Journal of Thermal Analysis, Vol. 50 (1997) 843-856

ANALYSIS OF THERMODYNAMIC PARAMETERS OF GLASS FORMING METALLIC MELTS

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(Received January 9, 1996; in revised form November 22, 1996)

Abstract

The temperature dependence of the Gibbs free energy difference (ΔG) between the undercooled liquid and the corresponding equilibrium solid has been analysed for metallic glass forming systems in the frame of the expression obtained by expanding free energies of the undercooled liquid and solid phases in the form of Taylor's series expansion. The enthalpy difference (ΔH) and the entropy difference (ΔS) between the undercooled liquid and solid phases have also been analysed. The study is made for five different metallic glass forming materials, $Au_{77}Ge_{13.6}Si_{9.4}$, $Au_{53.2}Pb_{27.5}Sb_{19.3}$, $Au_{81.4}Si_{18.6}$, $Mg_{85.5}Cu_{14.5}$ and $Mg_{81.6}Ga_{18.4}$ and a very good agreement is found between calculated and experimental values of ΔG. The ideal glass transition temperature (T_k) and the residual entropy (ΔS_R) of these materials have also been studied due to their important role in assigning the glass formation ability of materials.

Keywords: thermodynamic parameters

Introduction

The advent of metallic glasses by the rapid quenching techniques has resulted in a revival of renewed interests in the nucleation and growth kinetics in liquid alloys. One of the important parameters necessary for the understanding of the classical theories of the nucleation and growth is the Gibbs free energy difference (ΔG) between the undercooled liquid and the corresponding equilibrium solid phases. But the metastability of melts precludes the experimental determination of the specific heat of the undercooled liquids over entire temperature range of undercooling. It can be measured with sufficient accuracy at temperatures close to the melting temperature (T_m) and at glass transition temperature (T_g). Thus the behaviour of the thermodynamic parameters for T_m to T_g can only be obtained by extrapolating the high temperature data [1, 2]. Due to such experimental difficulties, there is a need to have an analytical expression for the estimation of ΔG. The earlier investigators [3–6] attempted to express ΔG in terms of

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measured parameters, such as entropy of fusion (ΔS_m), melting temperature (T_m) etc. Most of these expressions are based on assumptions related to the temperature dependence of ΔC_p or its magnitude.

Recently, Lele *et al.* [7] have demonstrated that an expression for ΔG can be derived by expanding free energies of the liquid and solid phases around their values at T_m in the form of Taylor's series. The aim of the present work is to study the Gibbs free energy difference (ΔG) for five different samples of metallic glasses $Au_{77}Ge_{13.6}Si_{9.4}$, $Au_{53.2}Pb_{27.5}Sb_{19.3}$, $Au_{81.4}Si_{18.6}$, $Mg_{85.5}Cu_{14.5}$ and $Mg_{81.6}Ga_{18.4}$ in the temperature range T_m to T_g in the frame of the expression based on the Taylor series expansion. A non-glass forming alloy $Bi_{55}Pb_{45}$ and a pure metal liquid Pb have also been included in the present investigation to see the applicability of the expression for ΔG for non-glass forming liquids. The temperature dependence of enthalpy ΔH and entropy difference ΔS between the liquid and solid phases have also been studied for these materials on the basis of expression obtained in the frame of Taylor's series expansion.

As pointed out by Kauzmann [8], a liquid loses its entropy at a faster rate than the solid resulting in an iso-entropic temperature T_K at which both solid and liquid phases have the same entropy. T_K is often known as the ideal glass transition temperature and it is an important factor in the estimation of the viscosity [9–11] of the undercooled liquid as well as glass forming ability [12] of materials. T_K has been calculated for the above stated glass forming materials and compared with the values obtained on the basis of experimental data. The residual entropy has also been estimated due to its significant role in the prediction of glass forming ability of materials.

