

Viscous behaviour of glass-forming liquids: a thermodynamic approach

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Abstract. The temperature dependence of the viscosity of the undercooled melts exhibits an important role in the study of nucleation, crystal growth and the glass-forming ability of materials. Several attempts have been made to study the viscous behaviour of the glass-forming melts and these investigations are mainly based on free volume theory as well as on the configurational entropy model. In the present investigation, an attempt has been made to correlate the thermodynamic parameters with the viscosity of the glass-forming melts and to study the temperature dependence of the viscosity of undercooled liquids on the basis of the free volume theory as well as on the basis of the configurational entropy model of Adam and Gibbs. The entire study is confined on the expression for thermodynamic parameters reported by the authors recently. The expression obtained has been successfully applied to study the temperature dependence of the viscosity of the metallic, molecular and oxide glass-forming liquids.

Keywords. Viscosity; free volume; configurational entropy; Kauzmann temperature; thermodynamic parameters.

1. Introduction

The viscosity (η) and the Gibbs free energy difference (ΔG) between the undercooled liquid and the corresponding equilibrium solid are key factors in metastable solidification of undercooled melts. The viscosity (η) is also known to be one of the most sensitive variable controlling the glass-forming ability of materials and it is found that there is a large increase in η with progressive undercooling (Uhlmann 1972; Davies 1976). The metastability of liquids precludes the experimental determination of η of an amorphous alloy between the glass transition temperature (T_g) and the equilibrium melting temperature (T_m) due to inability to prevent crystallization. η of the glass-forming melts can be measured at low temperatures near T_g and at high temperatures above T_m . Due to these experimental difficulties, theoretical approaches or crude approximations are commonly used to estimate the viscosity at intermediate temperatures by connecting low and high temperature data of viscosity by simple equations. However, where T_g is well separated from the crystallization temperature (T_c), it is possible to measure η experimentally.

Several expressions (Vogel 1921; Raman 1923; Doolittle 1951; Macedo and Litovitz 1965; Cohen and Grest 1979) have been proposed for the temperature dependence of η . The simplest expression for η is the standard Arrhenius-type equation (Dunn 1926)

$$\eta = A_1 \exp(E/RT), \quad (1)$$

where E is the activation energy for viscous flow, R the gas constant and A_1 a constant. The above is applicable only in a narrow temperature range for simple liquids and viscosities of associated and network liquids generally do not follow this equation. The

commonly used expression for describing the temperature dependence of η is given by Vogel (1921) and Fulcher (1925) as

$$\eta = A_2 \exp\left(\frac{B_2}{T - T_0}\right), \quad (2)$$

where A_2 and B_2 are constants and T_0 the characteristic temperature. Often the temperature dependence of viscosity can not easily be explained on the basis of the above stated equation over the entire temperature range of interest with a single set of constants A_2 , B_2 and T_0 (Pok and Turnbull 1972).

There are basically two approaches to obtain an expression for the temperature dependence of η , namely the free volume theory (Doolittle 1951; Cohen and Turnbull 1959) and the configurational entropy model (Adam and Gibbs 1965). The expressions proposed by Eyring and his co-workers (Glasstone *et al* 1941; Hirai and Eyring 1958, 1959; Ree *et al* 1962) and Cohen and Turnbull (1959) are basically based on the diffusion theory while the procedure developed by Adam and Gibbs (1965) is confined on the configurational entropy of undercooled liquids. Recently, the authors (1996) reported an expression for the Gibbs free energy difference (ΔG) between the undercooled liquid and the corresponding equilibrium solid using the hole theory of liquids (Frankel 1955; Hirai and Eyring 1958, 1959) and the expression obtained has been successfully applied to study the various thermodynamic parameters of metallic, molecular and oxide glass-forming melts. The aim of the present investigation is to study the temperature dependence of the viscosity of the glass-forming melts using expressions for the thermodynamic parameters reported by the authors recently. The viscous behaviour of glass-forming liquids has been studied on the basis of the free volume theory as well as on the basis of the configurational entropy model proposed by Adam and Gibbs (1965). The expression obtained is also found to encompass many empirical relations under appropriate approximations. The expression obtained has been successfully applied to study the temperature dependence of η of the metallic ($\text{Au}_{0.77}\text{Ge}_{0.136}\text{Si}_{0.094}$), oxide (B_2O_3) and molecular (2-methyl pentane) glass-forming liquids.

