Thermodynamic and viscous behaviour of undercooled liquids [1]

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Abstract

The Gibbs free energy difference (ΔG) between the undercooled liquid and the corresponding equilibrium solid phases and the viscosity (η) of the undercooled liquid are key variables in the metastable solidification of glass-forming melts. Novel expressions have been developed for ΔG recently by the authors using the hole theory of liquids as well as by expanding the free energies of liquid and solid phases in the form of the Taylor series. These expressions have also been used to derive the temperature-dependence of the viscosity of the undercooled melts. The present article summarises the procedures for obtaining the expressions for ΔG; their application in obtaining the temperature-dependence of the viscosity and relaxation phenomenon are also discussed. The procedure for the estimation of the ideal glass transition temperature has been reviewed together with its importance in the glass-forming ability of materials. Glass formation has been discussed in terms of minimum volumes of constituent atoms, concentration–concentration fluctuations, driving force for nucleation and phase diagram features. The glass-forming ability of materials is also explained in terms of the ratio of specific heat difference to the entropy difference between liquid and solid phases at the melting point. Finally an attempt has been made to review the procedure for the estimation of the heat of crystallisation in terms of the viscosity of the melt.

Keywords: Gibbs free energy; Glass-forming ability; Heat of crystallisation; Hole theory; Ideal glass transition temperature; Relaxation phenomena; Undercooled liquids; Viscosity

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1. Introduction

Undercooling of melts is recognised as an important route for the production of novel metastable phases and microstructures. Their ease of formation and thermal stability are dependent on the thermodynamic properties of various metastable and stable phases which can occur in a given alloy system. Measurements of the thermodynamic properties of undercooled melts at large departures from equilibrium are always difficult and sometimes impossible. Consequently, development of methods for assessing the thermodynamic properties of undercooled liquids (more generally for stable phases in the temperature ranges where they are metastable) is useful and important. These methods also naturally lead to a description of the viscous behaviour of such phases. In this communication, we shall outline procedures developed for this purpose.

Undercooling of liquids leads to the formation of glasses if nucleation of crystalline phases can be avoided. The glass transition temperature depends, among other things, on the rate of cooling. To avoid an entropy catastrophe, Kauzmann [1] proposed the existence of an ideal glass transition temperature. The availability of a thermodynamic description of undercooled liquids also enables one to estimate the ideal glass transition temperature. Empirical relationships expressing the temperature-dependence of the viscosity also lead to alternative estimates of this temperature. Procedures for evaluating the ideal glass transition temperature are discussed and values compared with experimental observations.

We have next considered various factors governing glass formability. An evaluation of the critical cooling rate for glass formation is also discussed. The review concludes with an estimation of the enthalpy of crystallisation of glasses.

2. Thermodynamic parameters of undercooled melts

Experimental measurements of the thermodynamic parameters of the undercooled melts can be made only in a restricted range of temperature below the melting temperature T_m because of their strong tendency to crystallise. The behaviour of the thermodynamic parameters from T_m to the glass transition temperature T_g can only be predicted by extrapolation of high temperature data [2,3] to the low temperature region. The Gibbs free energy difference ΔG between undercooled liquid and the corresponding equilibrium solid phases is an important parameter in the study of the nucleation and growth processes. It also plays a significant role in the study of the stability of amorphous phases. Elementary thermodynamic relations can, in principle, be used to estimate ΔG and other thermodynamic parameters from a knowledge of the experimental data of the specific heat difference ΔC_p between the phases. As indicated above, the metastability of the liquid precludes the experimental determination of ΔC_p. Because of experimental difficulties, some expressions have been proposed [4–8] for estimation of ΔG. Most of these expressions are based on various types of assumption related to either the temperature-dependence of ΔC_p or its magnitude.

We [9] have recently reported a better expression for ΔG by deriving the temperature-dependence of ΔC_p in the framework of the hole theory of liquids. It has also been demonstrated [10–12] that an accurate description of ΔG can also be provided by the use of the Taylor series expansion. These methods can be applied to estimate other thermodynamic parameters. Both procedures have been reviewed in the present section.

2.1. The hole theory of liquids

According to the hole theory, the liquid state is described as a quasi-crystalline lattice with a considerable number of vacant sites or holes; the number of holes is usually derived by minimising the change in the free energy due to introduction of holes into a lattice. Following earlier work of Frankel [13] as well as Hirai and Eyring [14, 15], the change in the free energy ΔG associated with the introduction of N_h holes in a lattice having N_a atoms or molecules at a temperature T can be expressed as

$$\Delta G = N_h(\varepsilon'_h + p v_h) + k T \left[N_h \ln \frac{N_h}{N_h + n N_a} + N_a \ln \frac{n N_a}{N_h + n N_a} \right] - T \Delta S_h \tag{1}$$

where ε'_h represents the energy required for the formation of a hole of volume v_h; $n = v_a/v_h$, represents the relative volume of hole and atoms; v_a is the hard core volume per atom or molecule; p represents the external pressure; k stands for the Boltzmann constant and ΔS_h is the change in the entropy associated with the formation of a hole. Following Flory [16] and Sanchez [17] and minimising ΔG, Dubey and Ramachandrarao [9] obtained N_h as

$$N_h = n N_a g/(1 - g) \tag{2}$$

$$g = \exp\left[-\frac{(\varepsilon'_h + p v_h)}{k T} - A \right] \tag{3}$$

with $A = 1 - 1/n$. An expression for ΔC_p can be obtained by realising that $\Delta C_p = \mathrm{d}\Delta H/\mathrm{d}T$, where ΔH is the change in enthalpy. As a result ΔC_p takes the form

$$\Delta C_p = n R(\varepsilon_h/R T)^2 g \tag{4}$$

where ε_h is the hole formation energy per mole and R is the gas constant.

An expression for ΔG can be obtained by utilising the above equation for ΔC_p and the thermodynamic relationships

$$\Delta G = \Delta H - T \Delta S \tag{5}$$

$$\Delta H = \Delta H_m - \int_T^{T_m} \Delta C_p \mathrm{d} T \tag{6}$$

$$\Delta S = \Delta S_m - \int_T^{T_m} (\Delta C_p/T) \mathrm{d} T \tag{7}$$

where ΔH_m and ΔS_m are enthalpy of fusion and entropy of fusion, respectively, ΔH represents the enthalpy difference between the undercooled liquid and equilibrium

solid and ΔS is the entropy difference between the phases. The resulting expression for ΔG is given by

$$\Delta G = \Delta S_m \Delta T - nR\left[\gamma \delta \Delta T g_m - T(g_m - g)\right] \tag{8}$$

with $\Delta T = T_m - T$, $\gamma = (\varepsilon_h/R\,T_o)$, $\delta = (T_o/T_m)$, g_m is the value of g at $T = T_m$, and T_o is the ideal glass transition temperature. Expanding the exponential terms of g and g_m in Eq. (8) yields

$$\Delta G = \Delta S_m \Delta T - \Delta C_p^m \frac{\Delta T^2}{2T}\left[1 - \frac{\gamma \delta}{3}\frac{\Delta T}{T} + \sum_{n=4}^{\infty}(-1)^n\left(\gamma\delta\frac{\Delta T}{T}\right)^{n-2}\left(\frac{2}{n!}\right)\right] \tag{9}$$

where ΔC_p^m represents the value of ΔC_p at $T = T_m$. During the analysis of ΔG for a variety of materials, it is observed that the magnitude of the summation term in the above equation is negligible in comparison to other terms in the same bracket and can be ignored. Thus, the expression for ΔG can be expressed as

$$\Delta G = \Delta S_m \Delta T - \frac{\Delta C_p^m}{2T}\Delta T^2\left[1 - \frac{\gamma\delta}{3}\frac{\Delta T}{T}\right] \tag{10}$$

The magnitude of $\gamma\delta$ for a variety of substances varies little and is less than unity. At the same time, the contribution of term $\gamma\delta/3\Delta T/T$ is very small compared to unity in the temperature range T_m to T_g and can be neglected without much loss of accuracy. As a result, Eq. (10) can be approximated as

$$\Delta G = \Delta S_m \Delta T - \Delta C_p^m \frac{\Delta T^2}{2T} \tag{11}$$

The expression for ΔG reported in Eq. (11) requires ΔS_m, ΔC_p^m and T_m all of which can be measured easily. At the same time, it does not contain any parameter related to holes. It is interesting to compare the expression for ΔG reported by Dubey and Ramachandrarao with the earlier expressions. The first term in Eq. (11) represents the linear approximation for ΔG reported by Turnbull [4]

$$\Delta G = \Delta S_m \Delta T \tag{12}$$

on the basis of the assumption $\Delta C_p = 0$. Hoffman [5] assumed a constant but non-zero ΔC_p and proposed

$$\Delta G = \Delta S_m \Delta T(T/T_m) \tag{13}$$

Thompson and Spaepen [6] also assumed a constant value of ΔC_p and related it to entropy of fusion through a relationship

$$\Delta C_p = \alpha \Delta S_m \quad \text{and} \quad \alpha = \frac{1}{\ln(T_m/T_o)}$$

They reported an expression for ΔG which takes the form

$$\Delta G = \Delta S_m \Delta T \frac{2T}{T_m + T} \quad \text{for } \alpha = 1.0 \tag{14}$$

The expressions reported in Eqs. (9)–(11) are capable of explaining the temperature dependence of ΔG very satisfactorily in the temperature range T_g to T_m for the variety of materials, metallic glasses, oxide glasses and polymeric glasses as shown in Figs. (1a), (1b) and (1c), respectively. It gives a very good response for pure metals also, as illustrated in Fig. 1(d) for Ga. In Table 1A, an attempt is made to compare the values of ΔG obtained by the use of earlier expressions and Eq. (9) which clearly shows the greater accuracy of the expression for ΔG reported by Dubey and Ramachandrarao [9].

