Thermodynamic behaviour of undercooled melts

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Abstract. The Gibbs free energy difference (ΔG) between the undercooled liquid and the equilibrium solid phases has been studied for the various kinds of glass forming melts such as metallic, molecular and oxides melts using the hole theory of liquids and an excellent agreement is found between calculated and experimental values of ΔG. The study is made for non-glass forming melts also. The temperature dependence of enthalpy difference (ΔH) and entropy difference (ΔS) between the two phases, liquid and solid, has also been studied. The Kauzmann temperature (T_0) has been estimated using the expression for ΔS and a linear relation is found between the reduced glass transition temperature (T_g/T_m) and (T_0/T_m). The residual entropy (ΔS_R) has been estimated for glass forming melts and an attempt is made to correlate ΔS_R, T_g, T_0, and T_m which play a very important role in the study of glass forming melts.

Keywords. Undercooled melts; Gibbs free energy; Kauzmann temperature; metallic glasses; residual entropy.

1. Introduction

The production of metallic glasses by rapid solidification techniques has recently received sufficient attention and resulted in a revival of interests in nucleation and growth kinetics in liquid alloys, The Gibbs free energy difference (ΔG) between the undercooled liquid and the equilibrium solid phases is found to be an important parameter in the classical theory of nucleation and growth processes while the entropy difference (ΔS) between the liquid and solid phases plays an important role in the viscosity of these melts. The Gibbs free energy difference (ΔG) can be estimated by using the thermodynamic relations from a knowledge of the experimentally measured values of specific heat difference (ΔCp) between the undercooled melt and equilibrium solid phases. But the experimental measurements of the specific heat of the glass forming melts in their super-cooled states can be carried out only in a restricted temperature range below the melting temperature (T_m) due to their strong tendency to crystalliza-tion which prevents any direct measurements of the thermodynamic quantities. It can at best be measured near the melting temperature and at the glass transition tempera-ture (T_g). Often, the behaviour of the thermodynamic parameters from T_g to T_m is obtained by extrapolating the high temperature data to low temperature region.

Due to experimental problems, several investigators (Turnbull 1950; Hoffman 1958; Jones and Chadwick 1971; Thompson and Spaepen 1979) have tried to suggest appro-priate analytical expressions for ΔG in terms of experimentally measured parameters such as entropy of fusion (ΔS_m), T_m, etc. Most of these expressions are inadequate for describing the temperature dependence of ΔG over a large degree of undercoolings.

Recently an expression for ΔG has been obtained by Dubey and Ramachandrarao (1984) based on the hole theory of liquids. Following the earlier work of Dubey and his coworkers (Dubey and Ramachandrarao 1984; Pandey *et al* 1987), the aim of the

present work is to study ΔG for various kinds of glass forming melts such as metallic, molecular and oxide glass formers. ΔG has been estimated for $Au_{77}Ge_{18.6}Si_{9.4}$, $Au_{81.4}Si_{18.6}$, $Mg_{85.5}Cu_{14.5}$, $Mg_{81.6}Ga_{18.4}$, glycerol, ethanol, 2-methyl pentane, B_2O_3, SiO_2 and GeO_2 in the temperature range T_g to T_m and an excellent agreement is obtained between calculated and experimental values of ΔG. The study is also made for three samples of non-glass forming melts, Pb, Ga and $Bi_{55}Pb_{45}$, in the temperature range $0.5\ T_m$ to T_m. The expressions for the entropy difference (ΔS) and enthalpy difference (ΔH) between the liquid and solid phases have been derived using the hole theory of liquids and the applicability of the expression obtained has been tested by estimating ΔS and ΔH for one sample from each kind of glass forming melts $Mg_{85.5}Cu_{14.5}$ (metallic), glycerol (molecular), and SiO_2 (oxide) and one sample of non-glass forming melt, Pb. A very good agreement is found between calculated and experimental data.

The expression derived for ΔS has been further used to obtain an expression for the Kauzmann temperature T_0 (which is also known as the ideal glass transition temperature) as well as for the residual entropy (ΔS_R) of glass forming melts and T_0 and ΔS_R are calculated for the above stated glass forming melts. Attempt has been made to correlate T_0 and T_g and a linear relation has been obtained between T_g/T_m and T_0/T_m for each kind of glass forming melts. The role of the characteristic temperatures T_0, T_g and T_m in the estimation of the 'frozen-in' entropy (ΔS_R) has been studied and a linear relation is found between $\Delta S_R/\Delta S_m$ and $(T_g - T_0)/T_m$. Attempt has also been made to study the variation of the residual entropy with the ratio $(\Delta Cp^m/\Delta S_m)$ of the specific heat and entropy difference between two liquid and solid phases, at $T = T_m$. The glass forming ability of material has been discussed in terms of the residual entropy of melts.

