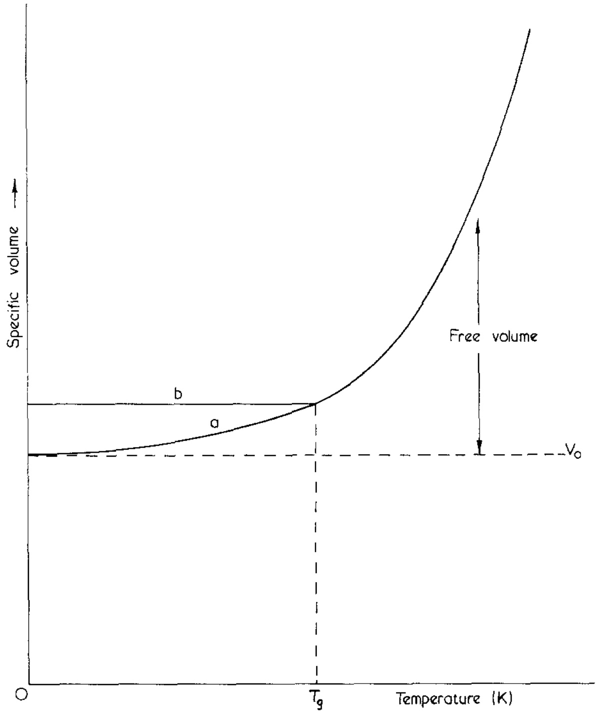

Figure 1 Schematic representation of the temperature dependence of free volume (a) in a liquid exhibiting no glass transition, and (b) in a liquid undergoing glass transition at T_g. V_0 is the specific volume of the liquid at absolute zero temperature. Only change in free volume is considered; thermal expansion due to thermal vibration is neglected.

Williams *et al.* [19] that the ratio of relaxation times at any temperature T to the value at the glass transition temperature T_g can be expressed by a universal equation capable of explaining the viscous behaviour of polymeric and inorganic materials irrespective of their molecular constitution. By comparing their equation with the Doolittle equation, Williams *et al.* [19] observed that the relative free volume for a variety of these materials is ~ 0.025 at the glass transition temperature. Fox and Flory [20] had earlier suggested that the glass transition in undercooled liquids is brought about by the fall of the relative free volume to a very small but constant value.

Theoretical basis for the empirical Doolittle equation was provided by Bueche [21] and Cohen and Turnbull [1, 22]. Bueche assumed that molecular vibrations in a liquid occasionally open up voids large enough to permit a molecular jump. The creation of a void requires the cooperative movement or vibration of a number of molecules. At high densities and low temperatures, the formation of the required voids becomes increasingly difficult and the undercooled liquid exhibits a glass transition. Cohen and Turnbull [1], on the other hand, started with the assumption that atomic transport in a hard-sphere fluid becomes possible only when a void of volume greater than a critical value v^* is formed. Further, the total free volume Nv_f, where v_f is the average free volume per atom and N the Avogadro number, was assumed to be partitioned randomly. The critical void was postulated to arise from a redistribution of free volume without attendant changes in energy at constant total volume. Below the glass transition temperature the free volume is nearly zero and temperature independent. At $T < T_g$ no density fluctuations capable of redistributing the free volume can arise. On increasing the temperature, a rapid increase in free volume results above T_g and is redistributed over the entire sample. Cohen and Turnbull [1] related the self-diffusion constant, D, to the probability $p(v)$ of finding a free volume between v and $v + dv$ by the following equation

$$D = gu \int_{v^*}^{\infty} a(v)\, p(v)\, dv \qquad (4)$$

where g is a geometric factor with a magnitude of $\frac{1}{6}$. u is the gas kinetic velocity given by $(3kT/m)^{1/2}$, where k is the Boltzmann constant and m is the mass of the molecule. The probability $p(v^*)$ of finding a free volume exceeding v^* was obtained by maximizing the number of ways of distributing the free volume. Such a procedure ultimately results in the following expression for D:

$$D = \tfrac{1}{6}\, a^* u \exp\left(-\gamma \frac{v^*}{v_f}\right) \qquad (5)$$

where a^* is approximately equal to the molecular diameter and γ is an overlap factor of the order of $\frac{1}{2}$ to unity, i.e. a factor to correct for the overlap of adjacent voids. This analysis was further refined by Turnbull and Cohen [22] to include the consequences of back-scattering. Equation (5) was shown to be valid in the high density regime where $v^* \gg v_f/\gamma$. Several reviews of this work are now available [23–25].

According to Frenkel [26], and Eyring and co-workers [11–13], the thermal expansion coefficient of liquids represents primarily the creation of additional free volume with rising temperature by way of creation of "holes". These hole theories are discussed in the following section.

3. Hole theory of liquids

The spatial distribution of the free volume of a liquid is partly discontinuous and partly accommodated by an increase in the minimum interatomic spacing. In the original hole theories of liquids, the latter is neglected and the discontinuous increase is attributed entirely to the formation of holes. While one can easily visualize holes as lattice vacancies and interstitial spaces in the case of crystalline solids, as first pointed out by Frenkel [26], the distinction between interstices and vacancies is less clear in the case of liquids. Consequently, holes have to be treated simply as abnormal gaps between atoms, gaps which arise and collapse spontaneously.

Treating holes as cavity fluctuations in a continuous medium, Frenkel [26] attempted to obtain an average size and distribution of sizes of cavities and the energy for the formation of a cavity of average size. The result indicated that the formation energy of an average cavity is equal to kT, where k is the Boltzmann constant, a value in complete disagreement with the experimental data on temperature dependence of viscosity. Frenkel [26] therefore concluded that it it necessary to modify his assumption of a continuous size distribution and to postulate, arbitrarily, that only holes exceeding a critical size and requiring a minimum amount of work for their formation exist in the liquid. He further argued that the size distribution of holes must be quite narrow; in effect he proposed that all holes have virtually the same size.

