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Article

Endothermic Effects on Heating Physically Aged Sucrose Glasses and the Clausius Theorem Violation in Glass Thermodynamics

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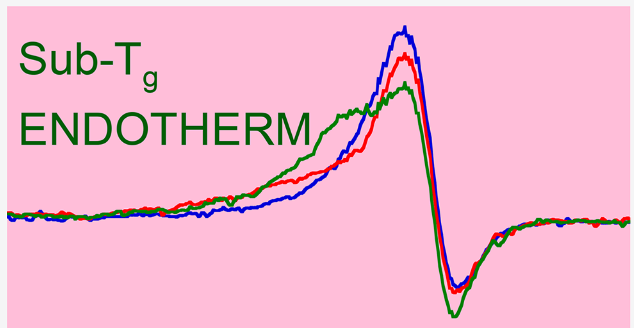
ABSTRACT: Experimental heat capacity, $C_{p,\mathrm{app}}$, of some physically aged polymers had shown an endothermic peak or a shoulder on heating when the material was still in the glassy state. In the first part of this paper, we report observation of a similar feature in a molecular glass, sucrose, indicating increase in the enthalpy and entropy from kinetic unfreezing of molecular motions in the solid state. Aging decreases $C_{p,\mathrm{app}}$ of glass. Increase in the aging time, t_{age}, or aging temperature, T_{age}, interferes with the onset temperature of $C_{p,\mathrm{app}}$ increase toward the liquid state value. When the endothermic feature is not obvious in the $C_{p,\mathrm{app}}-T$ plots of the glassy state, its presence may be discerned in a plot of $\mathrm{d}C_{p,\mathrm{app}}/\mathrm{d}T$ against T. Molecular motions producing this feature have implications for the state point in a potential energy landscape of an aging *glass*. In the second part of the paper, we use the $C_{p,\mathrm{app}}$ data to examine how much our violation of the Clausius theorem affects the entropy determined from the $C_{p,\mathrm{app}}\,\mathrm{d}\ln T$ integral. In addition to calculating this integral for a closed cycle of (irreversible) cooling and heating paths, we suggest an analysis which uses the $\delta C_{p,\mathrm{app}}\,\mathrm{d}\ln T$ integrals ($\delta C_{p,\mathrm{app}}$ is the difference between the $C_{p,\mathrm{app}}$ of the aged and the unaged glass) measured *only* on the heating paths. The closed cycle $C_{p,\mathrm{app}}\,\mathrm{d}\ln T$ integral value is negligibly small. The $\delta C_{p,\mathrm{app}}\,\mathrm{d}\ln T$ integral value increases with t_{age}. It is equal to the enthalpy lost on aging divided by T_{age}. Clausius theorem violation has no significant effect on determination of the entropy from $C_{p,\mathrm{app}}\,\mathrm{d}\ln T$ integral of an aged glass.



1. INTRODUCTION

One of the characteristic features of a glass is that its properties change exothermally with time, more rapidly at a high temperature than at a low temperature, T.[1,2] When a glass is aged at a high T, the net change observed in the magnitude of a physical property is relatively small, and when it is aged at a relatively low T, the net change observed in the magnitude is large.[3] This spontaneous occurrence asymptotically brings the out-of equilibrium state of a glass closer to its equilibrium state of the metastable liquid at a fixed aging temperature, T_{age}. The phenomenon is known as structural relaxation on isothermal physical aging of a glass to a lower enthalpy, entropy, and volume.

When a physically aged glass is heated, the plot of its heat flow rate, $\mathrm{d}H/\mathrm{d}t$, against T in differential scanning calorimetry or the plot of the apparent heat capacity, $C_{p,\mathrm{app}}$, determined from it usually shows either a small time-dependent decrease or, depending upon the heating rate, q_{h}, a broad exothermic dip. (To avoid confusion, we use $C_{p,\mathrm{app}}$ for the time-dependent heat capacity measured in the liquid−glass−liquid transition range and of a glass.) Thereafter, $\mathrm{d}H/\mathrm{d}t$ or $C_{p,\mathrm{app}}$ rapidly increases to a value above the liquid state value, thus producing an overshoot, and then decreases to the liquid state's C_p value. (See for example the $C_{p,\mathrm{app}}-T$ plots in refs 3 and 4 and the plots in papers published by the polymer physics group at Universität Rostock, who has also studied a variety of polymers by fast scanning chip calorimetry in ref 5). The rapid increase indicates rapid onset of kinetic unfreezing of the overall glass structure.[1,2,5] For convenience of description we denote the onset temperature of kinetic unfreezing as T^{onset}. Increase in the aging time, t_{age}, at an aging temperature, T_{age}, shifts T^{onset} to higher T. Note that T^{onset} has occasionally been taken as the "glass transition temperature" for a certain q_{h} and is denoted by "T_{g}". This "T_{g}" is neither the same as the glass to liquid transition temperature, $T_{\mathrm{g}\to\mathrm{l}}$, observed on heating at the same q_{h} as q_{c} or the *kinetic freezing or glass formation temperature*, $T_{\mathrm{l}\to\mathrm{g}}$, observed on cooling the liquid. So we distinguish T^{onset} from $T_{\mathrm{g}\to\mathrm{l}}$ and also from $T_{\mathrm{l}\to\mathrm{g}}$, the latter determined from the $C_{p,\mathrm{app}}-T$ plots measured on cooling a liquid. It is known that $T_{\mathrm{l}\to\mathrm{g}}$ is high when q_{c} is high and low when q_{c} is low. A liquid

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cooled at different rates produces glasses of different $T_{l\to g}$ values and of different structure and properties, and cooling at the same rate repeatedly produces glass of the same structure and properties (see also note in ref 6).

Polymer glasses have shown also a different effect of physical aging in the dH/dt against T plots obtained from differential scanning calorimetry, DSC.[2,7−15] It was observed as an endothermic peak when an aged polymer glass was heated from $T \leq T_{age}$, and the sample was still in the out-of-equilibrium state of a rigid glass.[2,7−16] The endothermic peak has been called sub-T_g peak, and we refer to it as such, not as sub-T^{onset} peak. It is seen when molecular motions in the glassy state begin to cause an appreciable recovery of the enthalpy and entropy lost on physical aging. The sub-T_g peak has been observed in the DSC scans of freeze-dried poly(methyl methacrylate) by Shultz et al.,[11] of polyvinyl chloride by Hodge and co-workers,[12,13] and in the $C_{p,app}-T$ plots of polystyrene by Chen and Wang,[14] and it has been modeled for polyvinyl chloride by Hodge and Berens.[15] Most recently, it has been observed in the $C_{p,app}-T$ plots of polyamide-11,[16] a relatively fast crystallizing polymer. The width of sub-T_g peaks in the DSC scans of polymers is typically 20−30 K.[12] We are unaware of sub-T_g peak appearing in the $C_{p,app}-T$ plots obtained by adiabatic calorimetry method.

The shape and magnitude of the sub-T_g peak, its temperature, and its broadness vary with q_c of the liquid, with T_{age}, with t_{age} at that T_{age}, and with q_h of the glass.[11−13] For certain combinations of these variables, the sub-T_g peak shifts toward T_g and merges with the sigmoid shape increase in $C_{p,app}$ that characterizes T^{onset}.[11−13] The peak is reduced to a sub-T_g shoulder-like feature for polyvinyl chloride[12] and polystyrene,[13] which resembles the kinetic-unfreezing endotherm of the type seen at T^{onset} without a $C_{p,app}$-overshoot. Here, we use the terms sub-T_g peak, sub-T_g endotherm, enthalpy recovery peak,[16] and sub-T_g feature interchangeably, insisting that T_g is close to $T_{l\to g}$. An exceptionally broad (∼80 K and in some case more than 120 K) peak has also been observed on heating some polymers which had been aged at T of ∼120 K or more below their $T_{l\to g}$ values and which have been discussed in terms of two-step or two-mode enthalpy relaxation (see ref 17 for further details of such studies).

