

ANALYSIS OF THERMODYNAMIC PARAMETERS OF GLASS FORMING POLYMERIC MELTS

R. K. Mishra and K. S. Dubey

Department of Applied Physics, Institute of Technology, Banaras Hindu University
Varanasi-221005, India

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Abstract

The temperature dependence of the Gibbs free energy difference (ΔG), enthalpy difference (ΔH) and entropy difference (ΔS) between the undercooled melt and the corresponding equilibrium solid has been analysed for glass forming polymeric materials by calculating ΔG , ΔH and ΔS within the framework of the hole theory of liquids. The study is made for nine samples of glass forming polymeric melts; polypropylene oxide (PPO), polyamid-6 (PA-6), polytetramethylene oxide (PTMO), polyethylene oxide (PEO), polystyrene (PS), polypropylene (PP), polyethylene (PE), polyethylene terephthalate (PET) and polybutadiene (PB) and three simple organic liquids: tri- α -naphthyl benzene (tri- α -NB), *o*-terphenyl (*o*-ter) and phenyl salicylate (salol) in the entire temperature range T_m (melting temperature) to T_g (glass transition temperature). The ideal glass transition temperature (T_K) and the residual entropy (ΔS_R) of these samples have also been studied due to their important role in the study of the glass forming ability of materials.

Keywords: polymeric glasses, thermodynamic of undercooled melts, thermodynamic parameters

Introduction

The advent of rapid solidification technique has well established that all kinds of materials can form glasses irrespective of their physical and chemical properties. The thermodynamic behaviour of the undercooled melt is important for understanding the viscosity, glass forming abilities, nucleation and growth kinetics etc. The Gibbs free energy difference (ΔG) between the undercooled liquid and the corresponding equilibrium solid phases is found to be an important parameter in the understanding of the classical theory of nucleation and growth processes while the entropy difference (ΔS) between the liquid and solid phases has a significant role in the study of viscosity of the undercooled melts. Elementary thermodynamic procedures can in principle be applied to estimate ΔG , ΔS and ΔH (enthalpy difference between undercooled liquid and solid phases) with the aid of the specific heat difference (ΔC_p) between the undercooled liquid and corresponding equilibrium solid. But the experimental determinations of the specific heat of the undercooled melts are always difficult and some-

times impossible due to their strong tendency to crystallize. It can at best be measured close to the melting temperature T_m and at the glass transition temperature (T_g) in the case of glass forming melts. Consequently, owing to these experimental difficulties, it would be desirable to have reliable analytical expressions for the estimation of the thermodynamic parameters expressions for the estimation of the thermodynamic parameters of undercooled liquids. Several investigators [1–5] suggested expressions for ΔG in terms of more easily measured quantities such as heat of fusion (ΔH_m), T_m etc. However, most of these expressions did not consider the appropriate temperature dependence of ΔC_p and consequently these expressions were inadequate for describing the correct temperature dependence of ΔG over a large degree of undercooling.

Recently, following the earlier work of Dubey and Ramachandrarao [6, 7] an expression for ΔG has been reported by Mishra and Dubey [8, 9] based on the hole theory [10, 11] of liquids and it requires the knowledge of the specific heat difference ΔC_p^m at T_m and entropy of fusion (ΔS_m). These parameters can be experimentally measured relatively easily. The aim of the present investigation is to study the thermodynamic behaviour of the glass forming polymeric melts. The study was made by analyzing the temperature dependence of ΔG , ΔH and ΔS in the temperature range T_m to T_g for nine different glass forming polymeric melts; polypropylene oxide (PPO), polyamid-6 (PA-6), polytetramethylene oxide (PTMO), polyethylene oxide (PEO), polystyrene (PS), polypropylene (PP), polyethylene (PE), polyethylene terephthalate (PET) and polybutadiene (PB). Three simple organic liquids tri- α -naphthyle benzene (tri- α -NB), *o*-terphenyl (*o*-ter) and phenyl salicylate (salol) are also included in the present study.

The ideal glass transition temperature T_K has also been estimated for all samples and an attempt is made to establish a correlation between T_K and T_g as well as between T_K and $\Delta C_p^m/\Delta S_m$. The residual entropy (ΔS_R) has been analysed by estimating ΔS_R for all samples. The role of T_K , T_g and T_m in the estimation of the residual entropy has also been studied. An attempt has been made to obtain a correlation between $\Delta S_R/\Delta S_m$ and $(T_g - T_K)/T_m$.