2. Free energy, enthalpy and entropy of undercooled liquids

According to the hole theory, a liquid state is described as a quasi-crystalline lattice with a considerable fraction of vacant sites of holes and the hole concentration is usually derived by minimizing the change in the free energy associated with the introduction of holes into a lattice. Following Frenkel (1955) as well as Hirai and Eyring (1958, 1959), the change in the free energy (ΔG) due to introduction of N_h hole into a lattice having N_α atoms or molecules at a temperature T can be expressed as

$$\Delta G = N_h(\varepsilon_h + pv_h) + K_B T\left[N_h \ln \frac{N_h}{N_h + nN_\alpha} + N_h \ln \frac{nN_\alpha}{N_h + nN_\alpha}\right] - T\Delta S_h,$$

(1)

here ε_h is the energy required for the formation of a hole of volume v_h, p the external pressure, K_B represents the Boltzmann constant, $n = v_\alpha/v_h$ is a measure of the relative volume of a hole and an atom, v_α the hard core volume per atom or molecule and ΔS_h the entropy change associated with the formation of a hole.

Following Flory (1953), Sanchez (1974) and Dubey and Ramachandrarao (1984) and minimizing the ΔG, an expression for N_h can be obtained as

$$N_h = nN_\alpha(g/(1 - g)),$$

(2)

$$g = \exp\left\{ -\left(\frac{\varepsilon_h + pv_h}{K_B T}\right) - A\right\},$$

(3)

with

$$A = 1 - 1/n.$$

The temperature dependence of ΔCp can be derived by realizing $\Delta Cp = d/dt(\Delta H)$. According to Flory (1953) and Sanchez (1974), the enthalpy change associated with the formation of hole is given by

$$\Delta H = (1 - g)\varepsilon_h N_h,$$

and can be used to obtain the temperature dependence of the specific heat difference between the liquid and solid phases. Realising $\Delta Cp = d/dt(\Delta H)$, and following Dubey and Ramachandrarao (1984) one can have

$$\Delta Cp = nR\left(\frac{E_h}{RT}\right)^2 g, \tag{4}$$

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

It is usually found that ΔCp increases with increase in the undercooling below T_m. The process of increase in ΔCp cannot go on indefinitely and as per Kauzmann paradox, ΔCp should attain a maximum value at some undercooled temperature to avoid the entropy catastrophe. The temperature at which ΔCp becomes maximum can be assumed to be the same at which ΔS becomes zero, i.e. the ideal glass transition temperature T_0. As a result, one gets

$$E_h/RT_0 = 2. \tag{5}$$

Similar relation has also been obtained by Sanchez (1974) in connection with the viscous behaviour of polymeric melts. Consequently, (4) reduces to

$$\Delta Cp = \Delta Cp^m (T_m/T)^2 e^{-2\delta\Delta T/T}, \tag{6}$$

with $\delta = T_0/T_m$ is the reduced ideal glass transition temperature.

The expression for ΔCp stated in (6) can be used to derive an expression for ΔG with the aid of basic thermodynamic relations

$$\Delta G = \Delta H - T\Delta S, \tag{7}$$

$$\Delta H = \Delta H_m - \int_T^{T_m} \Delta Cp\, dT, \tag{8}$$

$$\Delta S = \Delta S_m - \int_T^{T_m} (\Delta Cp/T)dT. \tag{9}$$

Appropriate substitution of (6) and simplification of (7) yield an expression for ΔG as

$$\Delta G = \Delta S_m \Delta T - \frac{\Delta Cp^m}{4\delta^2}[2\delta\Delta T - T(1 - e^{-2\delta\Delta T/T})], \tag{10}$$

under the approximations,

$$1 - e^{-2x} = 2x\frac{3-x}{3+2x}, \tag{11a}$$

and

$$e^{2x} - 1 = 2x \frac{3+x}{3-2x},$$ (11b)

the expression for ΔG stated in (10) reduces to

$$\Delta G = \Delta S_m \Delta T - \Delta Cp^m \frac{\Delta T^2}{2T\left(1 + \frac{2}{3}(\delta \Delta T/T)\right)},$$ (12)

which can further be simplified as

$$\Delta G = \Delta S_m \Delta T - \Delta Cp^m \frac{\Delta T^2}{2T}\left(1 - \frac{2}{3}\delta \frac{\Delta T}{T}\right).$$ (13)

The expression stated in (13) requires the knowledge of ΔCp^m, ΔS_m and T_m which can be measured easily. The parameter δ can also be estimated with the aid of ΔCp^m and ΔS_m which has been discussed in the next section.

The use of (6) and (9) yields an expression for ΔS as

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

In view of the approximation stated in (11), expression for ΔS takes the form

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

which can be further approximated as

$$\Delta S = \Delta S_m - \frac{\Delta Cp^m \Delta T(T_m + T)}{2T^2}\left[1 - \frac{2}{3}\delta \frac{\Delta T}{T}\left(\frac{2T_m + T}{T_m + T}\right)\right].$$ (16)

The expression for ΔH can also be derived with the aid of (6) and (8) and takes the form

$$\Delta H = \Delta H_m - \frac{\Delta Cp^m T_m}{2\delta}(1 - e^{-2\delta \Delta T/T}).$$ (17)

Use of approximation stated in (11) yields to a more simplified form

$$\Delta H = \Delta H_m - \Delta Cp^m \frac{\Delta T}{T} T_m \left(1 - \delta \frac{\Delta T}{T}\right).$$ (18)

Thus, ΔS and ΔH can be estimated with the aid of ΔS_m, ΔCp^m and T_m which can be measured easily.