In a similar way, the expression for ΔH can also be derived with the help of Eqs. (4) and (6) and the resulting expression can be expressed as

$$\Delta H = \Delta H_m - n\varepsilon_h(g_m - g) \tag{15}$$

equivalently,

$$\Delta H = \Delta H_m - \Delta C_p^m T_m \frac{\Delta T}{T}\left[1 - \frac{\gamma\delta}{2}\left(\frac{\Delta T}{T}\right) \sum_{n=3}^{\infty} (-1)^{n-1}\left(\gamma\delta\frac{\Delta T}{T}\right)^{n-1}\frac{1}{n!}\right] \tag{16}$$

Neglecting the lower value terms, one gets

$$\Delta H = \Delta H_m - \Delta C_p^m T_m \frac{\Delta T}{T}\left[1 - \gamma\delta\frac{\Delta T}{2T}\right] \tag{17}$$

One can also derive an expression for the entropy difference ΔS between the undercooled liquid and equilibrium solid with the aid of Eq. (4) and (7) and expression
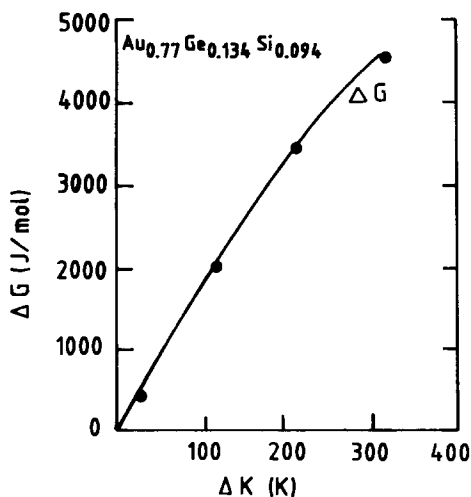

Fig. 1(a). The temperature-dependence of the Gibbs free energy difference between the undercooled liquid and the equilibrium solid phases in $Au_{0.77}Ge_{0.136}Si_{0.094}$. The experimental values are based on experimental ΔC_p data [3, 89].
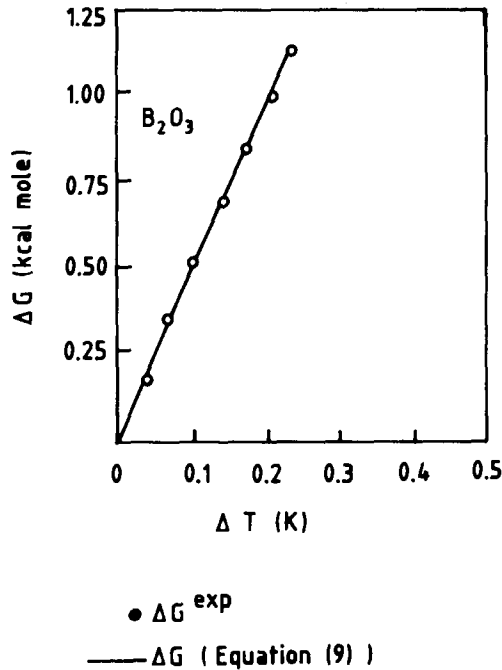
Fig. 1(b). The temperature-dependence of the Gibbs free energy difference between the undercooled liquid and the equilibrium solid phases in B_2O_3. The experimental values are based on the measured value of ΔC_p [90,91].

obtained can be expressed as

$$\Delta S = \Delta S_m - nR\left[(1 + \gamma\delta)g_m - \left(1 + \gamma\delta\frac{T_m}{T}\right)g\right] \tag{18}$$

which can be approximated as

$$\Delta S = \Delta S_m - \Delta C_p^m \Delta T\frac{(T_m + T)}{2T^2} \tag{19}$$

The expressions for ΔH and ΔS play an important role in the study of the temperature-dependence of the viscosity of glass-forming liquids. These are discussed in more detail in the next section.

2.2. The Taylor series expansion method

An expression for ΔG has also been obtained by the authors [10] by expanding the free energies of the phases viz., undercooled liquid and solid, around their values at T_m
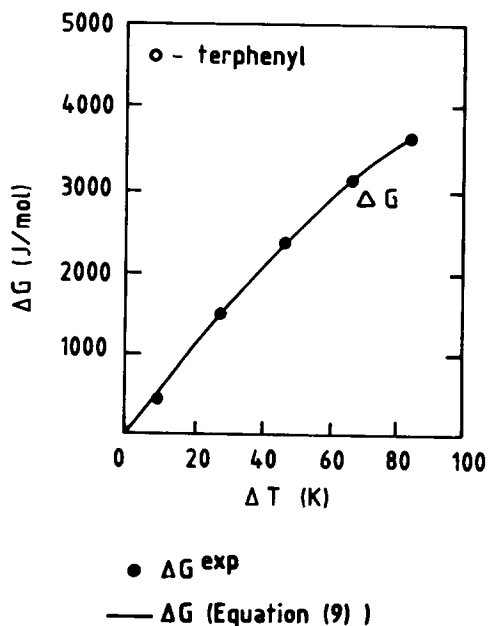
Fig. 1(c). The temperature-dependence of the Gibbs free energy difference between the undercooled liquid and the equilibrium solid phases in o-terphenyl. The experimental values were obtained using measured ΔC_p data [92].
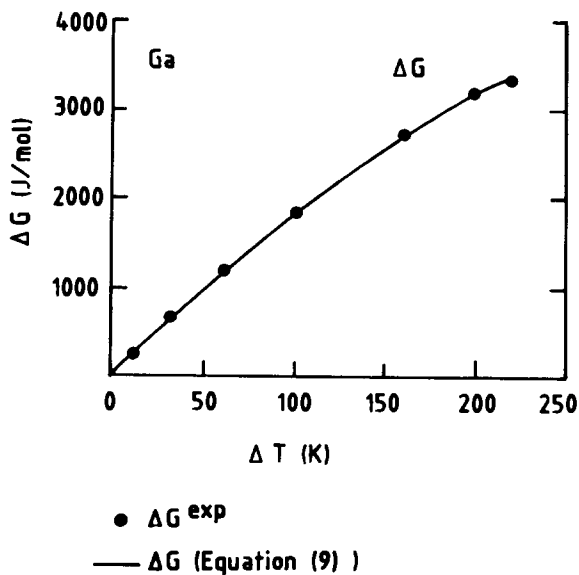

Fig. 1(d). The temperature-dependence of the Gibbs free energy difference between the undercooled melt and the equilibrium solid phases in Ga. The experimental values were obtained using experimental ΔC_p data [89,93].

Table 1A

Free energy differences ΔG between the liquid and equilibrium solid phases of $Au_{0.814}Si_{0.186}$ obtained from various expressions. The experimental values are based the measured values of ΔC_p [2]

T/K	$\Delta T/K$	$\Delta G/(J\,mol^{-1})$					
		Turnbull [4]	Hoffmann [5]	JC [7]	TS [6]	Eq. (9)	Experimental
600	36	557	526	549	541	549	550
500	136	2105	1655	1979	1833	1971	1973
400	236	3653	2298	3237	2821	3183	3194
300	336	5202	2454	4266	3334	4067	4076
290	346	5356	2442	4354	3355	4131	4163
(T_g)							

Table 1B

Free energy difference between the undercooled liquid and corresponding equilibrium solid phases obtained using Eq. (24). The experimental values are obtained using experimental ΔC_p [40, 97–104]

	$\Delta G/(J\,mol^{-1})$									
	Glycerol		o-Terphenyl		1, 3, 5-Tri-α-naphthylbenzene		2-Methylpentane		Ethanol	
T/T_m	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
0.95	889	889	883	884	2066	2068	305	305	246	246
0.90	1713	1716	1686	1693	3996	4009	591	592	480	480
0.85	2470	2478	2390	2415	5757	5802	854	859	700	703
0.80	3150	3169	2977	3036	7313	7422	1090	1103	905	911
0.75	3747	3786	3425	3543	8626	8843	1295	1320	1093	1105
0.70	4253	4322	–	–	–	–	1462	1508	1261	1282
0.65	4649	4772	–	–	–	–	–	–	1406	1440
T_g/T_m	4761	4890	3487	3619	9185	9479	1554	1619	1575	1640

in the form of Taylor's series expansion as

$$G^i = G_m^i - \left|\frac{\partial G^i}{\partial T}\right|_{T_m} \Delta T + \frac{1}{2!}\left|\frac{\partial^2 G^i}{\partial T^2}\right|_{T_m} \Delta T^2 - \frac{1}{3!}\left|\frac{\partial^3 G^i}{\partial T^3}\right|_{T_m} \Delta T^3 + \frac{1}{4!}\left|\frac{\partial^4 G^i}{\partial T^4}\right|_{T_m} \Delta T^4$$

(20)

where i stands for phases L and S corresponding to undercooled liquid and equilibrium solid phases, respectively, and derivatives are taken at $T = T_m$. The expansion of series extends the free energy versus temperature (G vs T) curves of each phase into their metastable regions. Using the appropriate forms of the thermodynamic derivatives of

G^i and noting that $G^L - G^S$ is zero at $T = T_m$, Eq. (20) can be expressed [10] as

$$\Delta G = G^L - G^S = \Delta S_m \Delta T - \frac{\Delta C_p^m}{2T_m} \Delta T^2 \left[1 + \frac{\Delta T}{3T_m} + \frac{\Delta T^2}{6T_m^2} + \frac{\Delta T^3}{10T_m^3} + \cdots \right]$$
$$+ \left| \frac{\partial \Delta C_p}{\partial T} \right|_{T_m} \frac{\Delta T^3}{6T_m} \left[1 + \frac{2\Delta T}{4T_m} + \frac{3\Delta T^2}{10T_m^2} + \cdots \right] \tag{21}$$

Each series in the parentheses is a logarithmic series and can be summed to yield

$$\Delta G = \Delta S_m \Delta T - \Delta C_p^m \frac{\Delta T^2}{(T_m + T)} + \left| \frac{\partial \Delta C_p}{\partial T} \right|_{T_m} \frac{\Delta T^3}{(T_m + T)} \tag{22}$$

It should be noted that while summing the series, where necessary the approximation

$$\ln(T_m/T) = 2\Delta T/(T_m + T) \tag{23}$$

is used to simplify the expression. The contributions due to third term and other high order terms are very small compared to the contribution due to first two terms and it is sufficient to use

$$\Delta G = \Delta S_m \Delta T - \Delta C_p^m \frac{\Delta T^2}{T_m + T} \tag{24}$$

for the estimation of ΔG.

The expression for ΔG stated in Eq. (24) has been used successfully to estimate the Gibbs free energy change of the variety of materials and very good agreement is found between the calculated and experimental values of ΔG which can be seen in Table 1B for polymeric materials [18].

A similar Taylor's series expansion can also be carried out to get an expression for ΔS and the resulting expression takes the form

$$\Delta S = \Delta S_m - 2\Delta C_p^m \frac{\Delta T}{T_m + T} + \left| \frac{\partial \Delta C_p}{\partial T} \right|_{T_m} \frac{\Delta T^2}{(T_m + T)} - \frac{1}{4} \left| \frac{\partial^2 \Delta C_p}{\partial T^2} \right| \frac{\Delta T^3}{T_m + T} + \cdots \tag{25}$$

The expression for ΔS stated in Eq. (25) can be used to estimate the iso-entropic temperature or ideal glass transition temperature. At the same time, it can also be used in the study of relaxation behaviour of glass-forming liquids, which will be discussed in the next section.

3. Viscous behaviour of glass-forming melts

The theories of viscosity proposed by Cohen and Turnbull [19] and Hirai and Eyring [14, 15] are basically diffusion theories and the viscosity η and self-diffusion coefficient D can be related by the equation

$$\frac{D\eta}{kT} = \frac{1}{2\pi} \left(\frac{N_a}{V} \right)^{1/3} \tag{26}$$

where k is the Boltzmann constant, N_a is the Avogadro number and V is the molar volume. The free volume theory of viscosity is based on the idea that a certain critical volume must be available to a molecule before it performs a diffusive motion. The importance of the free volume in molecular transport has been stressed by a number of investigators [19–25]. Doolittle [20] proposed an empirical relationship for viscosity based on the free volume concept and expressed it as

$$\eta = A \exp(B/f_T) \tag{27}$$

where A and B are constants and f_T represents the relative free volume fraction. A theoretical explanation of the Doolittle equation was given by Cohen and Turnbull [19, 21, 22] as well as Bueche [26].

