Thermal Behaviour of Zr\textsubscript{65}Cu\textsubscript{17.5}Ni\textsubscript{10}Al\textsubscript{7.5} Glassy Alloy

\textit{Daisman P.B. Aji\textsuperscript{1}, Triyono, and Yusep Mujalis}

Department of Mechanical Engineering, Universitas Trisakti
Jl. Kyai Tapa 1, Grogol, Jakarta, Indonesia 11440

Email: daisman.aji@trisakti.ac.id

Abstract. Estimating entropy of glass cannot be performed using the time-dependent and irreversible part of the heat capacity (\(C_p\)) which is measured in the glass-formation range. The difference of the estimate and the real change in entropy can be determined by calculating the change in the \(C_p dT\) and \(C_p d\ln T\) integrals before and after isothermal annealing by using DSC. In this paper, we report this estimation difference for Zr\textsubscript{65}Cu\textsubscript{17.5}Ni\textsubscript{10}Al\textsubscript{7.5} glassy alloy. The minimized annealing results in the \(C_p d\ln T\) integrals for the cooling and the heating paths approach the same value. We affirm that entropy is an ensemble-averaged value since the Clausius limits show that the estimation of the residual entropy is not affected significantly by irreversibility and its value can be estimated from the \(C_p\) data.

1. Introduction

Glass formation on cooling a liquid is characterized by two features: (i) properties measured in the glass-formation temperature range depending on the observation time, and (ii) structure of the glass formed spontaneously relaxes with time toward the equilibrium state of lower enthalpy, \(H\), and lower volume. When a glass is heated, its structure relaxes at a faster rate, and its apparent (measured) specific heat \(C_p\) decreases initially. When the temperature is sufficiently high its value is regained by a broad peak-like overshoot in the \(C_p\) against \(T\) plot. The temperature at which the structure of a liquid kinetically freezes on cooling is known as the fictive temperature, \(T_f\). It is estimated from the enthalpy change, i.e., by using the area confined by the \(C_p\) against \(T\) plot measured during cooling a liquid through the vitrification range at a fixed cooling rate \(q_c\). The glass-softening temperature \(T_g\) is defined as the temperature at which the structural relaxation time of a glass on heating at 20 K/min rate reaches 100 s. When \(q_c\) is higher than this rate, \(T_f\) of the glass formed is higher than its \(T_g\), and when \(q_c\) is low, \(T_f\) of the glass formed is lower.

Quenching of a liquid \((q_c > 10^5 \text{ K/min})\) produces a glass of \(T_f\) much higher than \(T_g\). When such a glass is heated at a fixed rate, the heat released on its structural relaxation appears as a rapid decrease in its measured \(C_p\) by a large amount. On further heating, a relatively small overshoot appears in \(C_p\) before the state of equilibrium melt is reached. When \(C_p\) data during the cooling is not available, \(T_f\) has been determined by analyzing the area under the \(C_p\) against \(T\) plot obtained by heating a glass at a fixed rate,
Such studies are currently used to define how \( T_f \) decreases with time and in doing so, \( T_f \) at a given instant is taken as the temperature on the super cooled liquid curve at which the extrapolated \( H \) of glass would be equal to that of the super cooled liquid [1,2]. Thus, \( T_f \) becomes a useful measure of thermal history of a glass. On structural relaxation at a fixed \( T_f \), \( C_p \) of a glass decreases monotonically with time according to a stretched exponential equation. The decrease contains the relaxation of several components, the main one being configurational [3].

Residual entropy, \( S_{\text{res}} \), of a glass, i.e., its entropy at zero Kelvin, is estimated by using relations of reversible thermodynamics. Gutzow and Schmelzer [4] have listed the \( S_{\text{res}} \) data of a large number of glasses. But these values appear to be in contrast with the precepts of statistical thermodynamics, according to which, \( S_{\text{conf}} = k_B \ln \Omega \), where \( k_B \) is the Boltzmann constant and \( \Omega \) the number of configurations of equal energy. Since the structure of a non-crystalline solid is fixed, \( \Omega = 1 \), and thus its \( S_{\text{conf}} \) should be equal to zero. Therefore, it would appear that a glass, like a perfect crystal, should obey the third law, i.e., its entropy should be zero at 0 K, irrespective of the method by it has been produced and whatever its thermal history. Since \( S_{\text{res}} \) is equal to the frozen-in configurational entropy, which decreases on structural relaxation, its value decreases as a glass structurally relaxes. This suggests that there is a conflict between the finite \( S_{\text{res}} \) obtained from classical thermodynamics and the zero value for \( S_{\text{res}} \) obtained from statistical thermodynamics.