Sucrose is one of the essential constituent in food products. It is also widely used in pharmaceutical industry for stabilizing the glassy states of certain curative drugs and proteins. Because of these attributes, numerous calorimetric studies have been performed on melting of sucrose with or without decomposition, on glass formation on cooling its melt, and on the effects of physical aging of its glassy state.[18−21] However, the data and the conclusions obtained by different groups differ. For example, (i) the melting temperature of sucrose is different in different studies[21−23] and reported to be dependent upon q_h, more dependent in DSC studies than in fast differential scanning chip calorimetry studies,[21](ii) the glass-to-liquid transition temperature differs widely in the range 52−70 °C (325−343 K) according to the list of values Urbani et al.[18] have provided for "T_g" or of $T_{g\to l}$, defined here as T^{onset}; the list contains values reported by different groups until the year 1997. Recent studies have reported yet a different value.[19,20] By using reversing heat capacity method in a quasi-isothermal temperature-modulated-DSC technique, Magoń et al.[21] have estimated T_g of 331 K. We will discuss these aspects also here.

As part of our investigations on the effect of sucrose on unfolding of native proteins, we have studied the *glass formation of sucrose during cooling of its melt* and also the structural relaxation of sucrose glass observed after aging for different time periods at a fixed T_{age} and for different T_{age}. This paper reports the study. We find that the sub-T_g endotherm also appears in studies of aged sucrose glass, but its magnitude is small compared to that for polymers,[5,7−16,24,25] melt-spun metal-alloy glasses,[24,25] and As_2Se_3 glass,[25] likely due to relatively short t_{age} and/or high T_{age} in our study. We also suggest a procedure for revealing the sub-T_g feature when it is not obvious in the $C_{p,app}-T$ plots, and we argue that occurrence of the sub-T_g endotherm is a manifestation of a phenomenon intrinsic to a glass structure. The feature may be affected by a contribution to $C_{p,app}$ from the JG relaxation, but the feature is not attributable to JG relaxation. Modeling of the dH/dt and $C_{p,app}-T$ plots in terms of nonlinear, nonexponential structural relaxation[1,2] has shown a sub-T_g endotherm as both a peak and a shoulder shifting to a higher T as t_{age} was increased.[13−15,24,25]

Properties of a material in the liquid−glass−liquid transition range are thermally irreversible along the cooling and heating paths The $C_{p,app}$ value is time-dependent and shows thermal hysteresis. Since the Clausius theorem forbids entropy determination from a $C_{p,app}\,d\ln T$ integral on an irreversible path,[26,27] there has been a concern about the merits of the entropy data of the glassy state, as described in a review paper.[28] In the second part of this paper, therefore, we use the $C_{p,app}$ data of sucrose glasses to examine the effect of violating the Clausius theorem[26,27] on entropy determination from the $C_{p,app}\,d\ln T$ integral. We do so in two ways: (i) by determining, as previously,[29−32] the $C_{p,app}\,d\ln T$ integral of a closed cycle of cooling and heating paths without aging the glass and (ii) by determining the $\delta C_{p,app}\,d\ln T$ integral ($\delta C_{p,app}$ is the difference between $C_{p,app}$ of an aged and an unaged glass) only on the heating path, which is a simpler procedure (see also ref 33). We find that violation of the Clausius theorem has an insignificant effect on determining the entropy of glass also in the presence of endothermic feature, and the $\delta C_{p,app}\,d\ln T$ integral gives a value that increases with t_{age}, and this value is equal to the enthalpy lost on isothermal aging divided by T_{age}.

2. EXPERIMENTAL METHODS

Analytical grade crystalline sucrose of purity of ≥99.5% (catalog number 84097) was purchased from Sigma-Aldrich Co. and used in its as-received state. We used a differential calorimeter (DSC) Perkin Elmer model 8500, equipped with intracooler III assembly as refrigeration system. Dry nitrogen was used as purge gas at flow rate of 30 mL/min. The mass of the empty aluminum pans, with crimp-sealed covers, used as reference and sample cells was within 0.02 mg. An accurately determined mass of the sample (approximately 12 mg) was used in crimp-sealed pans.

The instrument was calibrated for temperature with three high purity standard materials, indium, naphthalene, and cyclohexane. Energy calibration was performed with indium. A baseline, which takes into account the differential instrument asymmetry, was measured for all $C_{p,app}$ scans by using empty reference and empty sample cells and 80 and 20 K/min cooling and heating rates, and this baseline was subtracted from the heat flow data obtained with empty reference cell and sample containing cell. At the beginning, as well as at the end of each scan, the cells were held isothermally for 1 min duration and the difference of heat flow resulting at the end of each isotherm observed for the sample cell and the empty cell baselines was

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used to calculate, by linear interpolation in T, a further baseline, which was also subtracted. Thus, the instrument's asymmetric drift in heat flow with time was also taken into account.

To test the adequacy of the above procedure for determining C_p and $C_{p,\mathrm{app}}$, we performed a separate set of experiments in which the heat flow was calibrated by using 35.5 mg of sapphire as a heat capacity standard. The results obtained after the calibration showed that C_p and $C_{p,\mathrm{app}}$, measured in the T range of our study agreed with those measured in the above-described procedure to better than 1%. For comparison, some of the data obtained from this procedure are shown as an example in Figure 1A.

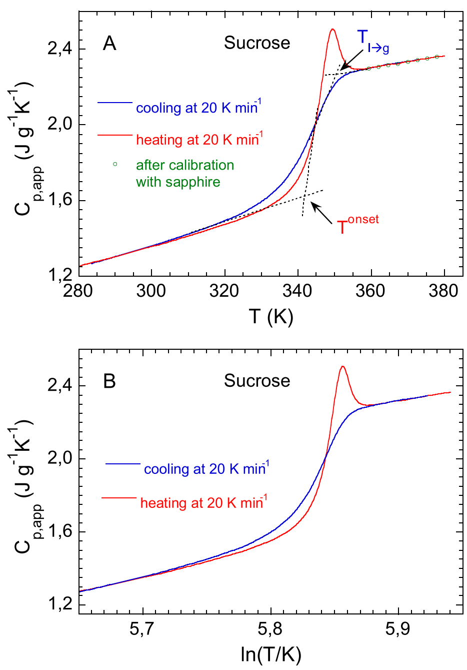

Figure 1. (A) $C_{p,\mathrm{app}}$−T plots of the glass obtained during the cooling at 20 K/min rate and during the heating at the same rate without aging (full curves). $C_{p,\mathrm{app}}$ results were obtained after calibration of the heat flow with a sapphire reference sample (open circles). (B) Corresponding plot of $C_{p,\mathrm{app}}$ against $\ln T$ used for determining the entropy change. $T_{\mathrm{l}\to\mathrm{g}}$ and T^{onset} are as marked.

We first determined the melting point of crystalline sucrose powder in the crimp sealed pan as follows. For this purpose, we used a freshly prepared cell with the sample, heated it at 80 K/min to 423 K, and then further heated it at 10 K/min to 469 K and kept it isothermally for 30 s at 469 K to ensure complete melting of sucrose. The onset temperature of melting observed on heating to 469 K at 10 K/min rate was 461 K. As there was no indication of decomposition of sucrose, which is an exothermic process, the melt contained the lowest amount of impurities, if any. It was then cooled to 300 K at 80 K/min rate, and this produced sucrose glass.

The glass was heated inside the calorimeter at 20 K/min to 383 K, a temperature 78 K below the onset temperature of melting (461 K). Thermal cycling experiments needed to investigate the physical aging effect were performed by heating the sample to the highest temperature of 383 K, cooling to 293 K at 80 K/min to form glass, keeping the glass for 1 min to thermally stabilize at 293 K and then heating it to the required T_{age} and keeping it at that T_{age} for a planned period, t_{age}. Thereafter the glass was cooled to 293 K and then heated at 20 K/min rate to 383 K to bring it into liquid state. The heating scans were obtained for all parts of the cycle but the C_p data reported here were calculated for only those scans that were relevant to this study and for which baselines had been measured. Specifically, these data are the ones obtained for the last part of the cool−age−heat cycle in which the sample was heated at 20 K/min to 383 K. The procedure was repeated using the same T_{age} but different (longer or shorter) t_{age}. The entire procedure was repeated for a second T_{age} and different t_{age} values, for a third T_{age}, and last for a fourth T_{age}. Multiple thermal cycles between 383 and 293 K of the unaged sample gave values of C_p which were the same in the last cycle and the first cycle. All values given here are per gram of the sample. These may be multiplied by the mol wt of sucrose (=342.3 g/mol) to obtain values in per mole of sucrose.

