Chapter 3

Thermodynamic Properties of metallic glasses and polymers

3.1 Introduction

Glasses are in excited state, from physics point of view. They will relax and eventually transform to the crystalline ground state if sufficient time is provided at any given temperature. The reason is that any metallic glass, rapidly cooled below its melting temperature, *Tm*, will not get sufficient time to arrange it's atoms in a regular periodic fashion. So, a thermodynamically stable state is not achieved by all the metallic glasses. It is well known that metallic liquids can extend the periods of time for being undercooled and avoiding crystallization from occurring [2.1]. The stability of the undercooled melt against nucleation of a crystalline phase is a good indicator of glass forming ability.Whole phenomena of being glass, depends upon the properties in the highly undercooled liquid state which include temperature dependent thermodynamic properties such as specific heat, entropy, enthalpy and Gibbs free energy.

According to classical nucleation theory [2.2, 2.3] thermodynamic and kinetic factors are used to evaluate the nucleation rate. [3.4]According to classical thermodynamics ΔG is a function of the heat capacity difference between metastable liquid and crystalline solid. The specific heat at high undercooling is an important characteristic for crystallization or glass formation. Gibbs free energy difference ΔG between the undercooled liquid and the corresponding crystalline solid, is the the most important factor in the analysis of the kinetics of crystallization at high undercooling . [In the supercooled liquid, the bulk glass forming alloys show a low driving force for crystallization. The low driving force leads to low nucleation rates and enhances glass forming ability (GFA). Metallic glasses are stable against crystallization in highly undercooled liquid state upto above 100K above the glass transition temperature. It opens a new vision into the dynamic and thermal properties of highly undercooled metallic liquids. It also provides a chance to prove theoretical concepts about glass transition itself for metallic materials.

Theoretical evaluation of ΔG, ΔS (entropy difference between solid and liquid phase) and

ΔH (enthalpy difference between the solid and liquid phase) with the aid of the specific heat difference (ΔCp) between the under cooled liquid and corresponding equilibrium solid can be done with fundamental thermodynamic procedures. The experimental determination of the specific heat of the under cooled melts is always tough due to their strong tendency to crystallize. It can be measured close to the melting temperature Tm and at the glass transition temperature Tg in the case of glass forming melts. These experimental difficulties lead us towards reliable analytical expressions for the estimation of the thermodynamic parameters. Several researchers have proposed expressions for ΔG.

They were not satisfactory for describing the correct temperature dependence of ΔG over a large degree of under cooling because most of these expressions did not deal with the appropriate temperature dependence of ΔCp. Considering these limitations, two different ΔG expressions are derived, using appropriate variation of ΔCp with temperature. These

expressions give good account for ΔG in most of the bulk glass forming melts.

A quantitative measure of the stability of a glass as compared to its corresponding crystalline state can be obtained by calculating the thermodynamic parameters such as the Gibbs free energy difference (ΔG), entropy difference (ΔS) and the enthalpy difference (ΔH) between the super-cooled liquid and the corresponding crystalline phase.

3.2 Thermodynamic Properties: Gibbs Free Energy Difference, ΔG, Entropy Difference, ΔS & Enthalpy Difference, ΔH

Stability of a metallic glass is depended on the Gibbs free energy between two phases; amorphous and crystalline. It becomes more stable when the Gibbs free energy of the amorphous phase is lower than that of the competing crystalline counter phase. By way of explanation, the system becomes stable when the change in Gibbs free energy, ΔG (= $Gglass$ - $Gcrystal$) exhibit minimum value. Mathematically, it can be written as below equation;

$\Delta G = \Delta H - T\Delta S$ (2.2)

where, ΔH and ΔS represents the enthalpy difference and entropy difference respectively

and the Δ symbol represents the change in these quantities between the final and initial states.The system becomes stable when the value of ΔG is the lowest. For getting a minimum value of ΔG, one should either decrease the value of ΔH or increase the value of ΔS

or both.

Now, we are going to consider about ΔH and ΔS. *First, we consider entropy difference* Δ Since entropy is nothing but a disorder in a system. In other words, the value of different ways in which the constituent atoms arrange is called entropy and this value will increase with increasing number of components in the amorphous alloy system. Thus, in multi component systems, the free energy will be lower because of the increment in entropy even if ΔH remains constant.

On the other side, value of ΔH will be differ because of the chemical interaction between the

different constituent elements.

The free energy of the system can be decreased in other cases at a constant temperature if there is a large interfacial energy between the liquid and solid phases or in case of low chemical potential due to low enthalpy.

Since all other cases seem to be troublesome for decreasing the free energy, except the increment in ΔS in an alloy system. Increment in ΔS also results in an increase in the degree of dense random packing of atoms, due to that ΔH decreases and consequently solid-liquid interfacial energy increases [2.1.]. Thus, the simplest way to decrease the free energy would be to increase ΔS by having a large number of components in the alloy system.

Furthermore, smaller value ofΔS indicates a better GFA, because it increases the disorder of the super-cooled liquid state and hence excesses its amorphicity. ΔS decreases more & more and reaches a minimum value at Tg, as supercooling increases and then finally, the material

gets converted into solid phase. It is presumed with a possibility of vanishingΔS that the entropy of glassy phase becomes equal to the entropy of the crystalline phase if a liquid is cooled below its Tg. Hence the glassy phase becomes as stable as the crystalline phase when $\Delta S \rightarrow 0$. The temperature at which this happens is known as Kauzmann temperature (TK). However, practically the super-cooling of a melt below its Tg is not possible since the material gets converted into solid well before TK (i.e., at Tg). Hence, the concept of an amorphous material having equal entropy as that of its crystalline counterpart becomes self-contradictory. This concept was given by Walter Kauzmann in 1948 [3.5] and it is termed as "Kauzmann paradox" .

Thus, Gibbs free energy difference, ΔG, the difference of free energy between amorphous metallic alloy and its crystalline counterpart, entropy difference, ΔS and enthalpy difference, ΔH are important parameters in order to know the thermal stability of metallic glass.

The Gibbs free energy change (ΔG) on crystallization of these multicomponent undercooled systems and polymers is an crucial parameter in nucleation process because he nucleation frequency has an exponential dependence on ΔG. Therefore, the evaluation of ΔG as a function of temperature is very important in the analysis of nucleation phenomena.

The heat capacities of liquid and corresponding crystalline phase must be known for the estimation of the exact temperature dependence of ΔG.

As we know, the nature of undercooled liquid is metastable hence the heat capacity data is not available easily. So, we have to estimate the value of the functional dependence of ΔG on undercooling (ΔT), theoretically.

There are so many expressions available for ΔG in the literature [3.6-3.15]. These expressions are formed on some kind of assumption for the

temperature dependence of the heat capacity. However, most of these expressions for ΔG is based on the assumption that under cooling ΔT (= $T_m - T$) is small. This is the limitation for the validity of the different proposed expressions for ΔG over small temperature interval. Now a days, scenario is changed as the BMG forming alloys have a large undercooled regime. Hence, an expression of ΔG is needed which can enhance the validity of small underccoling.

In the this chapter, a novel equation for ΔG is presented, which is suitably applicable and more reliable for BMG systems with wide undercooled region as well as polymers.

3.2.1 Theory

From the thermodynamic point of view, thermodynamic driving force for crystallization should be lower for the better glass former. The thermodynamic driving force for crystallization is given by ΔG. In order to understand the impact of

ΔG in the nucleation theory, we should consider the factors that can influence nucleation. The steady state homogeneous nucleation frequency per unit volume, I_v^{hom}, at a temperature T below the equilibrium freezing point or liquidus temperature T_l, is given by [3.16] :

$$I_v^{\mathrm{hom}} = \frac{D_n(T)N_v}{a_0^2}\exp[-\Delta G^*/kT] \tag{3.1}$$

where D_n (T) is the atomic diffusivity at the liquidus/nucleus interface, N_v is the volume density and a_0 the mean effective diameter of the diffusing species, k is Boltzmann's constant and ΔG^* is the critical free enthalpy barrier for nucleation.

For spherical nuclei the isotropic interfacial enthalpy σ between solid and liquid is

$$\Delta G^* = 16\pi\sigma^3/3\Delta G_v^2 \tag{3.2}$$

where ΔG_v^2 or, say ΔG in the present context, is the free energy difference between liquid and crystal phases and which is a function of temperature T.

The difference in Gibbs free energy between the liquid and crystalline phases is given by

$$\Delta G = \Delta H - T\Delta S \tag{3.3}$$

where

$$\Delta H = \Delta H_m - \int_T^{T_m} \Delta C_p dT \tag{3.4}$$

and

$$\Delta S = \Delta S_m - \int_T^{T_m} \Delta C_p \frac{dT}{T} \tag{3.5}$$

T_m is the melting temperature, ΔS_m is entropy of fusion and ΔH_m is the enthalpy of fusion. They are related to each other by the following relation:

$$\Delta S_m = \frac{\Delta H_m}{T_m} \tag{3.6}$$

ΔC_p is defined as $C^l{}_p - C^x{}_p$ is the difference in specific heats of the two phases.