3. The ideal glass transition temperature T_0 and the residual entropy ΔS_R

The problem associated with a purely kinetic definition of the glass transition was pointed out by Kauzmann (1948). One of the problems is ΔS becoming negative at some

temperature below T_g. He further argued that a liquid loses its entropy at a faster rate than the corresponding equilibrium solid. Consequently one can assume an iso-entropic temperature (T_0) at which both liquid and solid phases have equal entropy. Gibbs and DiMarzio (1958) as well as Adam and Gibbs (1965) have pleaded that such a transition should be of the second order while Cohen and Grest (1979) reported in favour of the first order. Recalling (14) and setting to zero at $T = T_0$, one can have an expression for the estimation of T_0 in terms of ΔCp^m, ΔS_m and T_m of the form

$$\Delta S_m - \frac{\Delta Cp^m}{2\delta}[(1 + 2\delta) - 3e^{-2(1-\delta)}] = 0. \tag{19}$$

The solution of the transcendental equation can be achieved by iterative procedure. However an approximate and more simplified form of the expression for estimating δ can be obtained under the approximation stated in (11) as

$$4\delta^3 - \left[10 + \frac{5\Delta Cp^m}{\Delta S_m}\right]\delta^2 + \frac{4\Delta Cp^m}{\Delta S_m}\delta + \frac{\Delta Cp^m}{\Delta S_m} = 0, \tag{20}$$

which shows that the value of δ is entirely governed by the ratio $\Delta Cp^m/\Delta S_m$. It may be noted that generally δ^3 is found to be much smaller compared to δ^2 and an approximate value of the ideal glass transition temperature T_0 is given by

$$T_0 = T_m \frac{2s + (9s^2 + 10s)^{1/2}}{5(2+s)}. \tag{21}$$

where

$$s = \frac{\Delta Cp^m}{\Delta S_m}.$$

According to the statistico-mechanical quasi-lattice theory of Gibbs and DiMarzio (1958), the configurational entropy becomes zero at the iso-entropic temperature T_0. The apparent entropy difference between the hypothetical glass and crystal at $T - 0$ K is the same as the configurational entropy of the liquid frozen-in at T_g. In other words, it can also be understood that some amount of entropy is blocked in the glassy configuration at T_g and is usually referred to as the residual entropy or 'frozen-in' entropy. Thus the residual entropy is given by

$$\Delta S_R = \Delta S \quad (\text{at } T = 0 \text{ K}) = \Delta S(T_g)$$

$$= \frac{\Delta Cp^m}{4\delta^2}\left[\left(1 + 2\delta\frac{T_m}{T_g}\right)e^{-2\delta\Delta T_g/T_g} - 3e^{-2(1-\delta)}\right], \tag{22}$$

where

$$\Delta T_g = (T_m - T_g).$$

Use of (11) yields a simplified form of ΔS_R as

$$\Delta S_R = \Delta Cp^m[1\cdot5 - 2(T_0/T_g) + 0\cdot5(T_0/T_g)^2]e^{-2(1-\delta)}, \tag{23}$$

which can also be stated as

$$\Delta S_R = \Delta S_m\left[1 - \frac{\Delta Cp^m}{\Delta S_m}\left\{T_{gr}^{-2} - 1 - \frac{2}{3}\delta(2T_{gr}^{-3} - 3T_{gr}^{-2} - 1)\right\}\right], \tag{24}$$

as a function of ΔCp^m and ΔS_m. Here $T_{gr} = T_g/T_m$ is the reduced glass transition temperature.

Expressions stated in (21–24) show that the residual entropy is mainly governed by the characteristic temperatures T_g, T_m and T_0.

4. Results and discussions

The experimental values of ΔG have been calculated with the help of experimentally measured values of ΔCp and using (7). Generally, experimental data of ΔCp is represented by the equation

$$\Delta Cp = A + BT + CT^2 + D/T + E/T^2, \tag{25}$$

where A, B, C, D and E are constants. The material constants are reported in tables 1a and b. To test the expression for ΔG reported in (13), ΔG has been calculated for various types of glass forming melts in the temperature range T_m to T_g, which includes $Au_{77}Ge_{13.6}Si_{9.4}$, $Au_{81.4}Si_{18.6}$, $Mg_{85.5}Cu_{14.5}$ and $Mg_{81.6}Ga_{18.4}$ (metallic glass formers), glycerol, 2-methyl pentane and ethanol (molecular glass formers) and B_2O_3, GeO_2 and SiO_2 (oxide glass formers) and results obtained are illustrated in figures 1–3 for metallic, molecular and oxide glass forming melts respectively. To see the applicability of the expression reported in (13) for non-glass forming melts, ΔG is also calculated for Ga, Pb and $Bi_{55}Pb_{45}$ in the temperature range T_m to $T_m/2$ and results obtained are shown in figure 4. An excellent agreement between calculated and experimental values of ΔG can be seen in figures 1–4 for the glass forming as well as for non-glass forming melts.