3. RESULTS

First we point out that there has been a disagreement on the melting point of sucrose. Countering the doubts raised on whether sugars actually melt, Roos et al.[22] carefully studied the melting of sucrose by several different methods. They found that melting of the sucrose crystals was complete during the final heating at 1 K/min to 185 °C (458 K), and the melting point of sucrose is about 458 K. This is comparable to the value of 461 K we observed for q_c of 10 K/min, but it differs much from Magoń et al.'s[21] finding of the melting point of 424.4 K for formally zero heating rate and 483 K for 60 000 K/min heating rate. So some of the thermodynamic data obtained by different groups are not in complete agreement with each other which makes it difficult to provide standard data for sucrose crystal, liquid, and glass. As mentioned earlier here, the T^{onset} denoted as "T_g" also differs among different groups.[18−21]

It is instructive to compare the $C_{p,\mathrm{app}}$ values of the glassy state in Figure 1 against the $C_{p,\mathrm{app}}$ values plotted by Magoń et al. and listed in their Table 2.[21] The values for q_h of 20 K/min from Figure 1A are 1.25 J/(g K) at 280 K, 1.36 J/(g K) at 300 K in the glassy state, and 1.48 J/(g K) at 320 K in the liquid state. From Magoń et al.'s[21] plots for q_h of 10 K/min seen in their Figure 8, we obtain $C_{p,\mathrm{app}}$ of the glassy sucrose as 411 J/(mol K) (1.20 J/(g K)) at 280 K, as 456 J/(mol K) (1.33 J/(g K)) at 300 K, and as 506 J/(mol K) (1.48 J/(g K)) at 320 K. One expects the $C_{p,\mathrm{app}}$ values for different cooling/heating rate to differ because different rates produce different glasses whose $T_{\mathrm{g}\to\mathrm{l}}$, as well as T^{onset} differ. The difference between the respective $C_{p,\mathrm{app}}$ values may be partly due to the difference in the glass structure and partly due to the incipiently degraded state of the sucrose samples formed by melting sucrose at respectively different heating rates and so at different temperatures and different temporal duration of exposure to high temperatures which facilitate degradation. The latter is important in view of the reported variation of the melting point of sucrose with the heating rate in Table 3 of ref 21.

On the basis of their DSC and TMDSC studies, Magoń et al.[21] have recommended C_p values of 801.37 J/(mol K) (2.34 J/(g K)) of their sucrose melt at 380 K in their Table 2. The value measured here is 2.36 J/(g K) in Figure 1. So despite the different extents of possible degradation of the respective samples during melting, these two C_p values for liquid sucrose are the same within experimental errors.

It is also known that $C_{p,\mathrm{app}}$ of the glass is generally higher than C_p of the crystal phase. For example, $C_{p,\mathrm{app}}$ of glassy sucrose at 280 K in Figure 1 is 1.25 J/(g K), which is higher

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than C_p of 399.15 J/(mol K) (or 1.166 J/(g K)) for crystalline sucrose at 280 K, as listed in Table 2 of ref 21. We point out that the C_p values of sucrose listed by NIST vary among different groups, and Magoń et al.[21] have listed in their Table 2 the "smoothed experimental data of values from measurement of heat capacity by adiabatic calorimetry according to ref [30]". (See also ref 34 here.) The NIST compilation provided data from several groups, including those from Putnam and Boerio-Goates[35] who provided a list of corrected values of C_p of *crystalline* sucrose. Their C_p/R = 57.706 at 331.92 K[35] gives C_p = 1.402 J/(g K). In Figure 1A here, $C_{p,\mathrm{app}}$ of the glassy sucrose at 332 K is 1.58 J/(g K), which, as expected, is higher than C_p of 1.40 J/(g K) of crystalline sucrose. The difference would be more for rapid-cool formed or unaged glass than for slow-cool formed or aged glass.

In the study of glassy state, we first determined the glass formation temperature $T_{l\to g}$ of sucrose from the $C_{p,\mathrm{app}}-T$ plot obtained by cooling the melt from 383 to 293 K at 20 K/min rate and then determined its so-called T^{onset} from the $C_{p,\mathrm{app}}-T$ plot obtained by heating immediately after to 383 K at the same rate. Figure 1A shows the $C_{p,\mathrm{app}}$ plot against T, and Figure 1B shows the $C_{p,\mathrm{app}}$ plot against ln T; the latter is provided for the purpose of discussing the effect of violation of Clausius theorem by using the $C_p\,d\ln T$ integral for an irreversible thermal path. As determined from the usual extrapolation, the value of $T_{l\to g}$ is 350.3 K and that of T^{onset} is 341.7 K, as indicated in Figure 1A. For comparison, we note that Magoń et al.[21] obtained T_g from the midpoint value of the heating endotherm showing a $C_{p,\mathrm{app}}$-overshoot in normal DSC scan. It was 337.95 K for 10 K/min heating of the glass (Figure 8, ref 21). From the midpoint of the endotherm in Figure 1A, we obtain 344 K for 20 K/min heating of the glass, which is 6 K higher than their T_g value.[21] In Figure 1A the midpoints of the heating and cooling curves do not agree, and therefore we take $T_{l\to g}$ as 350.3 K as the glass formation temperature of sucrose on cooling the melt at 20 K/min. From the midpoint of the reversing heat capacity measured by quasi-isothermal TMDSC on cooling Magoń et al.[21] (modulation period of 100 s and amplitude of 0.5 K), reported T_g of 331.26 K (Figure 10, ref 21). Fast scanning calorimetry on heating at 60 000 K/min gave T_g of 364 K.[21] From the plots obtained on cooling the melt from 383 to 293 K at q_c of 80 K/min, we obtain $T_{l\to g}$ of 354.4 K (not shown here), which we refer to as T_g of the sucrose glass formed, aged, and studied here. The sub-T_g endotherm here refers to the endothermic feature observed in the T-range below this T_g of 354.4 K.

The glass formed on cooling at 80 K/min rate was then heated at 200 K/min rate to a certain T_{age}, aged for a time period t_{age}, cooled to 293 K at q_c of 80 K/min, and then heated at 20 K/min rate. Figure 2A shows the plot of $C_{p,\mathrm{app}}$ against T obtained without aging, i.e., for t_{age} = 0. The procedure was repeated after t_{age} of 1, 3, 10, 100, and 300 min at T_{age} of 313 K. The $C_{p,\mathrm{app}}-T$ plots obtained on heating at 20 K/min rate are included in Figure 1A. Figure 2B shows the similarly obtained C_p-T plots for samples aged at 323 K for t_{age} = 0, 1, 3, 10, 100, and 265 min.

Figure 3A shows the corresponding plots of the samples aged at T_{age} of 333 K for t_{age} = 0, 1, 3, 10, and 100 min, and finally Figure 3B shows the plots of the samples aged at T_{age} of 343 K for t_{age} = 0, 1, 3, 10, and 30 min. From the main plots in Figures 2 and 3, we took the $C_{p,\mathrm{app}}-T$ data from 300 to 307 K and have plotted these against T on an enlarged scale in the insets of Figures 2 and 3.