Using the molecular–kinetic theory, Adam and Gibbs [27] reported a procedure to develop an expression for the temperature-dependence of η on the basis of the configurational entropy of liquids. Ramachandrarao and co-workers [18, 28–30] have studied the viscous behaviour of the glass-forming melts in the framework of both the free volume concept and the configurational entropy concept of Adams and Gibbs [27]. They also rederived the WLF equation [31–33] to study the relaxation behaviour of glass-forming melts. These procedures are reviewed in the present section.

3.1. The free volume approach

Defining the free volume in the term of the excess volume arising from holes, Ramachandrarao et al. [28] were able to express the relative free volume fraction f_T as

$$f_T/f_m = 1 + \sin\left[\frac{\pi}{2}\{(T - T_m)/(T_m - T_o)\}\right] \tag{28}$$

where f_m stands for the relative free volume fraction at $T = T_m$. Consequently, use of Eq. (26) gives an expression for η. Taking the proper value of constants they reported the temperature-dependence of the viscosity of metallic glass $Au_{0.77}Ge_{0.136}Si_{0.094}$ as

$$\log \eta_{10} = 1.8968 + \frac{0.3919}{f_T} \tag{29}$$

which explains experimental data at both low and high temperatures and its response is much better compared to those given by expressions reported by Chen and Turnbull [3] and Polk and Turnbull [34], as can be seen from Fig. 2(a).

Following the earlier work of Ramachandrarao et al. [28] and defining the free volume fraction with reference to the ideal glass transition temperature T_o, Dubey and Ramachandrarao [29] expressed f_T as

$$f_T = \frac{V_T - V_{T_o}}{V_{T_o}} = \frac{g - g_o}{1 - g} \tag{30}$$

where V_T and V_{T_o} are the volumes of the liquid at temperatures T and T_o, respectively, g and g_o are the volume fractions of holes at temperatures T and T_o, respectively, and
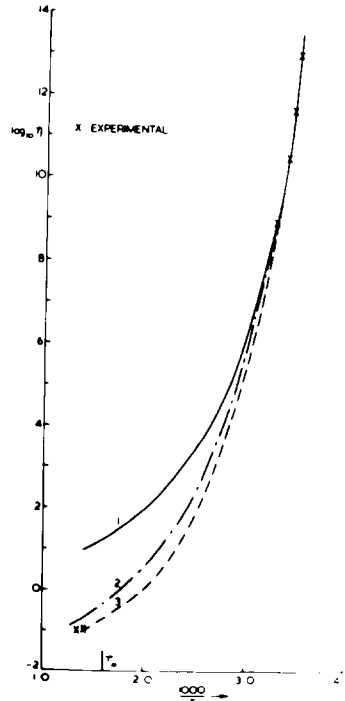
Fig. 2(a). The temperature-dependence of the experimental [3] and calculated viscosity of an $Au_{0.77}Ge_{0.136}Si_{0.094}$ alloy. Curve 1 is from an equation given by Chen and Turnbull [3], curve 2 is based on an expression reported by Polk and Turnbull [34] and curve 3 is based on Eq. (29). Points (*) represent experimental data.

are the same as defined in Eq. (3). Substituting for f_T in Eq. (27) and taking g as in Eq. (3), one gets

$$\eta = A_1 \exp\left\{\frac{(1-g)B_1}{g-g_o}\right\} = A_2 \exp\frac{B_2}{(g-g_o)} \tag{31}$$

where As and Bs are constants. By appropriate substitution of g and g_o in the terms for thermodynamic parameters ΔG, ΔH and ΔS as stated earlier in Eqs. (8), (15) and (18), Dubey and Ramachandrarao [29] expressed η in the form

$$\ln \eta = \ln A_3 + \frac{n\varepsilon_h B_3}{T\Delta S\left[1 + \dfrac{\Delta G - \Delta G_O}{T\Delta S}\right]} \tag{32}$$

equivalently,

$$\ln \eta = \ln A_4 + \frac{n\varepsilon_h B_4}{\Delta H - \Delta H_o} \tag{33}$$

where As and Bs are constants. ΔG_o and ΔH_o represent the values of the corresponding parameters at T_o. Substitution of Eq. (11) for ΔG in Eq. (32) gives

$$\ln \eta = \ln A_5 + \frac{B_5 \varepsilon_h (1 - \Delta C_p^m / \Delta S_m)}{RT} + B_6 \frac{\Delta C_p^m}{2\Delta S_m} (T_m/T)^2 \tag{34}$$

The above results clearly show that even the use of the concept of the free volume results in an expression for viscosity in terms of thermodynamic parameters. These expressions are capable of predicting the correct temperature-dependence of η of the glass-forming melts; this has been illustrated in Figs. 2(b) and 2(c) for the metallic glass $Au_{0.77}Ge_{0.136}Si_{0.094}$ and o-terphenyl, respectively [29].

3.2. The configurational entropy approach

In view of the molecular–kinetic theory proposed by Adam and Gibbs [27], the viscosity η of glass-forming liquids can be expressed as

$$\ln \eta = A \exp \left(\frac{C}{T \Delta S_c} \right) \tag{35}$$

where A and C are constants and ΔS_c, the configurational entropy is given by

$$\Delta S_c = \int [C_p(\text{liquid}) - C_p(\text{glass})] \, d \ln T \tag{36}$$

Most often, the experimentaly determined value of $\Delta C_p(\text{glass})$ is very close to that of the crystal and shows similar temperature-dependence [35]. As a result of it, the
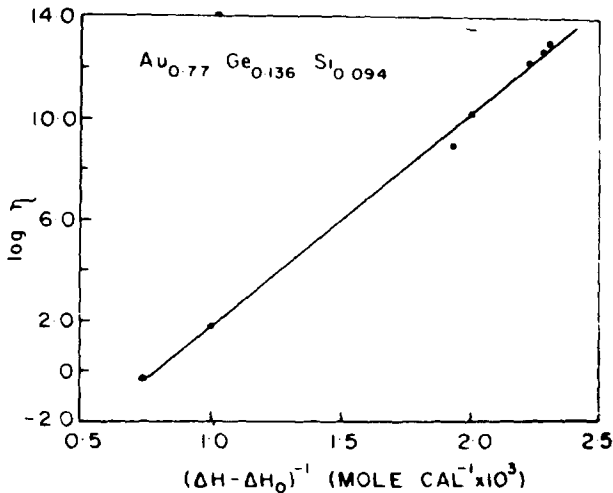

Fig. 2(b). The variation of the viscosity of the undercooled melt of an $Au_{0.77}Ge_{0.136}Si_{0.094}$ alloy with the thermodynamic function $(\Delta H - \Delta H_o)^{-1}$. Circles are experimental data [3] while solid line represents calculated values using Eq. (33).
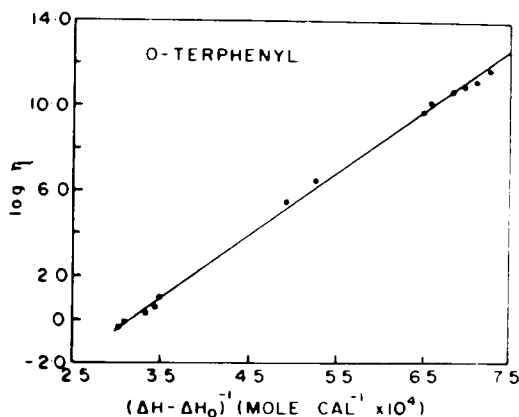
Fig. 2(c). The variation of the viscosity of the undercooled melt of o-terphenyl with the thermodynamic function $(\Delta H - \Delta H_o)^{-1}$. Circles represent experimental data [92,94] while the solid line represents the calculated values obtained using Eq. (33).

expression for ΔS stated in Eq. (25) can be used in place of ΔS_c. As pointed out by Kauzmann, ΔS vanishes at the ideal glass transition temperature T_o. Replacing T by T_o in Eq. (25) gives

$$\Delta S_m - 2\Delta C_p^m \frac{\Delta T_o}{T_m + T_o} + \left|\frac{\partial \Delta C_p}{\partial T}\right|_{T_m} \frac{\Delta T_o^2}{T_m + T_o} - \frac{1}{4}\left|\frac{\partial^2 \Delta C_p}{\partial T^2}\right|_{T_m} \frac{\Delta T_o^3}{T_m + T_o} + \cdots = 0 \quad (37)$$

with $\Delta T_o = T_m - T_o$

Using Eq. (25) and (37) together with Eq. (23), one can express ΔS as

$$\Delta S = \Delta C_p^m \ln(T_m/T_o) - \left|\frac{\partial \Delta C_p}{\partial T}\right|_{T_m} [T_m \ln(T/T_o) - \Delta T_o] + \cdots \quad (38)$$

Substitution of Eq. (38) for ΔS in Eq. (35) and consideration of higher derivatives of ΔC_p yields an expression for η of the form

$$\ln \eta = \ln A + \frac{B(1 + T_o/T)}{(T - T_o)[1 + A_1(T - T_o) + A_2(T - T_o)^2 + A_3(T - T_o)^3 + \cdots]} \quad (39)$$

where $B = C/2\Delta C_p^m$, A_1, A_2, A_3, etc. are constants and depend on ΔC_p^m and its derivatives with respect to T at $T = T_m$ and T_o.

When ΔC_p varies linearly with temperature, as reported by several workers, [36–40], Eq. (39) reduces to

$$\ln \eta = \ln A + \frac{C}{2\Delta C_p^m} \frac{(1 + T_o/T)}{(T - T_o)\left[1 - \frac{\alpha \Delta T_o}{T_m}\left(1 - \frac{T - T_o}{2\Delta T_o}\right)\right]} \quad (40)$$

with

$$\alpha = T_m \left[\frac{\partial}{\partial T} (\ln \Delta C_p) \right]_{T_m}$$

when ΔC_p is independent of temperature, Eq. (39) reduces to

$$\ln \eta = \ln A + \frac{C'}{2(T - T_o)}(1 + T_o/T) \tag{41}$$

with $C' = C/\Delta C_p^m$. In the vicinity of the glass transition temperature T_g, T_o/T is approximately 0.75, and Eq. (39) reduces to the frequently used Vogel–Fulcher equation [41, 42]

$$\ln \eta = \ln A + \frac{C''}{(T - T_o)} \tag{42}$$

with

$$C'' = 0.875 C'.$$

In general C'' (constant) of the Vogel–Fulcher equation should be temperature-dependent at least to the extent of

$$C = \frac{C'}{2}(1 + T_o/T) \tag{43}$$

These results clearly show that the Vogel–Fulcher equation is, in fact, an approximate expression arising from the more general expression of the form stated in Eq. (39) obtained by Dubey and Ramachandrarao [18]. The complexity of the viscous behaviour and consequently the curvature in the $\ln \eta$ vs $1/T$ curve are due to the temperature-dependence of ΔC_p. All other constants except A and B can be estimated from thermodynamic parameters and they depend on ΔC_p and its derivatives. It should also be noted that Eq. (39) with a single set of A and B is capable of explaining the temperature-dependence of η in the entire temperature range of interest. To show the validity of Eq. (39), the variation of calculated and experimental values of η with function

$$f(T) = \frac{1 + T_o/T}{(T - T_o)\left[1 - \frac{\alpha \Delta T_o}{T_m}\left(1 - \frac{T - T_o}{2\Delta T_o}\right)\right]}$$

is shown in Figs. 2(d) and 2(e) for 1, 3, 5-tri-α-naphthylbenzene and 2-methylpentane. For both materials ΔC_p is a linear function of T. These figures show the applicability of expression stated in Eq. (39) for viscosity with a single set of constants over a wide range of viscosity 10^{13}–10^{-1} poise.