Hence, the expression for ΔG becomes

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m} - \int_T^{T_m} \Delta C_p dT + T\int_T^{T_m} \Delta C_p \frac{dT}{T} \tag{3.7}$$

Thus, we need experimental specific heat data for the undercooled and the crystal phases of a material, and then, experimental ΔG values can be calculated with the help of Eq.(3.7). In case of non-availability of ΔC_p data, one has to switch over to approximations. The linear or hyperbolic forms of variation of ΔC_p with temperature are the simplest available options to estimate ΔG in the undercooled region. The two types of variation of ΔC_p with temperature are represented as

$$\Delta C_p = AT + B \qquad \text{(a)}$$

$$\Delta C_p = C/T + D \qquad \text{(b)}$$

It is tough to derive the two constants, *A* & *B* or *C* & *D*, in absence of ΔC_p data at any two different temperatures. Owing to this difficulty, most of workers in this field, have taken the simplest assumption that is to take $A = 0$ and make $\Delta C_p = B$ i.e. constant through Eq.(a).

It is observed that, the ΔC_p = constant assumption work quite well in most of the bulk glass forming alloys, in which, the specific heat of undercooled liquid $C_p{}^l$ does not vary much with temperature. Hence, $\Delta C_p = C_p^l - C_p^x$ remains nearly constant throughout the entire undercooled region.

However, few glass forming systems possess exceptionally high glass forming ability (GFA). In such cases, the specific heat of undercooled liquid $C_p{}^l$ varies much with temperature. In such systems ΔC_p increases considerably with undercooling. Therefore, to evaluate ΔG correctly an appropriate hyperbolic assumption, given by Eq.(b), has to be considered.

Thus, we can summarize that an appropriate variation of ΔC_p should be considered while deriving an analytical expression for ΔG.

3.2.2 Earlier proposed Expressions for Calculation of Thermodynamic Parameters ΔG, ΔS and ΔH expressions

Several models [3.6-3.15] of varying degrees of complexity have been proposed for the dependence of ΔG on undercooling. All analytical expressions depend on some kind of assumption for the temperature dependence of the heat capacity.

The simplest expression for ΔG was given by Turnbull [3.6] where ΔC_p was assumed to be zero. So, using $\Delta C_p = 0$, Eq.(3.7) simplifies to

$$\Delta G = \frac{\Delta H_m}{T_m}\Delta T \tag{3.8}$$

As, ΔC_p is most often non-zero, the expression given by Turnbull shows very large deviation.

The most widely used expression for estimation of ΔG is the one given by Thompson and Spaepen [3.10]. They have assumed linear variation of ΔC_p given by Eq.(a) and further taking $A = 0$ and making $\Delta C_p = B = constant$. Using this assumption Eq. (3.7) simplifies to

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m} + \Delta C_p\left(T\ln\left(\frac{T_m}{T}\right) - \Delta T\right) \tag{3.9}$$

To simplify Eq. (3.9), TS have used the following approximation:

$$\begin{aligned} \ln\left(\frac{T_m}{T}\right) &= \ln\left(1 + \frac{\Delta T}{(T_m + T)/2}\right) \\ &\cong \frac{2\Delta T}{T_m + T} \end{aligned} \tag{3.10}$$

Also, using Kauzmann phenomena [3.16] which states that the entropy difference ΔS, which is configurational in nature, decreases with the decrease in temperature and vanishes at a temperature, T_K, known as Kauzmann temperature, TS approximated ΔC_p in following way

Assuming ΔC_p to be constant, Eq. (3.5) for ΔS reduces to

$$\Delta S = \frac{\Delta H_m}{T_m} + \Delta C_p \ln\left(\frac{T}{T_m}\right) \tag{3.11}$$

Since $\Delta S = 0$ at $T = T_K$

$$\Delta C_p = \alpha \frac{\Delta H_m}{T_m} \tag{3.12}$$

where $$\alpha = \frac{1}{\ln\left(T_m / T_K\right)}$$

(3.13)

Using this, they have derived an expression given as

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m}\left(\frac{(1-\alpha)T_m + (1+\alpha)T}{T_m + T}\right) \tag{3.14}$$

Still in order to evaluate ΔG one requires the knowledge of T_K, which is not easily known. So, TS suggested that, if no experimental data are available, the best approximation for ΔC_p is when $\alpha \cong 1$.

Hence, Eq. (3.14) reduces to

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m}\left(\frac{2T}{T_m + T}\right) \tag{3.15}$$

It is clear that in derivation of ΔG, TS have used two approximations one is approximating the logarithmic term and second considering $\alpha \cong 1$. Approximation of Eq. (3.10) is strictly valid only for small ΔT and as reported by TS, in the temperature range of interest ($T_m/2 < T < T_m$) this leads to errors in ΔG of less than 4% at the largest undercooling [3.14]. But, for the multicomponent metallic glass forming alloys, which exhibits a large undercooled regime, this error is greater than 5%. Also, it is observed that α values calculated in most of bulk metallic glasses are always greater than one. Because of these two limitations, the ΔG values obtained using TS expressions show large deviations.

Eq. (3.14) reduces to Hoffman [3.12] expression if $\alpha = 1 + T_m/T$

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m}\left(\frac{T}{T_m}\right) \tag{3.16}$$

The expression given by Singh & Holtz [3.15] is

$$\Delta G = \frac{\Delta H_m}{T_m}\Delta T\left(\frac{7T}{T_m + 6T}\right) \tag{3.17}$$

In order to account for the wide undercooled region of the multicomponent metallic alloys Lad et al [3.18] modified the Eq.(2.15) by considering

$$\ln\left(\frac{T_m}{T}\right) \equiv \frac{\Delta T}{T}\left(1 - \frac{\Delta T}{2T}\right) \tag{3.18}$$

Eventually they derived expression for ΔG as

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m}\left(1 - \frac{\Delta T}{2T}\right) \tag{3.19}$$

This expression, when utilized to estimate ΔG for various metallic glass forming alloys, gives good results. But, when applied for the alloys which posses very high glass forming ability, it was found that the calculated values showed deviation a large undercooling. Hence, in order to obtain satisfactory results for such systems Lad et al [3.20] have extended the Taylor series expansion of Eq.(3.10) upto second order to give:

$$\ln\left(\frac{T_m}{T}\right) = \ln\left(1 + \frac{\Delta T}{(T_m + T)/2}\right)$$
$$\cong \frac{\Delta T}{(T_m + T)/2} - \frac{1}{2}\left(\frac{\Delta T}{(T_m + T)/2}\right)^2$$

$$\ln\left(\frac{T_m}{T}\right) \cong \frac{4T\Delta T}{(T_m + T)^2} \tag{3.20}$$

The new expression for ΔG derived by them is given by

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m}\left(\frac{4T^2}{(T + T_m)^2}\right) \tag{3.21}$$

Eq. (3.21), gives good account of ΔG in most of the systems. But, since the derivation again involves the approximation of the logarithmic term, the results obtained are not in excellent agreement with the experimental points.

Another quite extensively used expression for ΔG is the one given by Dubey and Ramchandrarao (DR) [3.16]:

$$\Delta G = \Delta S_m \Delta T - \frac{\Delta C_p^m (\Delta T)^2}{2T}\left[1 - \frac{\Delta T}{6T}\right] \tag{3.22}$$

The above expression is an approximate formula and the exact one derived by DR based on hole theory of liquids leads to the following expression for ΔG

$$\Delta G = \Delta S_m \Delta T - \eta \operatorname{Re}^{(-\gamma\delta + A)}\left[\gamma\delta\Delta T - T(1 - e^{\gamma\delta\Delta T/T}\right] \tag{3.23}$$

where $\Delta T = T_m - T$, $\gamma = \frac{E_h}{RT_K}$ and $\delta = \frac{T_K}{T_m}$. The other terms have their usual meaning and the same can be seen in the work of DR [3.16].

However, it is obvious from Eq.(3.23) that it involves evaluation of many parameters like η, γ, δ, T_K, and E_h, which in turn, requires the knowledge of ΔC_p at two temperatures (taken at T_m and T_g by DR).

An expression derived by Battezzati and Garrone , Eq.(3.24) does not involve the approximation of the logarithmic term

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m} - \gamma \frac{\Delta H_m}{T_m}\left[\Delta T - T \ln \frac{T_m}{T}\right] \tag{3.24}$$

with

$$\gamma = \left(1 - \frac{\Delta H_x}{\Delta H_m}\right) \Big/ \left(1 - \frac{T_x}{T_m}\right) \tag{3.25}$$

where ΔH_x and T_x are heat and temperature of crystallization respectively.

Normally, γ has been taken to be 0.8 for glass forming liquids and ΔG has been reported using this value in Eq. (3.24.) for multicomponent amorphous alloys and even for bulk metallic glass Battezzati and Baricco [3.12] have reported an experimental study of thermodynamic properties in a ZBLAN glass-forming system in which γ has been taken to be ~ 3.5.

Moreover, the correct evaluation of γ in multicomponent amorphous systems is difficult owing to the following practical reasons:

I. Bulk amorphous alloys normally possess multicomponent nature and therefore crystallize in multiple steps. It is difficult to make a choice of the step to be taken for derivation of γ.

II. T_x is a function of heating rate and; even ΔH_x is not constant at all heating rates.

The above two points pose difficulty in evaluating γ and one often gets γ value which is not unique. In fact, upper limit to γ is obtained [3.12] as the input experimental parameter ΔH_x represents only a lower limit of the value.