Expression for ΔG, ΔH and ΔS

Following Lele *et al.* [7], Gibbs free energies of the undercooled liquid and its corresponding equilibrium solid phases can be expanded around their values at the melting temperature T_m in the form of Taylor's series as

$$G^{i} = G^{i}_{m} - \left[\frac{\partial G^{i}}{\partial T}\right]_{T_m} \Delta T + \frac{1}{2}\left[\frac{\partial^2 G^{i}}{\partial T^2}\right]_{T_m} \Delta T^2 - \frac{1}{3!}\left[\frac{\partial^3 G^{i}}{\partial T^3}\right]_{T_m} \Delta T^3 + \frac{1}{4!}\left[\frac{\partial^4 G^{i}}{\partial T^4}\right]_{T_m} \Delta T^4 - \ldots\ldots \quad (1)$$

where i stands for phases L and S corresponding to liquid and solid phases respectively and $\Delta T=(T_m-T)$ represents the degree of the undercooling. The various derivatives of G^i are taken at $T=T_m$ and at constant pressure. The expansion extends the free energy *vs.* temperature (G *vs.* T) plot of each phase into their metastable regions. Substitution of the appropriate forms of the various derivatives of G yields an expression for ΔG as $\Delta G=G^L$ (Liquid)–G^S (Solid)

$$\Delta G = \Delta S_m \Delta T - \frac{\Delta C_p^m \Delta T^2}{2T_m}\left[1 + \frac{\Delta T}{3T_m} + \frac{1}{6}\left(\frac{\Delta T}{T_m}\right)^2 + \frac{1}{10}\left(\frac{\Delta T}{T_m}\right)^3 + \ldots\right] + \tag{2}$$

$$+\left[\frac{\partial \Delta C_p}{\partial T}\right]_{T_m} \frac{\Delta T^3}{6T_m}\left[1 + \frac{\Delta T}{4T_m} + \frac{3}{10}\left(\frac{\Delta T}{T_m}\right)^2 + \frac{1}{5}\left(\frac{\Delta T}{T_m}\right)^3 + \ldots\right] -$$

$$-\left[\frac{\partial^2 \Delta C_p}{\partial T^2}\right]_{T_m} \frac{\Delta T^4}{24T_m}\left[1 + \frac{3}{5}\left(\frac{\Delta T}{T_m}\right) + \frac{2}{5}\left(\frac{\Delta T}{T_m}\right)^2 + \frac{2}{7}\left(\frac{\Delta T}{T_m}\right)^3 + \ldots\right] + \ldots \tag{3}$$

where ΔS_m and ΔC_p^m are entropy and specific heat differences between the liquid and solid phases at T_m respectively. Subsequent terms have higher order derivatives of ΔC_p. Each of the series in the square brackets is based on logarithmic series and can be summed to yield.

$$\Delta G = \Delta S_m \Delta T - \frac{\Delta C_p^m \Delta T^2}{(T_m + T)} + \left[\frac{\partial \Delta C_p}{\partial T}\right]_{T_m} \frac{\Delta T^3}{2(T_m + T)} - \left[\frac{\partial^2 \Delta C_p}{\partial T^2}\right]_{T_m} \frac{\Delta T^4}{3!(T_m + T)}\left(1 + \frac{T}{2\Delta T}\right) + \ldots \tag{4}$$

It is needed to state that while simplifying the above stated equation, where necessary, the approximation

$$\ln(T_m/T) = \frac{2\Delta T}{(T_m + T)} \tag{5}$$

has been taken. During the numerical analysis, it is also observed that the contribution due to the third and subsequent terms in Eq. (4) are small compared to the first two terms and without much loss of accuracy, one can use

$$\Delta G = \Delta S_m \Delta T - \frac{\Delta C_p^m \Delta T^2}{(T_m + T)} \tag{6}$$

for the estimation of Gibbs free energy difference between the liquid and solid phases.

In the similar way the expressions for ΔS and ΔH can also be obtained by expanding the enthalpy and entropy of both the phases solid and liquid in the form of Taylor's series and one can have

$$\Delta H = \Delta H_m - \Delta C_p^m \Delta T + \left[\frac{\partial \Delta C_p}{\partial T}\right]_{T_m} \frac{\Delta T^2}{2} - \left[\frac{\partial^2 \Delta C_p}{\partial T^2}\right]_{T_m} \frac{\Delta T^3}{3!} + \ldots \tag{7}$$