2. Thermodynamic parameters

Following the earlier work of Dubey and Ramachandrarao (1984) and incorporating the modifications suggested by Sanchez (1974) and Flory (1953), various thermodynamic parameters the Gibbs free energy difference (ΔG), enthalpy difference (ΔH) and entropy difference (ΔS) between the undercooled liquid and solid phases of the glass-forming melts have been studied by the authors (1996) on the basis of the hole theory (Frankel 1955; Hirai and Eyring 1958, 1959) of liquids. According to the earlier report of authors (1996), the specific heat difference ΔC_p between the undercooled liquid and the equilibrium solid can be expressed as

$$\Delta C_p = nR \left(\frac{E_h}{RT}\right)^2 g = \Delta C_p^m \left(\frac{T_m}{T}\right)^2 e^{-2\delta \cdot \Delta T/T}, \quad (3)$$

and

$$g = \exp\left[-\left(\frac{\epsilon_h + pv_h}{K_B T} + A\right)\right], \quad (4)$$

with $A = 1 - 1/n$. $\Delta T = T_m - T$ represents the degree of undercooling, E_h the hole formation energy per mole, v_h the volume of a hole. $n = v_a/v_h$ is a measure of the relative volume of a hole and an atom, v_a the hard core volume per atom or molecule, $\delta = T_0/T_m$, T_0 the ideal glass transition temperature, p the external pressure and g the volume fraction of holes at temperatures T . ΔC_p^m is the specific heat difference between the liquid and solid phases at $T = T_m$. K_B is the Boltzmann constant and ϵ_h the energy required for the formation of a hole.

The expressions for ΔG , ΔH and ΔS can be obtained with the aid of basic thermodynamic relations

$$\Delta G = \Delta H - T\Delta S, \quad (5)$$

$$\Delta H = \Delta H_m - \int_T^{T_m} \Delta C_p dT, \quad (6)$$

$$\Delta S = \Delta S_m - \int_T^{T_m} (\Delta C_p/T) dT, \quad (7)$$

and the expression for ΔC_p as stated in (3). Consequently one can have

$$\Delta G = \Delta S_m \Delta T - \frac{\Delta C_p^m}{4\delta^2} [2\delta \Delta T - T(1 - e^{-2\delta \Delta T/T})], \quad (8)$$

$$\Delta H = \Delta H_m - \Delta C_p^m \frac{T_m}{2\delta} [1 - e^{-2\delta \Delta T/T}], \quad (9)$$

$$\Delta S = \Delta S_m - \frac{\Delta C_p^m}{4\delta^2} \left[(1 + 2\delta) - \left(1 + 2\delta \frac{T_m}{T} \right) (e^{-2\delta \Delta T/T}) \right], \quad (10)$$

where ΔH_m and ΔS_m are enthalpy of fusion and entropy of fusion respectively. As argued by Kauzmann (1948) that a liquid loses its entropy at a faster rate than the solid resulting in the two phases having the equal entropy at some temperature T_0 well above the absolute zero and below the glass transition temperature (T_g). The iso-entropy temperature T_0 is usually referred to as the Kauzmann temperature or the ideal glass transition temperature. Introducing the Kauzmann temperature T_0 and volume fraction g as stated in (4) the expression for ΔH stated in (9) takes the form of

$$\Delta H = \Delta H_0 + \frac{\Delta C_p^m T_m}{2\delta g_m} (g - g_0), \quad (11)$$

where g_0 and g_m represent volume fractions of holes at temperatures T_0 and T_m respectively.

As stated earlier, according to Kauzmann ΔS becomes zero at $T = T_0$. In view of it, the expression for ΔS stated in (10) results as

$$\Delta S_m = \frac{\Delta C_p^m}{4\delta^2} [(1 + 2\delta) - 3e^{-2(1-\delta)}]. \quad (12)$$

Using the approximations

$$e^{2x} - 1 \simeq 2x \frac{3+x}{3-2x}, \quad (13a)$$

and

$$1 - e^{-2x} \simeq 2x \frac{3-x}{3+2x}, \quad (13b)$$

and taking the help of (12), expression for ΔS stated in (10) reduces to

$$\Delta S = \frac{\Delta C_p^m e^{-2(1-\delta)} (T - T_0)(3T - T_0)}{2\delta^2 T^2}. \quad (14)$$