Recently, Ji and Pan have proposed an expression for ΔG assuming hyperbolic variation of ΔC_p in undercooled region

$$\Delta G = \frac{2\Delta H_m \Delta T_m}{T_m}\left[\frac{T}{T_m + T} - \frac{\Delta T^2 T_m}{3\left(T_m + T\right)^3}\right] \tag{3.26}$$

This expression is derived considering $\Delta C_p = \Delta H^m / T$ for hyperbolic temperature variation of ΔC_p. At $T = T_m$ and using their expression,

$$\Delta C_p^m = \Delta H^m / T_m \quad .$$

In fact, the above expression for $\Delta C_p{}^m$ could be obtained assuming ΔC_p to be constant between T_K and T_m and inserting $\Delta C_p = \Delta C_p{}^m$ and taking $\alpha = 1$ (following Thompson & Spaepen) from Eq.(3.12),

$$\Delta C_p^m = \frac{\Delta H_m}{T_m}$$

Assumption of constant ΔC_p at one instance and obtaining temperature variation at the other are self contradictory. Moreover, values obtained using Ji & Pan approach under estimate ΔC_p and also at $T = T_m$, $\Delta C_p^m = \Delta H^m / T_m$ provides the reference values of $\Delta C_p{}^m$ which is much below the experimental values. Eventually the expression derived for ΔG does not account well for bulk glass forming alloys.

ΔC_p to be constant work well for most of these systems.

Heena et al derived following expression considering ΔC_p to be constant

Then, for $\Delta C_p = AT+B$, assuming $A = 0$; $B = \Delta C_p = constant$ Following the argument of vanishing ΔS at the Kauzmann temperature T_K, using the Eq.(3.12) for ΔC_p, they derived following expression

$$\Delta G = \frac{\Delta H_m}{T_m}\left[\alpha T \ln\frac{T_m}{T} + \Delta T(1-\alpha)\right] \tag{3.27}$$

For bulk glass forming alloys having excellent GFA it is observed that the specific heat increases considerably with undercooling. In such systems the hyperbolic variation for ΔC_p given by $\Delta C_p = C/T + D$ is to be considered. Again in order to estimate the values of the constants C and D, the knowledge of ΔC_p data at two different temperatures is required. In absence of ΔC_p data it can be assumed that $D = 0$ and $C = \Delta C_p{}^m T_m$, since the value of *constant D* is very low (almost negligible) compared to C.
Heena et al derived one more expression for such case as discussing above.

They considered, ΔC_p at any temperature $T_K < T < T_m$ in the undercooled region can be expressed as

$$\Delta C_p = \frac{\Delta C_p^m T_m}{T} \tag{3.28}$$

$\Delta C_p{}^m$ being the specific heat difference at the melting point. Substituting ΔC_p from Eq.(3.28) in Eqs.(2.7), we get;

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m} - \Delta C_p^m T_m \left[\ln \frac{T_m}{T} - \frac{\Delta T}{T_m} \right] \qquad (3.29)$$

Now, ΔS can be obtained by differentiating ΔG with respect to T i.e.

$$\Delta S = -\frac{\partial \Delta G}{\partial T} = \frac{\Delta H_m}{T_m} \left[\alpha \ln \left(T / T_m \right) + 1 \right] \qquad (3.30)$$

substituting above eq. in Eq.(3.3) we can get the expression for ΔH as:

$$\Delta H = \frac{\Delta H_m}{T_m} \left[T_m - \alpha \Delta T \right] \qquad (3.31)$$

The expression for ΔS in case of hyperbolic dependence of ΔC_p on T can be obtained by partial differentiation of Eq.(3.29), hence

$$\Delta S = \frac{\Delta H_m}{T_m} - \Delta C_p^m \, T_m / T + \Delta C_p^m \qquad (3.32)$$

and ΔH can be obtained using equations (3.29) and (3.32) in Eq. (3)

$$\Delta H = \frac{\Delta H_m}{T_m} - \Delta C_p^m T_m \ln \left(T_m / T \right) \qquad (3.33)$$

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3.2.3 Equations for *ΔG* assuming Hyperbolic Variations of *ΔC*p with Temperature

The difference in Gibbs free energy ΔG is expressed as

$$\Delta G = \left(\Delta H_m + \int_T^{T_m} \Delta C_p dT \right) - T \left(\Delta S_m + \int_T^{T_m} \frac{\Delta C_p}{T} dT \right) \qquad (3.34)$$

The choice of proper ΔC_p variation is important to evaluate ΔG accurately. The linear or hyperbolic forms of variation of ΔC_p with temperature are the simplest available options to estimate ΔG in the undercooled region.

Derivation of ΔG assuming hyperbolic variation ΔC_p with temperature

Assumption of constant ΔC_p works quite well for most of the glass forming systems and provides fairly close results for ΔG. But, for few systems having outstanding glass forming ability (GFA), temperature variation of ΔC_p has to be accounted for in some form. For bulk glass forming alloys having excellent GFA it is observed that the specific heat increases considerably with undercooling. In such systems the hyperbolic variation for ΔC_p given by $\Delta C_p = C/T + D$ is to be considered. Again in order to estimate the values of the constants C and D, the knowledge of ΔC_p data at two different temperatures is required. In absence of ΔC_p data it can be assumed that $D = 0$ and $C = \Delta C_p^m T_m$, since the value of *constant* D is very low (almost negligible) compared to C.

Hence, ΔC_p at any temperature $T_K < T < T_m$ in the undercooled region can be expressed as

$$\Delta C_p = \frac{\Delta C_p^m T_m}{T} \tag{3.35}$$

ΔC_p^m being the specific heat difference at the melting point. Substituting ΔC_p from Eq. (3.28) in Eqs.(3.7), we get;

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m} - \Delta C_p^m T_m \left[\ln \frac{T_m}{T} - \frac{\Delta T}{T_m} \right] \tag{3.36}$$

This equation, assuming hyperbolic variation of ΔC_p differs only in a temperature term with respect to Eq. (3.9) (taking ΔC_p = constant) from which expression for ΔG given has been derived.

Now, we consider the below approximation and substituting into Eqn (3.36)

$$\ln\left(\frac{T_m}{T}\right) \equiv \frac{\Delta T}{T}\left(1 - \frac{\Delta T}{2T}\right)$$

We can get the following new expression for ΔG in case of hyperbolic dependence of ΔC_p on T,

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m} - \Delta C_p^m T_m \Delta T \left[\frac{1}{T} - \frac{\Delta T}{2T^2} - \frac{1}{T_m} \right] \tag{3.52}$$

Eq. (3.52) is the new expression for multi component BMG forming alloys with large undercooled region. It is derived by taking the hyperbolic variation of ΔC_p, and it involves approximation for the logarithmic term.

3.3 Results and Discussions

3.3.1 Gibbs Free Energy Difference, Entropy Difference and Enthalpy Difference for Six Glass Forming Polymeric Melts

The temperature dependence of the Gibbs free energy difference (ΔG), entropy difference (ΔS) and enthalpy difference (ΔH) between the undercooled melt and the corresponding equilibrium solid has been analysed for glass forming polymeric materials. It is done by calculating ΔG, ΔS and ΔH for four samples of glass forming polymeric melt, polyethylene (PE), polytetramethylene oxide (PTMO), polyamid-6 (PA-6), polypropylene oxide (PPO) and two samples of simple organic liquids: *o*-terphenyl (*o*-ter), tri-α-naphthyl benzene(tri-α-NB), in the entire temperature range melting temperature(T_m) to glass transition temperature(T_g). The expression for ΔG, ΔS and ΔH has been derived assuming hyperbolic dependence of ΔC_p on T.

. The result of tri-α-NB shows excellent match with experimental data. This is simple organic liquid and no polymerization undergoes. So we can say that polymerization may have effect on Glass Forming Ability (GFA) of material. Lad et al (Eq.3.21) are somewhat closer and the possible reason is ΔCp may not vary much.

Figures 1-6 show the results of ΔG as function of T in the undercooled region for three polymeric melts and two simple organic liquids obtained using Eq (3.21), (3.22) ,(3.29) and present Eq.(3.52).The parameters used for the calculations of ΔG for these systems are given in table.1. The results for these systems (fig.1-6) are calculated with our present Eq. (3.52), Lad et al Eq.(3.21),Mishra etalEq(3.22) ,Heeana et al Eq(3.29) and compared with the experimental results of [19]. We can see the fair agreement of the present results obtained through Eq. (3.52) with experimental data.

The tri-α-NB shows the good agreement and close matching of our present Eq.(3.52)and Eq(3.29) with experimental curves up to large degrees of undercooling.

All three polymeric and simple organic liquid samples (fig.1-6) have a large deviation of the curves obtained using the formulation given by Lad et al Eq.(6).

Figures 6-12 show the result of ΔS as function of T in the undercooled region for two samples of glass forming polymeric melts and one simple organic liquid obtained using our present Eq. and Mishra et al Eq., The graphs for PA6, PPO and tri-α-NB show results for ΔS of our present Eq. and seem to be matching with experimental curve.