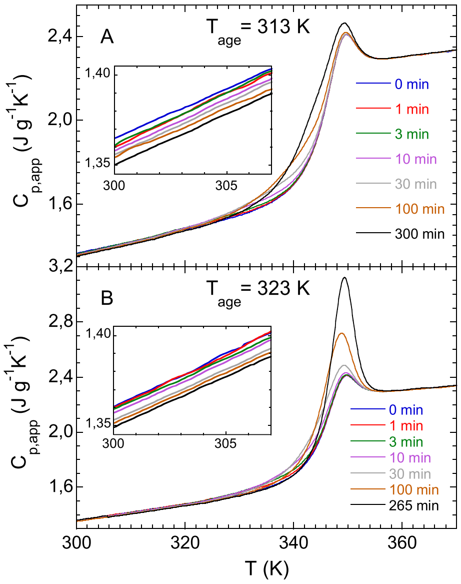

Figure 2. (A) $C_{p,\mathrm{app}}-T$ plots of the glass obtained after t_{age} of 0, 1, 3, 10, 100, and 300 min at T_{ann} of 313 K. The inset contains the plots for the glassy state on an amplified scale. It shows that $C_{p,\mathrm{app}}$ of the glass decreases on aging. (B) Corresponding plots and inset for the glass aged at 323 K for t_{age} = 0, 1, 3, 10, 100, and 265 min.

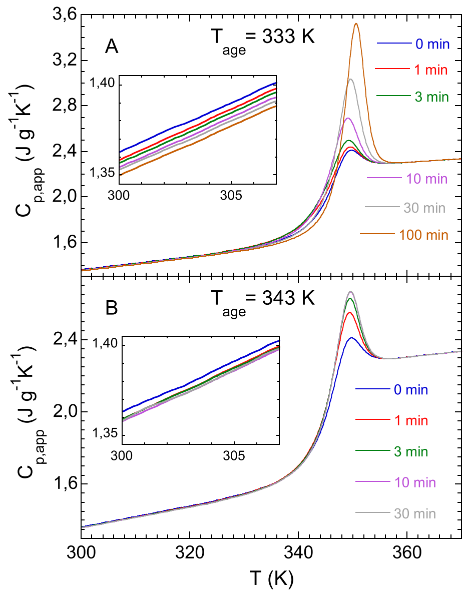

Figure 3. (A) $C_{p,\mathrm{app}}-T$ plots of the glass obtained after t_{age} of 0, 1, 3, 10, 30, and 100 min at T_{age} of 333 K. The inset contains the plots for the glassy state on an amplified scale. It shows that $C_{p,\mathrm{app}}$ of the glass decreases on aging. (B) Corresponding plots and inset for the glass aged at 343 K for t_{age} = 0, 1, 3, 10, and 30 min.

We took from Figures 2 and 3 the $C_{p,\mathrm{app}}-T$ plots for t_{age} of 3 min and for t_{age} of 30 min and show these plots in Figure 4 for comparing the effects of t_{age} at different T_{age}. The plots for the unaged sample and the samples aged for 3 min at T_{age} of 313, 323, 333, and 343 K are given in Figure 4A, and the plots for the unaged sample and for the samples aged for 30 min at the same four T_{age} values are given in Figure 4B. The endothermic feature is evident in the plots at 323, 333, and 343 K in Figure 4A and only in the plot at 313−323 K in Figure 4B. The insets in Figure 4A and Figure 4B provide the $C_{p,\mathrm{app}}-T$ plots on a

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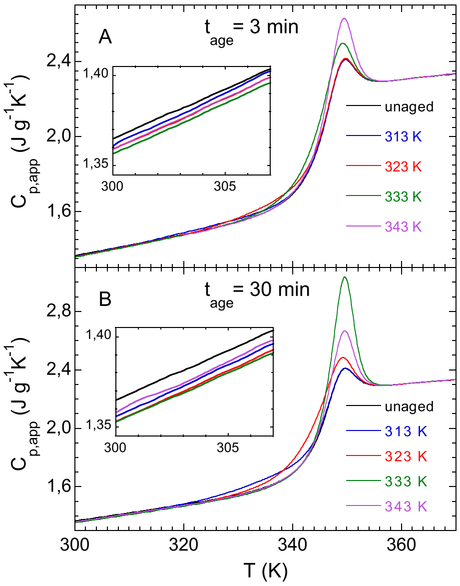

Figure 4. (A) $C_{p,app}-T$ plots of the sucrose glass obtained after aging for 3 min at 313, 323, 333, and 343 K. (B) $C_{p,app}-T$ plots of the glass obtained after aging for 30 min at 313, 323, 333, and 343 K. The plot for the unaged sample is included in both panels. The inset contains the plots for the glassy state on an amplified scale. They show that $C_{p,app}$ of the glass decreases on aging more for 30 min aging than for 3 min aging and $C_{p,app}$ decreases with increase in the aging temperature for both 3 and 30 min aging.

magnified scale at 300−307 K. These show that the lowest $C_{p,app}$ value is reached for T_{age} of 333 K.

In all glass samples of our study, T_g or $T_{l\to g}$ is fixed by q_c which is 80 K/min. Its value is 354.4 K. The onset temperature of the endothermic rise on heating, denoted as T^{onset}, depends upon the extent of structural relaxation that has occurred on heating and/or aging of glass. It corresponds to an approximate value of the fictive temperature.[1,2] As mentioned earlier here, the viscosity or the relaxation time of the state at T^{onset} is not known and it has been ambiguously referred to as the glass transition temperature and unjustifiably denoted as "T_g" for a certain relaxation time value.[33] By using T^{onset} for the onset temperature of the fast approach of $C_{p,app}$ to the equilibrium liquid state, we distinguish it from T_g taken here as close to $T_{l\to g}$. Reference 33 may be consulted for discussion of the formal difference between $T_{l\to g}$, and $T_{g\to l}$ and also for the assumed values of the relaxation time at these two temperatures.

4. DISCUSSION

4.1. General Aspects of Cooling, Heating, and T^{onset}.

During cooling of a liquid, the rates of density and structure fluctuations become progressively slower. When these rates become *slightly* lower than q_c, the structure of the liquid becomes arrested on the time scale of q_c at a temperature $T_{l\to g}$; it becomes mechanically rigid or glass on that time scale and remains so on further cooling. Thus, a glass inherits the structure of its metastable liquid at T in the vicinity of $T_{l\to g}$. Kinetic freezing to a glassy state occurs over a temperature range whose width varies with q_c and the distribution of structural relaxation times. There is no sharp change in a property or in its temperature derivative at $T_{l\to g}$, and the magnitude of a property is time-dependent. Glasses formed by cooling a liquid at different rates have different $T_{l\to g}$ values, different structures, and different electronic, vibrational, mechanical, electrical, and thermodynamic properties. During cooling from $T_{l\to g}$ toward 0 K, faster modes of motion in the distribution of relaxation times and the JG relaxation kinetically freeze gradually. Thermodynamics of this characteristic feature of the glassy state was recently discussed.[36] When a glass is heated, the $C_{p,app}-T$ plot obtained generally shows an endothermic rise and often an overshoot of $C_{p,app}$ before its value reaches the liquid state's C_p value. The shape of the $C_{p,app}-T$ plots obtained on heating characteristically differs from those of the plot obtained on cooling, and the two plots cross each other. These features are evident in the $C_{p,app}-T$ plots in Figure 1 for $q_h = q_c$. Similar crossing of the plots is observed even when $q_h \neq q_c$ and/or when the glass has been physically aged.[1−4]

As mentioned earlier here, cooling a liquid at different rates produces different glasses. For aging studies, we cooled the sucrose melt at 80 K/min rate to form glass, thereby producing glasses of the same $T_{l\to g}$ and of the same structure and properties. This avoided the complications inherent to the study in the analysis of the data obtained for glasses that were formed by using different q_c. Aging of a glass for different t_{age} and/or at different T_{age} itself produces glasses of different structures and properties, and the shapes of the $C_{p,app}-T$ plots obtained on their heating differ.