Eyring and associates [11–13] start with the assumption that a liquid can be considered to possess a quasi-crystalline lattice and contain vacant lattice sites which are treated as holes. Each hole is characterized by a constant volume v_h and a temperature-independent energy of formation, ϵ_h, at constant pressure. These assumptions are akin to those made by Frenkel. However, important differences arise between Hirai and Eyring's treatment and that of Frenkel owing to differences in the assumed size for the holes. Frenkel [26] considered the holes to be atom-sized while Hirai and Eyring [12, 13] consider them to be much smaller. The assumed hole size can have noticeable influence on the free energy of the liquid and on the proposed number of holes in it.

The equilibrium number of holes, N_h, is determined by maximizing the decrease in free energy associated with the introduction of holes. The first step is, therefore, to arrive at an expression for the change in free energy of the liquid, ΔG, which is given by

$$\Delta G = \Delta E + P\Delta V - T\Delta S \tag{6}$$

ΔE represents the change in internal energy of the liquid due to introduction of N_h holes and its magnitude is $N_h\epsilon_h$. The work of expansion caused by an increase in volume of $N_h v_h$ is presented by $P\Delta V$. The change in entropy ΔS at temperature T arises from two different sources: the vibrational entropy contribution ΔS_h due to the formation of the hole, and ΔS_m, the change in entropy due to the mixing of N_h holes and N_a atoms. The contribution ΔS_h is considered to be small and the total change ΔS is dominated by ΔS_m [12, 13]. Two different methods have been used in the literature [26, 12, 13]. Two different methods have been used in the literature [26, 12, 13] for evaluating ΔS and consequently for the evaluation of N_h. The first of these assumes ideal mixing of atoms and atom-sized holes and the change in entropy is represented by

$$\Delta S = -k\left\{\frac{N_h}{N_a}\ln\left[N_h/(N_h+N_a)\right] + \ln\left[N_h/(N_h+N_a)\right]\right\} \tag{7}$$

where N_a is the number of atoms, each having a volume v_a considered to be independent of temrature. It is to be emphasized that the ideal mixing approximation assumes that the two species being mixed are of the same size, i.e. $v_a = v_h$. Under these conditions Equation 7 can be rewritten as

$$\Delta S = -k\left[\frac{f_T}{1-f_T}\ln f_T + \ln(1-f_T)\right] \tag{8}$$

in terms of the relative free volume f_T. Substituting the value of S from Equation 7 into Equation 6 and putting $\partial\Delta G/\partial N_h = 0$ yields the result

$$N_h = N_a \exp\left(\frac{-\epsilon_h - Pv_h}{kT}\right) \tag{9}$$

Analyses of the transport properties of liquid metals [1] have indicated that the volume of a hole, v_h, in these liquids is in fact far smaller than the volume per atom (or molecule), v_a, in the corresponding liquid at atmospheric pressure and zero absolute temperature. Accordingly, use of Equation 7 has been discarded and an alternative method employed for estimating the change in entropy of mixing holes of volume v_h and atoms of volume v_a [12, 13].

Furthermore, thermodynamic investigations on solutions of polymers have emphasized the need for the development of an alternative expression for the entropy of mixing capable of taking into consideration substantial differences in the sizes of solvent and solute molecules [17, 27]. Consequently, it has been recognized that the change in entropy on mixing of molecules of dissimilar sizes is better represented by the expression

$$\Delta S = -k\left\{\left(\frac{N_A}{N_A+N_B}\right)\ln\phi_A + \left(\frac{N_B}{N_A+N_B}\right)\ln\phi_B\right\}, \tag{10}$$

where N_A and N_B are the number of molecules of species A and B respectively, and ϕ_A and ϕ_B are their volume fractions. The expression is similar to Equation 7 except that mole fractions are replaced by volume fractions in the logarithmic terms. Equation 10 has been derived from lattice models of the liquid state [27], statistical thermodynamic arguments [28] and from a consideration of free volumes [29].

When ΔS, calculated by an equation of the form of Equation 10, is substituted into Equation

6, the following expression for the equilibrium number of holes is obtained:

$$N_h = \frac{N_a v_a}{v_h} \exp\left(\frac{-\epsilon_h - P v_h}{kT}\right) \tag{11}$$

In what follows, we shall restrict ourselves to atomic, as distinct from molecular melts. We shall begin by considering melts consisting of only one species of atoms of volume v_a.

On the basis of Equation 11, the total volume V of the liquid, which is the sum of the volume of holes and atoms, can be expressed as

$$V = N_a v_a \left[1 + \exp\left(\frac{-\epsilon_h - P v_h}{kT}\right)\right] \tag{12}$$

The above equation was utilized by Hirai and Eyring [12] to obtain expressions for the compressibily, β, and volume thermal expansion, α, of liquids, using the well known identities

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T .$$

The result, in each case, was expressed as the sum of two terms:

$$\alpha = \alpha_0 + \alpha_h \quad \text{and} \quad \beta = \beta_0 + \beta_h \tag{13}$$

where

$$\alpha_0 = \frac{1}{v_a}\left(\frac{\partial v_a}{\partial T}\right)_P \quad \text{and} \quad \beta_0 = -\frac{1}{v_a}\left(\frac{\partial v_a}{\partial P}\right)_T$$

represent the expansion coefficient and compressibility of the "occupied volume", i.e. the component of the change of α and β which is due to variation in interatomic spacing. The second terms in the expressions for α and β represent the contributions due to the changing number of holes and are given by

$$\alpha_h = \left(\frac{\epsilon_h}{kT^2}\right) \exp\left(\frac{-\epsilon_h - P v_h}{kT}\right) \tag{14a}$$

and

$$\beta_h = \left(\frac{v_h}{kT}\right) \exp\left(\frac{-\epsilon_h - P v_h}{kT}\right) \tag{14b}$$

Hirai and Eyring [12] further consider the liquid state to be characterized by the equilibrium between holes and phonons. The disappearance of a hole, for example, creates elastic strain which propagates with the velocity of an elastic wave. The excess energy is taken up by the changed lattice. The creation of N_h holes increases the internal energy of the liquid and the change in number of holes with temperature entails an additional heat capacity. On this assumption, the total specific heat of the liquid can likewise be separated into two components, as was done for α and β. Therefore,

$$C_p = C_{pl} + C_{ph}$$

where C_{pl} is the contribution from lattice vibrations and C_{ph} is due to changes in the equilibrium number of holes. The latter is given on a molar basis by

$$C_{ph} = E_h \left(\frac{\partial N_h}{\partial T}\right)_P \tag{15}$$

where E_h is the energy of one mole of holes. Differentiating Equation 11 and substituting in Equation 15 gives

$$C_{ph} = R\frac{v_a}{v_h}\left(\frac{E_h}{RT}\right)^2 \exp\left(\frac{-E_h - P\Delta V}{RT}\right) \tag{16}$$

At atmospheric pressure the $P\Delta V$ term in the above expression can be neglected.