Expressions for thermodynamic parameters ΔG , ΔH and ΔS

Using the hole theory [10–12] of liquid state proposed by Frankel [10] as well as by Hirai and Eyring [11, 12] and following Flory [13], Sanchez [14] and Dubey and his co-workers [6–9, 15], hole concentration N_h can be expressed as

$$N_h = nN_a \frac{g}{1-g} \quad (1)$$

$$g = \exp\left(-\frac{\epsilon_h + pv_h}{K_B T} - A\right) \quad (2)$$

where $A = 1 - 1/n$, $n = v_a/v_h$, v_h is the volume of a hole while v_a is the hard core volume per atom or molecule, N_a is the number of atoms or molecules of lattice, K_B is the

Boltzmann constant, ϵ_h is the energy required to form a hole and p stands for the external pressure. As a result, the enthalpy change associated with the formation of a hole is given by [6]

$$\Delta H = (1-g)\epsilon_h N_h \quad (3)$$

Realising $\Delta C_p = d\Delta H/dT$ and following Dubey and his co-workers [6–9, 15], the temperature dependence of ΔC_p can be written as

$$\Delta C_p = nR \left(\frac{E_h}{RT} \right)^2 g \quad (4)$$

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

Usually below T_m , ΔC_p exhibits increasing nature with an increase in the degree of undercooling (ΔT) and this increasing tendency of ΔC_p cannot be continued indefinitely. In view of the Kauzmann [16] paradox, ΔC_p should attain a maximum value at T_K which results in $E_h = 2RT_K$. A similar result was also obtained by Sanchez [14] based on the viscous behaviour of polymeric melts. Thus, expression for ΔC_p stated in Eq. (4) can be written as

$$\Delta C_p = \Delta C_p^m \left(\frac{T_m}{T} \right)^2 e^{-2\delta\Delta T/T} \quad (5)$$

where $\delta = T_K/T_m$ and $\Delta T = T_m - T$.

Incorporating the temperature dependence of ΔC_p stated above, an expression for ΔG can be derived with the aid of basic thermodynamic relations

$$\Delta G = \Delta H - T\Delta S \quad (6)$$

$$\Delta H = \Delta H_m - \int_T^{T_m} \Delta C_p dT \quad (7)$$

$$\Delta S = \Delta S_m - \int_T^{T_m} \frac{\Delta C_p}{T} dT \quad (8)$$

The expressions obtained for ΔG can be written as

$$\Delta G = \Delta S_m \Delta T - \frac{\Delta C_p^m}{4\delta^2} [2\delta\Delta T - T(1 - e^{-2\delta\Delta T/T})] \quad (9)$$

Using the approximations

$$e^{2x} - 1 \cong 2x \frac{3+x}{3-2x} \quad (10a)$$

and

$$1 - e^{-2x} \cong 2x \frac{3-x}{3+2x} \quad (10b)$$

Equation (9) can be approximated to a simpler expression as

$$\Delta G = \Delta S_m \Delta T - \Delta C_p^m \frac{\Delta T^2}{2T} \left(1 - \frac{2}{3} \delta \frac{\Delta T}{T} \right) \quad (11)$$

The temperature dependence ΔH can be studied with the aid of Eqs (5) and (7) as

$$\Delta H = \Delta H_m - \frac{\Delta C_p^m T_m}{2\delta} (1 - e^{-2\delta\Delta T/T}) \quad (12)$$

Under the approximation stated above in Eqs (10a) and (10b), expression for ΔH stated in Eq. (12) can be approximated to

$$\Delta H = \Delta H_m - \Delta C_p^m T_m \frac{\Delta T}{T} \left(1 - \delta \frac{\Delta T}{T} \right) \quad (13)$$

Substitution of Eq. (5) into Eq. (8) yields an expression for ΔS as

$$\Delta S = \Delta S_m - \frac{\Delta C_p^m}{4\delta^2} \left[(1+2\delta) - \left(1+2\delta \frac{T_m}{T} \right) e^{-2\delta\Delta T/T} \right] \quad (14)$$

Within the framework of approximations stated above Eqs (10a) and (10b), ΔS reduces to

$$\Delta S = \Delta S_m - \Delta C_p^m \frac{\Delta T(T_m+1)}{2T} \left[1 - \frac{2}{3} \delta \frac{\Delta T}{T} \left(\frac{2T_m+T}{T_m+T} \right) \right] \quad (15)$$

Analysis of thermodynamic parameters ΔG , ΔH and ΔS of polymeric melts

The Gibbs free energy difference ΔG of glass forming polymeric melts has been studied by several investigators [16–26] taking different kinds of approximation related to ΔC_p . Most of these studies are based on the assumption of either a constant value of ΔC_p or $\Delta C_p=0$. Smith [18] reported ΔG of polymeric materials by using ΔC_p in terms of ΔH_m .