As noted here earlier, T^{onset} depends upon the thermal history of a glass. Its value varies with q_h, and viscosity, self-diffusion coefficient, or relaxation time at T^{onset} is not known.. Therefore, a change in T^{onset} refers to the change in T at which an unknown structure of a glass begins to transform to its liquid for a certain q_h. Lack of definition of T^{onset} in terms of viscosity or relaxation time has led to reports of different values of T^{onset}, often referred to as "T_g", especially of sucrose. For example, in reviewing the subject, Urbani et al.[18] noted that in papers published until the year 1997, "T_g" of sucrose was reported to be in the 52−70 °C (325−343 K) range. Studies since then have reported its values as high as 78 °C (351 K at q_h of 10 K/min).[19] In one of the precise study, Dranca et al.[20] reported "T_g" of 390 K, as determined from the midpoint temperature of the sigmoid-shape DSC scan showing an overshoot, assuming that the slopes of the $C_{p,app}-T$ plots of the liquid and crystal are identical (ref 20, Figure 6). In some of these studies the sucrose samples had been heated to a temperature at which partial decomposition or caramelization occurs and then cooled at various q_c values to form glass and the glass was then heated at the same respective rates without aging. The effects of q_c and thermal history on "T_g" or T^{onset} were not considered in most cases.

Most recently, Magoń et al.[21] have reported "the glass transition temperature (T_g) of amorphous sucrose was at 331 K with a change in C_p of 267 J/(mol K) as it was estimated from reversing heat capacity by quasi-isothermal TMDSC on cooling". Their studies by fast scanning chip calorimetry on heating at 60 000 K/min "... showed that T_g was 364 K". As mentioned earlier here, they also found that the melting temperature was 424.4 K for formally zero heating rate and 483 K for 60 000 K/min heating rate; both differ from previously reported melting points.[22,23] For q_c of 80 K/min, $T_{l\to g}$ of 354.4 K determined here is, as expected, higher than T_g of 331 K determined from TMDSC and its value is closer to the T^{onset} of 340.5 K in Figure 1 for q_h of 20 K/min. It seems necessary therefore that the $C_{p,app}-T$ plot be obtained during the cooling of a liquid and $T_{l\to g}$ be determined,[33] as discussed

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in the papers showing that the second "T_g" of water was phenomenologically mistaken.[37,38]

4.2. Decrease in C_p of Glass on Aging. The insets in Figures 2, 3, and 4 show that aging decreases the $C_{p,app}$ of sucrose glass. Such decrease in $C_{p,app}$ has been rarely observed, and it is relatively small. In accurate determination of $C_{p,app}$ by adiabatic calorimetry it was found that annealed or aged glass of *o*-terphenyl[39] of dibutyl phthalate[40] and poly(isoprene)[41] has a lower $C_{p,app}$ than their respective quench-formed glasses (see Figure 4 in ref 39 and Figure 3 in ref 40 and Figure 3 in ref 41). The difference between the values for the unaged and for highly aged glass here is ~1.1% of $C_{p,app}$, which is at least 3 times the combined sensitivity, measurements errors, and repeatability of our data (see ref 42 for details.)

It is known that the configurational and vibrational contributions to $C_{p,app}$, enthalpy, and entropy decrease on cooling a liquid, and similar decreases occur on physical aging of a glass. When an aged glass is heated, the decrease is recovered in different ways for glasses aged at different T_{age} for different t_{age}. This difference is evident also in the $C_{p,app}$−T plots in the 300−307 K range shown as insets of Figures 2 and 3. They indicate that on aging, (i) the predominantly vibrational C_p of the glass decreases with increase in t_{age} at a fixed T_{age} and (ii) the decrease in C_p is higher when T_{age} is high (343 K, Figure 3B) than when it is low (313 K, Figure 2A).

The decrease in $C_{p,app}$ on aging of glass is due to (i) the kinetic freezing of fast degrees of freedom in the broad distribution of times,[36] (ii) a decrease in the JG relaxation's contribution,[36] and (iii) an increase in the phonon frequency, as previously discussed in the context of kinetics of isothermal decrease in $C_{p,app}$ of poly(styrene)[43] and of a molecular glass[44] by using the decrease in the real part of complex C_p ($C_p^* = C_p' + iC_p''$) measured by modulated scanning calorimetry.

4.3. Sub-T_g Endotherm of the Glassy State and Its Interpretation. Sub-T_g endothermic peaks had been observed in DSC scans of melt-spun (hyperquenched) metal alloy glasses. On heating, these glasses devitrified (crystallized) before their $T_{g\rightarrow l}$ or T^{onset} could be reached, and therefore their $T_{g\rightarrow l}$ or T^{onset} is not known. In these studies, the sub-T_g endotherm was called "reversible endotherm" (for review see refs 24 and 25). It was reversible not in the sense that the dH/dt was the same or showed a hysteresis on the cooling and heating paths through the sub-T_g endotherm but in the sense that it was observed again when the glass was cooled back to the same T_{age}, aged for the same t_{age}, and then heated to a T below its vitrification temperature. The endotherm had been interpreted in terms of changes in both the chemical short-range order, i.e., a preference for unlike neighbors, and topological short-range order in a metal-alloy glass and was modeled within the concepts of independent two-level systems (see discussion in refs 24 and 25). This interpretation was examined by DSC studies of six isothermally aged Ni-based glassy metal alloys and one network structure organic polymer[24] and for one metal alloy glass, two polymers, and As_2Se_3 glass.[25] These studies[24,25] investigated also the effect of (i) different t_{age} at a given T_{age}, (ii) the effect of different T_{age} for a given t_{age}, and (iii) the asymptotic recovery of the enthalpy and entropy with increase in t_{age} at a fixed T_{age}. (The term *annealing* in refs 24 and 25 has the same meaning as the term *aging* here.)

We now appropriately refer to the "reversible endotherm" as the sub-T_g endotherm. Its peak appeared at T at ~100 K below the devitrification temperature for melt-spun metal-alloy glasses and its width was also at least ~100 K.[24,25] The $T_{g\rightarrow l}$ or T^{onset} of the network structure polymer glass[24] was 393 K and its sub-T_g peak width was 30−40 K.[24] The sub-T_g peak shifted to higher T when t_{age} was increased. (See Figures 1−3 for a metal alloy glass and Figure 2 for a network polymer in ref 25.) A model calculation based on nonexponential, nonlinear structural relaxation showed a sub-T_g peak of about 50 K width (see Figure 5 in ref 24 and Figures 12 and 13 in ref 25) whose shape changed when T_{age} for a given t_{age} was decreased and when t_{age} for a given T_{age} was decreased. It was concluded that each mode of atomic diffusion in the distribution of times has its own "mini-glass-softening endotherm", and the sub-T_g peak is indicative of a broad distribution of diffusion times that stems from temporal and spatial variations in the molecular or atomic environment.

In a distribution of relaxation times those modes of motions that are the last ones to kinetically freeze on cooling to a certain T are the first ones to kinetically unfreeze on heating of an unaged glass from that T. Although JG relaxation has its own distribution of relaxation times and is expected to affect the sub-T_g endotherm, we stress that the sub-T_g endotherm is not attributable to recovery of the JG relaxation strength by kinetic unfreezing of molecular mobility in local regions in a glass structure.[36] The reasons are as follows: (i) Increase in T_{age} shifts the sub-T_g endotherm toward T^{onset}, and at such a high temperature, the JG relaxation time is orders of magnitude shorter than the time scale of heating. (ii) The endotherm appears only in aged samples, and its strength *increases with increase* in t_{age}; the JG relaxation strength in contrast decreases with increase in t_{age}. (iii) JG relaxation indicates density and structure fluctuations in randomly distributed local regions in a rigid glass structure,[36] and therefore its calorimetric feature is observed both on cooling a glass and thereafter on heating a glass, and the two paths show thermal hysteresis,[45] resembling the thermal hysteresis in the liquid−glass−liquid transition range in Figure 1 here but spread over a much broader T-range.[45] Unfortunately, $C_{p,app}$−T plots in the JG relaxation range of polymers and the sucrose glass are not available, but on the basis of the finding for a metal-alloy glass,[45] it is likely that the T-range of the JG relaxation would be much larger for sucrose than that of the sub-T_g peak. We also note that in an asymmetric distribution of relaxation times, all molecular motions would not formally freeze on cooling toward 0 K; only their contribution to a property would tend to become vanishingly small as faster modes of motions also gradually freeze out.