The temperature dependence of the thermodynamic parameters ΔS and ΔH has been studied for one sample of each group of glass forming melts; MgCu (metallic), glyceral (molecular), SiO_2 (oxide) in the temperature range T_m to T_g and one sample of non-glass forming melt Pb in the temperature range T_m to $T_m/2$ and are illustrated in figures 5–8 respectively. From figures 5–8, it can be seen that the agreement between calculated and experimental values of ΔH is very good for glass forming as well as for non-glass forming melts. With the help of these figures (figures 5–8), it can also be realized that the calculated values of ΔS are quite close to the experimental values for materials under study except Pb. The agreement between the calculated and experimental values of ΔS is not very satisfactory for Pb at the large undercoolings. As a result of it, one can say that expressions reported in (16) and (18) are capable to explain the temperature dependence of the thermodynamic parameters ΔS and ΔH respectively. To see the goodness of the expression reported in (13) for ΔG, a comparative study is made in table 2 for $Mg_{85.5}Cu_{14.5}$ with the results obtained using the expressions obtained by earlier workers (Turnbull 1950; Hoffman 1958; Thompson and Spaepen 1979) as

$$\Delta G = \Delta S_m \Delta T, \tag{26}$$

$$\Delta G = \Delta S_m \Delta T \frac{T}{T_m}, \tag{27}$$

$$\Delta G = \Delta S_m \Delta T \frac{2T}{(T_m + T)}. \tag{28}$$

Table 1a. The material parameters used in the study of the thermodynamic parameters ΔG, ΔH, ΔS, T_0 and ΔS_R.

Parameter	Material						
	$Au_{81.4}Si_{18.6}$	$Au_{77}Ge_{13.6}Si_{9.4}$	$Mg_{85.5}Cu_{14.5}$	$Mg_{81.6}Ga_{18.4}$	$Bi_{55}Pb_{45}$	Ga	Pb
a (J/mol/K)	266186	32·5264	15·17	17·75	0·22	4·3028	8·6149
b (J/mol/K^2)10^3	−53·764	−63·0822	−9·88	−12·83	—	−16·2343	−12·1629
c (J/mol/K^3)10^5	3·2949	3·4141	—	−1·0082	—	0·2053	—
d (J/mol)10^{-2}	—	1·3004	—	—	—	11·1901	—
e (JK/mol)10^{-4}	—	2·5188	—	—	—	—	—
ΔH_m (J/mol)	9445	10627	7838	7120	4178	5589	4802
ΔS_m (J/mol/K)	15·48	17·03	10·34	10·23	10·50	18·45	7·99
$\Delta C p_m$ (J/mol/K)	7·75	6·74	7·68	3·94	0·22	2·89	1·21
T_m (K)	636	625	758	696	398	303	601
T_g (K)	290	294	380	390	—	—	—

Table 1b. The material parameters used in the study of the thermodynamic parameters ΔG, ΔH, ΔS, T_0 and ΔS_R.

	Material					
Parameter	Glycerol	Ethanol	2-methyl pentane	B_2O_3	SiO_2	GeO_2
a (J/mol/K)	90·8646	51·5810	146·871	70·854	14·20	20·98
b (J/mol/K^2)10^3	39·06	− 167·3	− 798·5	− 73·416	− 1·9	− 9·87
c (J/mol/K^3)10^5	—	—	—	—	—	—
d (J/mol)10^{-2}	—	—	—	—	—	—
e (JK/mol)10^{-4}	—	—	—	141·12	392·1	177·7
ΔH_m (J/mol)	18371	5015	6260	22261	9621	44517
ΔS_m (J/mol/K)	62·70	31·64	52·36	30·79	4·82	32·05
$\Delta C p^m$ (J/mol/K)	79·42	25·06	51·41	20·47	11·39	8·19
T_m (K)	293	158·5	119·55	723	1996	1389
T_g (K)	186	91	79·5	550	1443	823
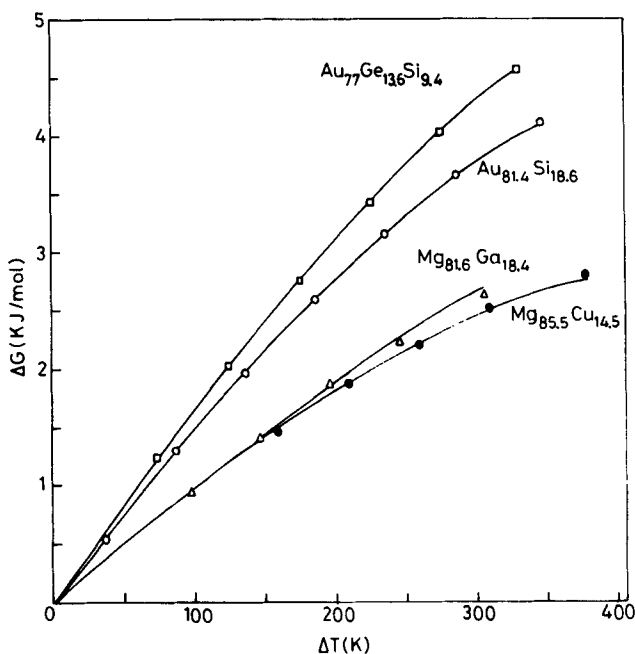
Figure 1. The Gibbs free energy difference, ΔG, for metallic glass formers. Closed circles, triangles, open circles and squares represent experimental values of ΔG for $Mg_{85·5}Cu_{14·5}$, $Mg_{81·6}Ga_{18·4}$, $Au_{81·4}Si_{18·6}$, $Au_{77}Ge_{13·6}Si_{9·4}$ respectively whereas lines are calculated values of the respective samples.