and

$$\Delta S = \Delta S_\mathrm{m} - \Delta C_\mathrm{p}^\mathrm{m} \ln (T_\mathrm{m}/T) + \left[\frac{\partial \Delta C_\mathrm{p}}{\partial T}\right]_{T_\mathrm{m}} T_\mathrm{m} \left[\ln (T_\mathrm{m}/T) - \frac{\Delta T}{T_\mathrm{m}}\right] - \frac{1}{2}\left[\frac{\partial^2 \Delta C_\mathrm{p}}{\partial T^2}\right]_{T_\mathrm{m}} T_\mathrm{m}^2 \left[\ln\left(\frac{T_\mathrm{m}}{T}\right) - \frac{\Delta T}{T_\mathrm{m}} - \frac{\Delta T^2}{2T_\mathrm{m}^2}\right] + \ldots.. \quad (8)$$

Taking the approximation stated above Eq. (5) and ignoring the smaller value terms, expressions for ΔH and ΔS yield to

$$\Delta H = \Delta H_\mathrm{m} - \Delta C_\mathrm{p}^\mathrm{m}\, \Delta T + \left[\frac{\partial \Delta C_\mathrm{p}}{\partial T}\right]_{T_\mathrm{m}} \frac{\Delta T^2}{2} - \ldots.. \quad (9)$$

and

$$\Delta S = \Delta S_\mathrm{m} - \frac{2\Delta C_\mathrm{p}^\mathrm{m} \Delta T}{(T_\mathrm{m} + T)} + \left[\frac{\partial \Delta C_\mathrm{p}}{\partial T}\right]_{T_\mathrm{m}} \frac{\Delta T^2}{(T_\mathrm{m} + T)} - \ldots.. \quad (10)$$

Temperature variation of ΔG, ΔH and ΔS

Materials parameters are stated in Table 1. The Gibbs free energy difference ΔG between the undercooled liquid and corresponding equilibrium solid have been evaluated for the five glass forming samples $Au_{77}Ge_{13.6}Si_{9.4}$, $Au_{53.2}Pb_{27.5}Sb_{19.3}$, $Au_{81.4}Si_{18.6}$, $Mg_{85.5}Cu_{14.5}$ and $Mg_{81.6}Ga_{18.4}$ with the aid of the expression stated in Eq. (6) and constants given in Table 1 and the results obtained are reported in Figs 1–5 respectively along with the experimental data. The experimental values of ΔG have been estimated with the aid of the following expressions

$$\Delta G = \Delta H - T\Delta S \quad (11)$$

$$\Delta H = \Delta H_\mathrm{m} - \int_{T}^{T_\mathrm{m}} \Delta C_\mathrm{p} \mathrm{d}T \quad (12)$$

$$\Delta S = \Delta S_\mathrm{m} - \int_{T}^{T_\mathrm{m}} \frac{\Delta C_\mathrm{p}}{T} \mathrm{d}T \quad (13)$$

and experimental data of ΔC_p in the form of

$$\Delta C_\mathrm{p} = a + bT + cT^2 + d/T + e/T^2. \quad (14)$$

Table 1 The material parameters used in the study of the various thermodynamic parameters ΔG, ΔH, ΔS, T_k and ΔS_R for glass forming and non-glass forming melts

Parameter	Material						
	$Au_{77}Ge_{13.6}Si_{9.4}$	$Au_{53.2}Pb_{27.5}Sb_{19.3}$	$Au_{81.4}Si_{18.6}$	$Mg_{85.5}Cu_{14.5}$	$Mg_{81.6}Ga_{18.4}$	$Bi_{55}Pb_{45}$	Pb
a/(J mol^{-1} K^{-1})	32.5264	−76.58	28.6186	15.17	17.75	0.22	8.6149
b/(J mol^{-1} K^{-2})$\times 10^3$	−63.0822	88.705	−53.7640	−9.88	−12.83	–	−12.1629
c/(J mol^{-1} K^{-3})$\times 10^5$	3.4141	–	3.2949	–	−1.0082	–	–
d/(J mol^{-1})$\times 10^{-2}$	1.3004	–	–	–	–	–	–
e/(J K mol^{-1})$\times 10^{-4}$	2.5188	1112.8	–	–	–	–	–
ΔH_m/J mol^{-1}	10627	8253	9845	7838	7120	4178	4802
ΔS_m/J mol^{-1} K^{-1}	17.03	15.78	15.48	10.34	10.23	10.50	7.99
ΔC_p^m/J mol^{-1} K^{-1}	6.74	10.50	7.75	7.68	3.94	0.22	1.21
T_m/K	625	523	636	758	696	398	601
T_g/K	294	318	290	380	390	–	–