3.3. Relaxation behaviour of glass-forming melts

Modifying the molecular–kinetic theory of Gibbs and DiMarzio [43], Adam and Gibbs [27] studied the temperature-dependence of relaxation behaviour of the glass-
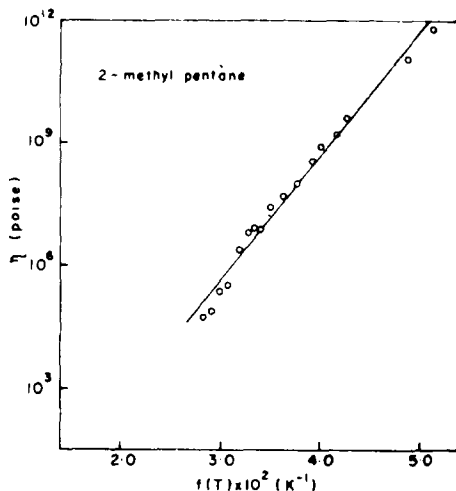
Fig. 2(d). Comparison of the temperature-dependence of the viscosity of an undercooled liquid as obtained from Eq. (40) (–) with experimental values (○) [95] for 1, 3, 5-tri-α-naphthylbenzene.
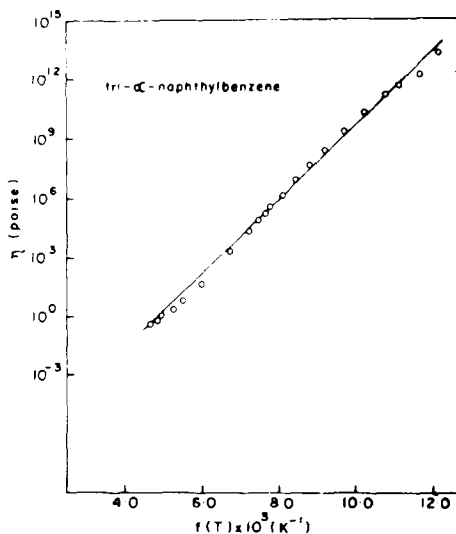
Fig. 2(e). Comparison of the temperature-dependence of the viscosity of undercooled liquid as obtained from Eq. (40) (–) with experimental values (○) [96] for 2-methylpentane.

forming liquids in the framework of configurational entropy and they obtained a relationship akin to the well-known William–Landel–Ferry (WLF) empirical equation [31–33]. The WLF equation takes the form

$$-\log a_{T_s}(T) = \frac{C_1(T - T_s)}{C_2 + (T - T_s)} \tag{44}$$

where $a_{T_s}(T) = \tau(T)/\tau(T_s)$, is the ratio of the relaxation times at temperature T and at some reference temperature T_s. C_1 and C_2 are constants. Changing the reference temperature from T_s to any other reference temperature. T'_s, changes C_1 and C_2 in a correlated fashion to a new set of values C'_1 and C'_2 as

$$C'_1 = \frac{C_1 C_2}{C_2 - (T_s - T'_s)} \tag{45}$$

$$C'_2 = C_2 - (T_s - T'_s) \tag{46}$$

Considering ΔC_p as independent of temperature above T_g, Adam and Gibbs reported the values of constants C_1 and C_2 in terms of the potential energy hindering the cooperative rearrangement per monomer segment ($\Delta\mu$), the configurational entropy $\Delta S(T_s)$ at $T = T_s$, the Kauzmann temperature, T_o, the critical configurational entropy (S_c^*), and $\Delta C_p^{T_g}$ (ΔC_p at T_g).

Using the expression for ΔG based on the Taylor series expansion reported by Lele et al. [10] and following the earlier work of Adam and Gibbs [27], Dubey et al. [30] studied the temperature-dependence of the relaxation phenomena of glass-forming liquids by rederiving the WLF equation. In view of Adam and Gibbs model, one can express

$$-\ln a_{T_s}(T) = \frac{\Delta\mu S_c^*}{k}\left[\frac{1}{T_s\Delta S_c(T_s)} - \frac{1}{T\Delta S_c(T)}\right] \tag{47}$$

where k is the Boltzmann constant. Differentiating ΔG as stated in Eq. (24) with respect to T one gets

$$\Delta S = \Delta S_m - \Delta C_p^m\left[\frac{4T_m^2}{(T_m + T)^2} - 1\right] \tag{48}$$

At the iso-entropic temperature, T_o, ΔS becomes zero. Hence we can eliminate ΔS_m and express ΔS by

$$\Delta S = \frac{4T_m^2\Delta C_p^m}{(T_m + T_o)^2}\left[\frac{(2T_m + T_o + T)(T - T_o)}{(T_m + T)^2}\right] \tag{49}$$

We can consider the entire ΔS to be the difference in configurational entropy between the melt and glass. This is in conformity with the experimental finding that the heat capacities of the polymer in its crystalline and amorphous states are almost identical [44, 45]. Use of Eqs. (47) and (49) furnishes

$$-\ln a_{T_s}(T) = \frac{\Delta\mu S_c^{*i}}{k}\frac{1}{T_s\Delta S_c(T_s)}\frac{(T - T_s)}{D} \tag{50}$$

with

$$D = (T - T_s) + (T_s - T_o)\left[1 - \frac{1 - \frac{3}{2}T_o/(T_m + T_o)}{1 + \frac{3}{2}[(T_s - T_o)/(T_m + T_o)] + T_s/(T - T_o)}\right] \tag{51}$$

The shift factor for the use of T_g as a reference temperature can be obtained replacing T_s by T_g in Eqs. (50) and (51). To satisfy Eqs. (45) and (46), it is necessary to replace T in

the coefficients of $(T_s - T_o)$ by T_g and of $(T_g - T_o)$ by T_s. Consequently this furnishes

$$-\ln a_{T_s}(T) = \frac{C_1(T - T_s)}{(T - T_s) + \alpha(T_s - T_o)} \tag{52}$$

and

$$-\ln a_{T_g}(T) = \frac{C_1'(T - T_g)}{(T - T_g) + \beta(T_g - T_o)} \tag{53}$$

with

$$\alpha = 1 - \frac{1 - \frac{3}{2}T_o/(T_m + T_o)}{1 + \frac{3}{2}[(T_s - T_o)/(T_m + T_o)] + T_s/(T_g - T_o)} \tag{54}$$

$$\beta = 1 - \frac{1 - \frac{3}{2}T_o/(T_m + T_o)}{1 + \frac{3}{2}[(T_g - T_o)/(T_m + T_o)] + T_g/(T_s - T_o)} \tag{55}$$

The WLF equation is generally valid in the temperature range $T_g \pm 50\,\mathrm{K}$ and the change in the magnitude of the coefficient of $(T_s - T_o)$ in the denominator of the above stated Eq. (50) is very small in the temperature range cited above. As a result, replacing T by T_s or T_g yields an average value of the coefficient. Consequently, α and β can be taken as constants. Comparing Eqs. (52) and (53) with the WLF equation, gives the expressions

$$C_1 = \frac{\Delta\mu S_c^*}{k} \frac{1}{T_s \Delta S_c(T_s)} \tag{56}$$

$$C_2 = \alpha(T_s - T_o) \tag{57}$$

$$C_1' = \frac{\Delta\mu S_c^*}{k} \frac{1}{T_g \Delta S_c(T_g)} \tag{58}$$

$$C_2' = \beta(T_g - T_o) \tag{59}$$

As suggested by Kauzmann [1], when kinetic processes do not intervene an undercooled melt is forced to exhibit glass transition at the ideal glass transition temperature T_o. As a result, it is quite reasonable to assume that ΔC_p attains its theoretical maximum at $T = T_o$ and it gives $T_o = T_m/2$. This has been found true for a large number of glass-forming melts [46]. Under this condition, expressions for α and β reduce to the simplified forms

$$\alpha = \frac{1}{1 + (T_o/T_s)(T_g - T_o)/(T_g + T_o)} \tag{60}$$

$$\beta = \frac{1}{1 + (T_o/T_g)(T_s - T_o)/(T_s + T_o)} \tag{61}$$

A relationship between T_s and T_g can also be derived with the help of Eqs. (60) and (61) as

$$T_s - T_g = \frac{1}{1 - \beta} \frac{\alpha - \beta}{\alpha} C_2 \tag{62}$$

Dubey et al. [30] have analysed a number of polymeric materials and have reported values of α and β of $0.921 \pm 1.4\%$ and $0.854 \pm 2.4\%$, respectively. The constancy of α and β implies that T_s/T_o and T_g/T_o vary in a correlated fashion. The average values of α and β predict $T_s - T_g = 50.6\,\mathrm{K}$ which is very close to the value $T_s - T_g = 50\,\mathrm{K}$ obtained using the WLF equation, whereas Adam and Gibbs reported $T_s - T_g = 55\,\mathrm{K}$. These findings together with constancy of product $C_1 C_2$ explain why WLF equation is so successful despite its empirical nature. These expressions are very useful for estimating the ideal glass transition temperature T_o using relaxation data.

4. The ideal glass transition temperature

As pointed out by Kauzmann [1] a liquid loses its entropy at a faster rate than the equilibrium solid, resulting in the two phases having the same entropy at some temperature T_o which is well above the absolute zero and below the T_g. T_o is also known as the iso-entropic temperature or the Kauzmann temperature. If a liquid maintains its configurational equilibrium on cooling to the temperature region where it attains a large viscosity, then below T_o the liquid will have lower entropy than the solid. Such a state cannot be achieved and the 'equilibrium' liquid must therefore transform into a solid at T_o despite kinetic hindrances. Such a transformation should be of the second-order as argued by Gibbs and DiMarzio [43] as well as Adam and Gibbs [27]. On the other hand, Cohen and Grest [47] considered it to be a first-order transition. T_o is an important parameter in the study of the thermodynamic and viscous behaviour of glass-forming liquids. Expressions for ΔS derived by Dubey and coworkers [9, 10] based on the hole theory (Eq. (18)) as well as the Taylor series expansion (Eq. (25)) can be used to estimate T_0 using thermodynamic data while Eqs. (39) and (50) are useful for estimation of T_o using relaxation data.

4.1. T_o Based on thermodynamic data

As discussed earlier, ΔS becomes zero at $T = T_o$. Recalling Eq. (18) and equating it to zero yields

$$\Delta S_m = \Delta C_p^m \left[\frac{(1 - \delta^2)}{2\delta^2} + \sum_{n=3}^{\infty} \frac{(1 - \delta)^{(N-1)}}{n!} \frac{(N - 1 + \delta)}{\delta^N} (\gamma \delta)^{N-2} \right]$$

with

$$\delta = T_o/T_m \tag{63}$$

Eq. (63) cannot be solved analytically without approximation. At the same time, it can be realised that contribution due to the summation term is relatively small compared to the first term. Ignoring the lower value terms, an expression for estimation of T_o can be obtained as

$$\frac{\Delta C_p^m}{\Delta S_m} \left[\frac{1 - \delta^2}{2\delta^2} - \frac{\gamma \delta}{6} \frac{(2 + \delta)(1 - \delta)^2}{\delta^3} \right] - 1 = 0 \tag{64}$$

which clearly shows that δ, i.e. T_o/T_m is mainly controlled by the ratio $\Delta C_p^m/\Delta S_m$ which can be measured easily. Dubey and Ramachandrarao [48] estimated the value of the ideal glass transition temperature T_o for a variety of materials and found the calculated values are very close to extrapolated values based on experimental measurements, as can be seen from Table 2.