3. Viscosity of undercooled liquids based on free volume theory

The free volume model of the viscosity is essentially based on the idea that a certain critical volume must be available to a molecule or an atom before performing a diffusive motion. It was Doolittle (1951) first of all who proposed an empirical relation between viscosity and free volume as

$$\eta = A \exp(B/f_T), \quad (15)$$

where A and B are constants and f_T the relative free volume fraction at temperature T . A theoretical explanation to this relation was given by Cohen and Turnbull (1959) Turnbull and Cohen (1961, 1970) as well as by Bueche (1959). The free volume can be defined as unfilled space between atoms or molecules of the material under study. It can also be defined in terms of the thermal expansion and the hole theory of liquids and has been summarized by Bondi (1954). Following the earlier work of Doolittle (1951) and Ramachandrarao *et al* (1977), the relative free volume f_T can be expressed as

$$f_T = \frac{V_T - V_{T_0}}{V_{T_0}}, \quad (16)$$

where V_T and V_{T_0} are volumes of material at temperatures T and at some reference temperature T_0 . Consequently, in terms of volume fractions of holes, it can also be expressed as

$$f_T = \frac{g - g_0}{1 - g}. \quad (17)$$

Utilizing the Doolittle equation as stated in (15) and using (17), one can have

$$\eta = A_3 \exp\left(\frac{B_3}{g - g_0}\right). \quad (18)$$

Here a term $(1 - g_0)$ has been absorbed in the constant B_3 . A_3 is also a constant. Use of (11) allows one to express

$$g - g_0 = (\Delta H - \Delta H_0) \frac{2\delta g_m}{\Delta C_p^m T_m}. \quad (19)$$

Taking the aid of (18) and (19) one can express the viscosity of the glass-forming melts in terms of thermodynamic quantities as

$$\ln \eta = \ln \eta_0 + \frac{2B_3 \delta g_m}{\Delta C_p^m T_m} \frac{1}{\Delta H - \Delta H_0} \equiv \ln \eta_0 + \frac{D}{\Delta H - \Delta H_0}, \quad (20)$$

which clearly shows the evaluation of η with the aid of enthalpy differences ΔH and ΔH_0 at temperatures T and T_0 respectively. Here D can be taken as a constant. Appropriate substitution of ΔH and ΔH_0 in terms of ΔG and ΔS and simplification of (20) yields

$$\ln \eta = \ln \eta_0 + \frac{D}{T\Delta S \left[1 - \frac{\Delta G_0 - \Delta G}{T\Delta S} \right]}, \quad (21)$$

where ΔG_0 stands for the Gibbs free energy difference at $T = T_0$ and η_0 is a constant. Using the approximation stated in (13), it can be shown that

$$\Delta G_0 - \Delta G = \frac{T\Delta S(1 - T_0/T)}{(1 - T_0/3T)(1 + 2T_0/T)}. \quad (22)$$

As a result of it, expression for η stated in (21) can also be expressed as

$$\ln \eta = \ln \eta_0 + \frac{DX(T)}{T\Delta S}, \quad (23)$$

where

$$(X^{-1}(T)) = \frac{\frac{8}{3} \frac{T_0}{T} \left(1 - \frac{T_0}{4T} \right)}{(1 + 2T_0/T)(1 - T_0/3T)}, \quad (24)$$

is a weak temperature dependence function. In view of (20) and (23), one can say that, the expression for η stated in (20) based on the free volume approach reduces to (23) which shows a relation between η and ΔS and it is similar to the expression proposed by Adam and Gibbs (1965). The temperature dependence of the viscosity can be obtained by substituting the expression for ΔS as stated in (14) and it will be discussed in the next section.

4. Viscosity of undercooled liquids based on configurational entropy

The viscosity of the glass-forming liquids has also been studied in terms of the configurational entropy (ΔS_c) of liquids by Adam and Gibbs (1965) using the molecular-kinetic theory and it can be expressed as

$$\eta = A_0 \exp \left(\frac{C_0}{T\Delta S_c} \right), \quad (25)$$

where constant C_0 is related to the potential energy hindering the cooperative rearrangement per monomer segment and the critical entropy and it is treated as a constant. A_0 is also a constant. The configurational entropy (ΔS_c) is given by

$$\Delta S_c = \int [C_p(\text{liquid}) - C_p(\text{glass})] d \ln T. \quad (26)$$

Often, the experimental value of C_p (glass) is very close to that of the crystal and shows similar temperature dependence (Gee and Melia 1970; Wong and Angell 1976).