Attempts to rationalize this conflict have been considered since the 1920s, and several recent papers [6,7] briefly describe its history. In discussing the mutually exclusive statistical and classical thermodynamics views, Kivelson and Reiss [8] focused on the possible loss of \( S_{\text{conf}} \) when a liquid vitrifies on cooling and concluded that \( S_{\text{res}} \) is unreal. Goldstein [5] critically discussed their views and concluded that arguments for the unreality of \( S_{\text{res}} \) are untenable in terms of both the second law of thermodynamics and known experiments and \( S_{\text{res}} \) is real. Since Goldstein, several authors [6,9,10] have discussed the configurational entropy, \( S_{\text{conf}} \), of a liquid and glass, by reviewing the evolution of the third law discussing theoretical aspects of the entropy of a non-equilibrium state [6] and describing experiments on the solubility and other properties of a glass [5,6,9], all concluding against the view that \( S_{\text{conf}} \) vanishes on vitrification. Reiss [10] appealed that \( S_{\text{res}} \) violates the causality principle, and suggested that the impression of \( S_{\text{res}} \) stems from inclusion of a path-irreversible segment in the thermodynamic cycle of the liquid and glass. Thus, \( S_{\text{res}} \) is an artifact from the use of the \( C_p \) data in this segment. He neither provided experimental evidence in support of his arguments nor suggested methods for testing it.

Goldstein [5] and Johari [9] have recently discussed experiments that may be used to resolve it. In an earlier paper, Johari [9] also described (thermodynamically) analogous kinetic freezing of defect diffusion in a crystal lattice and suggested that thermodynamic arguments [8,10] against the reality of \( S_{\text{res}} \) of glasses would apply equally well to crystals containing lattice defects. By using the spontaneous enthalpy decrease in a calorimetric experiment, and the known enthalpy of formation of vacancy, one can calculate the decrease in the (fractional) vacancy population, \( \chi \), and use it to estimate the decrease in \( S_{\text{conf}} \) from the relation \( S_{\text{conf}} = -R [\chi \ln \chi + (1-\chi) \ln(1-\chi)] \), where \( R \) is the gas constant. This may be compared against the change determined from the \( C_p \)dln\( T \) integral.

Since the \( C_p \) measured during the rate-heating of a glass includes the effects of spontaneous enthalpy loss from structural relaxation, the quantity determined from the \( C_p \)dln\( T \) integral is not the entropy change. This is evident from Clausius inequality, \( dS > dq_{\text{rev}}/T \), where \( dq_{\text{rev}} \) is the irreversible heat transfer at temperature \( T \). Nevertheless, it provides the upper and lower limits of the entropy, the Clausius limits when data are available for both the cooling and the heating paths. For maintaining a distinction between the real entropy change and the quantity determined from the \( C_p \)dln\( T \) integral on the cooling and heating paths through the glass-liquid transformation temperature range, we refer the quantity determined from the integral as \( \Delta S \) instead of \( \Delta S \), and \( T_f \) determined from it as \( T_f^\sigma \). The usual \( T_f \) determined from the \( C_p \)d\( T \) integral is denoted as \( T_f^H \). In principle, \( T_f^\sigma \) would not be equal to \( T_f^H \), and a slight difference between the two is also expected on geometric considerations of the two integrals. Therefore, if one finds \( T_f^\sigma \) to be closely similar to \( T_f^H \) it would show that the time-dependence of the
thermodynamic path between glass and liquid is insufficient to produce a significant difference between the Clausius limits, i.e. the upper and lower limits of the entropy change, from the real entropy change, and $S_{\text{res}}$ would be real. But if they are found to be very different then $S_{\text{res}}$ would be unreal. We need to substantiate this analysis by showing that the configurational and residual entropy of a glass is real. Here we do so by determining $T_f^H$ and $T_f^H$ for a Zr$_{65}$Cu$_{17.5}$Ni$_{10}$Al$_{7.5}$ metallic glass studied here and examine if $T_f^H$ and $T_f^H$ are determined from the $C_p$ data obtained here by simulations from the non-exponential, non-linear relaxation model for glass-liquid relaxation differ substantially.

We also performed new calorimetric study on Zr$_{65}$Cu$_{17.5}$Ni$_{10}$Al$_{7.5}$ melt and glass in order to use a direct approach for ascertaining whether $S_{\text{res}}$ could be an artefact of using $\Delta \sigma$. In this study, a sample was cooled at a certain rate to form a glass and the glass was heated at the same rate. By using the (time-dependent) $C_p - T$ data on the cooling and heating paths, we determine the Clausius limits. These experiments also show that $S_{\text{res}}$ cannot be zero.