In a similar way an expression for ΔS based on the Taylor series expansion stated in Eq. (38) can also be used for the estimation of T_o as

$$\Delta S_m - T_m \left|\frac{\partial \Delta C_p}{\partial T}\right|_{T_m} + \left\{\Delta C_p^m - T\left|\frac{\partial \Delta C_p}{\partial T}\right|_{T_m}\right\} \ln\left(\frac{T_o}{T_m}\right) = 0 \qquad (65)$$

The above stated equation is transcendental and can be solved by iterative procedures. However, to have an analytical expression, Eq. (65) can be solved in the framework of the approximation stated in Eq. (23) and the resulting expression can be expressed as

$$T_o = T_m - \left[\frac{(\Delta S_m + 2\Delta C_p^m) \pm \left\{(\Delta S_m + 2\Delta C_p^m)^2 - 8\Delta S_m T_m \left|\frac{\partial \Delta C_p}{\partial T}\right|_{T_m}\right\}^{1/2}}{2\left|\frac{\partial \Delta C_p}{\partial T}\right|_{T_m}}\right] \qquad (66)$$

If $T_m[\partial \Delta C_p/\partial T]_{T_m}$ is small enough compared to the other terms in Eq. (65), the expression for T_o stated in Eq. (66) can further be simplified to yield

$$T_o = T_m \left[\frac{2D - 1}{2D + 1}\right] \qquad (67)$$

Table 2
The ideal glass transition temperature T_o obtained using Eqs. (63) and (64) and $\Delta C_p^m/\Delta S_m$ of the glass-forming materials

No.	Substance	Melting temp. T/K	$\Delta C_p^m/\Delta S_m$	$\delta = T_o/T_m$	Calculated value of T_o/K	Extrapolated value of T_o/K
1	B_2O_3	723	0.6373	0.4695	339	411
2	$Ca(NO_3)_2 \cdot 4H_2O$	315.5	2.0196	0.6434	203	202
3	$Cd(NO_3)_2 \cdot 4H_2O$	333.4	1.7730	0.6081	202	198
4	$ZnCl_2$	591	1.3687	0.4488	265	260
5	As_2S_3	585	1.2466	0.4423	259	270
6	$H_2SO_4 \cdot 3H_2O$	236.72	1.2510	0.5497	130	135
7	CH_3COOLi	560	2.1292	0.6705	376	381
8	$(CH_3COO)_2 Mg$	335	1.8810	0.5943	199	209
9	Glycerol	293	1.2667	0.4598	135	132
10	Ethanol	158.5	0.7927	0.3891	62	58
11	2-Methylpentane	119.55	0.9819	0.5091	61	59
12	o-Terphenyl	328	1.4180	0.6121	200	248
13	$Mg_{0.814}Ga_{0.186}$	696	0.3845	0.3800	265	–
14	$Au_{0.814}Si_{0.186}$	636	0.5010	0.3145	200	200
15	$Au_{0.77}Ge_{0.136}Si_{0.194}$	625	0.3956	0.3168	198	241.3

where $D = \Delta C_p^m/\Delta S_m$. The values of T_o were estimated by Dubey and Ramachandrarao [18] for several materials using Eq. (66) and the results obtained, reported in Table 3, showed good agreement with experimental values.

4.2. T_o based on relaxation data

As discussed earlier, viscosity data can also be used to estimate T_o. From reports of earlier investigators [17, 49, 50], it is often found that $C_2' = T_g - T^x$, where T^x is the characteristic temperature of the Vogel–Fulcher equation [41, 42] and is the same as T_o of the empirical WLF equation [31, 33].

As discussed in an earlier section Dubey et al. [30] suggested that to estimate T_o correctly from viscosity data obtained at temperatures greater than T_g it was necessary to incorporate either α or β (depending on the reference temperature used, T_s or T_g respectively) in the WLF equation, i.e. one has to use $C_2 = \alpha(T_s - T_o)$ and $C_2' = \beta(T_g - T_o)$ as stated in Eqs. (57) and (59), respectively. Considering the universal nature of C_2 and using the values of T_s and T_g compiled by William and co-workers [31–33], Dubey et al. [30] calculated T_o for a large number of polymeric materials; their results are shown in Table 4.

Finally, it is necessary to compare the values of T_o derived from viscosity data with the values obtained from thermodynamic data. However, thermodynamic data are relatively scarce and we have attempted such a comparison for a few polymers only. The results obtained are reported in Table 5, which shows excellent agreement between T_o derived from thermodynamic data and that from viscosity or other relaxation data. These values are far better than those evaluated from the Adam and Gibbs model.

5. The glass-forming ability of materials

The rapid solidification technique has established that all kinds of materials can form glasses irrespective of their bonding. The criteria of glass-forming ability of materials based on thermodynamic and structural concepts have, however, tended to be specific to classes of materials. For example, glass formation from oxides [51] can be explained on the basis of relative sizes of cationic and anionic atoms, Zachariasen's random network hypothesis, Smekal's mixed bonding, Sun's bond strength, etc., whereas low-order symmetry of the molecules, slow rotational isomerization from the liquid state to that required for crystallisation, and a high liquid viscosity are mainly responsible for glass formation in polymers [52]. In metallic systems a large number of binary, ternary and more complex alloys are known to yield the glassy structure, whereas it is still difficult to produce pure metal glasses. A variety of parameters such as the stabilisation of dense random packing by the metalloid, electronegativity, size difference between constituent atoms, etc., are supposed to be the controlling factors for glass formation in metallic materials [53–55]. Uhlmann and his co-workers [56, 57] studied the glass-forming ability of materials in terms of the kinetic concept using the formal theory of transformation, kinetics proposed by Johnson and Mehl [58] and Avrami [59]. Plotting the time–temperature-transformation (T–T-T) diagrams, they estimated the

Table 3
The ideal glass transition temperature T_o based on the expressions derived by the use of the Taylor series expansion. T_o (extrapolated) are the values based on the experimental data related to the thermodynamic as well as other relaxation properties

No.	Material	T_m/K	ΔS_m	ΔC_p^m	$\left|\dfrac{\partial \Delta C_p}{\partial T}\right|$	T_o/K Eq. (66)	T_o/K Eq. (65)	T_o/K (extrapolated)
			(J mol⁻¹ K⁻¹)	(J mol⁻¹ K⁻¹)	(J mol⁻¹ K⁻²)			
1	Glycerol	293	62.7	79.42	-3.906×10^2	132	137	132
2	2-Methylpentane	119.5	52.36	51.41	-7.985×10^{-1}	58	60	59
3	o-Terphenyl	328	56.01	79.42	-4.933×10^{-1}	200	200	248
4	1-3-5-Tri-α-naphthyl benzene	472	90.02	90.86	-4.673×10^{-1}	247	255	280
5	Salol	316.6	30.94	23.66	-8.962×10^{-1}	206	230	221
6	As$_2$S$_3$	585	48.71	60.79	-1.959×10^{-2}	262	259	270
7	Ethanol	158.5	31.64	58.08	-1.673×10^{-1}	57	62	58

Table 4

Calculated values of T_o, α and β obtained on the basis of the experimental parameters T_s, T_g, C_2 and C_2'. Values of T_2, α and β in columns marked 'a' refer to the use of T_s, T_g and C_2 while those in columns marked 'b' were obtained with T_g, C_2' and C_2

Material	T_s/K	T_g/K	C_2'/K	T_o/K		T_g/T_2		α		β	
				a	b	a	b	a	b	a	b
Polyisobutylene	243	202	80.0	126.6	107.0	1.559	1.887	0.896	0.872	0.837	0.842
Polystyrene	408	354		300.3		1.179		0.943		0.886	
		373	50.0		316.8		1.177		0.943		0.890
Poly(vinyl acetate)	349	301		239.5		1.257		0.928		0.871	
		305	46.8		251.4		1.213		0.937		0.873
Poly(vinyl chloroacetate)	346	296	40.4	236.7	249.6	1.251	1.186	0.930	0.944	0.870	0.870
Poly(methyl acrylate)	324	276	45.0	213.9	223.9	1.290	1.233	0.923	0.934	0.863	0.864
Poly(methyl methacrylate)	423	378		325.7		1.161		0.947		0.891	
		381	80.0		291.2		1.308		0.912		0.891
Glucose	351	305		241.2		1.264		0.925		0.872	
Propylene glycol	217	160		105.2		1.521		0.909		0.814	
Butadiene–styrene, 75/25	268	212		157.6		1.351		0.920		0.834	
		210	25.6		179.4		1.171		0.953		0.836
Glycerol	238	187		125.9		1.485		0.906		0.828	
Hevea rubber		200	53.6		135.8		1.473		0.905		0.834
Polyethylene		231	73.2		144.8		1.595		0.886		0.854
Poly(propylene oxide)		198	24.0		169.1		1.171		0.954		0.830
Poly(-methyl styrene)		445	49.3		390.5		1.140		0.951		0.905
Poly(hexene-1)		218	20.2		194.0		1.124		0.963		0.840
Ethylene–propylene		242	40.7		194.2		1.246		0.934		0.851
Cellulose tributyrate in dimethyl phthalate											
21%	247	188	42.6	136.5	136.5	1.377	1.377	0.920	0.920	0.828	0.828
43%		193	38.6		146.4		1.318		0.897		0.828
Polyurethane	283	238	32.6	171.3	199.6	1.389	1.192	0.910	0.946	0.850	0.849
n-Butyl cellulose nitrate in diethyl phthalate 23%		300	96.6		189.1		1.586		0.877		0.871
		166	53.5		100.8		1.647		0.897		0.821
Average						1.340	1.36	0.921	0.924	0.854	0.854
						+12.5%	+21%	+1.4%	+2.8%	+2.4%	+2.4%

Table 5

The ideal glass transition temperature T_o for polymers. T_o^{Cal} is the value based on the thermodynamic data, while T_o^η is the value from relxation data using Eqs. (56)–(62). T_o^{WLF} is the value obtained using the conventional WLF equation and T_o^{AG} is value derived using Adam and Gibbs equation

Material	T_g/K	T_m/K	T_o^{Cal}/K	T_o^η/K	T_o^{WLF}/K	T_o^{AG}/K
Polyethylene	231	414	143.9	144.8	157.8	158.8
Hevea rubber	200	421	132.8	135.8	146.4	171.2
Polystyrene	354	513	299.3	300.3	306.4	331.1
Poly(propylene oxide)	198	348	171.0	169.1	174.0	190.1

critical cooling rate R_c and suggested that materials can be classified with reference to their glass-forming ability on the basis of the magnitude of R_c.