Consequently, the expression for ΔS given in (10) or (14) can be used in place of ΔS_c to obtain the temperature dependence of η . The resulting expression takes the form

$$\ln \eta = \ln \eta'_0 + \frac{C(1 + T_0/3T)}{(T - T_0)}, \quad (27)$$

where $C = 2/3 C_0 \delta^2 e^{2(1-\delta)}/\Delta C_p^m$ and can be treated as a constant.

The expression for viscosity obtained above as stated in (27) can be compared with the Vogel–Fulcher equation stated in (2). At high temperatures i.e. $T \gg T_0$, the term $T_0/3T$ is small compared to unity and expression for η in (27) reduces to the Vogel–Fulcher equation stated in (2) as

$$\ln \eta = \ln \eta'_0 + \frac{C}{T - T_0}, \quad (28)$$

with $B_2 = C$ and $A_2 = \eta'_0$. At low temperatures, i.e. near the glass transition temperature, $T_0/T \simeq T_0/T_g$ is approximately 3/4 and (27) yields

$$\ln \eta = \ln \eta'_0 + \frac{C_1}{T - T_0}, \quad (29)$$

where $C_1 = 1.25C$ and once again it reduces to Vogel–Fulcher equation with $B_2 = 1.25C$ which is in justification of the fact that the Vogel–Fulcher equation was able to explain the experimental data of η at low as well as high temperatures with the aid of different sets of constants (A_2 , B_2 and T_0 as stated in (2)). In view of these findings, it can be said that the constant B_2 in the Vogel–Fulcher expression should be temperature dependent to the extent

$$B_2 = C(1 + T_0/3T). \quad (30)$$

At the same time, it is interesting to note that the expression for η stated in (27) has less number of adjustable parameters than in the case of the Vogel–Fulcher equation. In the present case, T_0 is not an adjustable parameter and it can be calculated using thermodynamic parameters ΔC_p^m and ΔS_m with the aid of (12) while T_0 is treated as an adjustable parameter in the Vogel–Fulcher expression. The expression for the temperature dependence of η reported in the present work is much simpler than the expression reported by Dubey and Ramachandrarao (1992) using the expression for ΔS based on Taylor series expansion. The constants η'_0 and C can be estimated with the help of experimental data of η at any two temperatures (say T_g and T_m) and T_0 can be evaluated with the aid of ΔC_p^m and ΔS_m and (12). Thus, η of the glass-forming melts can be calculated in the temperature range T_g to T_m with the aid of ΔC_p^m , ΔS_m and experimentally measured η at T_g and T_m .

5. Results and discussion

To test the applicability of expressions for thermodynamic parameters ΔH and ΔS used in the present analysis, ΔH and ΔS have been calculated for $\text{Au}_{0.77}\text{Ge}_{0.136}\text{Si}_{0.094}$, B_2O_3 and 2-methylpentane belonging to metallic, oxide and molecular glass-forming liquids respectively in the temperature range T_g to T_m using the materials parameters stated in table 1 and results obtained are shown in figure 1. The experimental data of

Table 1. The materials constants used to study the temperature dependence of ΔH , ΔS and viscosity.

Parameters	$\text{Au}_{0.77}\text{Ge}_{0.136}\text{Si}_{0.096}$	B_2O_3	2-mp
$a(\text{J}/\text{mol}/\text{K})$	32.5264	70.8540	146.871
$b(\text{J}/\text{mol}/\text{K}^2) \times 10^3$	-63.0822	-73.4160	-798.5
$c(\text{J}/\text{mol}/\text{K}^3) \times 10^5$	3.4141	—	—
$d(\text{J}/\text{mol}) \times 10^{-2}$	1.3004	—	—
$e(\text{JK}/\text{mol}) \times 10^{-4}$	2.5188	141.12	—
$\Delta H_m(\text{J}/\text{mol})$	10627	22261	6260
$\Delta S_m(\text{J}/\text{mol}/\text{K})$	17.03	30.79	52.36
$\Delta C_p^m(\text{J}/\text{mol}/\text{K})$	6.74	20.47	51.41
$T_m(\text{K})$	625	723	119.55
$T_g(\text{K})$	294	550	79.5
$T_0(\text{K})$	199.4	336	60.82