The present investigation deals with the analysis of thermodynamic parameters ΔG , ΔH and ΔS of the glass forming polymeric melts as well as simple organic liquids on the basis of expressions stated in earlier section. The entire study is made by estimating ΔG , ΔH and ΔS of nine samples of polymeric materials and three organic simple liquids in the temperature range T_m to T_g . The material parameters used in the present work are taken from the report of earlier workers [27–30] and are listed in Table 1. The experimental values of ΔG , ΔH and ΔS were obtained by taking experimental value of ΔC_p of the form of

$$\Delta C_p = a + bT \quad (16)$$

where a and b are constants.

It is to be noted that the relation for ΔC_p stated above is found to be true for most of the polymeric as well as simple organic glass forming materials.

Table 1 The material parameters used (taken from the earlier reports [27–30]) in the study of the various thermodynamic parameters ΔG , ΔH and ΔS

Materials	$a/$ $\text{J mol}^{-1} \text{K}^{-1}$	$b \cdot 10^2/$ $\text{J mol}^{-1} \text{K}^{-2}$	$\Delta H_m/$ J mol^{-1}	$\Delta S_m/$ $\text{J mol}^{-1} \text{K}^{-1}$	$\Delta C_p^m /$ $\text{J mol}^{-1} \text{K}^{-1}$	T_m/K	T_g/K
PPO	47.22	7.21	8400	24.00	21.98	350	198
PA-6	136.90	19.91	21814	43.96	38.15	496	323
PTMO	85.53	17.94	12601	40.65	29.92	310	185
PEO	73.48	16.91	8401	24.71	15.98	340	206
PS	106.28	19.32	10101	19.69	7.17	513	373
PP	52.92	10.24	8802	19.56	6.84	450	263
PE	37.03	7.08	7499	18.29	5.83	410	195
PET	161.66	28.15	22600	41.62	8.80	543	342
PB	53.57	13.36	9198	24.86	4.14	370	171
<i>o</i> -ter	241.13	49.33	18371	56.01	79.32	328	243.15
Tri- α -NB	311.42	46.73	42489	90.02	90.86	472	342
Salol	307.48	89.64	9799	30.95	23.68	316.6	230

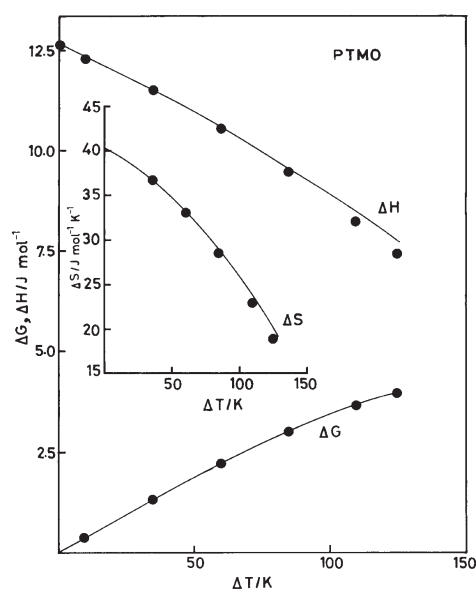


Fig. 1a Variation of thermodynamic parameters ΔG , ΔH and ΔS with temperature for PTMO on the basis Eqs (9), (12) and (14) respectively. Solid lines represent calculated values while circles are experimental values

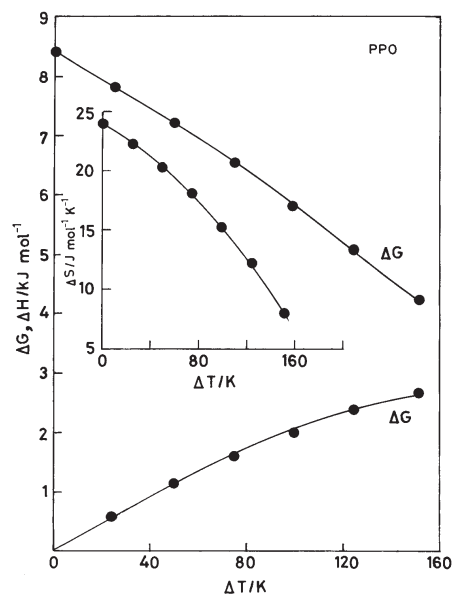


Fig. 1b Variation of thermodynamic parameters ΔG , ΔH and ΔS with temperature for PPO in frame of Eqs (9), (12) and (14) respectively. Solid lines represent calculated values while circles are experimental values

