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Thermal Behaviour of $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ Glassy Alloy

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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 $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ 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 ($q_c > 10^5$ 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,



q_h . 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 , 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_{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_{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, $S_{conf} = k_B \ln \Omega$, where k_B is the Boltzmann constant and Ω the number of configurations of equal energy. Since the structure of a non-crystalline solid is fixed, $\Omega = 1$, and thus its S_{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_{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_{res} obtained from classical thermodynamics and the zero value for S_{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_{conf} when a liquid vitrifies on cooling and concluded that S_{res} is unreal. Goldstein [5] critically discussed their views and concluded that arguments for the unreality of S_{res} are untenable in terms of both the second law of thermodynamics and known experiments and S_{res} is real. Since Goldstein, several authors [6,9,10] have discussed the configurational entropy, S_{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_{conf} vanishes on vitrification. Reiss [10] appealed that S_{res} violates the causality principle, and suggested that the impression of S_{res} stems from inclusion of a *path-irreversible* segment in the thermodynamic cycle of the liquid and glass. Thus, S_{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_{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, x and use it to estimate the decrease in S_{conf} from the relation $S_{conf} = -R [x \ln x + (1-x) \ln(1-x)]$, where R is the gas constant. This may be compared against the change determined from the $C_p d \ln T$ 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 $C_p d \ln T$ integral is not the entropy change. This is evident from Clausius inequality, $dS > dq_{irrev}/T$, where dq_{irrev} 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 $C_p d \ln T$ integral on the cooling and heating paths through the glass-liquid transformation temperature range, we refer the

quantity determined from the integral as $\Delta\sigma$ instead of ΔS , and T_f determined from it as T_f^σ . The usual

T_f determined from the $C_p dT$ integral is denoted as T_f^H . In principle, T_f^σ 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^σ 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_{res} would be real. But if they are found to be very different then S_{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^σ 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^σ 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_{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_{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 extrapolated from two temperatures in this method, one temperature below and one above the sigmoid shape part of the scan. This shows a step-like change at T_f' when the condition,

$$\int_{T^*}^{T_f'} (C_{p,liq} - C_{p,glass}) dT = \int_{T^*}^{T'} (C_{p,meas} - C_{p,glass}) dT \quad (1)$$

is fulfilled. Here, $C_{p,liq}$ is specific heat of the liquid, $C_{p,glass}$ 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 $C_{p,meas}$ is the measured C_p on heating from the glassy to liquid state. For use in the integral, $C_{p,glass}$ at $T > T_g$ is obtained from a curve drawn as an extension of the curve for $C_{p,glass}$ from $T < T_g$ to higher temperatures. This extension is either done by linear extrapolation from $C_{p,glass}$ or done by fitting the $C_{p,glass}$ data to a polynomial equation. The longer the extension, the greater is the error in the estimate of $C_{p,glass}$ 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 $d\ln T$,

$$\int_{T^*}^{T'_f} (C_{p,liq} - C_{p,glass}) d \ln T = \int_{T^*}^{T'} (C_{p,meas} - C_{p,glass}) d \ln T \quad (2)$$

Similarly, when the conditions of Eq. (2) are satisfied, $T_g^\sigma = T'_f$

Eqs. (1) and (2) are useful also when $q_h > q_c$, or when the glass has been annealed. But when $q_c \gg q_h$, 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,

$$\int_{T_{ref}}^{T_{eq}} (C_{p,2} - C_{p,1}) dT = \int_{T_g^H}^{T_f^H} (C_{p,liq} - C_{p,glass}) dT \quad (3)$$

where $C_{p,1}$ is the data from scan-1, $C_{p,2}$ that from scan-2, T_{ref} 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 $C_{p,liq}$ and $C_{p,glass}$ are as defined earlier. As mentioned earlier here, $C_{p,glass}$ 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^σ , we replace dT in Eq. (3), by $d \ln T$,

$$\int_{T_{ref}}^{T_{eq}} (C_{p,2} - C_{p,1}) d \ln T = \int_{T_g^\sigma}^{T_f^\sigma} (C_{p,liq} - C_{p,glass}) d \ln T \quad (4)$$

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

It is understood that values of T_f^H and T_f^σ can be estimated only with reference to either T_g^H or T_g^σ , 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^σ have the same values.

We now determine T_f^H of $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ glass heated at 20 K/min rate. In the main frames, curve 1 is the plot of C_p 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, ($C_{p,liq} - C_{p,glass}$), needed for determining T_f^H from Eq. (3). Values of T_g^H estimated from curve 2 are indicated in both figures, and its value 668 K is the same as before. Analysis yields T_f^H as 693 K. By using the corresponding plots, we determine T_f^σ of the $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ glass as 694.4 K.