2. Results

The quantity $dH/dt$ measured by DSC experiments was divided by the heating rate ($q_h = dT/dt$) and thus converted to $dH/dT$. This quantity is proportional to the $C_p$ of the sample, but for accuracy we use our original plots.

New experiments performed on Zr$_{65}$Cu$_{17.5}$Ni$_{10}$Al$_{7.5}$ glass yielded the quantity $dH/dT$. Its plot against $T$ for cooling the melt at 20 K/min

$T_g$ and $T_f$ can be determined from the plot of $C_p$ against $T$, or from a DSC scan. The method uses the $C_p$ or $dH/dT$ data obtained by heating at 10 K/min rate a glass that was formed on cooling the melt at the same rate. The rate of change of a function with $T$ is fulfilled. Here, $C_{p,\text{liq}}$ is specific heat of the liquid, $C_{p,\text{glass}}$ that of the glassy state and $T^*$ is any temperature above the transition region when the state is a liquid, $T'$ is the temperature well below the glass transition region, and $C_{p,\text{meas}}$ is the measured $C_p$ on heating from the glassy to liquid state. For use in the integral, $C_{p,\text{glass}}$ at $T > T_g$ is obtained from a curve drawn as an extension of the curve for $C_{p,\text{glass}}$ from $T < T_g$ to higher temperatures. This extension is either done by linear interpolation from $C_{p,\text{glass}}$ or done by fitting the $C_{p,\text{glass}}$ data to a polynomial equation. The longer the extension, the greater is the error in the estimate of $C_{p,\text{glass}}$ at $T > T_g$. One can estimate $T_f'$ of a glass for both cases, when $q_h = q_c = 10$ K/min, and when $q_h = 10$ K/min and $q_c = 80$ K/min. In both cases, $T_g$ was taken to be equal to $T_f'$. ($T_g$ itself is determined either by drawing a tangent to the maximum slope point and determining its intersection with the extended curve from the glassy state or by the midpoint temperature of the sigmoid-shape curve.) In the current practice of using $q_c = q_h = 20$ K/min, it is assumed that the calorimetric relaxation time at the $T_g$ obtained from the DSC scan is 100 s.

We first determine $T_f'$ in Eq. (1), which is in the range of sigmoid-shape increase. When $T_f'$ satisfies the conditions of Eq. (1), $T_g^H = T_f'$. We write Eq. (1) in terms of the corresponding $\Delta \sigma$ by replacing $dT$ by $d\ln T$,

$$
\int_{T_g^H}^{T_f'} (C_{p,\text{liq}} - C_{p,\text{glass}}) dT = \int_{T_g^H}^{T_f'} (C_{p,\text{meas}} - C_{p,\text{glass}}) dT
$$

(1)
Similarly, when the conditions of Eq. (2) are satisfied, \( T_g^{\sigma} = T_f^{\sigma} \)

Eqs. (1) and (2) are useful also when \( q_h > q_c \), or when the glass has been annealed. But when \( q_c >> q_h \), i.e., when a glass is formed by quenching, Eqs. (1) and (2) can still be used, but they require extrapolation from a very low temperature. Yue et al [10] described a procedure for estimating \( T_f \). Here we modified their procedure, the \( C_p dT \) integral for the enthalpy release is matched with the \( C_p dT \) integral for the enthalpy gain by using \( T_g^H \) determined by the break-point in the DSC heating scan for 20 K/min rate of a glass formed by cooling the melt at 20 K/min rate. Thus, to determine \( T_f \) for such glasses, one uses two DSC scans. One is obtained by heating the plot for a quenched glass referred here as scan-1, and the other by heating the same glass formed by cooling at 20 K/min, referred here as scan-2. \( T_f^H \) is determined by area-matching according to the relation,

\[
\int_{T_{eq}}^{T_g^H} (C_{p,\text{glass}} - C_{p,\text{liq}}) dT = \int_{T_f}^{T_g^H} (C_{p,\text{glass}} - C_{p,\text{liq}}) dT
\]

where \( C_{p,\text{glass}} \) is the data from scan-1, \( C_{p,\text{liq}} \) that from scan-2, \( T_{eq} \) is the temperature at which scan-1 begins to deviate from scan-2 at \( T < T_g^H \), \( T_{eq} \) is a temperature in the equilibrium liquid state, and \( C_{p,\text{liq}} \) and \( C_{p,\text{glass}} \) are as defined earlier. As mentioned earlier here, \( C_{p,\text{glass}} \) at \( T > T_g \) is extrapolated either linearly or by fitting a curved line to the measured data obtained at \( T < T_g \). The resulting error in \( T_f^H \) is higher the longer is the extrapolation of \( C_p \) to the liquid state.