From table 2, it can be seen that the results obtained on the basis of expression stated in (13) are the best and values of ΔG derived on the basis of (13) are the closest to the experimental values even for large undercoolings. At $T = T_g$ the error is only about 3·4% at the undercooling $\Delta T = 370$ K, while it is 36·6%, 31·5% and 8·8%, based on expressions proposed by Turnbull, Hoffman, and Thompson and Spaepen respectively.
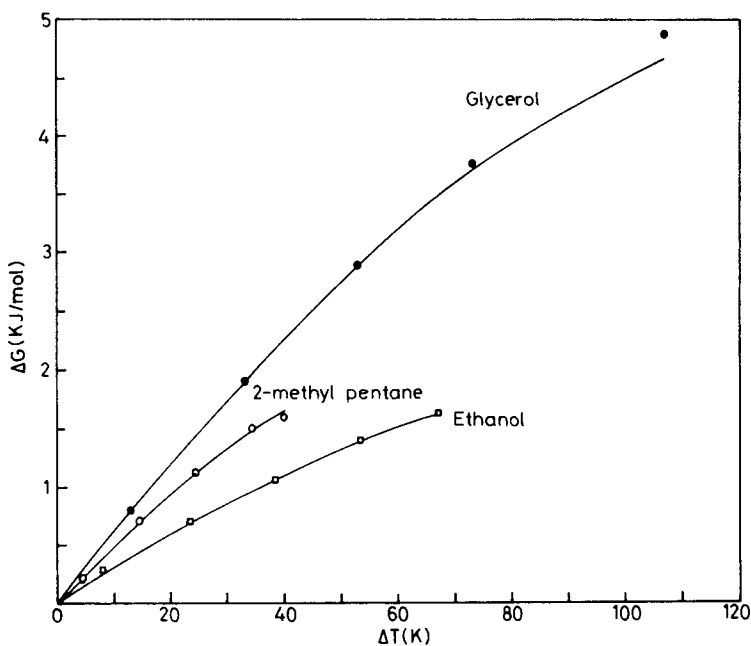
Figure 2. The Gibbs free energy difference, ΔG for molecular glass formers. Closed circles, open circles and squares represent experimental values of ΔG for glycerol, 2-methyl pentane and ethanol respectively whereas lines are calculated values of the respective samples.
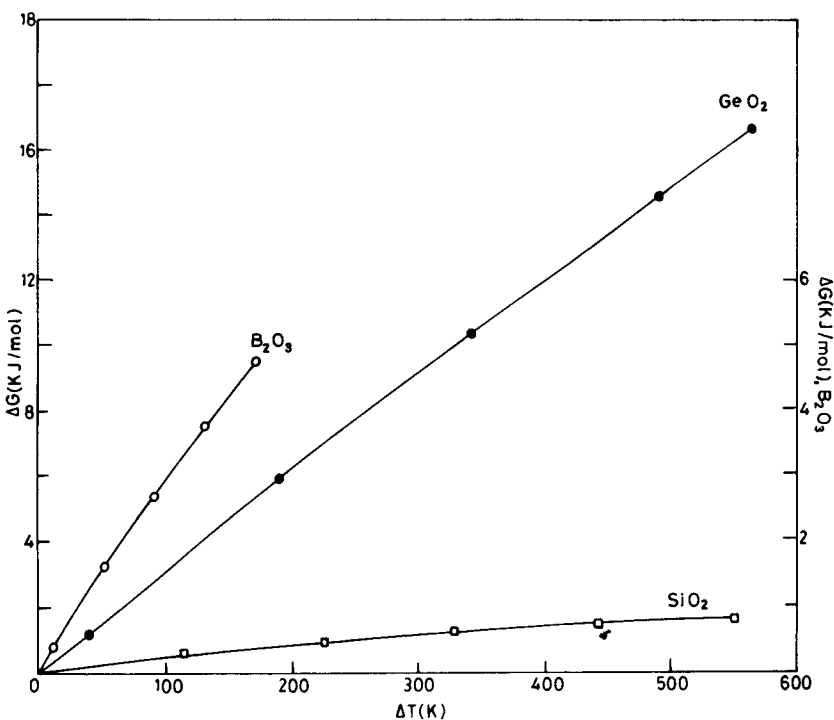

Figure 3. The Gibbs free energy difference, ΔG, for oxide glass formers. Squares, closed circles and open circles represent experimental values of ΔG for SiO_2, GeO_2 and B_2O_3 respectively whereas lines are calculated values of the respective samples.