When a liquid is progressively undercooled and transforms to a glass, a particular number of holes is frozen in. Their number (per mole) is given by Equation 11, at the glass transition temperature T_g. The exact value of T_g, and hence the exact concentration of the frozen-in holes, depends on the rate at which the liquid is cooled through the critical temperature range. With this proviso, it is clear that the thermal expansion coefficient, α, the compressibility β, and the specific heat C_p, all change discontinuously at T_g because the steady variation of N_h with T which determines α_h, β_h and C_{ph} is abruptly arrested at this temperature. We will denote these abrupt changes by $\Delta\alpha$, $\Delta\beta$, and ΔC_p.

In what follows, we shall adopt the hole theory with $v_h \neq v_a$ but shall link it in various ways with the most general free-volume model.

4. Estimation of hole formation energies and hole sizes in metallic glasses

As can be seen from the preceding discussion, in principle, a knowledge of the abrupt changes at T_g in thermal expansion coefficient and compressibility can be utilized to obtain the hole formation energy and size. However, since compressibilities of metallic glasses are known only below T_g and therefore $\Delta\beta$ is not known, the hole size has instead to be estimated from a knowledge of changes in specific heat, ΔC_p, and thermal expansion, $\Delta\alpha$. For this purpose, Equations 14 and 16 above are employed. Chen and co-workers have reported [4–9] densities and changes in thermal expansion and specific heats at T_g for a number of metallic glasses based on palladium and platinum. To illustrate the procedure, data from one alloy from each series (viz., $Pd_{0.48}Ni_{0.32}P_{0.2}$ and $Pt_{0.525}Ni_{0.225}P_{0.25}$) are utilized. Equation 14a can be rewritten for atmospheric pressure ($P \sim 0$) and $T = T_g$ as

$$T_g\alpha_h = T_g\Delta\alpha = \left(\frac{E_h}{RT_g}\right)\exp\left(\frac{-E_h}{RT_g}\right) \quad (17)$$

and solved graphically for (E_h/RT_g). Equation 17 is plotted in Fig. 2 in the form of the variation of $T_g\Delta\alpha$ as a function of (E_h/RT_g). For a given metallic glass produced by rapid solidification at a given cooling rate, $T_g\Delta\alpha$ has a fixed value. As can be seen from Fig. 2, two values of (E_h/RT_g) are in general possible for a given value of $T_g\Delta\alpha$. One of these has a very low value and is not physically meaningful since energies for hole formation in liquid metals are known to be several kilocalories per mole [11, 26]. Hence, only the higher of the two values is acceptable and is recorded for the alloys in Fig. 2 and Table I.

The hole volume v_h can then be obtained with the aid of Equation 16 and the known values of (E_h/RT_g) and v_a. Ideally, v_a is the volume per atom in the liquid at zero absolute temperature where no holes would be present in the liquid. V_a has therefore to be calculated by extrapolating the volume of a mole of liquid to zero absolute temperature with the aid of the known coefficient of thermal expansion and a measured density. Even though the thermal expansion coefficient is known, densities of the liquid alloys under consideration are not available. Therefore, to a first approximation, the value of v_a was obtained from the room-temperature values of the densities of amorphous alloys. The hole volumes obtained with these assumptions are shown in Table II.

5. Hole formation energy and viscous behaviour

Recently we demonstrated that the viscosity of undercooled metallic liquids ($Au_{0.77}Ge_{0.136}Si_{0.094}$ and $Pd_{0.775}Cu_{0.06}Si_{0.165}$) can be represented as a function of temperature by the Doolittle equation (Equation 3) [10]. For this purpose, the relative free volume f_T was assumed to be given by

$$f_T = \frac{V - V_0}{V_0} = \frac{N_h v_h}{V_0} \quad (18)$$

The equilibrium number of holes at a given temperature T was assumed to be given by Equation 9 of the present paper. A direct substitution of Equation 18 into Equation 3 should, in conjunction with experimental viscosity data, yield values of f_T at various temperatures. However, this approach leads to a set of non-linear simultaneous equations which are difficult to solve. To overcome the problem, a function of the type

$$\frac{f_T}{f_M} = 1 + \sin 2\pi\left(\frac{T - T_M}{T_M - T_0}\right) \quad (19)$$

was proposed in the earlier paper, to approximate the exponential temperature dependence of f_T. f_M is the relative free volume at the melting point T_M, and T_0 is a temperature at which relative free volume goes to zero. f_M was assumed to be 0.35*.

Equation 3 was then rewritten as

$$\ln\left(\frac{\eta_1}{\eta_2}\right) = B(1/f_{T_1} - 1/f_{T_2}), \quad (20)$$

where η_1 and η_2 are the viscosities at temperatures T_1 and T_2 respectively. Since f_M is assumed to be 0.35, f_T values given by Equation 19 are dependent only on the value of T_0. Further, since B is a constant, Equation 20 will be satisfied for all known values of η over the experimental temperature range only when T_0 is chosen correctly. In other words, a reproducible value for B will be obtained from different pairs of viscosity values only for the correct value of T_0. The value of T_0 was, therefore, determined by the method of successive approximations until a single value for B was obtained from arbitrarily chosen pairs of viscosity values at different temperatures. From

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*This value was obtained from Equation 8. As suggested by Gutzow [30], ΔS represents the difference in configurational entropy of a liquid and the solid in equilibrium with it and should be equal to the entropy of fusion at T_M.. Since the entropy of fusion of many metallic liquids is ~ 2 e.u., f_M should be ~ 0.35.