To estimate \( T_f^\sigma \), we replace \( dT \) in Eq. (3) by \( d\ln T \),

\[
\int_{T_{ref}}^{T_f^\sigma} (C_{p,2} - C_{p,1}) d\ln T = \int_{T_f}^{T_g^\sigma} (C_{p,\text{liq}} - C_{p,\text{glass}}) d\ln T
\]

and find the value of \( T_f^\sigma \) that satisfies the conditions of Eq. (4).

It is understood that values of \( T_f^H \) and \( T_f^\sigma \) can be estimated only with reference to either \( T_g^H \) or \( T_g^\sigma \), which in turn are determined for low values of both \( q_c \) and \( q_h \). When \( C_p - T \) data are not available, the heat flow rate (in W/mol) measured directly from a DSC scan may be divided by \( q_h \) to obtain \( (dH/dT) \) which may be used in place of \( C_p \).

To illustrate the method used, we determine \( T_g^H \) in Eq. (1) by using the \( C_p \) data for Zr\(_{65}\)Cu\(_{17.5}\)Ni\(_{10}\)Al\(_{7.5}\) glass. The data for the glass that had been formed by cooling its melt at 20 K/min. First, we chose a \( T \) in the range of sigmoid-shape increase in \( C_p \) and determined the areas of the shaded regions as shown in the insert. When the temperature chosen was such that the area shaded by horizontal lines was equal to the sum of the two areas shaded by vertical lines (to satisfy the conditions of Eq. (1)), that temperature is equal to \( T_g^H \). This temperature is 668 K. The same area matching but by using \( \Delta\sigma \) yields \( T_g^\sigma = 668 \) K. We conclude that the \( T_g \) thus estimated, \( T_g^H \) and \( T_g^\sigma \) have the same values.
We now determine the  of Zr65Cu17.5Ni10Al17.5 glass heated at 20 K/min rate. In the main frames, curve 1 is the plot of from the first scan, and curve 2 from the rescan, and curve 3 is an extrapolation from the glassy state which is used as a baseline to determine the difference, ( –  ), needed for determining from Eq. (3). Values of estimated from curve 2 are indicated in both figures, and its value 668 K is the same as before. Analysis yields as 693 K. By using the corresponding plots, we determine the of the Zr65Cu17.5Ni10Al17.5 glass as 694.4 K.

The values determined from the enthalpy and entropy integrals, or , and the values of , and , the ratio along with the values of and and the ratio are also listed in Tables 1 and 2. The ratio increases as increases. We estimate a combined error of about 4 % in the and in the  measurements, in our reading of the published data and in determining the path integrals. While geometrical considerations indicate that would differ slightly from , the difference is within the combined errors.

Table 1. The and from and from the integrals and from the integrals, the ratio of the two , the integrals used in determining , and their ratio.

| Material |  |  |  |  |  |  |  |  |
|-----------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Zr65Cu17.5Ni10Al17.5 | 668 | 668 | 693 | 694.4 | 4.86 | 8.7 | 1.00 | 657 |

(1) Values obtained when the assumed for the ultra-viscous liquid is taken as:
(a) zero, (b) - 4.57 x 10^4 Jg^-1 K^-2, and (c) 7.58 x 10^4 Jg^-1 K^-2.
(2) Values obtained when the assumed for the ultra-viscous liquid is taken as:
(a) zero, (b) - 9.65 x 10^4 Jg^-1 K^-2, and (c) 7.36 x 10^4 Jg^-1 K^-2.
(3) Values obtained when the assumed for the ultra-viscous liquid is taken as:
(a) zero, (b) - 7.96 x 10^5 Jg^-1 K^-2, and (c) 9.24 x 10^5 Jg^-1 K^-2.