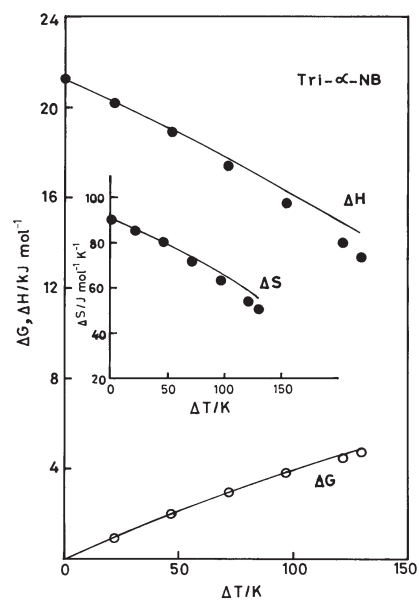


Fig. 1c Variation of thermodynamic parameters ΔG , ΔH and ΔS with temperature for tri- α -NB using Eqs (9), (12) and (14) respectively. Solid lines represent calculated values while circles are experimental values

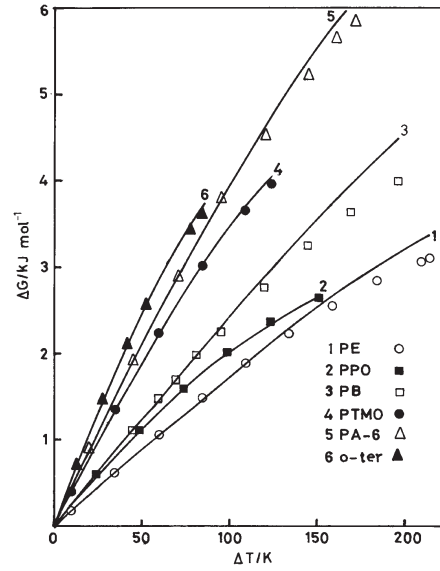


Fig. 2a Temperature dependence of ΔG for various melts. Solid lines represent calculated values using Eq. (11) while experimental values are stated by o, ■, □, ●, Δ and ▲ for PE, PPO, PB, PTMO, PA-6 and *o*-ter respectively

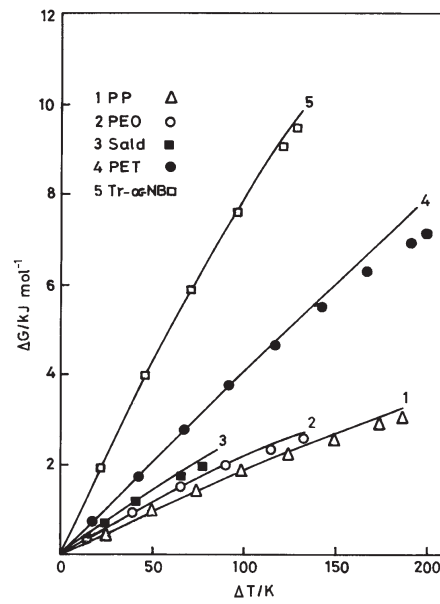


Fig. 2b Temperature dependence of ΔG for various polymeric melts. Solid lines represent calculated values using Eq. (11) while experimental values are stated by Δ, o, ■, ● and □ for PP, PEO, salol, PET and tri- α -HB respectively

Table 2 Free energy difference (ΔG) between the undercooled liquid and corresponding equilibrium solid phases of polyethylene (PE) evaluated using various expressions proposed by earlier workers and compared with that obtained in the present study using Eqs (9) and (11). The experimental values are evaluated using experimental data of ΔC_p

T/K	$\Delta T/K$	$\Delta G/J\ mol^{-1}$						Experimental
		Turnbull [1] Eq. (17)	Hoffmann [2] Eq. (18)	Jones and Chadwick [4] Eq. (19)	Thompson and Spacepen [3] Eq. (20)	Present Eq. (11)	Present Eq. (9)	
400	10	183	178	182	178	182	182	182
350	60	1097	937	1070	924	1068	1068	1063
300	110	2012	1472	1912	1388	1901	1902	1869
250	160	2926	1784	2700	1508	2658	2661	2555
200	210	3841	1874	3419	1196	3300	3314	3059
195 (T_g)	215	3932	1870	3487	1137	3356	3372	3096