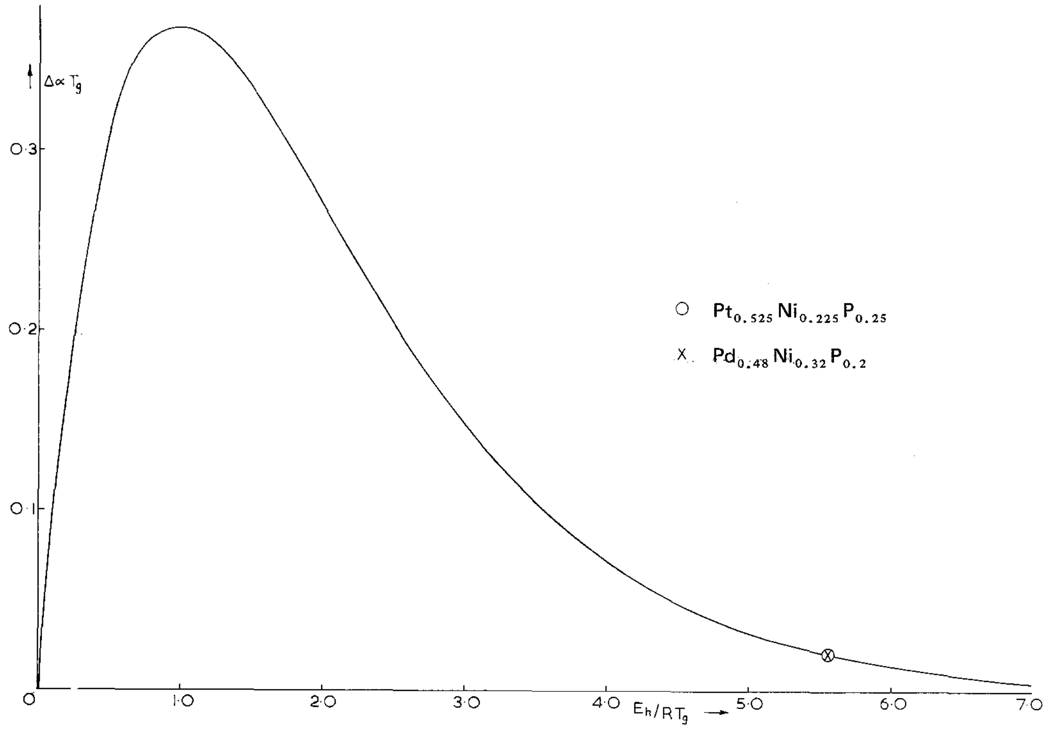

Figure 2 A plot of the theoretical $T_g\Delta\alpha$ product versus reduced hole energy, E_h/RT_g, Equation (17).

this value of T_0 and Equation 19, values of f_T were calculated for a range of temperatures. Equation 18 was now rewritten by substituting

$$f_T = \frac{N_h v_h}{V_0} = C\exp(-E_h/RT) \qquad (21)$$

with this substitution, Equation 18 can be written

$$\frac{f_T}{f_M} = \exp -\epsilon\left(\frac{\Delta T}{T}\right) \qquad (22)$$

where $\epsilon = -E_h/RT_M$ and $\Delta T = T_M - T$. E_h has determined from Equation 22 by plotting the calculated values of f_T against $(\Delta T/T)$, assuming $f_M = 0.35$. Analysis of experimental data due to Chen and Turnbull [4] and Chen and Goldstein [9] for the $Au_{0.77}Ge_{0.136}Si_{0.094}$ and $Pd_{0.775}Cu_{0.06}Si_{0.165}$ glasses by the foregoing procedure yielded values for E_h, A, B and C which are shown in Table I. It can be seen that for both the alloys, f_T at T_g was ~ 0.03 and B was ~ 1.0. These values are akin to those obtained by Doolittle [15, 16] for a number of organic liquids. The procedure was applied to $Pd_{0.82}Si_{0.18}$ alloy glass with the generalized assumptions that at T_g, $f_T = 0.03$, $\eta = 10^{13}P$ and $B = 1$. The values for E_h, A and C thus obtained are also included in Table I.

The earlier analysis [10] can be further improved to obtain a physical interpretation for the constant B, to eliminate certain unnecessary or

TABLE I Hole formation energies in metallic glasses*

Alloy	T_g (K) [3,5,7]	A	B	C	B'	f_{T_g} $\times 10^3$	f_M $\times 10^3$	f'_{T_g} $\times 10^3$	f'_{T_M} $\times 10^3$	$\Delta\alpha$ $\times 10^6$ [7]	E_h (kcal mol^{-1})
$Pd_{0.775}Cu_{0.06}Si_{0.165}$	643	1.06	1.11	11.95	0.0932	45.73	350	3.83	29.42	–	7.12
$Pd_{0.82}Si_{0.18}$	648	0.338	1.00	15.08	0.0647	29.05	350	1.93	22.76	–	8.06
$Au_{0.77}Ge_{0.136}Si_{0.094}$	294	0.0127	0.90	3.05	0.2838	20.17	350	9.89	114.02	–	2.70
$Pd_{0.48}Ni_{0.32}P_{0.2}$	585	–	–	–	–	–	–	3.60	–	34.5	6.55
$Pt_{0.525}Ni_{0.225}P_{0.25}$	486	–	–	–	–	–	–	3.95	–	44.7	5.35

*A, B, C, f_{T_g} and f_M refer to the old analysis [10]. B', f'_{T_g} and f'_{T_M} refer to the present analysis. E_h is unaltered by the change from the old to the new analysis.