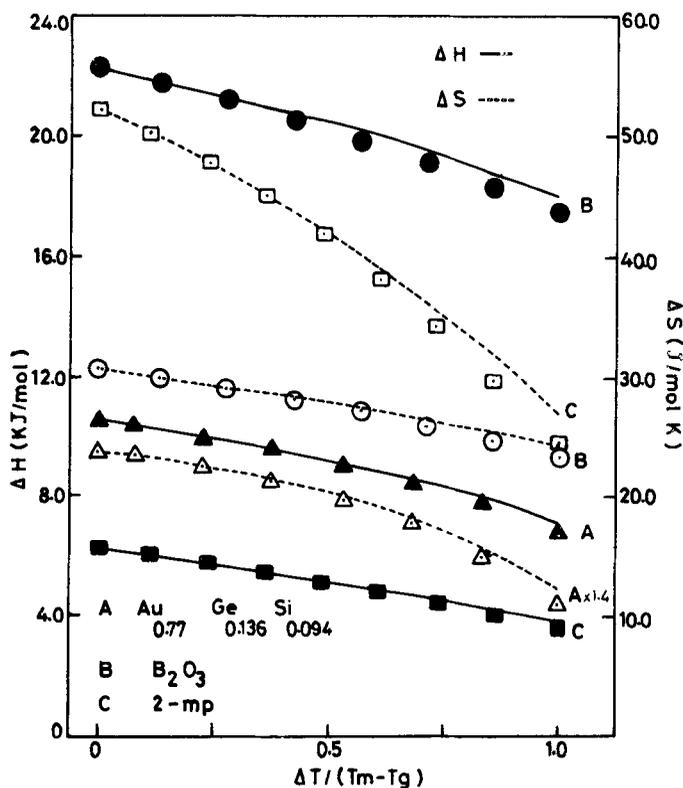


Figure 1. Variation of ΔH and ΔS with the reduced undercooling $\Delta T/(T_m - T_g)$. Curves A, B and C correspond to glass-forming melts $\text{Au}_{0.77}\text{Ge}_{0.136}\text{Si}_{0.096}$, B_2O_3 and 2-methylpentane respectively. Solid and dashed lines represent the calculated values of ΔH and ΔS respectively. Closed triangles, closed circles and closed squares represent the experimental values of ΔH for $\text{Au}_{0.77}\text{Ge}_{0.136}\text{Si}_{0.096}$, B_2O_3 and 2-mp respectively while open triangles, open circles and open squares denote the experimental data of ΔS of $\text{Au}_{0.77}\text{Ge}_{0.136}\text{Si}_{0.096}$, B_2O_3 and 2-mp respectively. For the sake of clarity ΔS of $\text{Au}_{0.77}\text{Ge}_{0.136}\text{Si}_{0.094}$ has been enlarged by a factor of 1.4.

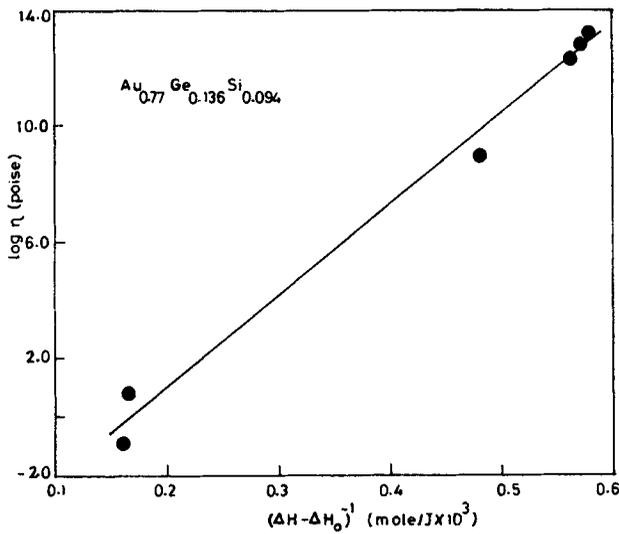


Figure 2. Variation of $\log \eta$ with $(\Delta H - \Delta H_0)^{-1}$ for the glass-forming melt $\text{Au}_{0.77}\text{Ge}_{0.136}\text{Si}_{0.096}$. Circles represent experimental data of η .