The T_g values determined from the enthalpy and entropy integrals, T_g^H or T_g^σ , and the values of T_f^H , and T_f^σ , the ratio T_f^σ / T_f^H along with the values of A_H and A_σ and the ratio A_H/A_σ are also listed in Tables 1 and 2. The ratio A_H/A_σ increases as T_g increases. We estimate a combined error of about 4 % in the $C_p - T$ and in the dH/dT measurements, in our reading of the published $C_p - T$ data and in determining the path integrals. While geometrical considerations indicate that T_f^H would differ slightly from T_f^σ , the difference is within the combined errors.

Table 1. The T_g s and T_f s of $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ as determined from the $C_p dT$ integrals and from the $C_p \ln T$ integrals, the ratio of the two T_f s, the integrals used in determining T_f s and their ratio, A_H/A_σ .

Material	T_g^H (K)	T_g^σ (K)	T_f^H (K)	T_f^σ (K)	A_H (J/g)	A_σ (mJg ⁻¹ K ⁻¹)	T_f^σ / T_f^H	1. A_H / A_σ (K)
$Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$	668	668	693	694.4	4.86	8.7	1.00	657

(1) Values obtained when the assumed dC_p/dT for the ultra-viscous liquid is taken as:

(a) zero, (b) $-4.57 \times 10^{-4} \text{ Jg}^{-1} \text{ K}^{-2}$, and (c) $7.58 \times 10^{-4} \text{ Jg}^{-1} \text{ K}^{-2}$.

(2) Values obtained when the assumed dC_p/dT for the ultra-viscous liquid is taken as:

(a) zero, (b) $-9.65 \times 10^{-4} \text{ Jg}^{-1} \text{ K}^{-2}$, and (c) $7.36 \times 10^{-4} \text{ Jg}^{-1} \text{ K}^{-2}$.

(3) Values obtained when the assumed dC_p/dT for the ultra-viscous liquid is taken as:

(a) zero, (b) $-7.96 \times 10^{-5} \text{ Jg}^{-1} \text{ K}^{-2}$, and (c) $9.24 \times 10^{-5} \text{ Jg}^{-1} \text{ K}^{-2}$.

Table 2. The T_g s and T_f s as determined from the $C_p dT$ integrals and from the $C_p \ln T$ integrals, the ratio of the two T_f s, the integrals used in determining T_f s and their ratio, A_H/A_σ .

Material	T_g^H (K)	T_g^σ (K)	T_f^H (K)	T_f^σ (K)	A_H (Jmol ⁻¹)	A_σ (Jmol ⁻¹ K ⁻¹)	T_f^σ / T_f^H	2. A_H / A_σ (K)
TNM-simulation ($q_c = 6 \times 10^6$ K/min, $q_h = 20$ K/min)	507	508	564	565	54.47	0.1461	1.00	373.1
TNM-simulation ($q_c = 60$ K/min, $q_h = 20$ K/min)	507	509	519	516	3.06	0.0121	1.00	252.9

Finally, we obtained the plots of normalized C_p by simulation and using the Tool-Narayanaswamy-Moynihan formalism. The simulation was performed to obtain the plots of normalized C_p against T . We used, $\ln A = -90.1$, $x = 0.5$, $\beta = 0.58$, $\Delta h^* = 323 \text{ kJ/mol}$ in all cases. For the slow cooling rate, we chose, $q_c = 60 \text{ K/min}$ and for heating $q_h = 20 \text{ K/min}$. For fast cooling, $q_c = 7 \text{ MK/min}$ and the same q_h of 20

K/min. From the plots obtained, we determined T_g^H and T_g^σ , T_f^H and T_f^σ , and the values of A_H and A_σ , as described above. These values and the ratios T_f^σ / T_f^H and A_H / A_σ 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_{glass} , and other in the liquid state, T_{liq} , as follows,

$$H_{cool} = c \int_{T_{liq}}^{T_{glass}} \left(\frac{dH}{dT} \right)_q dT ; \Delta H_{heat} = c \int_{T_{glass}}^{T_{liq}} \left(\frac{dH}{dT} \right)_q dT \quad (5)$$

$$\Delta \sigma_{cool} \geq c \int_{T_{liq}}^{T_{glass}} \left(\frac{dH}{dT} \right)_q d \ln(T) ; \Delta \sigma_{heat} \leq c \int_{T_{glass}}^{T_{liq}} \left(\frac{dH}{dT} \right)_q d \ln(T) \quad (6)$$