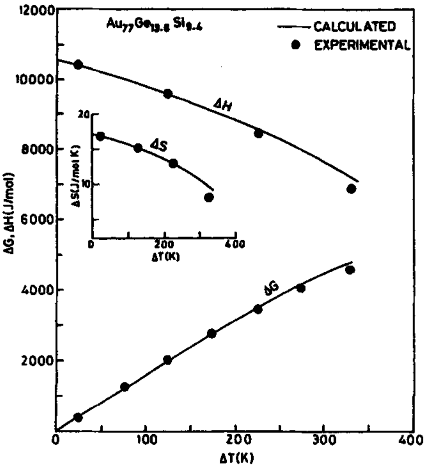

Fig. 1 Variation of thermodynamic parameters ΔG, ΔH and ΔS with temperature for glass forming metallic melt $Au_{77}Ge_{13.6}Si_{9.4}$. Solid lines represent calculated values while circles are experimental values

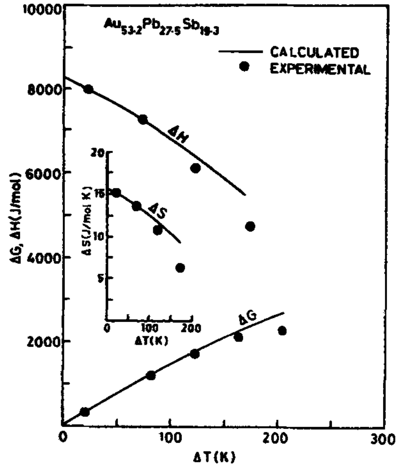

Fig. 2 Variation of thermodynamic parameters ΔG, ΔH and ΔS with temperature for glass forming metallic melt $Au_{53.2}Pb_{27.5}Sb_{19.3}$. Solid lines represent calculated values where as circles are experimental values

The experimental values of ΔC_p of $Au_{77}Ge_{13.6}Si_{9.4}$, $Au_{53.2}Pb_{27.5}Sb_{19.3}$, $Au_{81.4}Si_{18.6}$, $Mg_{85.5}Cu_{14.5}$ and $Mg_{81.6}Ga_{18.4}$ are taken from the report of Chen and Turnbull [2], Fecht *et al.* [13], Chen and Turnbull [1], Sommer *et al.* [14] and Predel and Hulse [15] respectively. With the help of Figs 1–5, it can be seen that the agreement between calculated and experimental values of ΔG is very good for all the five samples in the temperature range T_m to T_g.

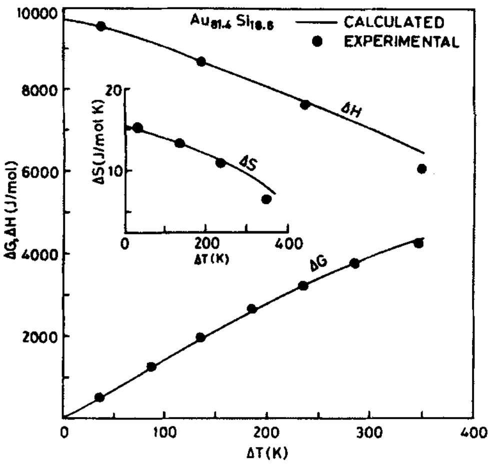

Fig. 3 Variation of thermodynamic parameters ΔG, ΔH and ΔS with temperature for glass forming metallic melt $Au_{81.4}Si_{18.6}$. Solid lines represent calculated values while circles are experimental values