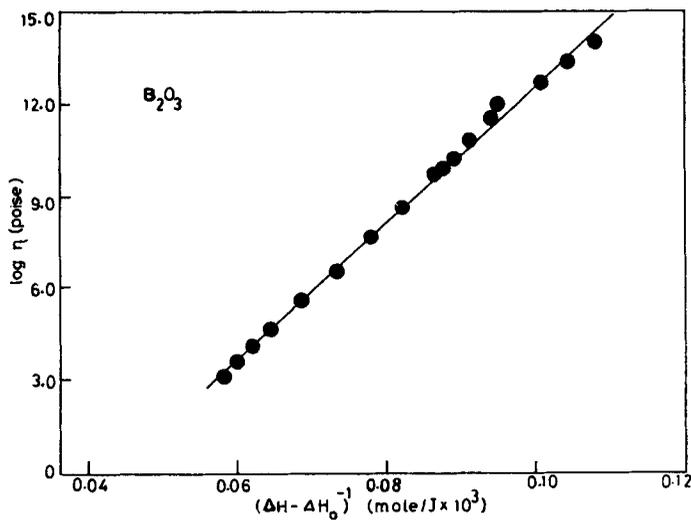


Figure 3. Variation of $\log \eta$ with $(\Delta H - \Delta H_0)^{-1}$ for the glass-forming melt B_2O_3 . Circles correspond to experimental values of η .

ΔC_p of these materials are available in literature (Thomas and Parks 1931; Douslin and Huffmann 1946; Greet and Turnbull 1967; Chen and Turnbull 1968; Angell and Rao 1972; Hultgren *et al* 1973) in the form of

$$\Delta C_p = a + bT = cT^2 + d/T + e/T^2, \quad (31)$$

where a, b, c, d and e are the materials constants. With the help of figure 1, it is very clear that the agreement between calculated and experimental values of ΔH and ΔS are quite good for all the three materials.

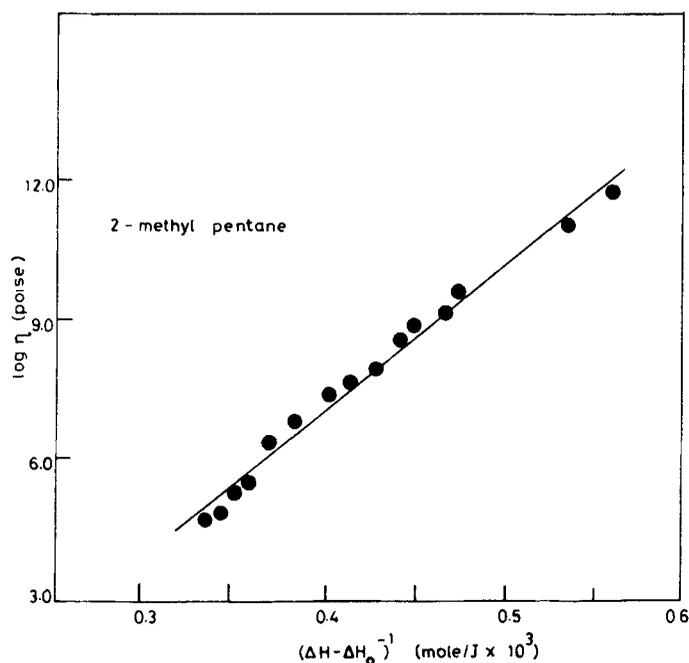


Figure 4. Variation of $\log \eta$ with $(\Delta H - \Delta H_0)^{-1}$ for the glass-forming melt 2-methylpentane. Circles denote the experimentally measured values of η .