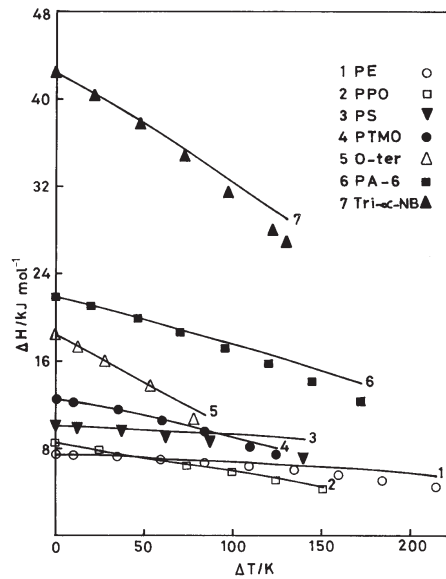


Fig. 3 Temperature dependence of ΔH for various samples. Solid lines represent estimated values on the basis of Eq. (13) while symbols \circ , \square , ∇ , \bullet , Δ , \blacksquare and \blacktriangle represent experimental values of ΔH for PE, PPO, PS, PTMO, *o*-ter, PA-6 and tri- α -NB respectively

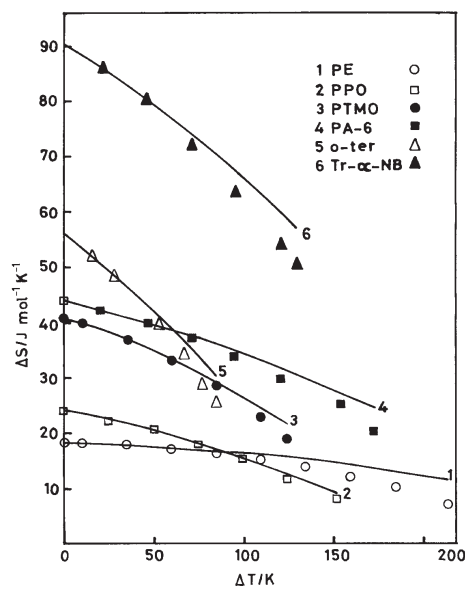


Fig. 4 Temperature dependence of ΔS for various samples. Solid lines represent estimated values in frame of Eq. (15) while symbols \circ , \square , \bullet , \blacksquare , Δ and \blacktriangle represent experimental values of ΔS for PE, PPO, PTMO, PA-6, *o*-ter and tri- α -NB respectively

To see the response of expressions for ΔG , ΔH and ΔS stated in Eqs (9), (12) and (14) respectively, ΔG , ΔH and ΔS of two polymeric materials (PTMO and PPO) and one simple organic liquid (tri- α -NB) have been calculated and the results obtained are illustrated in Figs 1(a), 1(b) and 1(c), respectively. To see the applicability of Eqs (11), (13) and (15), ΔG , ΔH and ΔS have been estimated for all samples and results obtained are shown in Figs 2(a and b), 3 and 4 for ΔG , ΔH and ΔS respectively. Results for some of the samples have not been included in these Figures for the sake of clarity.

From Figs 1a, b and c, it can be seen that the agreement between estimated and experimental values of ΔG is excellent in the entire temperature range of study for all the three samples PTMO, PPO and tri- α -NB. It can also be seen that the calculated values of ΔH and ΔS are very close to the experimental values of the respective parameters at low undercoolings, while some deviations are observed at large degree of undercoolings i.e. near T_g . Thus, one can say that the Eqs (9), (12) and (14) for ΔG , ΔH and ΔS respectively are able to explain the temperature dependence of the respective thermodynamic parameters quite satisfactorily.

Figures 2a and 2b, show that the agreement between calculated values of ΔG based on the Eq. (11) and experimental values is quite good in the temperature range T_m to T_g for most of the samples. However, some discrepancies are found at large degree of undercooling (near T_g) for a few materials. Figure 3 exhibits quite good closeness between experimental and estimated value of ΔH (Eq. (13)) for all materials at low ΔT . However, for large ΔT (near T_g) some deviations are found. Figure 4 shows that the agreement between calculated values of ΔS (Eq. (15)) and experimental values is very good particularly at low ΔT , while it shows some discrepancies at the large degree of undercooling. Thus, it can be concluded that these simple expressions (Eqs (11), (13) and (15)) can also be used to study the temperature dependence of the thermodynamic parameters.