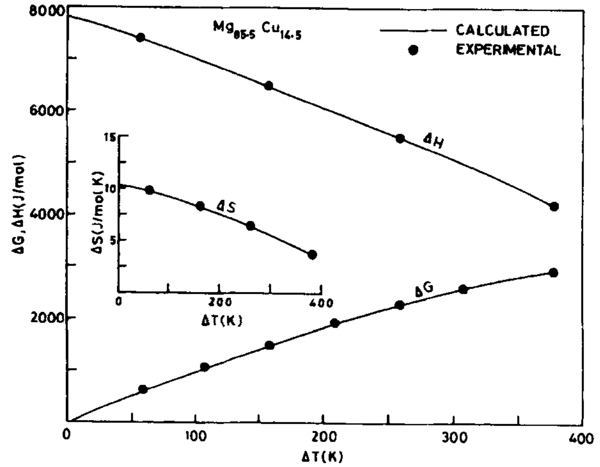

Fig. 4 Variation of thermodynamic parameters ΔG, ΔH and ΔS with temperature for glass forming metallic melt $Mg_{85.5}Cu_{14.5}$. Solid lines represent calculated values while circles are experimental values

In order to study the enthalpy and entropy differences between the two phases, undercooled liquid and solid phases, ΔH and ΔS have also been evaluated with the help of expressions reported in Eqs (9) and (10) and using the material parameters stated in Table 1. The experimental values of these thermodynamic parameters ΔH and ΔS are evaluated with the aid of Eqs (12) and (13) respectively. The results obtained are shown in the Figs 1–5 along with ΔG of the cor-

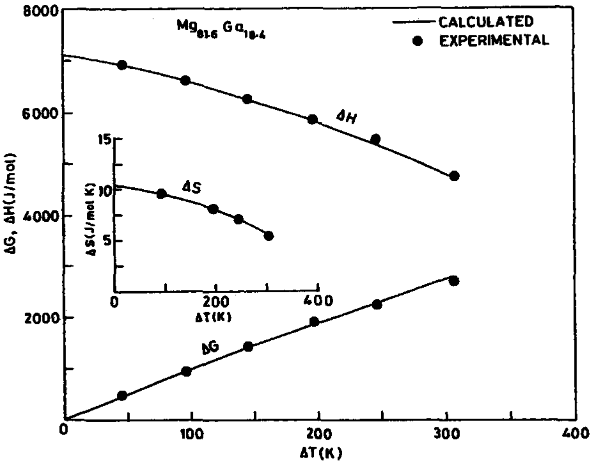

Fig. 5 Variation of thermodynamic parameters ΔG, ΔH and ΔS with temperature for glass forming metallic melt $Mg_{81.6}Ga_{18.4}$. Solid lines represent calculated values while circles are experimental values

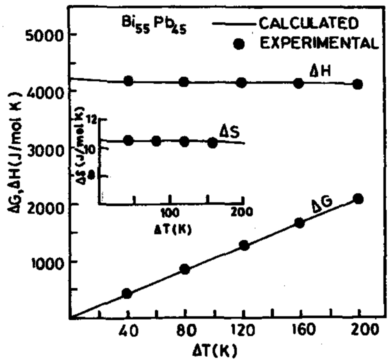

Fig. 6 Variation of thermodynamic parameters ΔG, ΔH and ΔS with temperature for non-glass forming metallic melt $Bi_{55}Pb_{45}$. Solid lines represent calculated values while circles are experimental values

responding sample. The agreement between calculated and experimental values is found to be very good. It is also interesting to note that the nature of variation of these thermodynamic parameters ΔG, ΔH and ΔS with temperature is almost similar for all samples (Figs 1–5). At the same time, the response of expressions obtained for ΔG, ΔH and ΔS on the basis of Taylor's series expansion is very good for glass forming metallic melts.

To see the response of these expressions for non-glass forming liquids, ΔG, ΔH and ΔS have also been estimated for $Bi_{55}Pb_4$ and Pb in the entire temperature range $0.5T_m$ to T_m and results obtained are depicted in Figs 6 and 7 for $Bi_{55}Pb_{45}$ and Pb respectively. The experimental data of ΔC_p for $Bi_{55}Pb_{45}$ and Pb are taken