Table 2. The and from and from the integrals and from the integrals, the ratio of the two , the integrals used in determining , and their ratio.

| Material |  |  |  |  |  |  |  |
|-----------|----------------|----------------|----------------|----------------|----------------|----------------|
| TNM-simulation | 507 | 508 | 564 | 565 | 54.47 | 0.1461 | 1.00 | 373.1 |
| (, ) | 507 | 509 | 519 | 516 | 3.06 | 0.0121 | 1.00 | 252.9 |

Finally, we obtained the plots of normalized against . The simulation was performed to obtain the plots of normalized against . We used, , 0.5, , 323 kJ/mol in all cases. For the slow cooling rate, we chose, , 60 K/min and for heating , 20 K/min. For fast cooling, , 7 MK/min and the same of 20
K/min. From the plots obtained, we determined $T_g^H$ and $T_g^\sigma$, $T_f^H$ and $T_f^\sigma$, and the values of $A_H$ and $A_\sigma$, as described above. These values and the ratios $T_f^\sigma / T_f^H$ and $A_H / A_\sigma$ are also listed in Table 2. The simulated plots of normalized $C_p$ are not shown.

To investigate whether or not the amount of entropy change on cooling a liquid to glass is the same as that on heating a glass to liquid, we integrate the respective cooling plots for the metallic glasses between two temperatures, one in the glassy state, $T_{\text{glass}}$, and other in the liquid state, $T_{\text{liq}}$, as follows,

$$
H_{\text{cool}} = c \int_{T_{\text{liq}}}^{T_{\text{glass}}} \left( \frac{dH}{dT} \right)_q dT; \quad \Delta H_{\text{heat}} = c \int_{T_{\text{liq}}}^{T_{\text{glass}}} \left( \frac{dH}{dT} \right)_q dT
$$

or

$$
\Delta \sigma_{\text{cool}} \geq c \int_{T_{\text{liq}}}^{T_{\text{glass}}} \left( \frac{dH}{dT} \right)_q d \ln(T) ; \quad \Delta \sigma_{\text{heat}} \leq c \int_{T_{\text{liq}}}^{T_{\text{glass}}} \left( \frac{dH}{dT} \right)_q d \ln(T)
$$

where $c$ is a material-dependent calibration constant, i.e., $C_p = c(dH/dT)_q$, $\Delta H_{\text{cool}} = (H_{\text{liquid}} - H_{\text{glass}})$ on cooling, $\Delta H_{\text{heat}} = (H_{\text{glass}} - H_{\text{liquid}})$ on heating, $\Delta \sigma_{\text{cool}}$ is higher than the real entropy change on cooling and $\Delta \sigma_{\text{heat}}$ is lower than the real entropy change on heating.

The plots are terminated at $T_{\text{glass}}$ and $T_{\text{liq}}$ where the data obtained on the cooling path appear to merge with those obtained for the heating path. For $Zr_{65}Cu_{17.5}Ni_{10}Al_{17.5}$ glass and liquid, $T_{\text{glass}} = 437.2$ K and $T_{\text{liq}} = 543$ K and the integrals were done with respect to the baseline with the value at $(dH/dT)_q$ at $T_{\text{glass}}$. The values of $\Delta H_{\text{cool}}$, $\Delta H_{\text{heat}}$, $\Delta \sigma_{\text{cool}}$ and $\Delta \sigma_{\text{heat}}$ are listed in Table 3. Here the ratios $x_H = (\Delta H_{\text{cool}} - \Delta H_{\text{heat}}) / \Delta H_{\text{cool}}$ and $x_\sigma = (\Delta \sigma_{\text{cool}} - \Delta \sigma_{\text{heat}}) / \Delta \sigma_{\text{cool}}$ are also listed.

We also simulated the plots of normalized $C_p - T$ plots for heating and for cooling by using the Tool-Narayanaswamy-Moyghan equation for $q_c = q_h = 20$ K/min in one case and for $q_c = q_h = 1$ K/min in the second case. These plots were analyzed in the same manner as the plots of $(dH/dT)_q$ for the metallic glasses and the various parameters obtained are listed also in Table 3.

Table 3. The cooling and heating rates $q$, the temperature limits of integration $T_{\text{glass}}$ and $T_{\text{liq}}$, the $\Delta H/c$ and $\Delta \sigma/c$ measured for cooling and for heating and the percentage differences, $x_H$ between $\Delta H_{\text{cool}}$ and $\Delta H_{\text{heat}}$ and $x_\sigma$ between $\Delta \sigma_{\text{cool}}$ and $\Delta \sigma_{\text{heat}}$.