In the result for ΔS of PA6 , our result Eq.and results obtained by Mishra et al match with experimental data qualitatively. However, quantitatively they deviate from experimental points.

Figures 13-18 are presenting the results of ΔH as a function of T in the undercooled region for two samples of glass forming polymeric melts and one simple organic liquid obtained using our present Eq. and that of Mishra et al Eq . The PA6 , PPO and tri-α-NB show excellent result for ΔH. The results using our present Eq. for both the systems are much nearer to experimental results.

Figures 1-6 show the results of Gibbs free energy differences ΔG as function of T in the undercooled region for five polymeric melts obtained using hole theory of liquids Eq, and hyperbolic variation of ΔC_p Eqs.(8) almost coinside with the experimental points [19] in the entire undercooled region. The parameters used for the calculations of ΔG for these systems are given in table.1. The good agreement of the present results obtained through equation (8) with experimental data can be observed.

The PE show good agreement and close matching of the two curves of Mishra expression Eq(3.22) and present expression Eq(3.52) with experimental curves up to large degrees of undercooling. The PB, PEO, PP and PTMO show good agreement of Mishra expression Eq and present expression Eq(3.52) with experimental curves. The plot using the Lad expression Eq(3.21) show a deviation from the experimental curves in all the samples. All five polymeric samples (fig.1-6) have a large deviation in Lad expression.

Figures 6-12 show the result of ΔS as function of T in the undercooled region for two samples of glass forming polymeric melts and one simple organic liquids. It is obtained from the derivative of the plotted ΔG using the hole theory of liquid [8];Eq.(9) and hyperbolic dependence of ΔC_p on T; Eq .The O-ter and the

PTMO show good result for ΔS using present eq.. For both the systems, the results are much nearer to experimental points while PE show deviation at lower(<250K) temperature range.

Figures 13--18 are presenting the results of ΔH as a function of T in the undercooled region for two samples of glass forming polymeric melts and one simple organic liquids. It is obtained using the hole theory of liquid [8]; eq(12) and hyperbolic dependence of ΔC_p on T; Eqs (13). The O-ter(fig.9) and the PTMO(fig.10) show wonderful result for ΔH. The results using present eq.(13) for both the systems are much nearer to experimental results while PE(fig.11) show deviation at lower(<280K) temperature range.

Table 3.1: Parameters used for the calculation of ΔG
for glass forming polymeric melts[8]

System	$T_i=T_g$ (K)	T_k (K)	T_m (K)	T_k/T_m (K)	ΔH_m (kJ/mol)	ΔC_p^m (kJ/mol-K)	ΔS_m (kJ/mol-K)
tri-α-NB	342	255.4	472	0.54	42.489	0.09086	0.09002
Salol	230	209.5	316.6	0.66	9.799	0.02368	0.03095
PET	342	253.6	543	0.47	22.600	0.0088	0.04162
PA6	323	252.5	496	0.51	21.814	0.03815	0.04396
PPO	198	156.7	350	0.45	8.4	0.02198	0.024