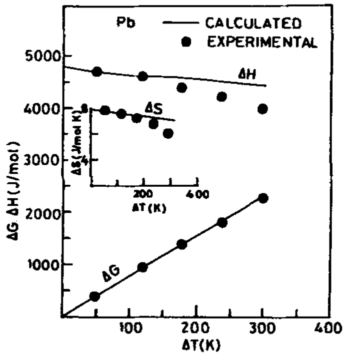

Fig. 7 Variation of thermodynamic parameters ΔG, ΔH and ΔS with temperature for non-glass forming melt Pb. Solid lines represent calculated values while circles are experimental values

from the report of Perepezko [16] and Thompson and Spaepen [5]. Once again a very good agreement between calculated and experimental values of thermodynamic parameters ΔG, ΔH and ΔS has been obtained in Figs 6 and 7 for non-glass forming materials in the temperature range T_m to $0.5T_m$, which confirms the capability of expressions obtained on the basis of Taylor's series expansion in explaining the thermodynamic parameters ΔG, ΔH and ΔS of unercooled liquids.

Table 2 Free energy difference (ΔG) between the liquid and equilibrium solid phases of $Mg_{85.5}Cu_{14.5}$ evaluated from various expression proposed by earlier workers and compared with that calculated using Eq. (6). The experimental value was evaluated using experimental data of ΔC_p

T/K	ΔT/K	ΔG/J mol^{-1}				
		Turnbull [3]	Hoffman [4]	Thompson and Spaepen [5]	Present Eq. (6)	Experimental
750	8	83	82	83	82	82
700	58	600	554	576	582	582
650	108	1117	958	1031	1053	1052
600	158	1634	1293	1444	1493	1488
550	208	2151	1561	1809	1897	1885
500	258	2668	1760	2121	2261	2239
450	308	3185	1891	2373	2582	2541
400	358	3702	1953	2557	2852	2783
380 (T_g)	378	3909	1959	2610	2944	2861

An attempt is made in Table 2 to compare the values of ΔG obtained by the use of earlier expressions [3–5]

$$\Delta G = \Delta S_m \Delta T \quad \text{(Turnbull [3])} \tag{15}$$

$$\Delta G = \Delta S_m \Delta T \frac{T}{T_m} \quad \text{(Hoffman [4])} \tag{16}$$

$$\Delta G = \Delta S_m \Delta T \left(\frac{2T}{T_m + T} \right) \quad \text{(Thompson and Spaepen [5])} \tag{17}$$

and the expression used in the present study. $Mg_{85.5}Cu_{14.5}$ is taken as an example. As can be seen from Table 2, the agreement between calculated and experimental data of ΔG is the best at all temperatures with a discrepancy of about 2.9% at T_g which can be compared with discrepancies of about 36.7%, 31.5% and 8.9% at the same temperature when expression proposed by Turnbull [3], Hoffman [4] and Thompson and Spaepen [5] are used respectively.

Ideal glass transition temperature (T_k) and residual (frozen-in) entropy (ΔS_R)

It was Kauzmann [8] first of all who pointed out the difficulties associated with a purely Kinetic description of the glass transition. One such a problem is the likelyhood of ΔS being negative at some temperature below T_g. The paradox was explained by Gibbs and DiMarzio [17] as well as Adam and Gibbs [11] by suggesting the glass transition as a second order transition. As suggested by Kauzmann, ΔS should be zero at some temperature T_k, the ideal glass transition temperature. It is also known as the Kauzmann temperature. The ideal glass transition temperature T_k can be estimated by setting ΔS=0 at T=T_k. The use of Eq. (8) facilitates an expression for the estimation of T_k as

$$\frac{b}{2}\left(\frac{T_m - T_k}{T_m}\right)^2 + (b-a)\left(\frac{T_m - T_k}{T_m}\right) + (\Delta C_p^m - a + b)\ln\left(\frac{T_k}{T_m}\right) + \Delta S_m = 0 \tag{18}$$

where

$$b = \frac{1}{2} T_m^2 \left[\partial^2 \Delta C_p / \partial T^2\right]_{T_m} \text{ and } a = T_m [\partial \Delta C_p / \partial T]_{T_m}$$