| Material | $q$ (K/min) | $T_{\text{glass}}$ (K) | $T_{\text{liq}}$ (K) | $\Delta H_{\text{cool}}/c$ (Jmol⁻¹) | $\Delta H_{\text{heat}}/c$ (Jmol⁻¹) | $x_H$ % | $\Delta \sigma_{\text{cool}}/c$ (Jmol⁻¹ K⁻¹) | $\Delta \sigma_{\text{heat}}/c$ (Jmol⁻¹ K⁻¹) |
|----------|-------------|-------------------------|---------------------|-----------------------------|-----------------------------|------|--------------------------------|--------------------------------|
| Zr-65Cu-17.5Ni-10Al-17.5 | 20          | 613                     | 707                 | 824.6                       | 823.4                       | 1.7  | 1.44                          | 1.39                          |
| TNM-simulation* | 20          | 415                     | 553                 | 56.3                        | 57.2                        | 0.25 | 0.102                         | 0.105                         |
| TNM-simulation* | 1           | 416                     | 541                 | 53.6                        | 53.1                        | 0.25 | 0.107                         | 0.101                         |

* $C_p$ integral values, i.e. $c = 1$.

3. Discussion

It is generally understood that the rate at which a liquid is cooled to form a glass determines its enthalpy as well as its frozen-in entropy. The rate at which a glass is heated determines the extent of its enthalpy loss by structural relaxation that shows up as a decrease in $C_p$ on initial heating. This decrease appears as a broad minimum before an endothermic overshoot indicating the enthalpy recovery before $C_{p, \text{liq}}$ is reached. This contrast the Reiss’s view [10] of the configurational entropy loss based on the Boltzmann equation in which the rate at which a liquid is cooled to form a glass only determines the
enthalpy. The entropy of a glass is zero and remains so until the equilibrium or liquid state is reached even when structural relaxation of a glass decreases the enthalpy. Since the measured \( C_p \) is time-dependent, Kivelson and Reiss [8] and Reiss [10] have argued that it cannot be used to obtain the entropy because \( dS > (dq_{\text{rev}} / dT) \). In thermodynamic studies in the glass-liquid transformation temperature range, one finds a spontaneous decrease in both \( C_p \) and enthalpy at any instant on both the cooling path and the heating path of a temperature cycle. But here we find that \( T^\sigma_f \) obtained is closely similar to \( T^H_f \).

Also, in all cases, \( T^\sigma_S \) is equal to \( T^S_S \) for all cases.

It is recognized that, (i) strictly speaking, there is a path-irreversible segment between the liquid and glass states, and (ii) liquid-like structural fluctuations do not occur in a (rigid) glass. Regarding (i), the above-given finding show that consequences of the path-irreversible segment are too small to make \( T^\sigma_f \) differ significantly from \( T^H_f \). This would suggest that for such purposes, calorimetric measurements meet the classical thermodynamics criteria for path-reversibility. Regarding (ii), one cannot deny Reiss [10] that \( S_{\text{rev}} \) violates the causality principle when Boltzmann equation is used, but a resolution of this violation would not be found in the difference of \( C_p \) values on the cooling and heating path in the glass-liquid transformation temperature range.

From the normalized \( C_p - T \) data obtained by simulations in a TNM model, we obtain \( T^\sigma_f \) slightly higher than \( T^H_f \), and the difference is more when the cooling rate is high, but it is not substantial and probably reflects the fact that geometrical considerations alone would not yield the same values of \( T^\sigma_f \) and \( T^H_f \) for an ideal set of data.

We now discuss the magnitudes of \( \Delta H_{\text{cool}} \) and \( \Delta H_{\text{heat}} \) values given in Table 3. Conservation of energy requires that \( \Delta H_{\text{cool}} \) be equal to \( \Delta H_{\text{heat}} \). This would be the case if \( T_{\text{glass}} \) was near 0 K or at a temperature such that structural relaxation effect were vanishingly small. Our experiments yield \( \Delta H_{\text{cool}} \) about 1\% higher than \( \Delta H_{\text{heat}} \). This may be not be due to a possible enthalpy loss on structural relaxation during the time period between the end of the cooling at \( T_{\text{glass}} \) and beginning of the heating from \( T_{\text{glass}} \). Briefly, if the loss were small the decrease in the slope of the \( H - T \) plot would be extremely small and would not appear in the measured \( C_p \) (or in \( dH/dT \)) in the usual study, and \( \Delta H_{\text{heat}} \) obtained from Eq. (1) would be higher than \( \Delta H_{\text{cool}} \) by an amount equal to this loss. But we find the opposite. The manner of resolving the cooling and heating scans also causes an error. To elaborate, cooling and heating curves are obtained in a continuous cycle in which the heat flow signal changes from positive to negative in a DSC experiment and the two curves are separated by vertically displacing one curve and inverting it. The 2\% higher value of \( \Delta H_{\text{cool}} \) would contain this error. The \( \Delta \sigma_{\text{cool}} \) determined from Eq. (6) is about 3\% higher than \( \Delta \sigma_{\text{heat}} \). This is partly attributable to this error plus the cumulative errors in the \( dH/dT \) measurements, in the uncertainty of determining \( T_{\text{glass}} \) at which the cooling and heating curves meet, and in the integration procedure which also cause \( \Delta H_{\text{cool}} \) and \( s \)

\( H_{\text{heat}} \) to differ.