Ramachandrarao and co-workers [60–63] studied the glass-forming ability of metallic materials in terms of minimum volume as well as concentration fluctuations. In view of Turnbull's [64] suggestions, Dubey and Ramachandrarao [65] reported the ease of glass formation on the basis of driving force for nucleation and phase diagram features. Using the kinetic concept, they [48] also studied the glass-forming ability of materials by deriving an expression to evaluate the nose temperature (T_n) of the T–T–T diagram and reported that $\Delta C_p^m/\Delta S_m$ and $\delta(= T_o/T_m)$ are mainly responsible for fixing the values of T_n. Thus glass-formation from materials can also be studied in terms of $\Delta C_p^m/\Delta S_m$ and the ideal glass transition temperature. These investigations are reviewed in this section.

5.1. Minimum volume criterion

From the results of several investigations [64, 66–69] related to the size differences of the constituent atoms, it is found that change in the atomic volume of the constituent elements play a significant role in the glass-forming ability of materials. It helps glass formation by reducing crystal growth and the homogeneous nucleation frequency by enhancing the viscosity of liquids. Consequently, the critical cooling rate for glass formation is lowered. In view of these findings Ramachandrarao [60] postulated that an alloy with the smallest possible molar volume should be the most prone to form a glass on rapid solidification, by virtue of its high viscosity. The Varley model [70] can be employed to estimate the volume change (ΔV) associated with alloying which helps to establish a relationship between atomic volume, atomic fraction and compressibility. If one considers a system consisting of N_A solvent and N_B solute atoms with atomic volumes V_A and V_B, respectively, the change in the mean atomic volume ΔV is given by [70]

$$\Delta V = \frac{X_A X_B (V_A - V_B)(V_B \varphi_B - V_A \varphi_A)}{V_B \varphi_B X_A + V_A \varphi_A X_B} \tag{68}$$

where φ_A and φ_B are isothermal compressibilities of pure A and B, respectively, and X_A and X_B are atomic fractions of solvent and solute, respectively. As stated earlier,

a decrease in the mean atomic volume enhances the viscosity, and a liquid of certain composition showing maximum decrease in volume can be expected to have the maximum viscosity. Thus the critical composition $\bar{X}_B$ can be evaluated by differentiating Eq. (68) and equating the results to zero. Then $\bar{X}_B$ is given by

$$\bar{X}_B = \frac{1}{1 \pm \sqrt{\dfrac{V_A \varphi_A}{V_B \varphi_B}}} \tag{69}$$

The use of Eq. (68) in the framework of the ideal volume V_{id} yields Eq. (69) for $\bar{X}_B$ as

$$X_B = \frac{1}{1 \pm \sqrt{\varphi_A/\varphi_B}} \tag{70}$$

Ramachandrarao [60] estimated $\bar{X}_B$ for a large number of alloys and found that the composition at which the binary liquid alloy volume is minimum invariably lies within the experimentally observed range of glass-forming composition in about 35 binary systems based on noble, alkaline earth and transition metals.

5.2. Criterion based on concentration fluctuations

Glass formation in metallic systems was first correlated by Turnbull [64] with the existence of deep eutectics in such systems. More generally, glass formation can be considered to be a reflection of the enhanced stability of the liquid phase in alloys. A quantitative measure of the liquid stability is provided by the concentration–concentration fluctuation structure factor in the longwave length limit, $S_{cc}^{(0)}$. Bhatia and Thornton [71] have shown that

$$S_{cc}^{(0)} = N_a \langle (\Delta C)^2 \rangle \tag{71}$$

where $\langle (\Delta C)^2 \rangle$ stands for the mean square fluctuations in concentration and ΔC is defined as

$$\Delta C = \frac{X_2 \Delta N_1 - X_1 \Delta N_2}{N_a} \tag{72}$$

where N_a is the Avogadro number. The fluctuations in particle density of components 1 and 2 of a binary system are denoted by ΔN_1 and ΔN_2, respectively, whereas the atomic fractions are denoted by X_1 and X_2. Bhatia and Thornton have further shown that

$$S_{cc}^{(0)} = \frac{RT}{\partial^2 \Delta G_m / \partial \chi_2^2} \tag{73}$$

where ΔG_m is the free energy of mixing per mole at temperature T. Experimentally, $S_{cc}^{(0)}$ can be found by diffraction experiments or through thermodynamic measurements. Ramachandrarao et al. [61] first attempted a correlation between the glass-forming composition range with the composition dependence of $S_{cc}^{(0)}$. It is well known

that $S_{cc}^{(0)}$ tends to zero for liquids of compound forming systems at the stoichiometry of the compound while for ideal solutions

$$S_{cc}^{id(0)} = X_1 X_2 \tag{74}$$

Ramachandrarao et al. [61] analysed the composition-dependence of $S_{cc}^{(0)}$ for a number of binary systems and showed that if glass formation occurred, it was confined to a composition range where the $S_{cc}^{(0)}$ values were close to $S_{cc}^{id(0)}$. This condition is necessary but not sufficient. Further, it is independent of the absence or occurrence of compound formation.

For a non-compound forming system, this criterion suggests that glass formation can occur over a wide composition range if the deviation from ideal solution behaviour is small. An example for this type is provided by the Pb–Sb system. For a system having a compound with stoichiometry $A_p B$, Lele [72] has shown that

$$S_{cc}^{(0)} = \begin{cases} X_2(1 - pX_2)[1 - (p+1)X_2] & \text{for } X_2 < 1/(1+p) \\ X_2(1 - X_2)[(1+p)X_2 - 1] & \text{for } X_2 > 1/(1+p) \end{cases} \tag{75}$$

where it was assumed that the liquid is fully associated in the terms of the model for associated solutions. This implies that for A–(B)-rich liquids, the only species present are A (B) and $A_p B$. The $S_{cc}^{(0)}$ values for such solutions are equal to those for ideal solutions only when

$$X_2 = \frac{2}{p+1} \tag{76}$$

Systems such as Al–La, Mg–Ca and Mg–Zn show a minimum in $S_{cc}^{(0)}$ at a stoichiometry corresponding to $A_2 B$. Glass formation is thus expected around $X_2 = 0.66$ and is, indeed, observed.

A more subtle effect is produced when interactions between the associates or complexes and the unassociated atoms are important. A comparison of the Mg–Ba and Mg–Sr systems throws light on this aspect. Glass formation is known to occur only in the latter. Sastry et al. [62] analysed the thermodynamic data for liquid alloys for these systems and showed the existence of complexes with stoichiometries $Mg_2 Ba$ and $Mg_2 Sr$ respectively. Glass formation could thus be expected at $X_{Mg} = 1/3$ for both systems. However, analysis using the regular associated solution model [63] showed strong repulsive interactions between the complex and unassociated atoms Mg–Ba and attractive interactions in Mg–Sr. As a result, the lowering of the free energy of mixing at the likely glass-forming composition was greater for Mg–Sr liquids than that for Mg–Ba liquids. This favours glass formation in Mg–Sr alloys.

5.3. Criterion based driving force for nucleation

In view of the Turnbull [64] findings, Donald and Davies [73] tried to extend the applicability of the concept of the eutectic depth by defining the ideal liquidus temperature T_L^o as a weighted mean of the melting temperature of the component metals; this also failed to predict the glass-forming ability of materials. Whang [74]

suggested plotting the empirical reduced liquidus temperature T_{LR} versus reduced eutectic composition X_{ER} to measure the glass-forming ability in systems showing extended solid solubility. He defined T_{LR} as $(T_L^o - T_L)/T_L$ where T_L is the observed liquidus temperature and

$$T_L^o = f_A T_A + f_B T_B \tag{77}$$

where f_A and f_B are atomic fractions of components A and B with melting temperatures T_A and T_B respectively. It should be noted that T_L^o is the same ideal liquidus temperature as defined by Donald and Davies. In general, Whang's approach predicts a wider glass-forming range than is experimentally observed.

On the basis of these findings, it can be concluded that the miscibility in solid enhances the entropy of the phase and stabilises it with respect to pure metal and also counteracts the entropic stabilisation of the liquid. Consequently, it leads to elevation of the liquidus temperature and a decrease in the liquidus slope, which makes us realise the importance of the solidus slope also. Thus it is necessary to consider both the slopes on either side of the eutectic. Dubey and Ramachandrarao [65] presented such a model and rationalised the asymmetries observed in respect of glass-forming composition ranges near the eutectic, using the driving force for nucleation together with phase diagram features of materials.

Following Lupis [75] as well as Ramachandrarao and Dubey [76], the driving force for nucleation can be expressed as

$$DG = \frac{(DT)^2}{2(X_e^L - X_e)^2} \left[\frac{\lambda^\alpha (\Delta S^{\alpha - L})^2}{\left. \frac{\partial^2 G^\alpha}{\partial X_2 \alpha^2} \right|_{X_2^\alpha = X_c^\alpha}} + \frac{\lambda^L (\Delta S^{L - \alpha})^2}{\left. \frac{\partial^2 G^L}{\partial X_2^{L2}} \right|_{X_2^L = X_c^L}} \right] + O[(DT)^3] \tag{78}$$

where $DT = T_L - T$

$$\Delta S^{\alpha\,L} = S^L - X_1^L S_1^\alpha - X_2^L S_2^\alpha \tag{79}$$

$$\Delta S^{L \cdot \alpha} = S^\alpha - X_1^\alpha S_1 - X_2^\alpha S_2 \tag{80}$$

$$\lambda^\alpha = \frac{X_e^L - X_2}{X_e^L - X_2^\alpha} \tag{81}$$

$$\lambda^L = 1 - \lambda^\alpha = \frac{X_2 - X_2^\alpha}{X_e^L - X_2^\alpha} \tag{82}$$

G^L and G^α are molar free energies of the L and α-phase, respectively. X_e^α and X_c^L represent the concentrations of component 2 in the α and L phases, respectively, that are in equilibrium at temperature T. X_2 is the concentration of component 2 in the alloy being considered. S_1^L, S_2^L, S_1^α and S_2^α are the partial molar entropies of components 1 and 2 in the L and α phases. $\Delta S^{\alpha\,L}$ and $\Delta S^{L \cdot \alpha}$ are also known as entropies of solution. $[(DT)^3]$ represents higher order terms of DT.

It is easy to show that the liquidus and solidus slopes, m_L and m_α, respectively, are given by

$$m_L = \frac{\partial^2 G^L}{\partial X_2^{L2}} \frac{X_2^L - X_2^\alpha}{\Delta S^{L-\alpha}} \tag{83}$$

and

$$m_\alpha = \frac{\partial^2 G^\alpha}{\partial X_2^{\alpha 2}} \frac{X_2^L - X_2^\alpha}{\Delta S^{\alpha - L}} \tag{84}$$

Consequently, Eq. (78) takes the form

$$DG = -\frac{(DT)^2}{2(X_c^L - X_e^\alpha)} \left[\frac{\lambda^L \Delta S^{L-\alpha}}{m_L} + \frac{\lambda^\alpha \Delta S^{\alpha\ L}}{m_\alpha} \right] \tag{85}$$

The term, $O[(DT)^3]$ is ignored due to its small contribution. The above equation is valid at deviations from the equilibrium that are not too large. The above equation clearly states that the free energy change is controlled by both solidus and liquidus slopes. Besides, the expected fractions of solid and liquid phases as well as the entropies of solutions $\Delta S^{L\ \alpha}$ and $\Delta S^{\alpha-L}$ play a significant role.