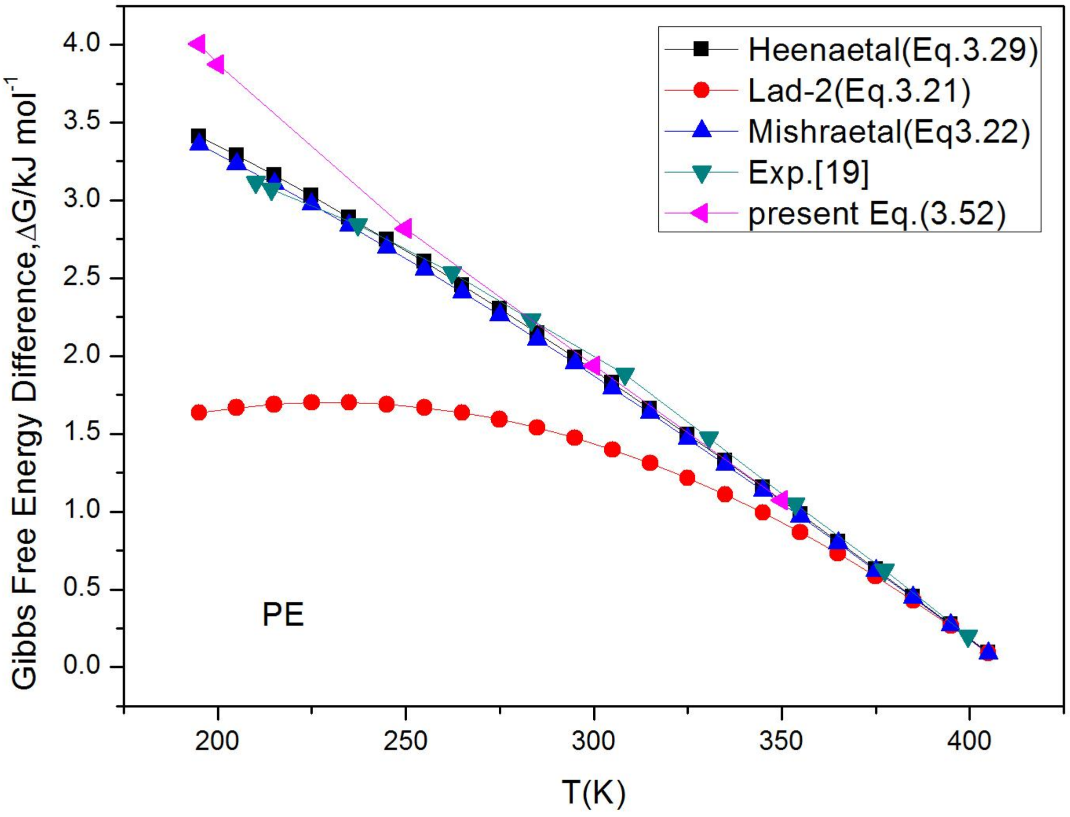


Fig. 3.1 Gibbs free energy difference, ΔG as a function of temperature for PE

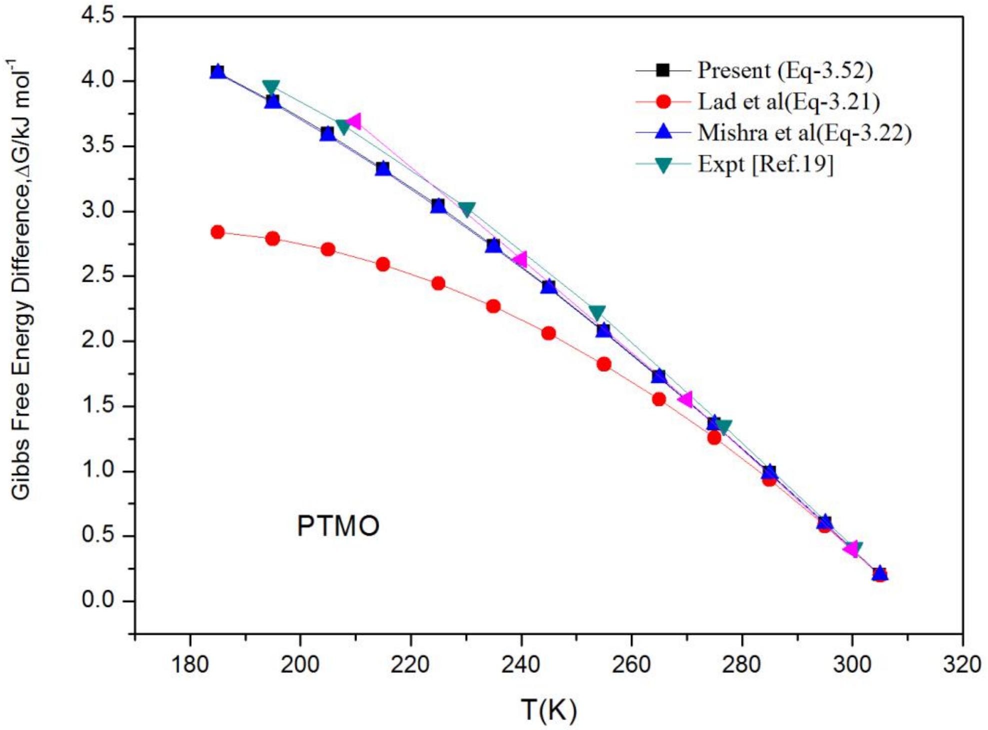


Fig. 3.2 Gibbs free energy difference, ΔG as a function of temperature for PTMO

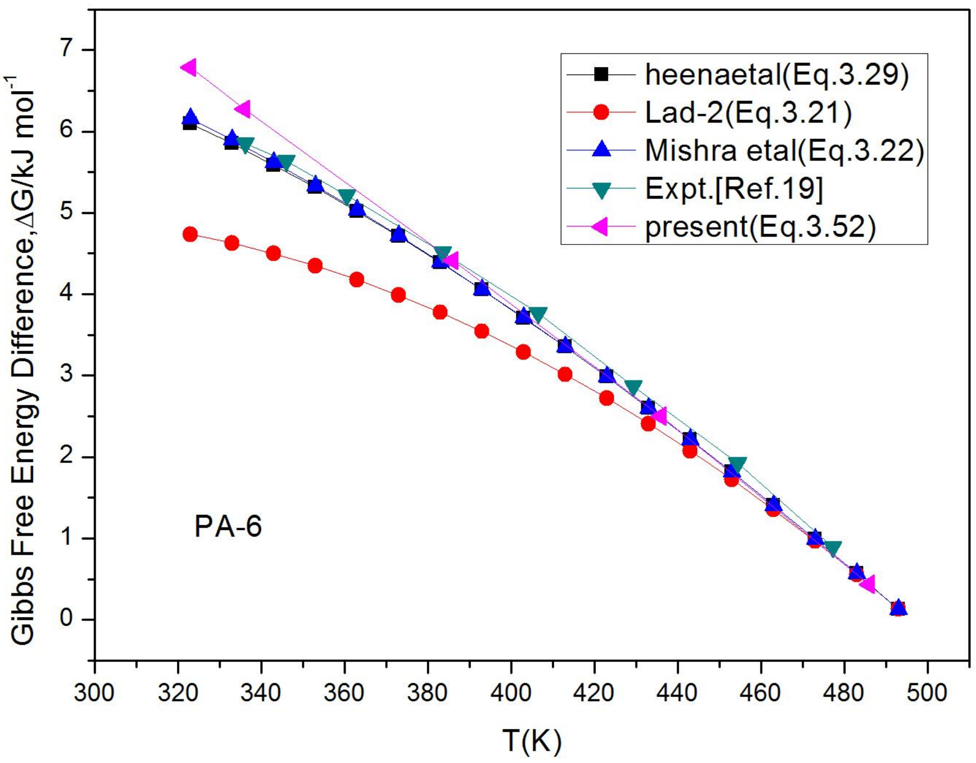


Fig. 3.3 Gibbs free energy difference, ΔG as a function of temperature for PA6

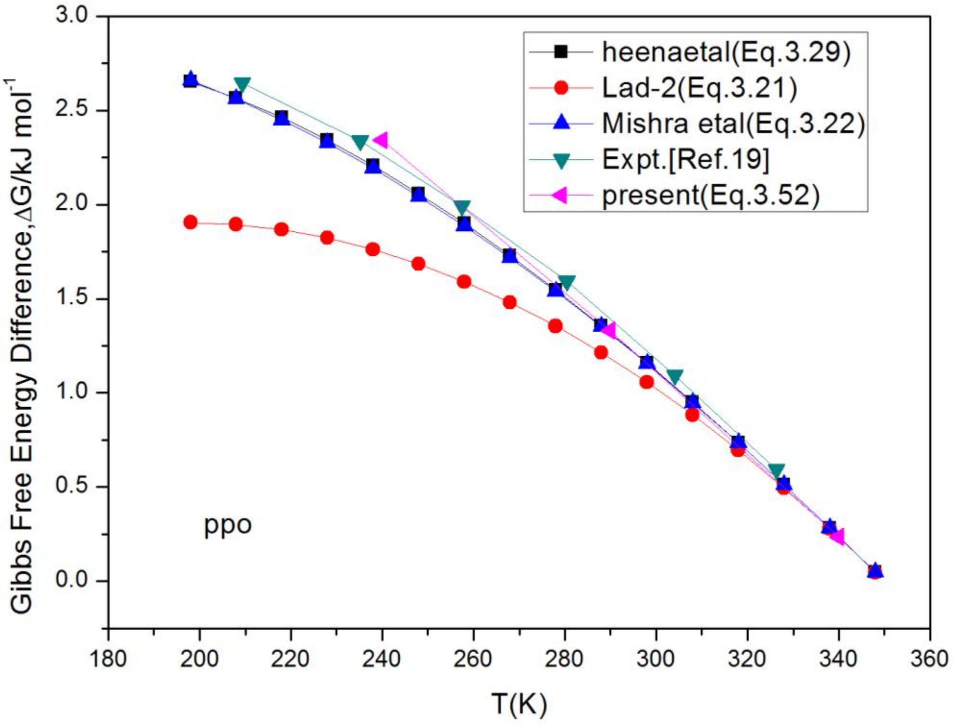


Fig. 3.4 Gibbs free energy difference, ΔG as a function of temperature for PPO

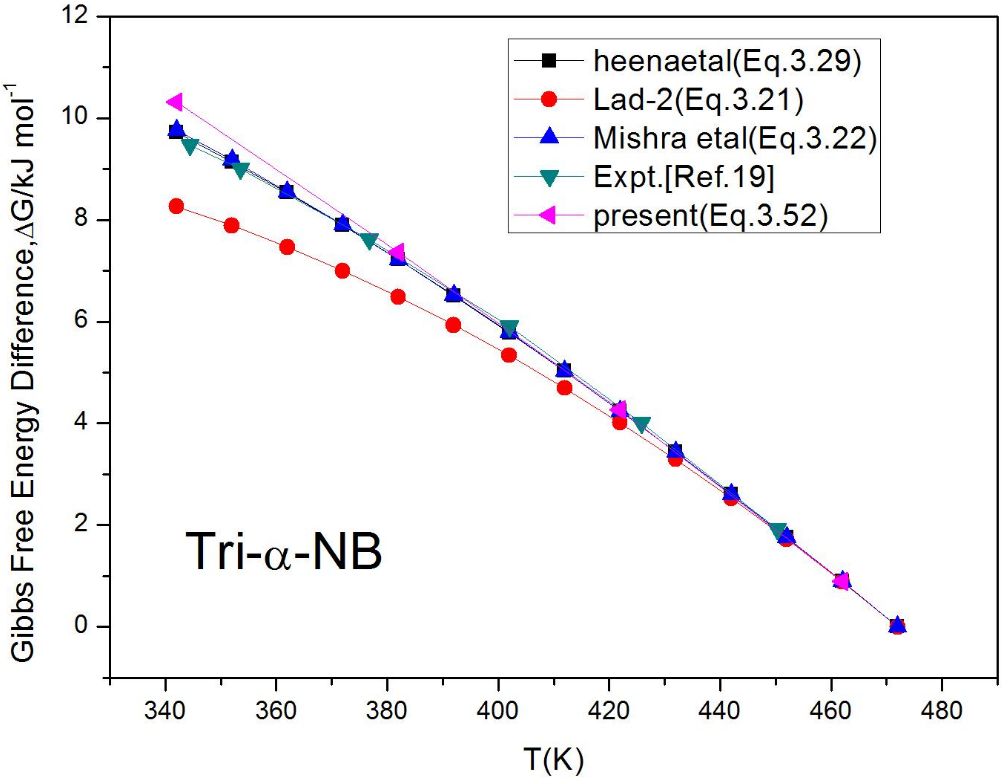


Fig. 3.5 Gibbs free energy difference, ΔG as a function of temperature for tri-α NB