The equation stated above is a tanscendental in nature and can be solved for T_k by iterative procedures. However, ignoring the term $\left[\partial^2 \Delta C_p / \partial T^2\right]_{T_m}$ and using the approximation stated earlier in Eq. (5), an approximate value of T_k can be derived in the form of a quadratic equation. Consequently, the expression for T_k can be stated as

$$T_k = T_m - \frac{(\Delta S_m + 2\Delta C_p^m) \pm \left\{ (\Delta S_m + 2\Delta C_p^m)^2 - 8\Delta S_m T_m \left[\frac{\partial \Delta C_p}{\partial T} \right]_{T_m} \right\}^{1/2}}{2\left(\frac{\partial \Delta C_p}{\partial T} \right)_{T_m}} \tag{19}$$

which can further be approximated to a simple expression

$$T_k = T_m \left[\frac{2\Delta C_p^m/\Delta S_m - 1}{2\Delta C_p^m/\Delta S_m + 1} \right] \tag{20}$$

by ignoring the term

$$\left[\partial \Delta C_p/\partial T \right]_{T_m}$$

According to the equilibrium theory of Gibbs and DiMarzio, the configurational entropy becomes zero at the ideal glass transition temperature T_k. Neglecting the differences in vibrational entropy between the hypothetical glass and equilibrium crystal at T_k, the zero-point entropy (the apparent entropy difference between glass and crystal at absolute zero, T=0 K should be equal to the configurational entropy of the liquid which was frozen at T=T_g) which is known as the residual entropy ΔS_R. It is also referred as frozen-in entropy. ΔS_R can be expressed as

$$\Delta S_R = \Delta S_m - \int_{T_g}^{T_m} \frac{\Delta C_p}{T} \mathrm{d}T \tag{21}$$

In view of ΔS=0 at T=T_k, Eq. (21) yields

$$\Delta S_R = \Delta C_p^m \ln(T_g/T_k) - \left[\frac{\partial \Delta C_p}{\partial T} \right]_{T_m} \left[T_m \ln(T_g/T_k) - (T_g - T_k \right] + \ldots.. \tag{22}$$

where higher order derivatives are ignored and can further be approximated as

$$\Delta S_R = 2\Delta C_p^m \frac{(T_g - T_k)}{(T_g + T_k)} \tag{23}$$

It should be noted that it is customary to express ΔC_p and ΔS_R and other thermodynamic data on the basis of per mole of beads as proposed by Wunderlich [18]. The definition of a bead is better in the case of large polymeric molecules. However in the case of glassy alloys (metallic glasses), it is usually preferred to express thermodynamic quantities in the form of per mole.

Table 3 The value T_k and ΔS_R for glass forming samples used in the present analysis

Material	$T_{k_{cal}}$ /K	$T_{k_{exp}}$ /K	T_g/T_m	T_k/T_m	$(T_g-T_k)/T_m$	$\Delta S_{R_{exp}}$ /J mol^{-1} K^{-1}	$\Delta S_{R_{cal}}$ /J mol^{-1} K^{-1}	$\Delta S_{R_{exp}}/\Delta S_{m_{exp}}$	$\Delta C_p^m/\Delta S_m$
$Mg_{85.5}Cu_{14.5}$	281	281	0.5031	0.3707	0.1306	3.60	3.60	0.3481	0.7427
$Au_{81.4}Si_{18.6}$	202	202	0.4559	0.3176	0.1383	6.33	7.58	0.4089	0.5006
$Au_{77}Ge_{13.6}Si_{9.4}$	198	199	0.4704	0.3190	0.1514	7.84	9.01	0.4603	0.3957
$Mg_{81.6}Gal_{8.4}$	252	252	0.5603	0.3615	0.1983	5.55	5.34	0.5425	0.3851
$Au_{53.2}Pb_{27.5}Sb_{19.3}$	296	313	0.6080	0.5984	0.0096	1.02	6.87	0.0647	0.6653