The second derivative of molar free energies of the α and L phases with respect to composition are always greater than or equal to zero. At the same time, λ^α and λ^L are positive fractions. Consequently, the terms in the square bracket of Eq. (78) are always positive; when the α phase is a solid solution with considerable solubility, $\partial^2 G^\alpha / \partial X_2^2$ will have a smaller value than for the pure metals. It will enhance the driving force for nucleation and lead to the attainment of a large degree of undercooling. As a result, the tendency of glass formation will decrease with increased solubility; alloys with a solid solution as a primary phase are, therefore, less prone to glass formation.

If one of the components of a eutectic alloy happens to be an intermetallic compound with fixed stoichiometry, $(\partial^2 G / \partial X_2^2)$ of the respective phase will be infinity leading to a decrease in the driving free energy. Thus for alloy compositions where the melt normally nucleates a stoichiometric intermetallic phase shows a greater tendency to glass formation. At the same time, eutectics with a solid solution and an intermediate phase should exhibit an asymmetry in the glass-forming composition range. These findings are in agreement with the experimental observations as shown in Fig. 3.

5.4. Critical cooling rate and $\Delta C_p^m / \Delta S_m$

Following Uhlmann [56], the time (t) for the transformation of a fraction (x) of the undercooled liquid can be expressed as

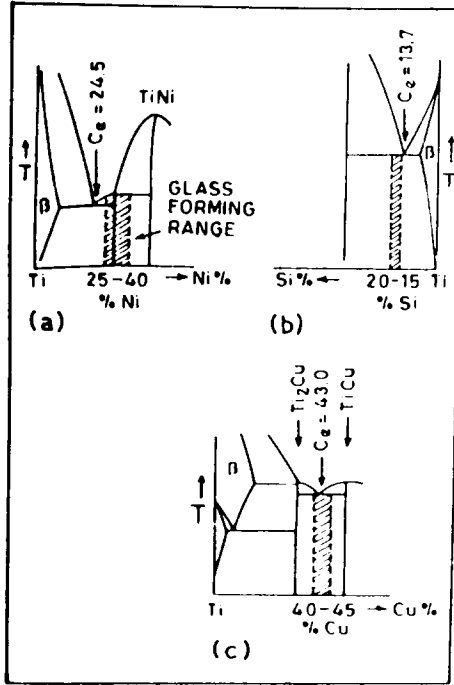$$t = \left[\frac{3X}{\pi I U^3} \right]^{1/4} \tag{86}$$

Fig. 3. Glass-formation ranges observed on melt-quenching a selected system.

where I is the homogeneous nucleation frequency and U is the growth rate in the liquid. I and U are given by

$$I = \frac{D_n N_9}{a_o^2} \exp\left(-\frac{\Delta G^*}{kT}\right)$$ (87)

and

$$U = \frac{f D_g}{a_o}\left[1 - \exp\left(-\frac{\Delta G}{RT}\right)\right]$$ (88)

where D_n and D_g are the coefficients of atomic diffusion involved in the processes of nucleation and growth, respectively, a_o is the average atomic or molecular radius, N_9 is the number density of atoms, and f is the fraction of sites at the interface on which growth can occur. ΔG is the driving force for the growth which is the Gibbs free energy difference between the liquid and solid phases as given in Eq. (10). ΔG^* is the free energy barrier for the formation of a critical nucleus.

Generally, D_g and D_n are taken to be the same and can be related to the shear viscosity η_T of the liquid through the Stockes–Einstein relationship [77]

$$D_g = D_n = D = \frac{kT}{3\pi q_o \eta_T}$$ (89)

For a spherical nucleus, ΔG^* is given by

$$\Delta G^* = \frac{16\pi\sigma^3}{3\Delta G_v} \tag{90}$$

where ΔG_v is the Gibbs free energy difference between the phases per unit volume, and σ is the solid–liquid interfacial energy and is difficult to estimate theoretically. Usually σ is evaluated by equating $\Delta G^*/KT$ to 50 at $\Delta T = 0.2\,T_m$. With all these assumptions and substitution, I and U can be expressed as

$$I = \frac{kN_3 T}{3\pi a_o^3 \eta_T} \exp\left[-\left(\frac{(16\pi\alpha^3)}{3K_1^3} \right) \frac{\Delta H_m^3}{\Delta G_v^2 RT} \right] \tag{91}$$

$$U = \frac{kfT}{3\pi a_o^2 \eta_T} \left[1 - \exp\left(-\frac{\Delta G}{RT} \right) \right] \tag{92}$$

The nose of the T–T-T curve is evaluated by the condition $dt/dT = 0$. Using the expressions for ΔG and η_T given in Eqs. (10) and (31) and realising the above stated condition, Dubey and Ramachandrarao [48] derived an equation for the estimation of the nose temperature T_n analytically with the aid of Eqs. (86), (91) and (92) which can be expressed as

$$\left(\frac{16\pi\alpha^3}{3RK_1^3} \right)\left(\frac{g_m}{1-g_0} \right)\left(\frac{\gamma\delta}{4B} \right)[2\Delta H(T_n) - 3\Delta G(T_n)]\left[\frac{\Delta H(T_n) - \Delta H_o}{\Delta C_p^m} \right]^2$$
$$\times \exp\left(\frac{\gamma\delta\Delta T_n}{T_n} \right) = \left(\frac{\Delta G(T_n)}{\Delta S_m} \right)^3 \tag{93}$$

with

$$\left(\frac{\Delta H(T_n) - \Delta H_o}{\Delta C_p^m} \right) = \left(\frac{T_m}{\delta} \right)\left(1 - \frac{T_o}{T_n} \right)\left[1 - \gamma\delta\left\{ \frac{1}{2\delta}\left(1 + \frac{T_o}{T_n} \right) - 1 \right\} \right] \tag{94}$$

$$\frac{\Delta G(T_n)}{\Delta S_m} = 1 + \left(\frac{\Delta C_p^m}{\Delta S_m} \right)\left(\frac{\Delta T_n^2}{2T_n} \right)\left(1 - \frac{\gamma\delta}{3}\frac{\Delta T_n}{T_n} \right) \tag{95}$$

$$2\Delta H(T_n) - 3\Delta G(T_n) = \Delta S_m\left[3T_n - T_m - \left(\frac{\Delta C_p^m \Delta T_n}{2\Delta S_m} \right) \right.$$
$$\left. \times \left\{ 3T_n + T_m - \left(\frac{\gamma\delta}{T_n} \right)(T_m^2 - T_n^2) \right\} \right] \tag{96}$$

$$\frac{B(1 - g_0)}{g_m} = [\ln(\eta_{T_g}/\eta_{T_m})]\left[1 - \exp\left\{ -\frac{\gamma\delta(T_m - T_o)}{T_m} \right\} \right]$$
$$\times \frac{\left[1 - \exp\left\{ -\frac{\gamma\delta T_m(T_g - T_o)}{T_g T_o} \right\} \right]}{\exp\left\{ \frac{\gamma\delta(T_m - T_g)}{T_g} - 1 \right\}} \tag{97}$$

and $\Delta T_n = T_m - T_n$, η_{T_g} and η_{T_m} are the viscosities of the undercooled liquid at T_g and T_m, respectively, K_1 can be taken as unity [56] and α is estimated by normalising ΔG^* as already discussed. $\Delta H(T_n)$ and $\Delta G(T_n)$ represent the values of the corresponding thermodynamic parameters at the nose temperature T_n. Thus, except for T_n, all the terms in Eq. (93) are either measurable (ΔC_p^m, ΔS_m, T_m, T_g, η_{T_m} and η_{T_g}) or evaluable (T_o and $\gamma\delta$). T_n can be evaluated by an iterative procedure. The method has further advantage that a knowledge of the temperature-dependence of viscosity is not required in the estimation of T_n. Knowing T_n, the critical cooling rate R_c can be evaluated from relationship

$$R_c = \frac{T_m - T_n}{t_n} \tag{98}$$

where t_n is the time for the crystallisation of volume fraction 10^{-6} of the liquid at temperature T_n and can be evaluated with the aid of Eqs. (86)–(88). The values of T_n and R_c are reported in Table 6 along with the values obtained on the basis T–T–T diagram as suggested by Uhlmann. The variation of R_c with δ is illustrated in Fig. 4(a).

Turnbull [78] and Davies [77] have attempted to correlate the critical cooling rate R_c with the reduced glass transition temperature T_g/T_m and it is reported that lower the value of T_g/T_m, greater is the rate of cooling required for glass formation. Through the analysis of Eq. (93) it can be realised that the nose temperature T_n is mainly determined by $\Delta C_p^m/\Delta S_m$ and $\delta = (T_o/T_m)$. Consequently the dominating nature of these parameters can be understood in assessing the value of R_c. In view of these findings, Dubey and Ramachandrarao [48] have attempted to correlate reduced ideal glass transition temperature δ with R_c to study the glass-forming ability of materials and it is reported (Fig. 4(a) and Table 6) that materials showing a large value of δ require a low value of rate of cooling for glass formation. A high value of δ implies high T_o and its proximity to the melting point T_m. It may, therefore, be considered that materials with a high value of δ are likely to form glasses more readily by requiring a lower degree of undercooling or lower rate of cooling. As discussed in the previous section (Table 2), δ is in itself a function of $\Delta C_p^m/\Delta S_m$ and its dependence on $\Delta C_p^m/\Delta S_m$ can be understood with the help of Fig. 4(b). Hence R_c should correlate with $\Delta C_p^m/\Delta S_m$. Fig. 4(c) shows that except for methylpentane, correlation between $\Delta C_p^m/\Delta S_m$ and R_c is indeed indicated. The results clearly indicate that material with a large value of $\Delta C_p^m/\Delta S_m$ are most suitable for glass formation.

6. Heat of crystallisation and viscosity

On the basis of earlier investigations related to the crystallisation kinetics of metallic glasses, it has been established that the apparent activation energy of crystallisation is equal to the activation energy for viscous flow [79–82]. Chen [83] has attempted to show that the equality of apparent activation energies can be used to obtain the viscosity from the thermal measurements. This procedure is helpful in the determination of viscosity at a temperature where creep measurements are not feasible due to the intervention of crystallisation. Using free volume as well as hole theories of liquids,
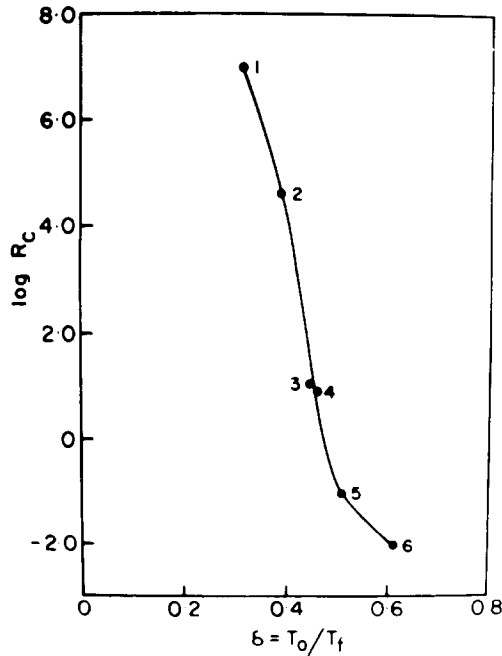
Fig. 4(a). The variation of the critical cooling rate R_c for glass formation with δ the ratio of the ideal glass transition temperature (T_o) to the melting temperature (T_m). The numbers indicated identify the materials as per Table 6.