It is well established that increase in t_{age} of a glass at a fixed T_{age} shifts its T^{onset} to a higher T.[1−3,12,15,43,44] The data in Figure 2A show that some of the $C_{p,app}$−T plots of the sample aged at 313 K instead shift to lower T when t_{age} is increased from 0 to 300 min; i.e., T^{onset} appears to decrease when t_{age} is increased. This is obviously due to interference of the T^{onset} endotherm by the sub-T_g endotherm. It is also evident in the modeling of the sub-T_g and T^{onset} endotherms in Figure 5 of ref 15, Figure 5 of ref 24, and Figures 12 and 13 of ref 25.

To show more clearly the sub-T_g feature in $C_{p,app}$ of a glass, we calculated the derivative of d$C_{p,app}$/dT from the data provided in Figures 2 and 3. The values are plotted against T for samples aged for different t_{age} values (i) at 313 K in Figure 5A, (ii) at 323 K in Figure 5B, (iii) at 333 K for in Figure 6A, and (iv) at 343 K in Figure 6B. In all cases, d$C_{p,app}$/dT is, as expected, greater than zero both in the glassy state at 300 K and in the liquid state at 370 K. As the "glass" approaches the

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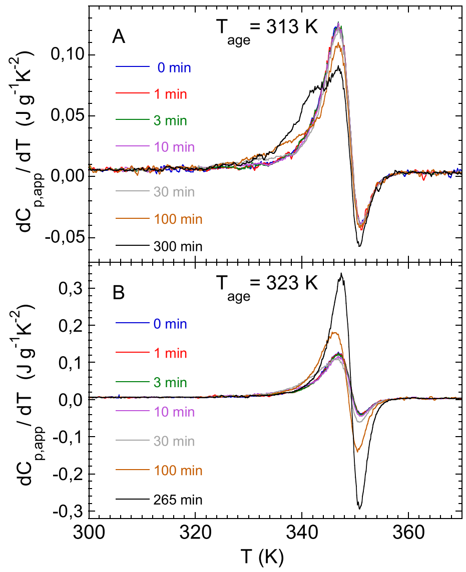

Figure 5. (A) Plots of ($dC_{p,app}/dT$) against T of the sucrose glass obtained after t_{ann} of 0, 1, 3, 10, 30, 100, and 300 min at 313 K. (B) Corresponding plots for samples annealed at 323 K. The plot for the unaged sample is included in both panels. It is denoted as 0 min.

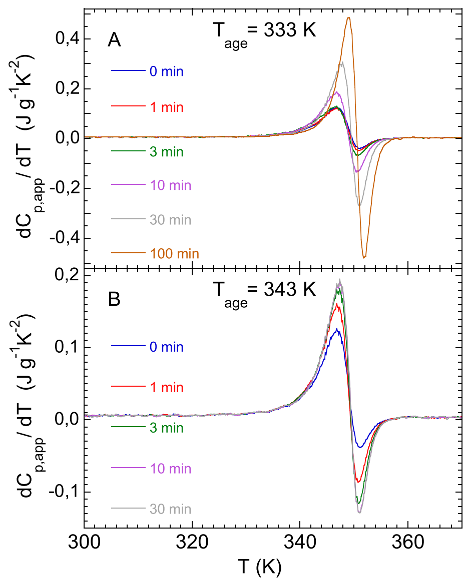

Figure 6. (A) Plots of ($dC_{p,app}/dT$) against T of the sucrose glass obtained after t_{ann} of 0, 1, 3, 10, 30, and 100 min at 333 K. (B) Corresponding plots for samples aged for 1, 3, 10, and 30 min at 343 K. The plot for the unaged sample is included in both panels. It is denoted as 0 min.

liquid state on heating, the plots show a peak at the point of inflection in the corresponding plot of $C_{p,app}$ against T in Figures 2 and 3; thereafter $dC_{p,app}/dT$ becomes zero at the overshoot peak temperature and then shows a peak on the negative side at the temperature where a point of inflection in the $C_{p,app}-T$ plot appears after the overshoot.

In Figure 5A, $dC_{p,app}/dT$ of the sample aged for t_{age} of 30 min at 313 K shows the beginning of a sub-T_g endothermic shoulder. Its magnitude increases when t_{age} is 100 min and reaches a still higher value when t_{age} of 100 min. In Figure 5 B, a sub-T_g shoulder is discernible for t_{age} of 10 and 30 min at T_{age} of 323 K. In Figure 6A, a weak shoulder appears for t_{age} of 1 and 3 min at T_{age} of 333 K. In Figure 6B, no such shoulder is observed at T_{age} of 343 K. In all cases increase in t_{age} causes the shoulder to merge with the rising $dC_{p,app}/dT$ values toward a peak. This shows that when the sub-T_g endotherm is not obvious in the $C_{p,app}-T$ plot, it may be discerned in the $dC_{p,app}/dT$ against T plot. Increase in t_{age} tends to merge this feature with the T_g endotherm. Similar analyses would be useful in future studies of structural relaxation in glasses.

The sub-T_g feature had been modeled by a four-parameter equation based on nonlinear and nonexponential kinetics of structural relaxation.[12,13,15,24,25] The nonlinear relaxation parameter was denoted as x and the nonexponential parameter as β; the latter can be represented as the sum of relaxation times in the range from zero to infinity. As discussed in numerous papers,[1−3,9,10,12,24,25] the model uses a description of change in T_f with time.[1−3] It was found that the $C_{p,app}$ data showing the sub-T_g endothermic peak for polymers may be modeled by the four-parameter equation with reasonable values of the x and β parameters, but the model-fit did not show the C_p overshoot as observed for monodisperse polystyrene[13,14] and also here for sucrose. Briefly, model-fitting of the sub-T_g endothermic plateau-like feature for monodisperse polystyrene[14] yielded unacceptable low value of $x = 0.12$ and $\beta = 0.39$, compared with $x = 0.43$ and $\beta = 0.68$ for polydisperse polystyrene.[13] The model itself requires a set of approximations,[1−3] the main one being that C_p and β values of the equilibrium state do not change on cooling from $T_{l\rightarrow g}$. But the two quantities do change with change in T of the equilibrium state of molecular glasses and polymers.[46,47] As mentioned earlier here, it is also unlikely that the sub-T_g feature indicates recovery of the JG relaxation by unfreezing of molecular motions in local regions dispersed in a sucrose glass structure[36] because (i) aging generally decreases the JG relaxation strength of a glass,[36,46] but aging here increases the strength of its sub-T_g feature, and (iii) JG relaxation shows a thermal hysteresis in the cooling and heating paths through the temperature range of its appearance,[36] which has not been observed for sucrose. Therefore, we attribute the rise in $C_{p,app}$ beginning at $T \sim 320$ K and ending at ∼335 K in Figure 2A to the onset of enthalpy and entropy recovery as faster modes of motion in the distribution of relaxation times in the sucrose glass unfreeze.

4.4. Sub-T_g Endotherm and the Potential Energy Landscape.

After recognizing the sub-T_g endotherm as a characteristic feature of glass, originating in the distribution of relaxation times, it is desirable to consider how its occurrence can be envisaged in the potential energy landscape (PEL) view.[48−50] This is particularly so because such effects were not known in 1969 when the concept of PEL for liquids was proposed[48] and have not been considered in further development of PEL since then.[49,50]

Briefly, PEL is a conceptual surface of potential energy in a configurational coordinate with a distribution of energy barriers and highly varied depths of potential energy minima in which the state point of a system moves upon thermal activation. During isothermal structural relaxation with time on aging, the state point continuously moves to a deeper minimum of higher curvature. This *decreases* the configurational and vibrational parts of the entropy of a glass. Experimentally, both parts of $C_{p,app}$ of a glass decrease with increase in t_{age} until the glass has reached its metastable equilibrium state in an apparently asymptotic manner. Hence, recovery of the configurational and vibrational entropy on

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heating an aged glass occurs by two thermally activated, sequential processes, the first of which is seen as a sub-T_g endotherm and the second as a relatively narrow T^{onset} endotherm that brings a glass to its liquid state. Separation between the two processes decreases on increasing T_{age} until the two become undiscernible.