Table 2 demonstrates a comparative study of the present result of ΔG for polyethylene with those obtained on the basis of the following expressions reported by earlier investigators [1–4].

$$\Delta G = \Delta S_m \Delta T \quad (\text{Turnbull [1]}) \quad (17)$$

$$\Delta G = \Delta S_m \Delta T - \Delta S_m \Delta T \frac{T}{T_m} \quad (\text{Hoffman [2]}) \quad (18)$$

$$\Delta G = \Delta S_m \Delta T - \Delta C_p^m \frac{\Delta T^2}{T_m + T} \quad (\text{Jones and Chadwick [4]}) \quad (19)$$

$$\Delta G = \Delta S_m \Delta T \frac{(3T - T_m)}{T_m + T} \quad (\text{Thompson and Spacepen [3]}) \quad (20)$$

From Table 2, it can be seen that the values of ΔG obtained by using Eqs (9) and (11) are the closest to the experimental results compared to values estimated on the basis of expressions used by earlier workers. At $T = T_g$, the deviation in the present

result is about 8.4 and 8.9% within the framework of Eqs (9) and (11) respectively which can be compared with 27, 39.6, 12.6 and 63.3% obtained by using Eqs (17), (18), (19) and (20) respectively.

Ideal glass transition temperature T_K

According to Kauzmann [16], a liquid loses its entropy at a faster rate than the corresponding equilibrium solid and consequently, both phases exhibit the same entropy at some particular temperature T_K which is referred as the ideal glass transition temperature or the Kauzmann temperature. It is usually found that T_K is well above 0 K and below T_g and can be evaluated by equating ΔS to zero at $T=T_K$. Use of Eq. (14) allows $\delta=T_K/T_m$ to be represented by the equation

$$4\delta^2 - \frac{\Delta C_p^m}{\Delta S_m} [(1+2\delta) - 3e^{-2(1-\delta)}] = 0 \quad (21)$$

The above equation is transcendental in nature and the value of δ can be obtained by iterative procedure. However, the following analytical expression can be obtained on the basis of approximations stated above in Eqs 10(a) and 10(b)

$$\delta^3 - 1.25(2+s)\delta^2 + s\delta + 0.25s = 0 \quad (22)$$

where $s = \Delta C_p^m / \Delta S_m$.

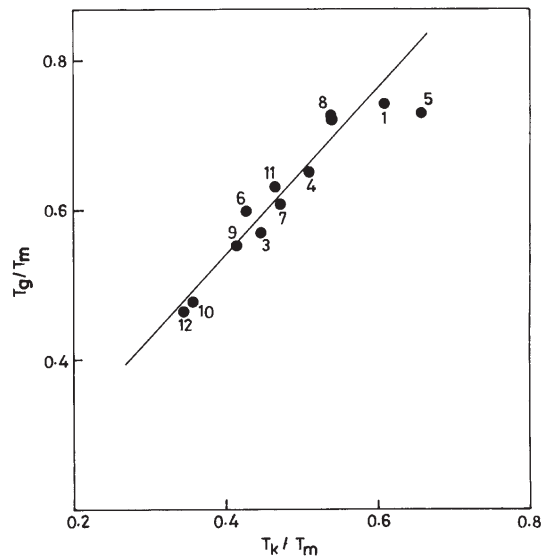


Fig. 5 Variation of reduced glass transition temperature (T_g/T_m) with reduced ideal glass transition temperature (T_K/T_m) for various samples. Numbers 1–12 represent for PPO, PA-6, PTMO, PEO, PS, PP, PE, PET, PB, *o*-ter, tri- α -NB and salol, respectively

Generally, δ^3 is found to be smaller compared to δ^2 due to the small value of δ . Ignoring δ^3 , an approximate value of δ can be estimated as

$$\delta = \frac{s + (2.25s^2 + 2.5s)^{1/2}}{2.5(s+2)} \quad (23)$$

Thus, the value of δ is essentially by the ratio of $s = \Delta C_p^m / \Delta S_m$

The Kauzmann temperature T_K has been evaluated for all samples and results obtained are reported in Table 3. Attempt has also been made to find a correlation between T_K and T_g as shown in Fig. 5 and the following simple empirical relation has been obtained

$$\frac{T_g}{T_m} = \frac{1.0987T_K}{T_m} + 0.102 \quad (24)$$

with a correlation coefficient $r=0.9692$.

Table 3 The value of T_K and ΔS_R for glass forming polymeric and simple organic materials. ΔS_R^{cal} and ΔS_R^{exp} refer to calculated and experimental values of ΔS_R respectively