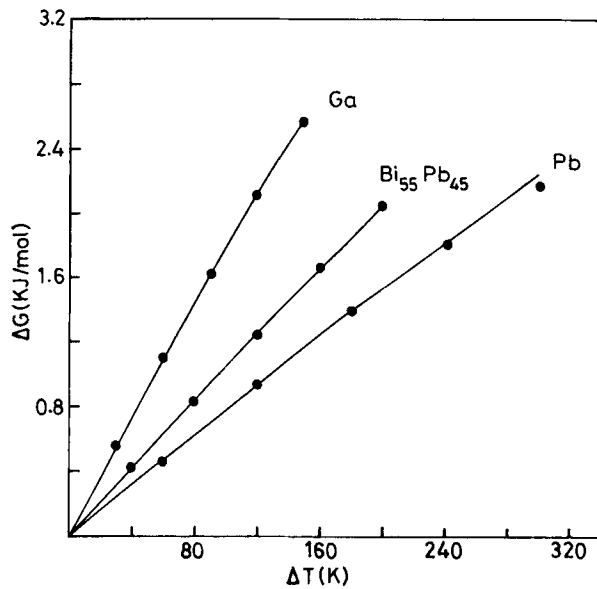**Figure 4.** The Gibbs free energy difference, ΔG, for non-glass forming melts. Closed circles and lines represent experimental and calculated values of ΔG of the respective samples.
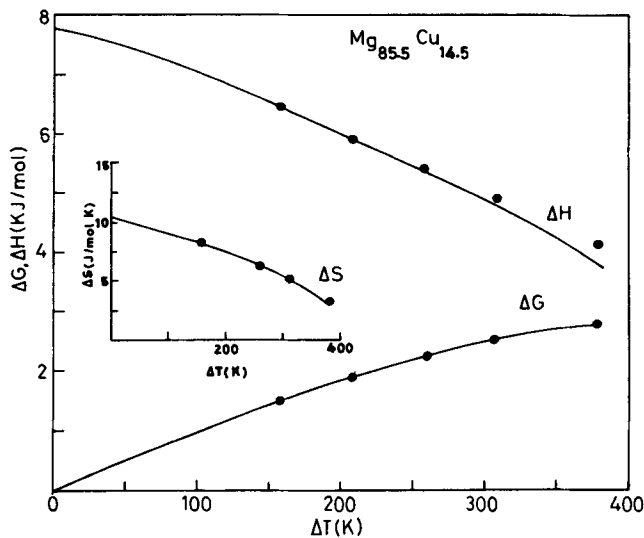

Figure 5. Variation of ΔG, ΔH and ΔS with undercooling ΔT for metallic melt $Mg_{85 \cdot 5}Cu_{14 \cdot 5}$. Circles represent experimental data of respective parameters while lines are calculated values.