A real glass contains nonequilibrium population of hydrogen bonds, molecular isomers, ion pairs, and entities formed by electrostatic and other type of interactions. Structural relaxation on aging tends to increase their population to the equilibrium value and thereby decrease the enthalpy and entropy. As PEL of a liquid and glass with $n + 1$ number of H-bonds (and/or other entities) would be different from the PEL of a liquid and glass with n number of hydrogen bonds (and/or other entities), we argue that global PEL of a glass would consist of parts that correspond to each of the all possible populations of H-bonds, isomers, ion pairs, and other entities. Therefore, the effects of aging may not be represented by motion of a state point within a set of basins or minima in a given PEL. Rather, it may be represented by motion of the state point to different parts of global PEL, each part containing a different set of basins, energy minima of different curvatures in configurational space, and different barrier height for configurational change. The state point of an aged glass is not in the same part of global PEL as the state point of the unaged glass. Recovery of thermodynamic properties seen as sub-T_g feature and the T^{onset} endotherms on heating would, in this view, occur by motion of a state point in a reverse order but through different parts of the global PEL.

4.5. Clausius Theorem, the Liquid−Glass−Liquid Transformation and Aging. Time-dependent processes are path-irreversible; they show thermal hysteresis of the cooling and heating paths. The T-range of path-irreversibility depends upon the time-period used for measurement relative to the kinetics of structural relaxation. Therefore, thermal hysteresis in a given T-range decreases when both q_c and q_h are decreased. If the state could be maintained in internal equilibrium, there would be no thermal hysteresis of $C_{p,app}$−T plots, and the plots on the cooling and heating paths would not cross each other. In such a case, the entropy can be determined from the $C_p \, d \ln T$ integral.

Determining entropy from the $C_p \, d \ln T$ integral in the liquid−glass−liquid range and at lower T is forbidden by the Clausius theorem because glass formation is a process of loss of internal equilibrium, a glass is an out-of-equilibrium state, and the time-dependent $C_{p,app}$−T paths on cooling and heating cross each other, as seen in Figure 1. Therefore refs 28−32 provide background to the perceived need for considering violation of the Clausius theorem in a view that regarded a glass to have no residual entropy or the 0 K entropy. Decrease in entropy on aging also is an irreversible process. This and the enthalpy change indicated by the sub-T_g feature add to this irreversibility. Nevertheless, irrespective of the thermal history, aging, or the structure of a glass, one returns to the same liquid state in a closed cycle thermal path. The Clausius theorem also forbids determining the entropy from $C_p \, d \ln T$ integral of an aged glass. In the following, we determine the consequences of violating this theorem.

According to the law of conservation of energy, the net change in the enthalpy is zero in a closed thermal cycle which may involve reversible and/or irreversible paths. According to the Clausius theorem, the entropy in a cyclic path is not zero when the path is irreversible. The theorem is stated as[26,27]

$$\oint \frac{\delta q}{T} \leq 0 \tag{1}$$

where δq is the amount of heat absorbed by the system at a temperature T. The equality in eq 1 holds when the process is reversible, and inequality holds when it is irreversible. The entropy is a state function, and the $C_{p,app} \, d \ln T$ integral is used to determine the entropy change exclusively for a reversible step in a process, i.e., one in which reversing the direction of change in T reverses the direction of change in the entropy and C_p. The real change in the entropy, $dS = (dq_{rev}/T)$, is higher than the value obtained from (dq_{irrev}/T). So although the Clausius theorem forbids the use of dq_{irrev}/T for determining the entropy change, it does not suggest how much difference it would make to a discussion if one purposely violated the theorem by evaluating the entropy from $C_{p,app} \, d \ln T$ integral.

According to the Clausius theorem, if the change in entropy, $d\sigma_{irrev}$, were determined for a cooling or heating path in the liquid−glass−liquid temperature range, the $C_{p,app} \, d \ln T$ integral would be less than the true entropy change, dS. In previous studies,[29−32] we determined $d\sigma_{irrev}$ from the $C_{p,app} \, d \ln T$ integral in a closed cycle cooling−heating path; its value was too small to show that the Clausius theorem has been violated or to invalidate the previously calculated residual entropy values. The analysis also helped define the Clausius limits for the entropy change on the cooling and heating paths.[31]

In the thermal hysteresis range, the $C_{p,app}dT$ integral for the cooling path from liquid to glass is equal to the heat absorbed on the heating path from glass to liquid, from a temperature in the glassy state (T_{gl}) to a temperature in the liquid state (T_{liq}). According to the law of conservation of energy, the net change in the enthalpy in a closed liquid−glass−liquid cycle is zero.

$$-\int_{T_{liq}}^{T_{gl}} C_{p,app}(\text{cool}) \, dT = \int_{T_{gl}}^{T_{liq}} C_{p,app}(\text{heat}) \, dT \tag{2}$$

or

$$\oint \Delta H = 0 \tag{3}$$

The entropy for a reversible process is given by

$$-\int_{T_{liq}}^{T_{gl}} C_{p,app}(\text{cool}) \, d \ln T = \int_{T_{gl}}^{T_{liq}} C_{p,app}(\text{heat}) \, d \ln T \tag{4}$$

or

$$\oint \Delta S = 0 \tag{5}$$

According to the Clausius theorem,

$$\oint C_{p,app} \, d \ln T \neq 0 \tag{6}$$

for an irreversible process, and calculating the entropy change from the $C_{p,app} \, d \ln T$ integral is forbidden. Nevertheless, we estimate this integral as follows. We use the difference between the $C_{p\ app}$(cool) values on the cooling path and the $C_{p,app}$(heat) values on the heating paths in the T range from 280 to 380 K from Figure 1 and plot the [$C_{p,app}$(cool) − $C_{p,app}$(heat)] value against $\ln T$ in Figure 7. The integrated values over the 280−380 K range are

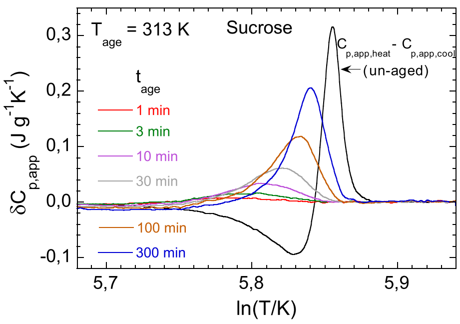

Figure 7. Difference, $\delta C_{p,\mathrm{app}} = [C_{p,\mathrm{app}}(\mathrm{aged}) - C_{p,\mathrm{app}}(\mathrm{unaged})]$, is plotted against ln T for glasses aged for different times at T_{age} of 313 K. The $C_{p,\mathrm{app}}$(unaged) refers to a glass that was formed by cooling at 80 K/min and then heated immediately at 20 K/min rate. (Data taken from Figure 2A.) Also plotted is the difference between the $C_{p,\mathrm{app}}$ of a glass formed by cooling at 20 K/min rate and thereafter heating at 20 K/min rate without aging. This plot is indicated by an arrow, and the data were taken from Figure 1A.

$$\oint \Delta H = 8 \times 10^{-4}\ \mathrm{J/g} \quad \text{and}$$
$$\oint C_{p,\mathrm{app}}\, \mathrm{d}\ln T = -2.3 \times 10^{-4}\ \mathrm{J/(g\,K)} \tag{7}$$

As expected, ΔH in the closed cycle is zero within the experimental and analysis errors.