incorrect assumptions and to make it consistent with the approach developed in the present paper. Since $v_a \neq v_h$, the equilibrium number of holes N_h has to be obtained from Equation 11 in preference to Equation 9. It is also no longer valid to put $f_M = 0.35$ since $v_a \neq v_h$ ($v_a = v_h$ was assumed in arriving at Equation 8 and in the calculation of f_M in the footnote on page 2493). It is sufficient to treat f_M as a constant for each alloy and carry out the earlier analysis purely in terms of normalized relative free volume, i.e. f_T/f_M. With the assumption that N_h is given by Equation 11, the relative free volume can now be expressed as

$$f'_T = \frac{N_h v_h}{V_0} = \frac{N_a v_a}{v_h}\,\frac{v_h}{V_0}\exp\left(\frac{-E_h}{RT}\right)$$

$$= \exp\left(\frac{-E_h}{RT}\right). \tag{23}$$

The prime indicates that the fractional volume is calculated for $v_h \neq v_a$. The ratio f'_T/f'_M is still given by Equation 19 and 22. This would leave the values of E_h and A unaltered while C becomes unity in Equation 21. Since Equations 19 and 22 are still valid, the new relative free volume, f'_T, is related to the earlier relative free volume, f_T, by

$$f'_T = \left(\frac{f_T}{0.35}\right) f'_M \tag{24}$$

Consequently, the new value of B in Equations 3 and 20, designated B' in the present analysis, is related to B of the earlier analysis by

$$B' = \left(\frac{B}{0.35}\right) f'_M \tag{25}$$

where f'_M is now obtained from Equation 23 in each case. The values obtained for B' for the $Au_{0.77}Ge_{0.136}Si_{0.094}$ and $Pd_{0.775}Cu_{0.06}Si_{0.165}$ alloys are shown in Table I. It is important to note that the revised analysis leads to the same values for viscosity at various temperatures, and the same E_h, as before.

The present analysis shows that f'_M is 0.113 in the case of $Au_{0.77}Ge_{0.136}Si_{0.165}$ alloy and 0.029 in the case of $Pd_{0.775}Cu_{0.06}Si_{0.165}$ alloy. Turnbull has calculated the ratio of the specific volume of the amorphous state to that of the crystal at 0 K and obtains a value of 1.125 for pure gold [31]. This implies that f'_M for gold is 0.125 and the proximity of this value to 0.113 obtained for the gold-based alloy justifies the present analysis. The large difference in the values for f'_M for the two alloys is striking. In this connection it may be remarked that the addition of silicon to palladium is known to decrease the molar volume of the liquid alloys by as much as 20% below the value derived on the asumption of ideal mixing at high temperatures [32].

To recapitulate, the sequence of calculation is as follows: E_h is calculated from experimental data on viscosity with the aid of Equation 19. Then from Equation 23, f'_M and f'_{T_g} are computed. Table I lists values of f_M and f_{T_g} (old analysis) and f'_M and f'_{T_g} (new analysis) for comparison. It will be seen that contrary to the long-held views of Fox and Flory [20] which were supported by our first analysis [10], the new approach does *not* indicate a constant value of f' at the glass transition temperature for the various glasses we have examined. However, it is interesting to observe that the ratio f'_{T_g}/f'_M is roughly constant and this is associated with the fact that T_g/T_M does not vary greatly from one glass to another.

The most important result of the revised analysis, however, stems from a comparison of Equation 3, with $B = B'$, and an expression for η based on the free volume approach due to Cohen and Turnbull [1]. For the purpose of this comparison it may be recalled that the self-diffusion coefficient D and the viscosity η of a liquid are related by the Stokes–Einstein equation

$$D = \left(\frac{k}{3\pi a_0}\right)\frac{T}{\eta} \tag{26}$$

where k is the Boltzmann constant and a_0 is the atomic diameter. Combining Equations 5 and 26, η can be expressed as

$$\eta = \eta_0 \exp\left(\gamma v^*/v_f\right) \tag{27}$$

The relative free volume f'_T of the present analysis and the average free volume per atom v_f of Cohen and Turnbull's analysis [1] can be related to each other as follows:

$$f'_T = \frac{N_h v_h}{N_a v_a} = \frac{v_f}{v_a} \tag{28}$$

and substituting for v_f from Equation 28 into Equation 27 we obtain

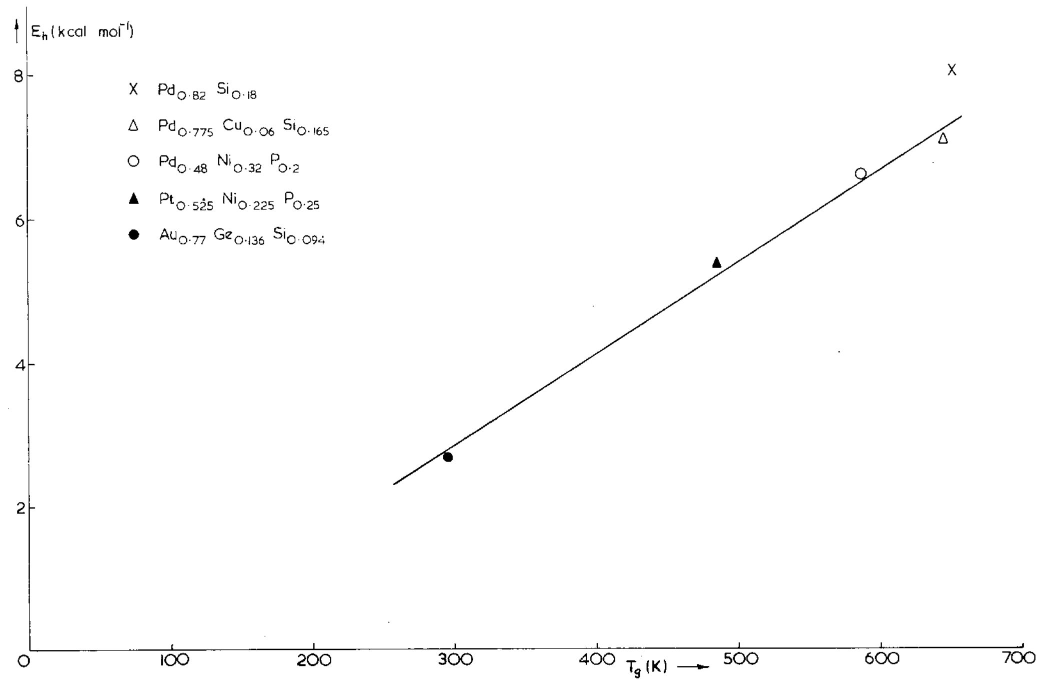

Figure 3 The empirical linear relationship between calculated hole energies and corresponding glass transition temperatures for a variety of metallic glasses.

$$\eta = \eta_0 \exp\left(\frac{\gamma v^*}{v_a f_T'}\right) \tag{29}$$

A comparison of Equations 3 and 29 suggests that $B' = (\gamma v^*/v_a)$. The overlap factor γ is generally taken to be unity. Hence, B' represents the ratio of the volume of a critical void necessary for flow in a hard-sphere liquid or glass and the volume per atom in the liquid at zero absolute temperature and atmospheric pressure*. It is significant that the values for v^*/v_a obtained from the present analysis of the data of the two alloy glasses (0.093 for $Pd_{0.775}Cu_{0.06}Si_{0.165}$ and 0.284 for $Au_{0.77}Ge_{0.136}Si_{0.094}$) are of similar magnitude to those calculated by Cohen and Turnbull [1] from an analysis of diffusion data of elemental liquid metals (from 0.0935 for Hg to 0.72 for Ga). This aspect is discussed further in Section 6.2.