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

The plots are terminated at T_{glass} and T_{liq} where the data obtained on the cooling path appear to merge with those obtained for the heating path. For $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ glass and liquid, $T_{glass} = 437.2$ K and $T_{liq} = 543$ K and the integrals were done with respect to the baseline with the value at $(dH/dT)_q$ at T_{glass} . The values of ΔH_{cool} , ΔH_{heat} , $\Delta \sigma_{cool}$ and $\Delta \sigma_{heat}$ are listed in Table 3. Here the ratios $x_H = (\Delta H_{cool} - \Delta H_{heat}) / \Delta H_{cool}$ and $x_\sigma = (\Delta \sigma_{cool} - \Delta \sigma_{heat}) / \Delta \sigma_{cool}$ are also listed.

We also simulated the plots of normalized $C_p - T$ plots for heating and for cooling by using the Tool-Narayanaswamy-Moynihan 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_{glass} and T_{liq} , the $\Delta H/c$ and $\Delta \sigma/c$ measured for cooling and for heating and the percentage differences, x_H between ΔH_{cool} and ΔH_{heat} and x_σ between $\Delta \sigma_{cool}$ and $\Delta \sigma_{heat}$.

Material	q (K/min)	T_{glass} (K)	T_{liq} (K)	$\Delta H_{cool}/c$ (Jmol ⁻¹)	$\Delta H_{heat}/c$ (Jmol ⁻¹)	x_H %	$\Delta \sigma_{cool}/c$ (Jmol ⁻¹)	$\Delta \sigma_{heat}/c$ (Jmol ⁻¹ K ⁻¹) 1)
Zr ₆₅ Cu _{17.5} Ni ₁₀ Al _{7.5}	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 $C_{p,liq}$ 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 $dS > (dq_{\text{irrev}}/dT)$. 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_f^σ obtained is closely similar to T_f^H . Also, in all cases, T_g^H is equal to T_g^σ 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_f^σ differ significantly from T_f^H . This would suggest that for such purposed, calorimetric measurements meet the classical thermodynamics criteria for path-reversibility. Regarding (ii), one cannot deny Reiss [10] that S_{res} 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_f^σ slightly higher than T_f^H , 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_f^σ and T_f^H for an ideal set of data.

We now discuss the magnitudes of ΔH_{cool} and ΔH_{heat} values given in Table 3. Conservation of energy requires that ΔH_{cool} be equal to ΔH_{heat} . This would be the case if T_{glass} was near 0 K or at a temperature such that structural relaxation effect were vanishingly small. Our experiments yield ΔH_{cool} about 1 % higher than ΔH_{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_{glass} and beginning of the heating from T_{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)_q in the usual study, and ΔH_{heat} obtained from Eq. (1) would be higher than ΔH_{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 ΔH_{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) _q measurements, in the uncertainty of determining T_{glass} at which the cooling and heating curves meet, and in the integration procedure which also cause ΔH_{cool} and H_{heat} to differ.

The corresponding values obtained by analyzing the data for C_p simulated from the Tool-Narayanaswamy-Moynihan model are also listed in Table 3. For the cooling and heating paths for $q = 20$ K/min, x_H differs by 0.3 %, and x_σ by 1.9 %, and for $q = 1$ K/min, x_H differs by 0.2 %, and x_σ by 1.8 %. It is between 1.8 % for x_σ found for the measured data for $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$.

$C_p d\ln T$ integral cannot be used for determining the entropy change in the glass-liquid transformation range because of the Clausius inequality, $dS > (dq_{\text{irrev}}/T)$. 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_{liq} 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 $q_c = q_h$ ($= 0.001$ 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 ~ 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 $\Delta\sigma_{cool}$ 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 $C_p d\ln T$ integral would not yield the entropy change. It only yields the upper bound value of the actual entropy change, ΔS , 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 ΔS . To avoid confusion with ΔS , we consistently use here the term $\Delta\sigma$ for estimates of the $C_p d\ln T$ integral in the liquid-glass transformation range.

S_{res} of $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ glass can not be estimated here, and the constant c used in Eqs. (5) and (6) to convert $(dH/dT)_q$ 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 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 $dH/dT)_q$ has little effect on $\Delta\sigma$ for $q_c = q_h$.

The data in Table 1 show that the T_f^σ / 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^σ / 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^σ 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^σ 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^σ .

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 $C_{p,liq}$ and $C_{p,glass}$ 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.

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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 $Mg_{65}Cu_{25}Tb_{10}$ 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., Baltés, A., Müller, 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 Gessellschaft, Offenbach, Germany, 2009, p. 125
- [14] Goldstein, M., *J. Chem. Phys.* **64** (1976) 4767