Thus, the expression for ΔG stated in (13) can be recommended in the use of nucleation and growth techniques. At the same time, it is interesting to note that present expression requires ΔCp^m, ΔS_m and T_m as input data which can be measured easily and more accurately and does not contain any adjustable parameter.
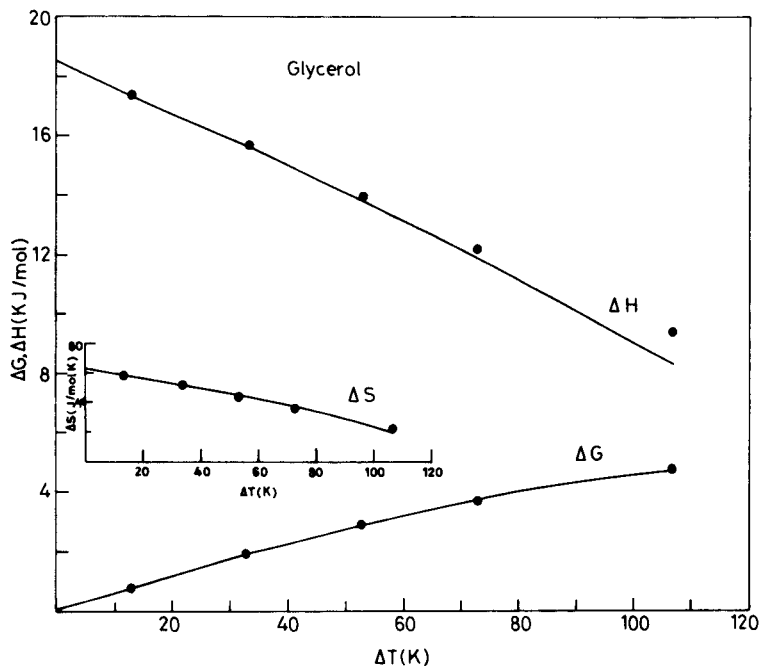
Figure 6. Variation of ΔG, ΔH and ΔS with undercooling ΔT for molecular melt glycerol. Circles represent experimental values of respective parameters whereas lines are calculated values.
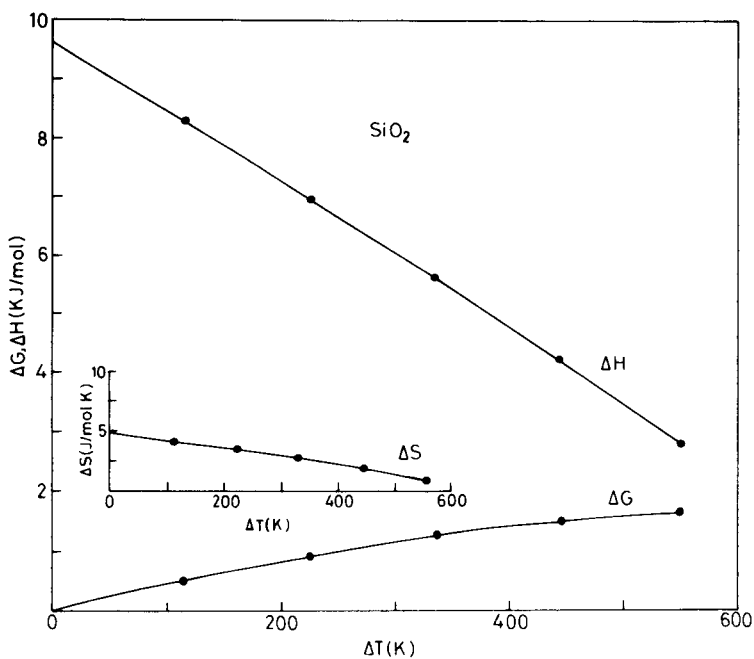

Figure 7. Variation of ΔG, ΔH and ΔS with undercooling ΔT for oxide melt SiO_2. Circles represent experimental values of respective parameters whereas lines are calculated values.
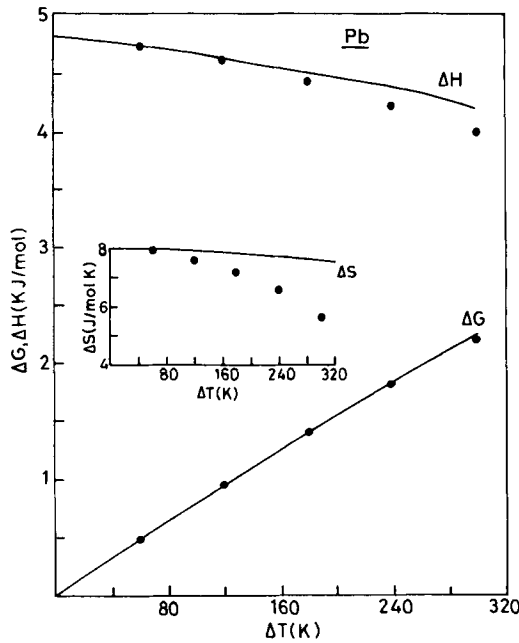
Figure 8. Variation of ΔG, ΔH and ΔS with undercooling ΔT for non-glass forming melt Pb. Circles represent experimental data of respective parameters while lines are calculated values.

The ideal glass transition temperature T_0 is calculated using (19) for glass forming melts and values obtained are reported in table 3. From table 3, it can be seen that the value of T_0 is very close to the extrapolated value of T_0 based on the experimental data. It can also be seen that the material with larger value of $\Delta Cp^m/\Delta S_m$ exhibits a larger value of $\delta = T_0/T_m$. During the analysis, it is also found that T_0 is mainly controlled by the ratio $\Delta Cp^m/\Delta S_m$. An attempt has been made to relate T_g and T_0 and a linear relation

$$T_g/T_m = a(T_0/T_m) + b, \tag{29}$$

is found between the reduced glass transition temperature and the reduced ideal glass transition temperature for each kind of glass forming melts. The values of constants a and b are reported in table 4 for metallic, molecular and oxide melts. A similar relation is also reported by Dubey and Ramachandrarao (1992) and Adam and Gibbs (1965) for organic materials.

The residual entropy (ΔS_R) of glass forming melts has been estimated and results are stated in table 3. ΔS_R is also evaluated using experimental data of ΔCp. It is found that calculated values of ΔS_R is close to that based on experimental data. Attempt has also been made to seek a relation between ΔS_R and characteristic temperatures T_0, T_g and T_m. A linear relation has been obtained between $\Delta S_R/\Delta S_m$ and $(T_g - T_0)/T_m$ of the form

$$\Delta S_R/\Delta S_m = m\frac{(T_g - T_0)}{T_m} + n, \tag{30}$$

where m and n are constants and are reported in table 4. These constants are found to be different for different kinds of glass forming melts. From table 3, it can be realized

Table 2. Free energy difference ΔG between the liquid and equilibrium solid phases of $Mg_{85.5}Cu_{14.5}$ evaluated from various expressions and compared with that calculated using (13). The experimental value was evaluated using experimental data of ΔCp.