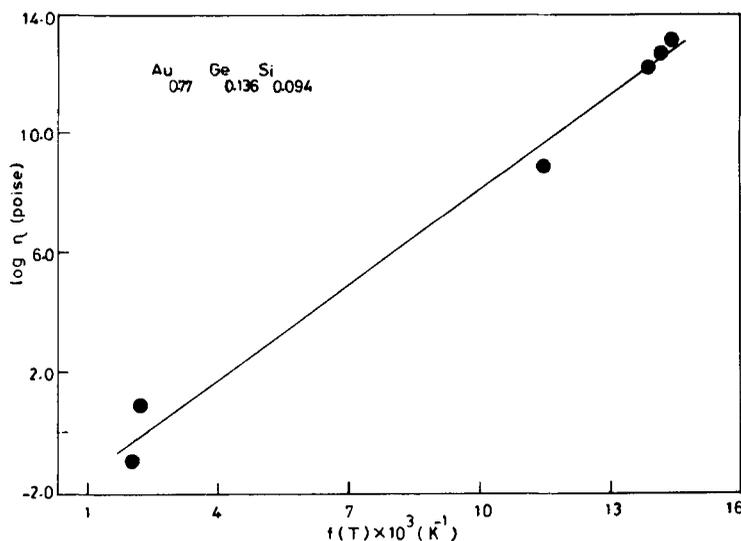


Figure 5. The temperature dependence of η of the metallic melt $\text{Au}_{0.77}\text{Ge}_{0.136}\text{Si}_{0.094}$ as predicted by (27). Circles represent the experimentally observed values of η .

To see the applicability of the expression for η reported in (20), the viscosity of $\text{Au}_{0.77}\text{Ge}_{0.136}\text{Si}_{0.094}$, B_2O_3 and 2-methylpentane (2-mp) have been shown as a function of $(\Delta H - \Delta H_0)^{-1}$ in figures 2, 3 and 4 respectively. The experimental values of the viscosity of the metallic glass $\text{Au}_{0.77}\text{Ge}_{0.136}\text{Si}_{0.094}$ are rare. Chen and Turnbull (1968)

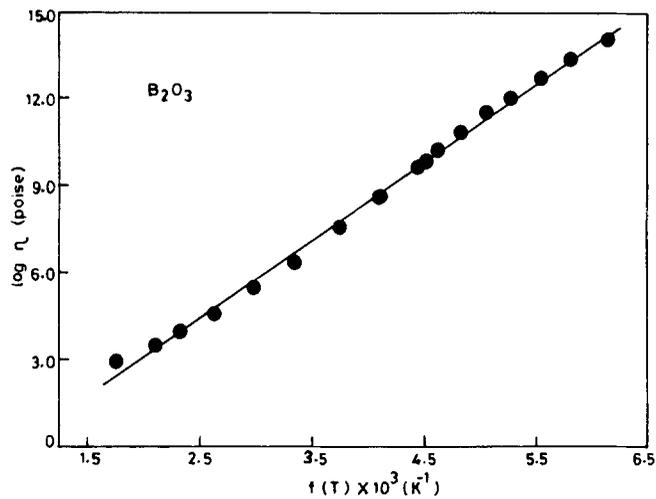


Figure 6. The temperature dependence of η of the glass-forming melt B_2O_3 as obtained by (27). Circles stand for experimental data on η .

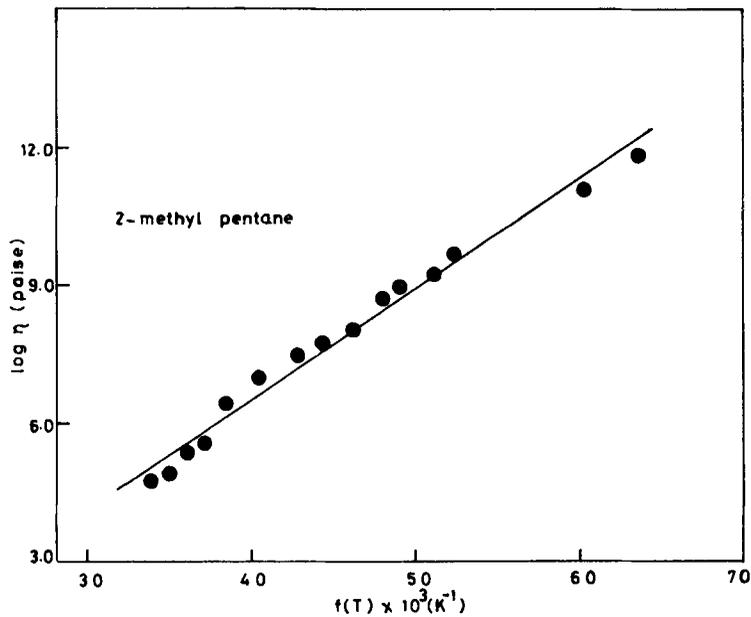


Figure 7. The temperature dependence of η of the glass-forming liquid 2-methylpentane as reported in (27). Circles represent the experimentally measured values of η .