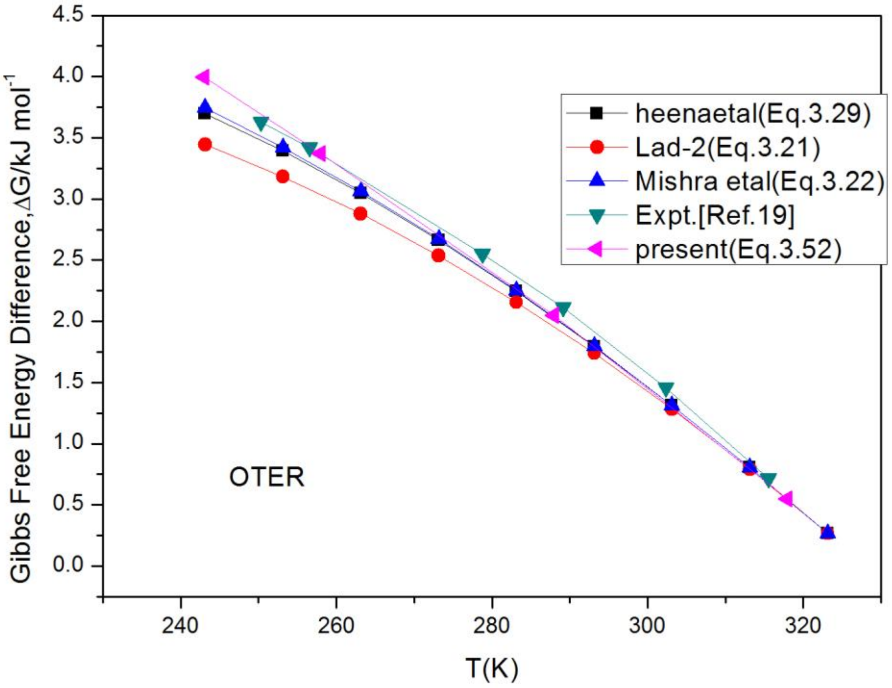


Fig. 3.6Gibbs free energy difference, ΔG as a function of temperature for OTER

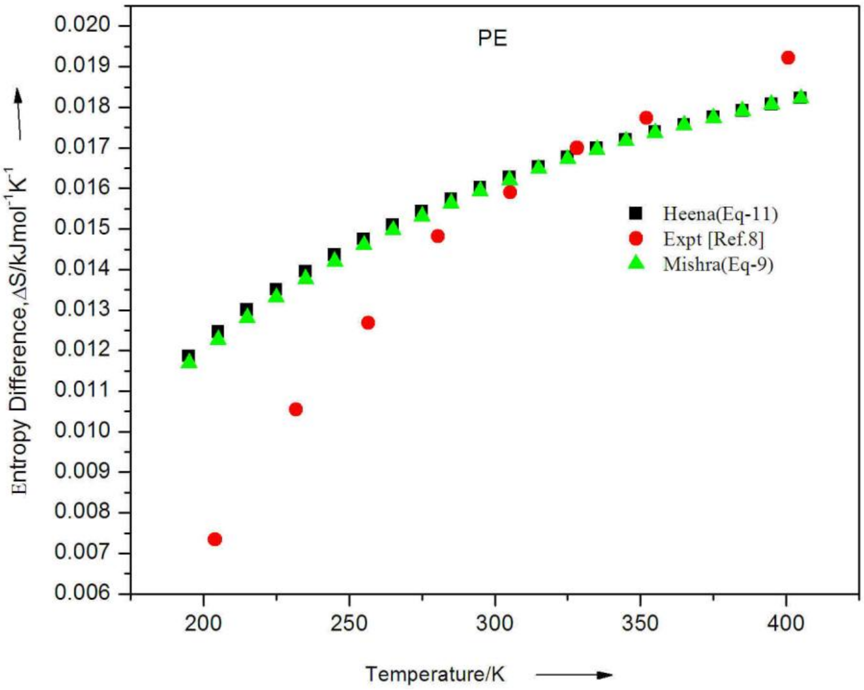


Fig. 3.7 Entropy difference, ΔS as a function of temperature for PE

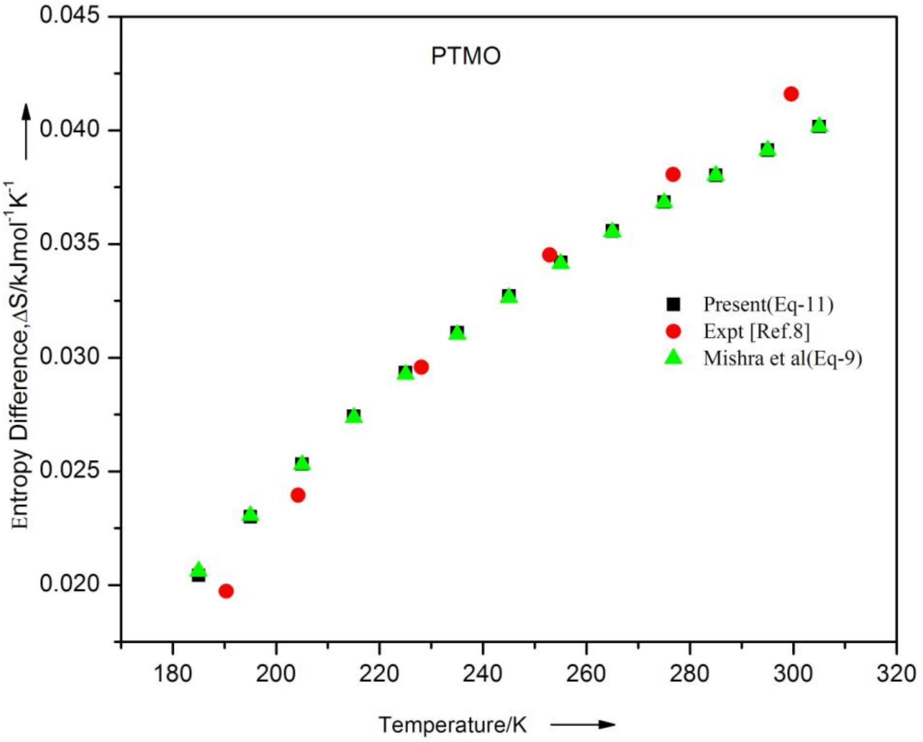


Fig. 3.8 Entropy difference, ΔS as a function of temperature for PTMO

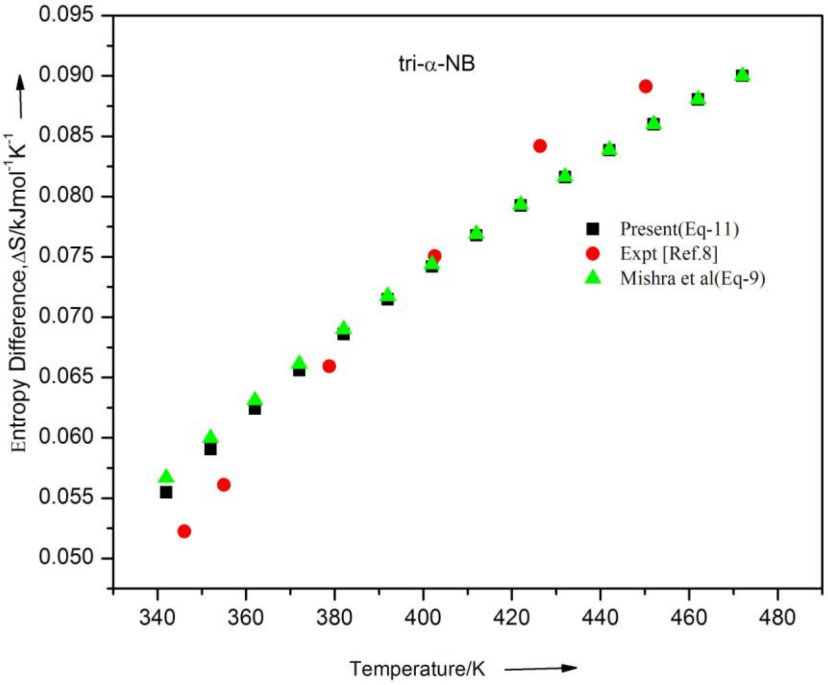


Fig. 3.9 Entropy difference, ΔS as a function of temperature for tri-α NB

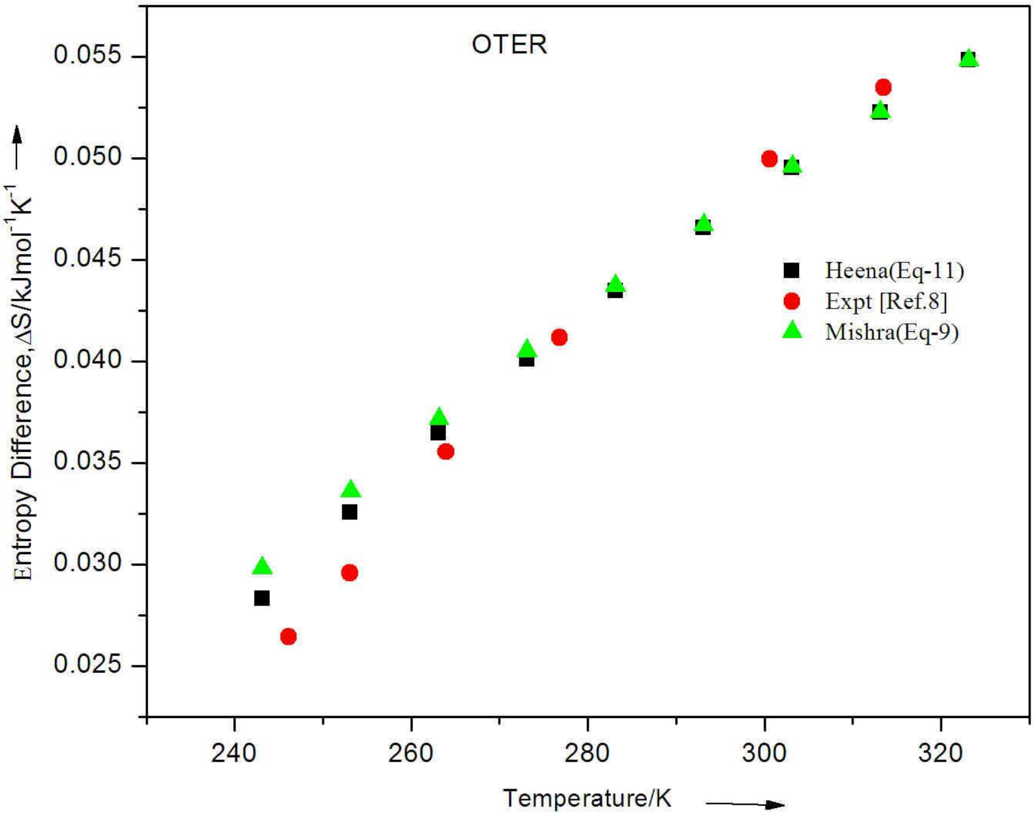


Fig. 3.10 Entropy difference, ΔS as a function of temperature for OTER