6. Discussion

6.1. Hole energy and glass transition temperature

An examination of Table I shows that the energy for hole formation scales as the glass transition temperature T_g. In Fig. 3 the values of E_h are plotted against T_g and the best fit straight line is drawn through the values which have been determined from experimental data on viscosity and thermal expansion. The straight line is represented by the equation:

$$E_h = 13.83\,T_g - 1400(\pm 290)\,\text{cals mole}^{-1}. \tag{30}$$

The conclusion that E_h varies linearly as T_g is not altogether surprising. The activation energy for viscous flow is composed of the energy for formation of holes and the activation energy for their migration. In general, the migration energy is assessed to be only 10 to 20% of the total activation energy for viscous flow [11]. To a first approximation then, the activation energy for viscous flow, E_{vis}, can hence be equated to E_h. A linear relationship has also been found for the variation of activation energy for viscous flow with respect to the melting point T_m in pure liquid metals [33]. Further, Spaepen and Turnbull [34] have shown that T_g/T_m is in the range 0.44 to 0.66 when both the temperatures are expressed in degrees Kelvin. Hence, the energy for hole formation can be expected to vary in a roughly linear way with T_g.

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*As mentioned in Section 3 the hole theory assumes that the hole size is equal to the critical void size necessary for flow, i.e. $v^* = v_h$.

TABLE II Hole Volumes and Radii in Metallic Glasses

Alloy	ΔC_p (cal deg K^{-1} $\cdot$ mol^{-1}) [3, 5, 38]	Density ($g\,cm^{-3}$) [2, 7, 48]	v_a ($Å^3$)	v_h($Å^3$)		v_h/v_a		r^*(Å)		Ionic radii Å [36, 37]
				from ΔC_p	from viscosity	from ΔC_p	from viscosity	from ΔC_p	from viscosity	
$Pd_{0.775}Cu_{0.06}Si_{0.165}$	2.0	10.48	14.39	1.69	1.34	0.117	0.093	0.74	0.68	Pd 2+ 0.80 4+ 0.65 to 0.55
$Pd_{0.82}Si_{0.18}$	3.06	10.25	14.95	0.73	0.97	0.049	0.065	0.56	0.61	Cu 1+ 0.96 2+ 0.72
$Au_{0.77}Ge_{0.136}Si_{0.094}$	5.65	15,12	18.02	1.32	5.11	0.073	0.284	0.68	1.07	Si 1+ 0.65 4+ 0.42 Au 1+ 1.37 3+ 0.85
$Pd_{0.48}Ni_{0.32}P_{0.2}$	2.50	9.83	12.84	1.16	–	0.090	–	0.65	–	Ge 2+ 0.73 4+ 0.44
$Pt_{0.525}Ni_{0.225}P_{0.25}$	4.40	15.85	12.92	0.70	–	0.054	–	0.55	–	Ni 2+ 0.69 P 3+ 0.44 5+ 0.35 Pt 2+ 0.80 4+ 0.65 to 0.55

6.2. Hole size and volume

The values for v^*/v_a in the metallic glasses at T_g and the hole volume v_h calculated therefrom, by the procedures illustrated in Sections 3 and 4, are shown in Table II. As remarked earlier the ratio v^*/v_a is seen to be in the range 0.05 to 0.30 for the glasses analysed and is of the same order of magnitude as that reported by Cohen and Turnbull [1] for pure liquid metals. By assuming the critical void to be spherical in shape, Cohen and Turnbull calculated its radius r^*. In each case, the critical radius r^* was found to be close to the ion core radius corresponding to the highest valence state of the metal, as is indeed appropriate to their initial postulate of a hard-sphere liquid. The present analysis also leads to a similar conclusion. The Goldschmidt ionic radii for the elements in their various valence states that constitute the alloys under consideration, along with the values for r^*, are shown in the last column of Table II. It is to be remarked that there is considerable discrepancy in the values for Goldschmidt atomic radii quoted in the literature [35]. Where there is considerable doubt, a range of values [36, 37] is quoted in Table II. As can be seen from the tabulated data, in all cases the calculated hole radius is close to the smallest ionic radius among the constituent metals, suggesting that the flow and other properties of both liquids and glasses are controlled by the movement of ions, rather than unionized atoms, into available holes. This confirms with the suggestion made by Eyring [11], and Cohen and Turnbull [1]. On the basis of the present analysis it would appear that it is the size of the metallic ions, rather than that of the smaller metalloid ions, which governs the transport properties.

It will be observed from Table II that the value for v^*/v_a obtained from viscosity data is always larger than that obtained from changes in specific heat at T_g. The discrepancy arises from uncertainties in the value of ΔC_p at T_g. The point is well illustrated by the data on $Pd_{0.775}Cu_{0.06}Si_{0.165}$ glass considered here. Chen reported ΔC_p to be 3.2 cal (deg K mol)$^{-1}$ [5] and 3.86 cal (deg K mol)$^{-1}$ [6]. In a later publication, Chen and Coleman reported [38] a value of only 2.0 cal (deg K mol)$^{-1}$ for the same glass in the annealed state. Equation 16, which was used to calculate v_h/v_a, assumes that an equilibrium concentration of holes is frozen-in at T_g. In practice, at the extremely rapid rates of quenching characteristic of the methods utilized in the production of metallic glasses, a non-equilibrium number of holes is frozen-in. This affects the value of ΔC_p recorded. On the other hand, the thermal expansion data were reported to have been obtained after stabilizing the glass and the viscosity data were obtained just above T_g. Hence the values of v^*/v_a obtained from viscosity data are more reliable. Experimental determination of changes in compressibily at T_g would be welcome to allow further comparisons.