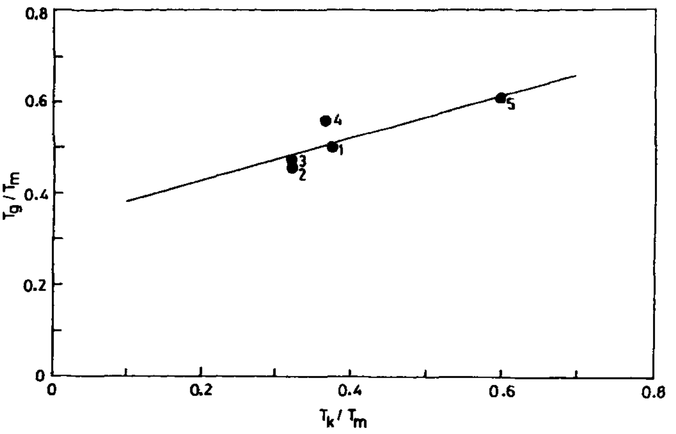

Fig. 8 Variation of reduced glass transition temperature (T_g/T_m) with reduced ideal glass transition temperature (T_k/T_m) for metallic glass formers. Numbers 1, 2, 3, 4 and 5 represent for $Mg_{85.5}Cu_{14.5}$, $Au_{81.4}Si_{18.6}$, $Au_{77}Ge_{13.6}Si_{9.4}$, $Mg_{81.6}Ga_{18.4}$ and $Au_{53.2}Pb_{27.5}Sb_{19.3}$ respectively

The ideal glass transition temperature (T_k) and the residual entropy (ΔS_R) have been calculated for all five samples using the constants given in Table 1 and results obtained are reported in Table 3. The variation of T_k with T_g has also been illustrated in the form of reduced temperature i.e. a plot of T_g/T_m *vs.* T_k/T_m is shown in Fig. 8 which show a linear relation

$$T_g/T_m = 0.4689 \quad (T_k/T_m) + 0.3347 \tag{24}$$

similar to the earlier finding of previous workers [9, 11] for polymeric materials.

Table 3 shows that the calculated value of ΔS_R is very close to the value of ΔS_R^{exp} based on the experimental data of ΔC_p. The variation of frozen-in entropy ΔS_R with $(T_g-T_k)/T_m$ can be understood with the help of Table 3 which clearly indicates that the reduced frozen-in entropy ($\Delta S_R/\Delta S_m$) increases with the increasing value of $(T_g-T_k)/T_m$ except in the case of $Au_{53.2}Pb_{27.5}Sb_{19.3}$. It can also be seen that reduced residual entropy increases with the decreasing value of $\Delta C_p^m/\Delta S_m$ which suggests a correlation between these parameters. As indicated by Dubey and Ramachandrarao [12] materials having larger value of $\Delta C_p^m/\Delta S_m$ is a better glass former. In view of these correlations, it can be said that material having lower value of reduced residual entropy ($\Delta S_R/\Delta S_m$) should form glass easily compared to the material having large value of $\Delta S_R/\Delta S_m$.

Conclusion

The expression for ΔG (Eq. (6)) based on Taylor's series expansion has been shown to yield correct estimates of Gibbs free energy difference even at large undercoolings for glass forming as well as non-glass forming melts. The expression for ΔH and ΔS (Eqs (9) and (10) respectively) are good enough to produce correct temperature dependence of the entropy difference and enthalpy difference between the liquid and solid phases and can be used to calculate ΔS and ΔH of undercooled liquids. A linear relation has been obtained between the reduced glass transition temperature (T_g/T_m) and the reduced ideal glass transition temperature (T_k/T_m) for metallic glass formers. The expression derived for ΔS_R (Eq. (23)) based on Taylor's series expansion is found to estimate the 'frozen-in' entropy correctly and calculated values are close to the experimental data. The reduced residual entropy ($\Delta S_R/\Delta S_m$) is mainly controlled by the characteristic temperature T_k, T_g and T_m. $\Delta S_R/\Delta S_m$ is found to increase with increasing $(T_g-T_k)/T_m$. It can also be concluded that material having lower value of $\Delta S_R/\Delta S_m$ exhibits higher value of $\Delta C_p^m/\Delta S_m$ and such materials can be a better glass formers as compared to those having large value of $\Delta S_R/\Delta S_m$.

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The authors are grateful to Prof. P. Ramachandrarao, N. M. L. Jamshedpur and Prof. S. Lele, Department of Metallurgical Engineering, B. H. U. for their interest in the present work. The part of work was done under C. S. I. R. project and we are also thankful to C. S. I. R., New Delhi for financial support.

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