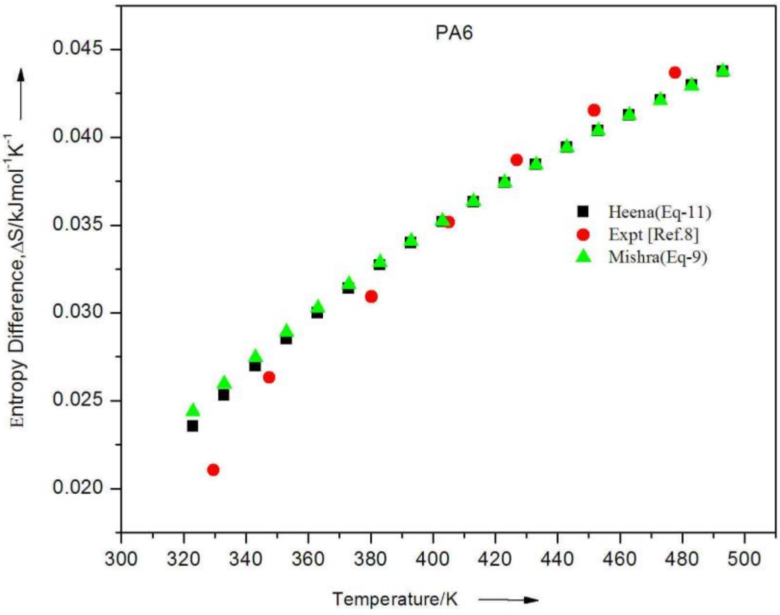


Fig. 3.11Entropy difference, ΔS as a function of temperature for PA6

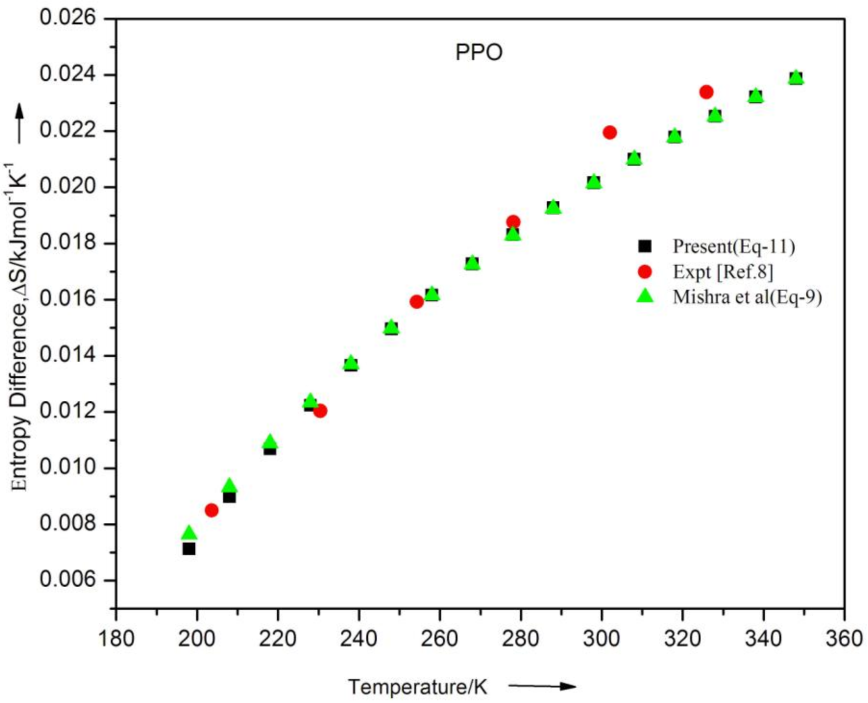


Fig. 3.12 Entropy difference, ΔS as a function of temperature for PPO

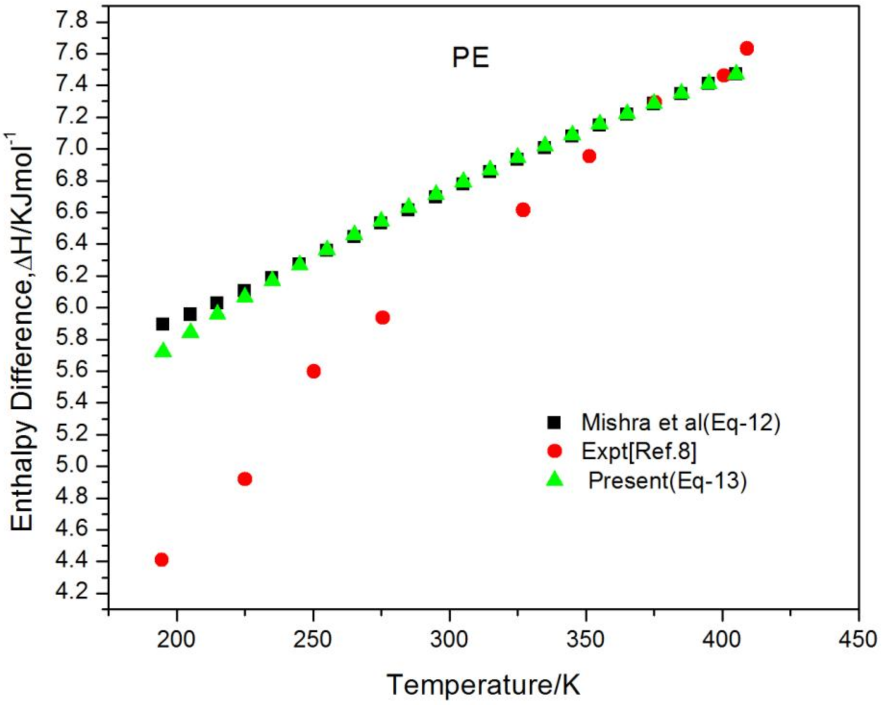


Fig. 3.13 Enthalpy difference, ΔH as a function of temperature for PE

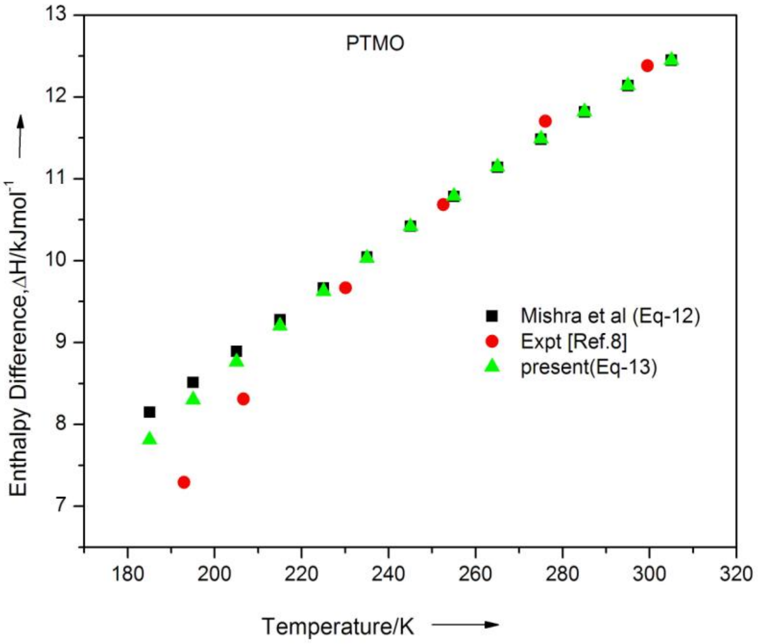


Fig. 3.14 Enthalpy difference, ΔH as a function of temperature for PTMO

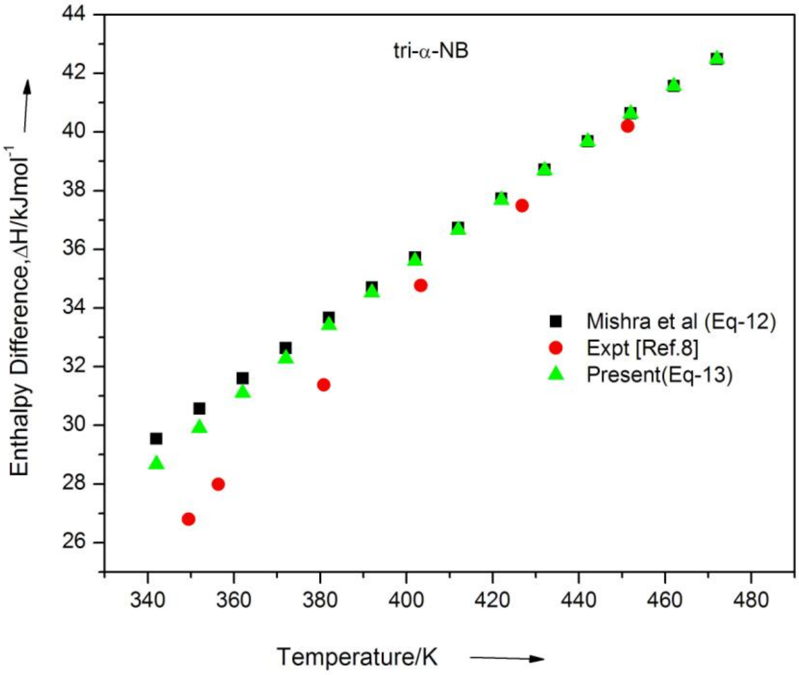
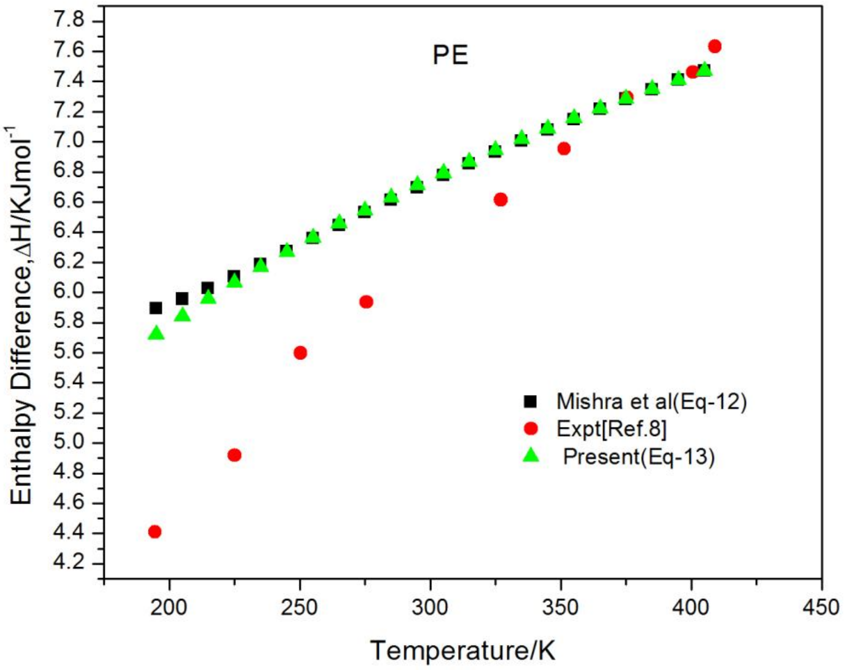