6.3. Diffusion in metallic glasses

Gupta *et al.* [39] determined the diffusion coefficient of radioactive silver in a $Pd_{81}Si_{19}$ alloy glass in the temperature range 480 to 550 K, far below T_g ($\sim$645 K). Their results show that the silver diffusion coefficient can be represented by

$$D = 2 \times 10^{-6} \exp(-29\,965/RT) \qquad (31)$$

and implies that extensive diffusive transport can occur below T_g.

It is possible to calculate the diffusion coefficient for palladium in $Pd_{82}Si_{18}$ glass at T_g from Equation 5 utilizing the v^* value obtained from ΔC_p at T_g, E_h value obtained by the earlier analysis, taking γ as unity and taking a^* to be the atomic diameter. Such a calculation yields a value for D at T_g (648 K) of 1.57×10^{-15} cm^2 sec^{-1} for Pd diffusion in $Pd_{82}Si_{18}$. This compares with a value of 1.57×10^{-16} cm^2 sec^{-1} obtained for the diffusion of radioactive silver at the temperature (648 K) in the $Pd_{81}Si_{19}$ glass, derived from Equation 31. The slower rate of silver diffusion is understandable since the Goldschmidt radius of Ag^+ ion (1.13 Å) is greater than that of Pd^{4+} ion (0.65 Å). It should, however, be remarked that the temperature dependence of D (Equation 31) is difficult to explain on the basis of the free volume theory. According to the postulates of the free volume theory and the hole theory, a relative free volume characteristic of the glass transition temperature T_g is frozen in at all temperatures below T_g. Hence the exponential term in Equation 5 should in fact be constant for all temperatures lower than T_g. The temperature dependence of D will then be solely controlled by the average kinetic velocity $\bar{u}$ in the pre-exponential term of Equation 5. Hence the diffusion coefficient D should vary as $T^{1/2}$, contrary to the experimental observation [39].

Diffusion in metallic glasses is in urgent need of more extensive investigation.

6.4. Hole energy in relation to formation and stability of metallic glasses

A characteristic feature of good glass formers is the strong temperature dependence of viscosity as represented by the Doolittle equation (Equation 3) and this is primarily determined by the relative free volume f_T. This in turn depends on the magnitude of hole formation energy E_h as represented by Equation 23. Materials with a high value of E_h should therefore be easy glass formers.

It has been observed that for non-metallic liquids, the ratio of the energy of evaporation (ΔE_{vap}) to the activation energy for viscous flow (E_{visc}) is close to 2.5 [11]. However, for metallic materials this ratio is in range of 8 to 25. Since ions and not neutral atoms are responsible for viscous flow in liquid metals, Eyring suggested that the quantity

$$\left(\frac{E_{vap}}{E_{vis}}\right)\left(\frac{r_{ion}}{r_{atom}}\right)^3 \qquad (32)$$

where r_{ion} and r_{atom} are the ionic and atomic radii respectively, is a good measure for comparing metallic and non-metallic materials. He gave reasons for supporting this quantity to be constant and showed that its value is indeed always in the range 3 to 4. The physical reality underlying Eyring's suggestion is that the activation energy for viscous flow is nearly the energy for hole formation and ΔE_{vap} is a measure of the cohesive energy of the liquid. In general, therefore, a high latent heat of evaporation should imply greater energy of hole formation.

The above observation leads us to the concept of reduced melting temperature, T_f, suggested by Cohen and Turnbull [40]. T_f is given by

$$T_f = kT_m/h_v \qquad (33)$$

where k and h_v are the Boltzmann constant and heat of evaporation per atom, respectively. It was suggested that a low value of T_f corresponds to a high glass-forming tendency. The general observation that many metallic glasses are either based on eutectic alloys or transition metals can be explained in terms of T_f. Eutectic alloys have low T_f by virtue of low T_m while transition metals have high values of h_v leading to a decrease in T_f. From the discussion of the previous paragraph it was concluded that a high value for E_h results when the latent heat of evaporation is high. Hence materials with a high value of E_h would also have a low value of T_f and be easy glass formers. Thus, the present approach in terms of E_h is consistent with the empirical finding of Cohen and Turnbull [40].

The formation of alloy glasses has been attributed to a number of other physically quite distinct considerations, ranging from crude space-filling criteria to electronic energy considerations [41–46]. A frequent explanation is based on the existence of local short-range order arising out of stronger unlike-neighbour bonds [44]. This view is in consonance with the present arguments since creation of a hole in locally ordered regions would require greater energy for hole formation than in disordered (i.e. chemically random) regions.

Further, the time for crystallization of a small fraction of liquid has been shown to be directly proportional to the viscosity [47]. From Equations 3 and 23 it can be inferred that the viscosity varies approximately as exp $[\exp(E_h/RT)]$. Hence, the time for the crystallization of a small volume is directly and strongly dependent on E_h. High values of E_h delay crystallization effectively and reduce the critical cooling rate for glass formation.

The essential conclusion that materials with high value for E_h are the easy glass formers is supported further by the data of Fig. 3. $Pd_{0.775}Cu_{0.06}Si_{0.165}$ and $Pd_{0.82}Si_{0.18}$ are known to be among the easiest glass formers [5]. Theoretical calculations show that the critical cooling rate required for the production of a $Au_{0.77}Ge_{0.13}Si_{0.094}$ glass is three to four orders of magnitude greater than the rates for palladium-based glasses [10, 48].

In general, all factors which promote glass formation and raise T_g also enhance the stability of a glass. The prime requisite for easy formation and retention of glassy alloys appears to be a high cohesive energy which is reflected in the high value of energy for hole formation.