The corresponding values obtained by analyzing the data for \( C_p \) simulated from the Tool-Narayanaswamy-Moyyinihan model are also listed in Table 3. For the cooling and heating paths for \( q = 20 \text{ K/min} \), \( x_f \) differs by 0.3\%, and \( x_r \) by 1.9\%, and for \( q = 1 \text{ K/min} \), \( x_f \) differs by 0.2\%, and \( x_r \) by 1.8\%. It is between 1.8\% for \( x_r \) found for the measured data for Zr57Cu21.5Ni10Al17.5.

\( C_p \text{d}f \) integral cannot be used for determining the entropy change in the glass-liquid transformation range because of the Clausius inequality, \( dS > (dq_{\text{rev}} / T) \). Also, the (time-dependent) \( C_p \) measured on the heating path through the glass-liquid range differs from the \( C_p \) measured on the cooling path, and classical thermodynamics is not used for systems whose properties change with time. Nevertheless, the Clausius inequality helps to ascertain the lower and upper limits of the actual entropy from \( C_p \) data when
measurements are made on both the cooling and heating paths. These are known as Clausius limits for the entropy. The Clausius limits give the upper and lower bound values of the entropy change, and the entropy at $T_{bg}$ is the same. A higher change in $\Delta \sigma$ would correspond to the lower entropy at $T_{glass}$ and a lower change in $\Delta \sigma$ to a higher entropy at $T_{glass}$. Thus $\Delta \sigma$ of a glass determined from the cooling path would be lower than the real entropy and that determined from the heating path would be higher.

Goldstein [5] also analyzed the errors in determining the entropy of a structurally relaxing glass from $C_p - T$ data obtained by using both the adiabatic calorimetry and DSC techniques. He did so by using several activation energies within the approximation of single-relaxation time and by using different $q_c$ and $q_h$. For $q_c = q_h (= 0.001 \text{ K/s})$, in his Table III, the minimum error in the entropy difference divided by the change in $C_p$ is 1.2%, and maximum error is $\sim 4.8\%$. He concluded that the error was negligibly small when adiabatic calorimetry was used, but it was a few percent when DSC was used. The error increased when $q_c$ was higher than $q_h$ and decreased when $q_c$ and $q_h$ were low. The $2\%$ difference between $\Delta \sigma_{coo}$ and $\Delta \sigma_{heat}$ noted in Table 3 is consistent with this estimate. In a more recent and closely related study, Fotheringham et al [12] have provided a comprehensive discussion of the subject by using data on two commercial optical glasses. They compared both the lower limit of $S_{res}$ resulting from the use of Clausius limits and the upper limit given by $S_{conf}$ of an equilibrium liquid with the same $T_f$ and found that the difference between $S_{res}$ and the Clausius limit is very small and negligible, in agreement with the earlier analyses. There is little doubt that the $C_p \frac{dT}{T}$ integral would not yield the entropy change. It only yields the upper bound value of the actual entropy change, $\Delta S$, on the cooling path and lower bound value on the heating path. The difference between the two extremes is usually orders of magnitude less than the lower bound value of the actual entropy. Unfortunately, this aspect has not been generally recognized and Gupta [13] regarded it as a measure of $\Delta S$. To avoid confusion with $\Delta S$, we consistently use here the term $\Delta \sigma$ for estimates of the $C_p \frac{dT}{T}$ integral in the liquid-glass transformation range.

$S_{res}$ of Zr50Cu27.5Ni10Al17.5 glass can not be estimated here, and the constant $c$ used in Eqs. (5) and (6) to convert $(dH/dT)_h$ to $C_p$ is not available for determining the upper and lower bound values of $S_{res}$. But one expects that $S_{res}$ would be close to the entropies of mixing, which is 7.98 J/(mol K). The real $S_{res}$ of the glass can differ by about $2\%$ from the values measured on the heating or on the cooling path. But this amount is not enough to suggest that $S_{res}$ would be reduced to zero if the limits of the Clausius inequality relative to the real entropy value are taken into account. Therefore, we deduce that the effect of time-dependence and enthalpy release on the measured $C_p$ (or $dH/dT)_h$ has little effect on $\Delta \sigma$ for $q_c = q_h$.