Materials	T_K/K	T_g/T_m	T_K/T_m	$(T_g - T_K)/T_m$	$\Delta S_R/\Delta S_m$		$\Delta C_p^m/\Delta S_m$
					calc	exp	
PPO	156.7	0.57	0.45	0.12	0.40	0.34	0.92
PA-6	252.5	0.65	0.51	0.14	0.56	0.54	0.87
PTMO	132.9	0.60	0.43	0.17	0.53	0.47	0.74
PEO	160.8	0.61	0.47	0.13	0.59	0.57	0.65
PS	278.1	0.73	0.54	0.18	0.86	0.85	0.36
PP	186.9	0.58	0.42	0.17	0.73	0.73	0.35
PE	145.2	0.48	0.35	0.12	0.63	0.60	0.32
PET	253.6	0.63	0.47	0.16	0.86	0.86	0.21
PB	126.9	0.46	0.34	0.12	0.77	0.76	0.17
<i>o</i> -ter	200.2	0.74	0.61	0.13	0.54	0.74	1.42
Tri- α -NB	255.4	0.72	0.54	0.18	0.63	0.72	1.01
Salol	209.5	0.73	0.66	0.06	0.71	0.73	0.77

A similar relation has also been reported by earlier workers [31, 32]. The average value of T_g/T_K in the present analysis is found to be $1.32 \pm 4.30\%$ as compared to $1.30 \pm 8.4\%$ reported by Adam and Gibbs [32] based on relaxation data on fifteen organic materials and $1.29 \pm 10.9\%$ reported by Bestul and Chang [33] based on the analysis of eleven different glass-forming organic materials.

As stated earlier, δ is mainly controlled by $\Delta C_p^m / \Delta S_m$ and it is interesting to seek a correlation between δ and $\Delta C_p^m / \Delta S_m$. Figure 6 illustrates the variation of δ with $\Delta C_p^m / \Delta S_m$ leading to the following relation

$$\delta = C \left(\frac{\Delta C_p^m}{\Delta S_m} \right)^m \quad (25)$$

with a correlation coefficient $r=0.9996$ and $C=0.4747$ and $m=0.5347$.

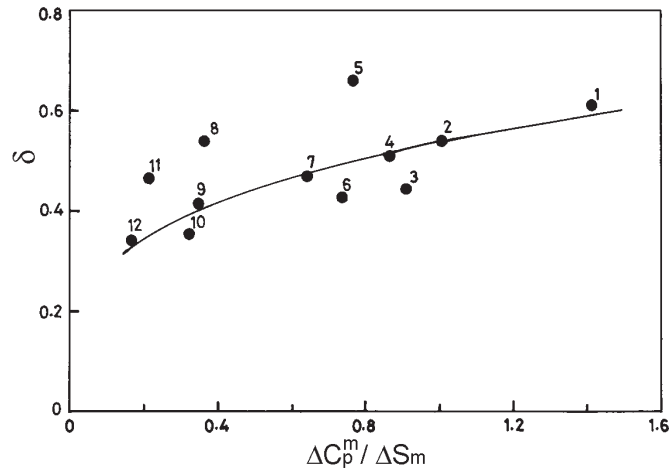


Fig. 6 Variation of $\delta=(T_K/T_m)$ with $\Delta C_p^m/\Delta S_m$ for glass forming materials. Numbers 1–12 represent for PPO, PA-6, PTMO, PEO, PS, PP, PE, PET, PB, *o*-ter, tri- α -NB and salol, respectively

Residual entropy ΔS_R

The residual or frozen-in-entropy of glassy state can be visualized on the basis of the statistico-mechanical quasi-lattice model proposed by Gibbs and DiMarzio [34] and accordingly the configurational entropy becomes zero at T_K . Ignoring the difference in vibrational entropy between the hypothetical glass and equilibrium crystal at T_K , the zero-point entropy should be equal to the configurational entropy of the liquid which is frozen-in at T_g . It is also referred to as residual entropy ΔS_R or frozen-in entropy. In other words, the residual entropy is the amount of entropy of the glass forming liquid that has been blocked in at T_g during the formation of glass and remains in the glassy state even at $T=0$ K. Introducing T_K and realizing that $\Delta S=0$ at $T=T_K$, an expression for ΔS_R can be obtained with the help of Eq. (14) as

$$\Delta S_R = \frac{\Delta C_p^m}{4\delta^2} \left[\left(1 + 2\delta \frac{T_m}{T_g} \right) e^{-2\delta(T_m - T_g)/T_g} - 3e^{2(1-\delta)} \right] \quad (26)$$

Use of the approximations stated in Eqs (10a) and (10b), yields following simplified expression

$$\Delta S_R = 2C_p^m \left[3 - 4 \left(\frac{T_K}{T_g} \right) + \left(\frac{T_K}{T_g} \right)^2 \right] e^{-2(1-\delta)}, \quad (27)$$

which can also be expressed in terms of ΔS_m and $\Delta C_p^m / \Delta S_m$ as

$$\Delta S_R = \Delta S_m \left[1 - \frac{\Delta C_p^m}{\Delta S_m} \left(T_{gR}^{-2} - 1 - \frac{2}{3} \delta (2T_{gR}^{-3} - 3T_{gR}^{-2} - 1) \right) \right] \quad (28)$$

where $T_{gR} = T_g / T_m$ is the reduced glass transition temperature.