6.5. Crystal vacancies and free volume theory

When a vacancy migrates in a metallic lattice, that is, during self-diffusion in a crystal, it is generally found that the activation energy for migration, E_m, does not differ greatly from the formation energy of vacancies, E_f, and this is true for a range of metals. Yet in a metallic glass, E_m is estimated to be as small as $0.35\,E_f$ to $0.1\,E_f$ [4, 49]. The difference between high E_m in a crystal and low E_m in a glass is evidently to be attributed to the looser packing of atoms in the glass: a different way of putting this is to assert that (even though in this paper we have made calculations on the basis that a majority of the holes in a glass are in a fairly narrow size range) the total free volume in a glass is widely dispersed throughout the structure. A crystal would be in a equivalent state if the vacancies it contains cease to be sharply localized and become distributed over a group of atoms. Is there any evidence that this can happen and, if and when it does, does E_m drop correspondingly? We might call this potential transition to a diffuse vacancy structure, the "free volume transition".

A suggestion to this effect derives from a simulation experiment in which bubbles on a soap solution represent a two-dimensional close-packed metal. Such a bubble raft can in effect be "heated' by subjecting the solution to mechanical vibration [50]. When that is done, it is found that as the "temperature" rises, any missing bubble sites, or vacancies, in the raft become progressively distributed. This is particularly pronounced when several vacancies are grouped close together. If this two-dimensional simulation has any resemblance to three-dimensional reality, it would suggest that one might expect to find a free volume transition near the melting temperature, if in that region the vacancy concentration is high enough to lead to a frequent close grouping of several vacancies. Kraftmakher and Strelkov [51] present evidence for vacancy concentrations approaching 0.01 in some refractory metals (though its validity is disputed), but there is no evidence of enhanced diffusion rates in this temperature range, as might be expected if E_m were to decrease as a result of a volume transition. It seems that for a free volume transition to appear, vacancy concentrations higher than 0.01 are needed, as well as high temperatures. This, it seems, can in fact happen as a consequence of radiation damage in a metal. During bombardment by energetic nucleons such as neutrons, displacement cascades are produced by the primary bombarding particle, i.e. regions are formed from which interstitials are transported outwards, leaving a vacancy-rich region at the cascade centre [52]. Such vacancy concentrations can collapse and form dislocation loops, and the kinetics of this process can be analysed in terms of an instantaneous diffusion coefficient [53, 54]. It is true that a cascade is briefly heated to a high temperature, but this temperature burst decays in a time much too short to assist significantly the vacancy transport process. When this is allowed for, one finds that in several metals, the vacancies segregate to dislocation loops (the "cascade collapse") at a modest temperature much faster than can be explained in terms of the normal mobility of the vacancies. Bullough and Eyre [53, 54] calculate that when vacancies are present in a concentration of the order of 10%, then the migration energy E_m is effectively reduced to about half its normal value.

It seems, on the basis of this detailed calculation, that really high vacancy concentrations lead to migration characteristics similar to those in metallic glasses, and this must be due to a free volume transformation, i.e. increased diffuseness or relaxation of vacancy structures, under these circumstances, even without the aid of temperatures close to the melting-point. This conclusion is quite separate from the hotly debated question of whether isolated vacancies in metals are or are not highly relaxed (i.e. diffuse in structure).

There is also evidence that in a non-metal, wüstite (FeO_x), a grouping of vacancies can lead to anomalously high diffusion rates [55]. A recent paper by Gorecki [56] is of interest in the present connection. Gorecki assembles extensive experimental evidence to show, more conclusively than did earlier authors, that the formation energy, E_F, for vacancies in a wide range of crystalline metals (A1, A2 and A3 structures) is closely proportional to the bonding energy (i.e. heat of vaporization), the absolute melting temperature and the heat of fusion per mole. The constants of proportionality are 19.2 cal $(\text{deg mol})^{-1}$ and 1.272 respectively. These empirical findings (which are of interest in the light of our finding that E_F for a hole in a metallic glass is proportional to T_g (Equation 30)) are then combined by Gorecki [56] with some theoretical analyses by Kraftmakher [51] to estimate a vacancy concentration at the melting temperature of ~ 0.004 for several metals. From the relationship of E_F to heat of fusion he calculates the fraction of holes in the molten metal near T_M and estimates this at 0.13. He deduces the value of this fraction by two independent methods: (1) from the experimental change in volume in a crystal when one vacancy is formed, and (2) from the observed volume increase on melting. He secures good agreement by the two methods of calculation. This again suggests that vacancies in crystals and holes in liquids can be regarded as similar entities.

Finally, Gorecki [56] suggests that metals melt when the vacancy concentration approaches 0.003, and the concentration then jumps by a factor of 30 to 40. Others, working through computer simulation [57, 58], have recently proposed that melting is a consequence of a critical dislocation density. It will be most interesting to see whether any theoretical basis can be discovered for the suggestion that melting results from the establishment of a critical vacancy concentration.

7. Conclusions

The present investigation clearly brings out the adequacy of the free volume theories, originally developed for explaining the behaviour of polymer and inorganic glasses, for interpreting the thermal and transport properties of metallic glasses. An analysis of the available experimental data pertaining to the changes in the specific heat and thermal expansion at the glass transition temperature, together with the temperature dependence of the viscosity of highly undercooled metallic melts, results in a valuable insight into the mechanism of transport in the glassy and liquid states of the alloys. The following conclusions are reached:

(1) The temperature dependence of the viscosity of metallic melts can be accurately represented by the Doolittle equation. Such a representation becomes physically meaningful only if the relative free volume is calculated from an expression for the number of holes that includes the ratio of the volume of a hole to the volume per atom in the liquid at absolute temperature. Such an expression can be arrived at by evaluating the entropy of mixing of holes and atoms with due consideration of the volume fraction (and not mole fraction) of holes and atoms.

(2) The relative free volume at the glass transition temperature was found to vary from one metallic glass to another. However, the ratio of the relative free volume at the glass transition temperature to that at the melting point was found to be roughly constant.

(3) The hole formation energies in palladium, platinum and gold-based glasses, evaluated from changes in thermal properties at the glass transition temperature and temperature dependence of viscosity of undercooled melts, vary linearly with the glass transition temperature.

(4) In each alloy glass the critical hole volume and size are nearly equal to those of the largest ion in its highest state of ionization. In accordance with theoretical predictions, transport in the melt and glass is controlled by the movement of these ions and not the neutral atoms.

(5) It is argued that a high energy for hole formation is a necessary condition for easy glass

formation. This observation is in conformity with several empirical criteria previously developed for explaining the ease of glass formation.

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