We now compare the closed cycle integral of $C_{p,\mathrm{app}}$ d ln T against the reported entropy of glassy sucrose.[21] A plot of the entropy against T of the glass and crystal states of sucrose is available in Figure 16 of ref 21, from which we obtain the entropy as ~430 J/(mol K) at 338 K. This value contains the residual entropy (the 0 K entropy) value of 18.4 J/(mol K). The C_p d ln T integral at 338 K is therefore 411.6 J/(mol K) or 1.20 J/(g K) at 338 K. The closed cycle integral of $C_{p,\mathrm{app}}$ d ln T in eq 7 is -2.3×10^{-4} J/(g K), which is 0.017% of the measured entropy of glassy sucrose at 338 K. We conclude that violation of the Clausius theorem by using the $C_{p,\mathrm{app}}$ d ln T integral in eq 7 on an irreversible path has insignificant effect on the determinination of the entropy of glassy sucrose.

We also use a new analysis for this purpose. It does not require $C_{p,\mathrm{app}}$ data in a closed thermodynamic cycle of eq 7. Instead it requires data obtained only on the heating path for two samples of glass, one unaged and the other aged, for different time periods. The integral of $C_{p,\mathrm{app}}$ dT from a temperature in the glassy state to a temperature in the liquid state gives the heat absorbed by the sample, and this heat would be higher for the more aged sample than for unaged sample. One may then use the difference, $\delta C_{p,\mathrm{app}} = [C_{p,\mathrm{app}}(\mathrm{aged}) - C_{p,\mathrm{app}}(\mathrm{unaged})]$ and plot it against ln T to obtain the $\delta C_{p,\mathrm{app}}$ ln T integral and compare its magnitude against the measured entropy of the glass. We calculated the δC_p value at each T from the data in Figure 2A for samples cooled at 80 K/min and heated at 20 K/min without aging and also after aging separately for 1−300 min at T_{age} of 313 K. From the plots of δC_p against T (not shown here) we determine the $\delta C_{p,\mathrm{app}}$ dT integral from 293 K in the glassy state to 370 K in the liquid state and denote it as δH. Its value is listed in Table 1. From the corresponding plots of $\delta C_{p,\mathrm{app}}$ against ln T shown in Figure 7, we determine the $\delta C_{p,\mathrm{app}}$ d ln T integral and denote it as $\delta\sigma$. The calculated $\delta\sigma$ values for different aging times are also listed in Table 1.

Table 1. Aging Time, t_{age}, and δH Value Obtained from the δC_p dT Integral and $\Delta\sigma$ Values Obtained from the δC_p d ln T Integral[a]

t_{age} (min)	δH (J/g)	$10^4 \times \Delta\sigma$, J/(g K)
1	0.086	2.4
3	0.27	7.9
10	0.47	13.8
30	0.77	22.5
100	1.30	37.4
300	1.77	50.3

[a]The temperature limits of integrals were from 293 to 370 K. In all cases the liquid was cooled at 80 K/min and then heated at 20 K/min. The aging temperature was 313 K.

The quantity δH is the enthalpy lost on isothermal aging for different t_{age}, and its value in Table 1 increases from 0.086 J/g for t_{age} of 1 min at 313 K to 1.77 J/g for t_{age} of 300 min. The quantity $\delta\sigma$ is also listed in Table 1. It varies from 2.4×10^{-4} J/(g K) for t_{age} of 1 min at 313 K to 50.3×10^{-4}J/(g K) for t_{age} of 300 min. According to the Clausius theorem, $\delta\sigma$ would be zero for a reversible (or nonspontaneous) process, not for an irreversible (spontaneous) process, and $\delta\sigma$ is not equal to the entropy lost. As discussed earlier here, the entropy of glassy state of sucrose is 1.20 J/(g K) at 338 K and $\delta\sigma$ is 0.02% of this entropy for t_{age} of 1 min and 0.4% for t_{age} of 300 min. This means that one may use the irreversible heating path from glass to liquid for obtaining the entropy without significant errors when t_{age} is short. The error increases when t_{age} is long. The method can be used also for two glass samples aged for different t_{age} at the same T_{age}.

The method of using $\delta C_{p,\mathrm{app}}$ of two differently aged glasses is equivalent to taking the difference between the entropy lost in one closed cycle in which t_{age} is zero or short and the entropy lost in the second closed cycle in which t_{age} is long. In our study, the melt was cooled to form the glass at the same rate in the two cycles and the glass heated at the same rate. But for examining the consequences of violating the Clausius theorem, q_c of the liquid and q_h of glass can also be different; i.e., $\delta C_{p,\mathrm{app}}$ may be the difference between the $C_{p,\mathrm{app}}$ of two samples formed at different rates, aged for different times at the same or different T_{age} and heated at different rates.

5. CONCLUSIONS

On heating, physically aged sucrose glass shows an endothermic increase in the $C_{p,\mathrm{app}}-T$ plots of its *glassy* state. The endothermic feature precedes the large endothermic increase due to the onset of kinetic unfreezing of the glass to the liquid state, and it is similar to that observed for polymer and metal alloy glasses but weaker. Its strength is high when T_{age} is high, or when t_{age} is long. When T_{age} is closer to $T_{g\to l}$, the feature becomes a small but high shoulder and almost undiscernible. In such cases its presence is resolved by plotting d$C_{p,\mathrm{app}}$/dT against T.

Aging of a glass decreases its $C_{p,\mathrm{app}}$. The effect is expected to be higher when a glass formed by rapid cooling is aged, and this may be tested by studying the effects of aging a glass formed by cooling at orders of magnitude higher rate (up to 60 000 K/s) by fast scanning calorimetry method, as in ref 21.

Increase in $C_{p,\mathrm{app}}$ on heating of aged sucrose glass toward its equilibium liquid state occurs in two steps. The T range of the first step in which the glassy state is maintained is slightly broader, as for a polymer,[12] depending upon q_c, T_{age}, t_{age}, q_h,

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and the material, than the second step that begins at T^{onset} and takes the glass to the liquid state through a C_p-overshoot. The two steps may be merged or further separated by controlling the thermal history of a glass.

Molecular motions biased toward decreasing the enthalpy and entropy on aging are not seen as density and structure fluctuations. So an interpretation of the sub-T_g endotherm in terms of such fluctuations would be inappropriate because the process is thermally irreversible. The sub-T_g endotherm is also not attributable to localized fluctuation that appears as JG relaxation in the dielectric, mechanical, and DSC studies.[36,45] They are likely to be due to the kinetic unfreezing of faster modes of motion in the broad distribution of relaxation times. The broad endothermic feature observed at T far below T^{onset} seems to be a continuation of the generally observed sub-T_g endotherm to a lower T, as indicated by modeling. If so, it too would be due to the unfreezing of faster modes of motion on heating an aged glass. This may be investigated (i) by studying liquids showing different distribution of relaxation times and (ii) by heating a glass rapidly to T in the middle of the sub-T_g endothermic peak and thereafter observing the rate of enthalpy release with time. We plan to perform such experiments.

In the potential energy landscape view, the loss of entropy on aging of glass is seen in terms of continuous motion of the state point in a configurational space to configurations of deeper and lower energy minima isothermally with time, and recovery of the entropy on heating is seen as motion of the state point to configurations of higher energy minima. Occurrence of sub-T_g endotherm and the implied increase in the entropy of the glass require that the potential energy minima be distributed such that motion of the state point to a different part of PEL occurs, especially as each part would consist of a state with a different populations of hydrogen bonds, molecular isomers, ion and ion pairs, and entities formed by electrostatic and other type of interactions.

While the net enthalpy change in a liquid−glass−liquid closed cycle with or without annealing is zero, the entropy change, which we determined from the $C_{p,\text{app}}\, \mathrm{d}\ln T$ integral by violating the Clausius theorem, is insignificantly small. The $C_{p,\text{app}}-T$ data analyzed by using the difference between two $C_{p,\text{app}}-\ln T$ integrals, one for heating the unaged sample and other for heating the isothermally aged sample, show that this integral is equal to the ratio of the enthalpy lost on aging divided by T_{age}. Although the use of the time-dependent C_p values for determining the entropy is forbidden by the Clausius theorem, the use of such C_p values in the $C_p\, \mathrm{d}\ln T$ integral has little consequence for determining the entropy of a glass.

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Notes

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