The residual entropy ΔS_R is evaluated for each sample and results obtained are reported in the form of ratio $\Delta S_R / \Delta S_m$ in Table 3. ΔS_R has also been estimated on the basis of experimental value of ΔC_p and results are listed in Table 3. It can be seen that the calculated values of $\Delta S_R / \Delta S_m$ are quite close to the experimental values. Attempt has been made to establish a relation between ΔS_R and characteristic temperatures T_K , T_g and T_m with the aid of Fig. 7 which shows the variation of $\Delta S_R / \Delta S_m$ with $(T_g - T_K) / T_m$. A linear relation has been achieved between $\Delta S_R / \Delta S_m$ and $(T_g - T_K) / T_m$ as

$$\frac{\Delta S_R}{\Delta S_m} = m \left(\frac{T_g - T_K}{T_m} \right) + C \quad (29)$$

having correlation coefficient $r=0.9855$ and $m=3.2679$ and $C=5218 \cdot 10^{-3}$.

Figure 7 and Table 3, indicate that materials having lower value of $(T_g - T_K) / T_m$ exhibit a lower value of $\Delta S_R / \Delta S_m$. This can be understood as follows. Material exhibiting low value of $\Delta S_R / \Delta S_m$ requires less amount of entropy trapping to form a glass

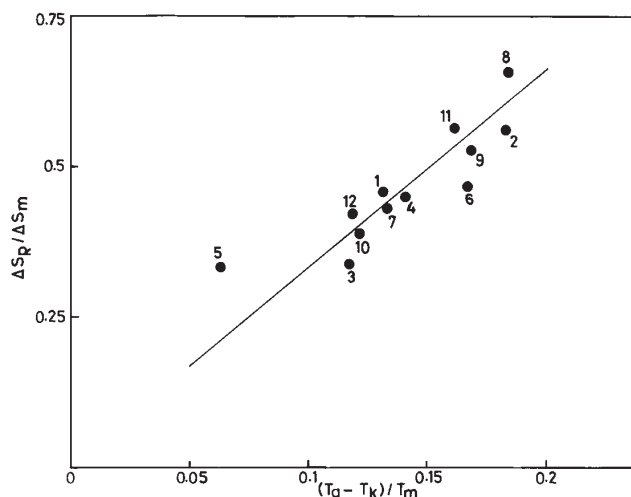


Fig. 7 Variation of $\Delta S_R / \Delta S_m$ with $(T_g - T_K) / T_m$ for various samples. Numbers 1–12 correspond to PPO, PA-6, PTMO, PEO, PS, PP, PE, PET, PB, *o*-ter, tri- α -NB and salol, respectively

and such material can have T_K close to T_g i.e. less value of $(T_g - T_0)/T_m$. Table 3 also indicates that material having lower value of $\Delta S_R/\Delta S_m$ shows a larger value of $\Delta C_p^m/\Delta S_m$. As reported by Dubey and Ramachandrarao [7], materials having larger value of $\Delta C_p^m/\Delta S_m$ are better glass formers compared to those showing lower values of $\Delta C_p^m/\Delta S_m$. In view of these findings, the glass forming ability of polymeric melts as well as simple organic liquids can be predicted in terms of $\Delta S_R/\Delta S_m$ also. The materials having lower values of $\Delta S_R/\Delta S_m$ can form glass more easily compared to those having larger $\Delta S_R/\Delta S_m$. A similar conclusion is also reported by Mishra and Dubey [35] for metallic materials.

Conclusions

The expressions for the thermodynamic parameters ΔG , ΔH and ΔS based on hole theory of liquids describe the correct temperature dependence of the respective parameters for glass forming polymeric as well as simple organic materials. A linear relation was obtained between (T_g/T_m) and (T_K/T_m) . While a simple power relation was obtained between $\delta(=T_K/T_M)$ and $\Delta C_p^m/\Delta S_m$. ΔS_R is mainly controlled by T_K , T_g and T_m . A linear relation is obtained between $\Delta S_R/\Delta S_m$ and $(T_g - T_K)/T_m$ which shows increasing nature of reduced residual entropy ($\Delta S_R/\Delta S_m$) with increasing $(T_g - T_K)/T_m$. It can also be concluded that the glass forming ability of material can also be studied on the basis of $\Delta S_R/\Delta S_m$.

* * *

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