Ramachandrarao [84] has demonstrated that the heat of crystallisation can be related to the viscous behaviour of glass-forming metallic melts.

According to the hole theory of liquids, introduction of holes into a liquid is considered to be impossible below the glass transition temperature T_g and all property changes which occur at T_g represent contributions due to holes at T_g. On the basis of these considerations, Hirai and Eyring [14] expressed

$$\Delta\alpha = \frac{\varepsilon_h}{R T^2} \exp\left[-\frac{(\varepsilon_h + P\vartheta_h)}{R T} \right] \tag{99}$$

$$\Delta\beta = \frac{\vartheta_h}{R T} \exp\left[-\frac{\varepsilon_h + P\vartheta_h}{R T} \right] \tag{100}$$

$$\Delta C_p = nR \left(\frac{\varepsilon_h}{R T} \right)^2 \exp\left[-\frac{\varepsilon_h + P\vartheta_h}{R T} \right] \tag{101}$$

where $\Delta\alpha$, $\Delta\beta$ and ΔC_p represent changes in thermal expansion (α), compressibility (β) and specific heat (ΔC_p), respectively, and other terms have the same meaning as defined earlier. The expression for heat of crystallisation can be derived using basic ther-
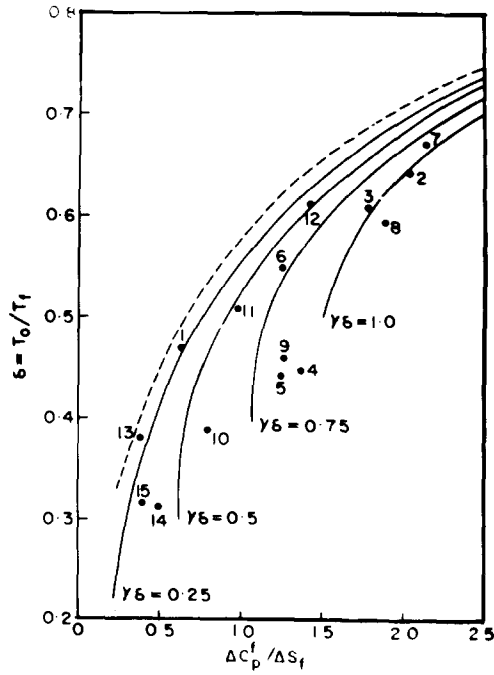
Fig. 4(b). The dependence of $\delta = T_o/T_m$ with $\Delta C_p^m/\Delta S_m$. The numbers in the plot refer to materials at the indicated serial numbers in Table 2.
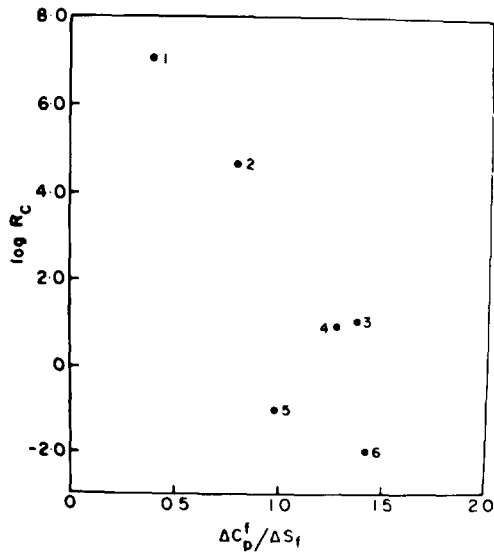

Fig. 4(c). The dependence of the critical cooling rate R_c for glass formation on $\Delta C_p^m/\Delta S_m$. The numbers shown identify the materials as per Table 6.

modynamic relationships and ΔC_p to yield

$$\Delta H_c = \Delta H_m - n\varepsilon_h \left[\exp\left(\frac{-\varepsilon_h}{RT_m}\right) - \exp\left(\frac{-\varepsilon_h}{RT_c}\right) \right] \tag{102}$$

Knowing the values of any two property changes listed above is sufficient to evaluate the characteristic parameters ε_h and ϑ_h which define a hole. These parameters can also be derived from the temperature-dependence of the viscosity of the liquid.

Utilising the expression for the free volume suggested by Ramachandrarao et al. [28, 85], the Doolittle empirical equation for viscosity as stated in Eq. (27) yields [84]

$$\eta = \eta_o \exp[(1/n)\exp(\varepsilon_h/RT)] \tag{103}$$

Generally, the viscosity is expressed in the form of the Vogel–Fulcher equation. A procedure has already been developed by Ramachandrarao et al. [28, 85] for recasting the viscosity data in the form of Eq. (103) which can be used to estimate parameters related to a hole, such as n, ε_h etc. An alternative and simple procedure has also been suggested by Ramachandrarao [84] for obtaining the temperature-dependence of the viscosity from the Vogel–Fulcher equation as given below. Eq. (103) can be rewritten as

$$\ln \eta = \ln \eta_o + (1/n)\exp(\varepsilon_h/RT)$$

and

$$\ln \frac{\partial \ln \eta}{\partial(1/T)} = \ln\left(\frac{\varepsilon_h}{nRT}\right) + \frac{\varepsilon_h}{RT}$$

These equations enable one to obtain n, ε_h and η_o with the help of experimentally measured values of η. Consequently, the heat of crystallisation ΔH_c can be determined with the aid of Eq. (102).

Conversely a knowledge of ΔH_c, ΔH_m and any other property change ($\Delta \alpha, \Delta \beta, \Delta C_p$ etc.) at T_g should be sufficient to estimate the viscosity and to obtain an expression for the viscosity of the kind given by Eq. (103).

Using experimental data [3, 86–88] related to the viscosity and to the heat of fusion, ΔH_m, Ramachandrarao calculated the heat of crystallisation for two metallic glasses $Au_{0.77}Ge_{0.136}Si_{0.094}$ and $Pd_{0.775}Cu_{0.06}Si_{0.165}$ as reported in Table 7. Comparison of the last two columns of Table 7 reveals the excellent agreement between observed and calculated values of the heat of crystallisation. He could not demonstrate the use of the reverse procedure for the determination of the viscous properties of glass-forming metallic melts from a knowledge of ΔC_p at T_g, ΔH_c and ΔH_m due to the non-availability of sufficient data on glass-forming melts.

7. Conclusions

The expressions for the Gibbs free energy difference ΔG between the undercooled melt and corresponding equilibrium solid phases derived by us on the basis of the hole

Table 6
Critical cooling rate R_c and the nose temperature T_n of six glass-forming materials based on T–T–T diagrams and on an approximate condition Eq. (93) for the nose temperature T_n

No.	Material	$\Delta C_p^m/\Delta S_m$	δ	Nose temperature T_n/K		Critical cooling rate R_c/K s^{-1}	
				Based on T–T–T diagram	Based on Eq. (17)	Based on T–T–T diagram	Based on Eq. (17)
1	Au$_{0.77}$Ge$_{0.136}$Si$_{0.094}$	0.3956	0.3168	432	436	1.07×10^7	1.04×10^7
2	Ethanol	0.7927	03891	118	121	4.39×10^4	3.48×10^4
3	ZnCl$_2$	1.3687	0.4488	459	462	12.38	11.87
4	Glycerol	1.2667	0.4598	229	230	8.91	8.75
5	2-Methylpentane	0.9819	0.5091	93	94	1.03×10^{-1}	9.61×10^{-2}
6	o-Terphenyl	1.4180	0.6121	268	270	1.07×10^{-2}	1.05×10^{-2}

Table 7
Viscosity and crystallisation data for the metallic glasses

Alloy	n	$\varepsilon_n/$ (kJ mol^{-1})	$\ln(\eta_0)/$ (kg^{-1} cm^{-1}))	T_c[3.102]/ (kJ mol^{-1})	T_m[3.87]/K /(kJ mol^{-1})	ΔH_m[3.87]/ (kJ mol^{-1})	$\Delta H_c^{(\text{Cal})}$/ (kJ mol^{-1})	ΔH_c^{ob}[3.102]/ (kJ mol^{-1})
Au$_{0.77}$Ge$_{0.136}$Si$_{0.094}$	3.524	11.30	−6.6686	300	625	10.63	6.53	6.19 ± 0.58
Pd$_{0.775}$Cu$_{0.06}$Si$_{0.165}$	2.714	22.27	−1.9264	675	1010	7.26	4.14	3.87

theory of liquids as well as Taylor series expansion are capable of estimating the correct temperature-dependence of ΔG for all kinds of metallic glasses, oxide glasses, polymeric glasses, etc. The temperature-dependence of the viscosity of the under-cooled melt can be explained very nicely with the help of expressions reported by us. It was also found that the well-known Vogel–Fulcher equation is a special form of the expression reported in this review. It is possible to give a correct mathematical explanation to the empirical WLF equation. Consequently it can be said that the expression reported by us is able to predict the correct temperature-dependence of relaxation phenomena. The ideal glass transition temperature, T_0 which plays a significant role in the estimation of the viscosity and the glass-forming ability of materials can be estimated correctly with the help of expression reported by us. It is also found that the values of T_0 estimated using thermodynamic data are nearly the same as obtained using relaxation data.

The binary liquid alloy with the smallest molar volume is found to be most prone to vitrification. The glass-forming composition range can be determined from the fractional negative deviation of the volume with respect to the ideal volume. The criterion based on concentration–concentration fluctuations suggests that any tendency for complex formation will be reflected in the deviation of the observed $S_{cc}^{(0)}$ from the ideal value $S_{cc}^{id(0)}$. It has been found that significant and systematic negative deviation from the ideal value or a tendency to zero of $S_{cc}^{(0)}$ is observed at stoichiometry corresponding to the complex in the melt. $S_{cc}^{(0)}$ exhibits a maximum and tends to the ideal value in the glass-forming composition range. It appears that complex formation is not to be directly related to the glass-forming tendency.

The existence of solid solubility in the constituent phases of a eutectic tends to enhance the driving force for nucleation. As a result, the observed glass-forming composition ranges tend to be asymmetric with respect to eutectic composition and lie closer to the stoichiometric compound or the pure metal in the eutectic. In pure metal metalloid eutectics, glass formation is more difficult in the composition range where the metalloid is a primary phase.

It is found that the ratio δ of the ideal glass transition temperature T_0 to the melting temperature T_m plays a dominant role in determining the glass-forming ability of materials. Consequently the ratio $(\Delta C_p^m / \Delta S_m)$ of the specific heat difference to the entropy difference between liquid and solid phases at the melting temperature is the controlling factor for glass formation. Materials with large value of $\Delta C_p^m / \Delta S_m$ can readily form glasses irrespective of the nature of the materials.

Reports related to crystallisation and viscous behaviour clearly indicate that the heat of crystallisation can be estimated with the help of the experimentally observed value of the viscosity. The procedure has also been found to furnish viscosity from the heat of crystallisation.

Acknowledgements

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