T(K)	ΔT(K)	ΔG (J/mol)				
		Turnbull (1950) Equation (26)	Hoffman (1958) Equation (27)	Thompson and Spaepen (1979) Equation (28)	Equation (13)	Experimental
750	8	83	82	83	82	82
700	58	600	554	576	582	582
650	108	1117	958	1031	1051	1052
600	158	1634	1293	1444	1484	1488
550	208	2151	1561	1809	1876	1885
500	258	2668	1760	2121	2217	2239
450	308	3185	1891	2373	2499	2541
400	358	3702	1953	2557	2743	2783
380 (T_g)	378	3909	1959	2610	2765	2861

Table 3. The value T_0 and ΔS_R for various glass forming samples used in the present analysis.

Material	T_m(K)	T_g(K)	T_0^{cal}(K)	T_0^{exp}(K)	δ	ΔS_R^{cal} (J/mol/K)	ΔS_R^{exp} (J/mol/K)	$\Delta S_R^{exp}/S_m$	$\Delta Cp^m/\Delta S_m$	$\dfrac{T_g - T_0}{T_m}$
Glycerol	293	186	155.4	137.4	0.4689	25.59	19.66	0.4081	1.2670	0.1658
Ethanol	158.5	91	66.9	63.1	0.3981	14.23	13.22	0.4497	0.7926	0.1760
2-methyl pentane	119.55	79.5	56.2	60.82	0.5087	24.42	26.94	0.4664	0.9818	0.1562
B_2O_3	723	550	277.5	336	0.4647	23.13	24.21	0.7512	0.6648	0.2959
SiO_2	1996	1443	1350	1358	0.6803	0.8144	0.8172	0.1689	2.363	0.0426
GeO_2	1389	823	317	290.5	0.2091	25.81	25.64	0.8053	0.2555	0.3833
$Au_{81.4}Si_{18.6}$	636	290	210.5	202	0.3176	6.33	5.77	0.4088	0.5006	0.1384
$Au_{77}Ge_{13.6}Si_{9.4}$	625	294	181.5	199.4	0.3190	7.84	8.66	0.4601	0.3957	0.1514
$Mg_{85.5}Cu_{14.5}$	758	380	300	281	0.3707	3.60	2.76	0.3480	0.7427	0.1306
$Mg_{81.6}Ga_{18.4}$	696	390	199.5	251.5	0.3613	5.55	6.84	0.5426	0.3851	0.1990

Table 4. The values of constants a, b, m, and n.

Kinds of materials	a	b	m	n
Metallic	1·27551	0·06056	2·5550	0·04423
Molecular	0·82521	0·24618	−0·79223	0·57291
Oxide	0·28842	0·56185	1·96431	0·10252

that material having smaller value of $(T_g - T_0)/T_m$ shows a lower value of $\Delta S_R/\Delta S_m$ which can be explained as follows. The material having lower value of ΔS_R requires trapping of less amount of entropy to form a glass and such material can exhibit T_0 near T_g i.e. material shows less value of $(T_g - T_0)/T_m$. It can also be seen that the material with lower value of $\Delta S_R/\Delta S_m$ shows a larger value of $\Delta Cp^m/\Delta S_m$. According to earlier report of Dubey and Ramachandrarao (1984–85), the material having large value of $\Delta Cp^m/\Delta S_m$ is a good glass former. In view of these findings, one can say that the material with lower value of $\Delta S_R/\Delta S_m$ exhibits a large value of δ and $\Delta Cp^m/\Delta S_m$ and is a good glass former. Thus, it can be said that δ, $\Delta Cp^m/\Delta S_m$ and $\Delta S_R/\Delta S_m$ are dependent on each other and can be used to measure the glass forming ability of materials.

5. Conclusion

The expression for ΔG reported in (13) is capable to estimate ΔG of all kinds of materials correctly at large undercooling also and expressions reported in (16) and (18) for ΔS and ΔH respectively can be used to study the temperature variation of these parameters. The value of the Kauzmann temperature T_0 is found to be close to the value extrapolated on the basis of experimental data. A linear relation is found between T_g/T_m and T_0/T_m for glass forming melts. Both, reduced ideal glass transition temperature $\delta(= T_0/T_m)$ and reduced residual entropy $(\Delta S_R/\Delta S_m)$ are mainly controlled by the parameter $\Delta Cp^m/\Delta S_m$ and T_m. A linear relation is also found between $\Delta S_R/\Delta S_m$ and $(T_g-T_0)/T_m$. The material having lower value of $\Delta S_R/\Delta S_m$ can form glass more easily. ΔS_R, T_0 and $\Delta Cp^m/\Delta S_m$ are dependent on each other and the glass forming ability of materials can be studied in the form of these parameters.

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