measured η over a narrow temperature range (285–305 K) near T_g and Pok and Turnbull (1972) subsequently measured η of the same at two temperatures 679 and 721 K. The earlier workers (Pok and Turnbull 1972) tried to explain these data using the Vogel–Fulcher equation and they found that one set of constants (A_2 , B_2 and T_0 in (2)) can not adequately fit the data over the entire temperature range. The experimental data of η for B_2O_3 and 2-mp are taken from the earlier report of Napolitano *et al* (1965) and Ling and Williard (1968) respectively. With the help of figures 2–4, it can be seen

Table 2. The slope (m), intercept (c) and correlation coefficient (r) are obtained in the analysis of (20) and (27).

Material	Based on (20)			Based on (27)			Viscosity range
	Intercept (c) (Poise)	Slope (m)	r	Intercept (c) (Poise)	Slope (m)	r	
$\text{Au}_{0.77}\text{Ge}_{0.136}\text{Si}_{0.094}$	-5.1764	31.0873×10^3	0.9941	-2.4247	1.0537×10^3	0.9942	$10^{-1} - 10^{1.4}$
B_2O_3	-9.6894	224.425×10^3	0.9991	-2.1687	2.6595×10^3	0.9984	$10^2 - 10^{1.4}$
2-mp	-5.3748	31.1816×10^3	0.9921	-3.1197	0.2399×10^3	0.9922	$10^4 - 10^{11}$

that the plot of $\log \eta$ against $(\Delta H - \Delta H_0)^{-1}$ is a straight line for all materials and correlation is also quite good. Thus, the viscosity of the glass-forming liquids can be estimated with a knowledge of enthalpy difference ΔH which can be calculated with the aid of ΔC_p^m , ΔS_m and T_m . During the numerical analysis, it has also been noticed that the contribution of term $(\Delta G_0 - \Delta G)/T \Delta S$ in (21) is small at low temperature i.e. around T_g as compared to its contribution at higher temperature i.e. near T_m .

The temperature dependence of the viscosity has also been derived on the basis of the configurational entropy of liquids introducing the temperature dependence of ΔC_p and the expression obtained is reported in (27). To see the validity of this expression, the experimentally determined values of η have been illustrated as a function of $f(T) = (1 + T_0/3T)/(T - T_0)$ for $\text{Au}_{0.77}\text{Ge}_{0.136}\text{Si}_{0.094}$, B_2O_3 and 2-mp in figures 5, 6 and 7 respectively which show the plot of $\log \eta$ against $f(T)$ is a straight line for all three materials. The intercepts and slopes are stated in table 2 along with the correlation coefficient r for the best fit straight line. With the help of figures 5–7, and the correlation coefficients stated in table 2, it can be seen that a single set of constants (η_0 , C and T_0) is able to fit the experimental data of the viscosity for all the three samples in the entire temperature range of study. In view of these results, one can say that the expression for η reported in (27) is able to represent the temperature dependence of the viscosity correctly for metallic, oxide and molecular glass-forming liquids. It can also be said that the constant B_2 in the Vogel–Fulcher expression (2) should be taken as temperature dependent as stated in (30). A similar temperature dependence of viscosity can also be derived using (20) or (23) based on the free volume theory.

6. Conclusion

The expressions for the thermodynamic parameters reported by the authors have been used to discuss the viscous behaviour of metallic, oxide and molecular glass-forming liquids on the basis of the free volume theory as well as on the basis of configurational entropy model. The expression for η reported in (20) based on the free volume theory is capable to explain the viscous behaviour of the glass-forming liquids with the help of single set of constants η_0 , D and T_0 . The expression derived for the temperature dependence of viscosity stated in (27) is a general form of the Vogel–Fulcher equation and it does not involve any more adjustable parameters compared to the Vogel–Fulcher equation. At the same time, it modifies the results in a significant fashion. The expression obtained is capable of reproducing the temperature dependence of viscosity with a single set of constants η_0 , C and T_0 over a wide range of viscosity (10^{-1} to 10^{14} poise) which suggests its great applicability. The viscous behaviour of the glass-forming melts can be studied with the aid of the thermodynamic parameters ΔC_p^m and ΔS_m and these two parameters can be measured experimentally.

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