The data in Table 1 show that the $T_f^\sigma/T_f^H$ ratio is close to 1 within the combined errors of $4\%$. Now, if use of $\Delta \sigma$ were incorrect, one would not find the ratio $T_f^\sigma/T_f^H$ equal to 1 for any of the glasses. This shows that the upper and lower limits of the entropy determined from use of $\Delta \sigma$ on the cooling and heating paths may be too close to make $T_f^\sigma$ differ from $T_f^H$ of these glasses within the combined errors. As mentioned earlier here, Goldstein [14] had estimated the error in the entropy change from the use of $C_p$ data for an irreversible process of glass relaxation. For adiabatic calorimetry measurements, he found that the error was negligible relative to the estimates of $S_{res}$ and the measured entropies of glass and liquid. The errors were significant when $C_p$ data were obtained from DSC, and also the errors were least when $q_c$ was the same as $q_h$. Our finding that $T_f^\sigma$ is the same as $T_f^H$ within the combined errors may appear to support his estimates. We also stress that such calculations do not indicate reversibility of the path, only that consequence of such calculation in terms of the upper and lower limits of the actual entropy is not large enough to make a significant difference between $T_f^H$ and $T_f^\sigma$. 

International Conference on Science and Innovated Engineering (I-COSINE)  
IOP Conf. Series: Materials Science and Engineering 536 (2019) 012004  
doi:10.1088/1757-899X/536/1/012004
4. Conclusion

We conclude that fictive temperature determined from the entropy change by using a large and broad, time-dependent irreversible segment of $C_p$ in the thermodynamic path between a glass and liquid is the same as that determined from the enthalpy change. Thus, $S_{res}$ of glass may not be an impression resulting from use of this irreversible segment. The two fictive temperatures differ, (i) when the $C_{p,\text{liq}}$ and $C_{p,\text{glass}}$ data are extrapolated to high temperatures without the help of data in the liquid state, and (ii) when the samples have a high strain energy and/or large surface area. Therefore, the fictive temperature of such glasses is not reliably determined.

The continuous decrease in the entropy from liquid to glass is much less than the decrease in the configurational entropy, which would be at least the entropy of mixing of the metal alloys. It seems that a resolution for the dichotomy between the statistical entropy and calorimetric entropy of glass would not be resolved by an appeal to the time-dependent $C_p - T$ path in the glass–liquid transformation temperature range.

Acknowledgement

The authors are grateful for the 2017/2018 grant in this research from the Faculty of Industrial Technology, Universitas Trisakti.

References

[1] Inoue, A., Kato, A., Zhang, T., Kim, S.G., and Masumoto, T., Mater. Trans. JIM 32 (1991) 609.
[2] J.W.P. Schmelzer, V.M. Fokin, A.S. Abyzov, E.D. Zanotto, I. Gutzow, Int. J. Appl. Glass Sci. 1, 16 (2010).
[3] E. Donth, The Glass Transition: Relaxation Dynamics in Liquids and Disordered Materials (Springer, Berlin, 2001).
[4] Aji, D.P.B. and Johari, G.P., Enthalpy and entropy change on structural relaxation of Mg65Cu25Tb10 glass, Thermochimica Acta 503-504 (2010) 121-131.
[5] Balanzat, E., Stanley, J.T., Marry, C., and Hillairet, J., Acta Metall. 33 (1985) 785.
[6] Inoue, A., Masumoto, T., and Chen, H.S., J. Mater. Sci. 20 (1985) 4057.
[7] Johari, G.P. and Shim, J.G., J. Non-Cryst. Solids 261 (2000) 52.
[8] Johari, G.P. and Perez, J., Mol. Phys. 83 (1994) 235.
[9] Hodge, I.M., J. Non-Cryst. Solids 169 (1994) 211.
[10] Reiss, H., J. Non-Cryst. Solids 355 (2009) 617.
[11] Yue, Y.Z., Christiansen, J. de C., and Jensen, S.L., Chem. Phys. Lett. 357 (2002) 20.
[12] Fotheringham, U., Baltes, A., Muller, R., and Conradt, R., J. Non-Cryst. Solids 355 (2009) 642.
[13] Gupta, P.K., in Proc. 10th Presentations of the Otto-Schott-Research Award, Bange, K. (Ed.), Verlag Deutschen Glastechnischen Gesselschaft, Offenbach, Germany, 2009, p. 125.
[14] Goldstein, M., J. Chem. Phys. 64 (1976) 4767.