Fig. 3.15 Enthalpy difference, ΔH as a function of temperature for tri-α NB



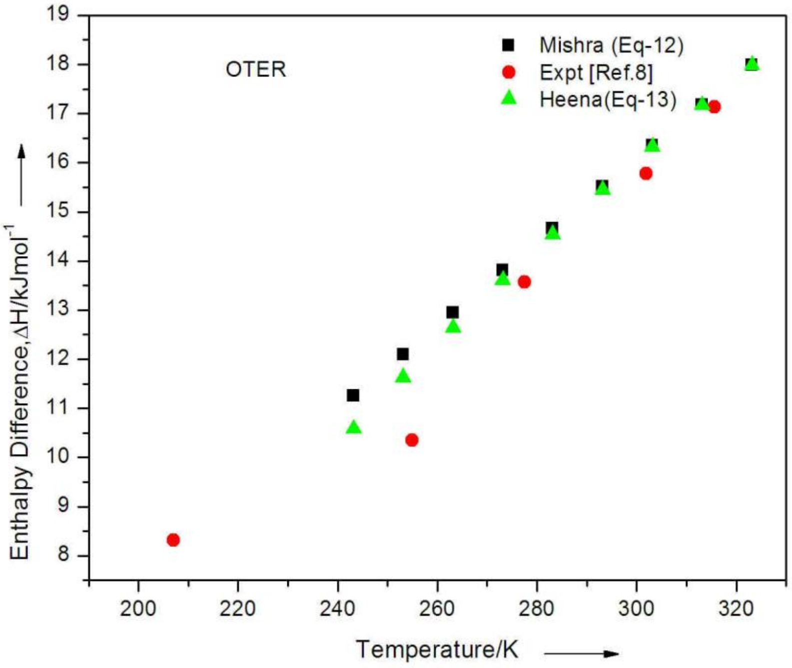


Fig. 3.16 Enthalpy difference, ΔH as a function of temperature for OTER

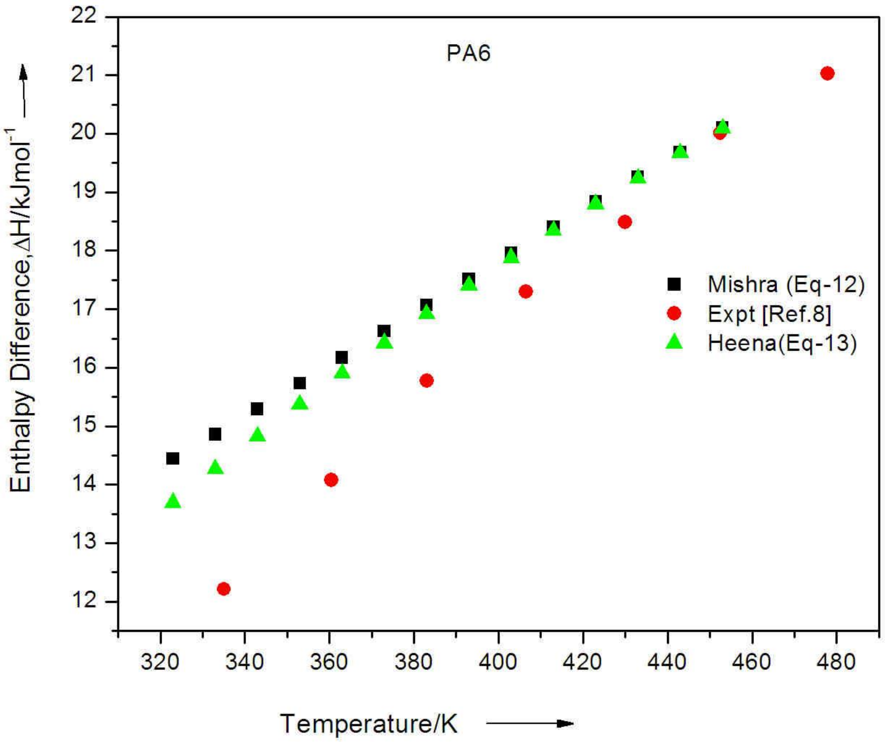


Fig. 3.17 Enthalpy difference, ΔH as a function of temperature for PA6

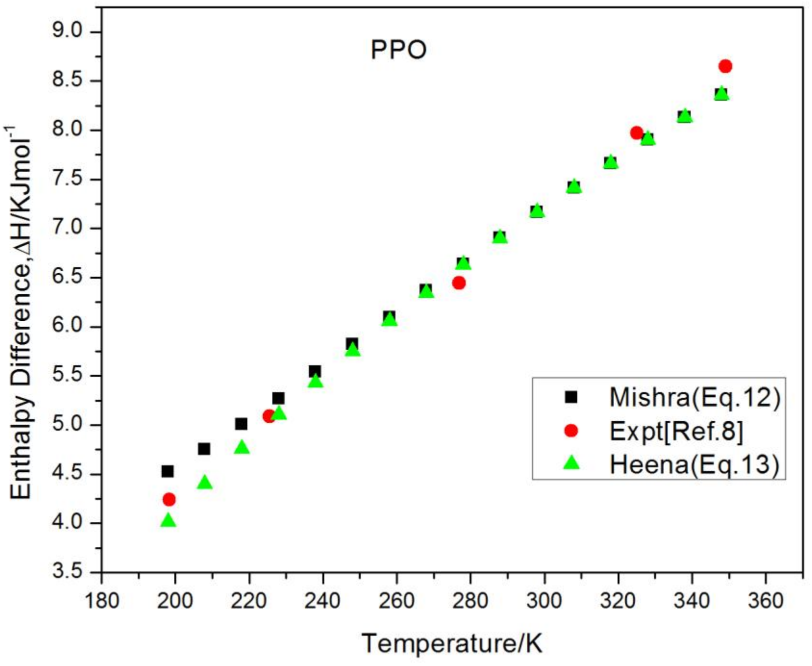


Fig. 3.18 Enthalpy difference, ΔH as a function of temperature for PPO

3.4 Conclusions

It is important to consider an appropriate variation of ΔCp with temperature while deriving an analytical expression for ΔG for bulk metallic glass forming alloys. All the earlier expressions for ΔG involve mainly two kinds of approximations. First the temperature dependence of ΔCp is assumed to be linear, and subsequently for simplified derivation it is approximated to be constant. Second, the logarithmic term appearing in the expression is

approximated with the help of a series expansion about Tm. These approximations in the expression for ΔG make it insensitive to the nature of the variation of ΔCp in the undercooled region and also limit its validity upto small undercooling (ΔT). Considering these limitations, three new expressions for ΔG, depending on the type of ΔCp variation (constant, hyperbolic and linear), are derived. Assumption of constant ΔCp in most of the glass forming alloys provides fairly accurate results and shows very small deviation even at temperature as low as $T \sim TK$. However, one of the indicators of enhanced GFA could be lower value of ΔG. Increased GFA, in turn, is associated with substantial increase in ΔCp and therefore hyperbolic variation of ΔCp has been taken and it accounts well for such systems which posses good glass forming ability. In case of magnetic liquid metals ΔCp rises linearly with temperature hence ΔG values derived using linear variation of ΔCp show excellent agreement with experimental results. The only difficulty involved in the present approach is the lack of prediction of the nature of variation of ΔCp (constant or hyperbolic) in the undercooled region i.e. there is no fixed criterion for choosing one of them a priori. The proposed expression for ΔG assuming linear and hyperbolic variation of ΔCp provides quite accurate results in the entire undercooled region of BMG forming alloys polymeric melts.ΔS and ΔH derived from so obtained ΔG values also lie very close to experimental points. Also, for polymer the ΔS values show good agreement with the experimental results compared to the earlier derived expressions. Hence, along with the exact variation of ΔCp the evaluation of the constants existing in ΔCp expressions is important in derivation of an expression for ΔG.

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