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Thermodynamic characterization of vapor-deposited amorphous solid [☆]

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Abstract

An adiabatic calorimeter designed for vapor-deposited sample has been applied to two molecular liquids, butyronitrile and 1-pentene, in order to characterize amorphous solid produced by vapor condensation. Comparisons are made between thermodynamic behavior of the vapor-deposited (VQ) and liquid-cooled (LQ) amorphous solids of both samples. It can be concluded that both the LQ and VQ solids exhibit essentially the same phenomena; the glass transition, residual entropy, and enthalpy relaxation. These are the reflection of the metastability and the non-equilibrium nature of both amorphous solids. From a quantitative viewpoint, however, the two types of amorphous solid behave differently. The VQ samples show the enthalpy relaxation occurring just above the temperature of deposition, and have larger residual entropy compared to the LQ samples. These results indicate the effective extraction of the kinetic energy of molecules during the process of condensation from vapor to amorphous solid.

Keywords: Calorimetry; Enthalpy relaxation; Metastable; Thermodynamics

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1. Introduction

It is well known that glass is a non-equilibrium amorphous solid and inherits its structure from the liquid [1]. A wide range of substances including monomeric and polymeric compounds of organic and inorganic origins have been vitrified by cooling their liquids. There is a large difference in glass-forming ability among these liquids. A good glass-former is readily undercooled to realize its glassy state by avoiding crystallization. The ability is inversely proportional to the crystallization tendency. Many liquids with poor glass-forming ability require an ultra-fast cooling technique [2] in order to by-pass the undesirable crystallization.

Vapor deposition is a powerful method for preparing amorphous solid from the vapor of the corresponding liquid with poor glass-forming ability. This is because the process can rapidly extract the thermal energy of molecules during production of the amorphous solid in a molecule-by-molecule fashion and avoid the passage through a liquid regime in which crystallization might take place [3]. A great deal of elaborate work has been accumulated on the glasses formed by liquid cooling [4]. Most of the works on vapor-deposited material, however, have thus far been carried out using rather simple instruments in order to investigate the qualitative aspect of properties, such as examining whether or not the glass transition exists in such amorphous solids [5].

In 1968, we constructed an adiabatic calorimeter for vapor-deposited sample and applied it to amorphous ice [6]. The experiment clearly showed the glass transition phenomenon at 135 K. Since then, we have improved the calorimeter to a sophisticated level [7]. In the present paper, we report thermodynamic characterization of vapor-deposited amorphous solid derived from some molecular liquids possessing good glass-forming ability. The experiments make it possible to compare thermal properties of non-crystalline solids prepared by vapor-condensation and liquid cooling. Here the thermal properties to be compared are the glass transition temperature, the residual entropy, and the rate of structural relaxation. Adiabatic calorimetry is particularly powerful in determining these properties in one experiment. The extremely high thermal stability of the adiabatic calorimeter enables easy detection of the spontaneous temperature drift of a sample due to irreversible enthalpy relaxation from a frozen-in non-equilibrium to the equilibrium state [8]. Analysis of the rate of spontaneous change in calorimetric temperature combined with the heat capacity data leads to kinetic parameters which govern the configurational enthalpy relaxation.

2. Experimental

In order to minimize the undesirable temperature rise of the deposited surface due to much heat of condensation, it is necessary to send a sample vapor into a calorimetric cell as slowly as possible. A typical flow rate is such that 1 g of amorphous deposit is produced during 100 h. This slow condensation rate requires the construction of an adiabatic calorimeter with a built-in cryo-refrigerator which can maintain the desired low temperatures for a long time.

Fig. 1 shows a schematic drawing of the calorimeter that satisfies the above conditions for the condensation. The calorimeter is essentially of a filling tube type [9]. Sample vapor is introduced in vacuo through a filling tube C into a calorimeter cell O installed in a cryostat with a built-in refrigerator F and H. The cryostat, enclosed by an outer vacuum jacket S, is partitioned into the inner and outer sides of the inner vacuum jacket Q. The adiabatic condition of the calorimeter is maintained by regulating the temperatures of both the adiabatic shields P, M, and

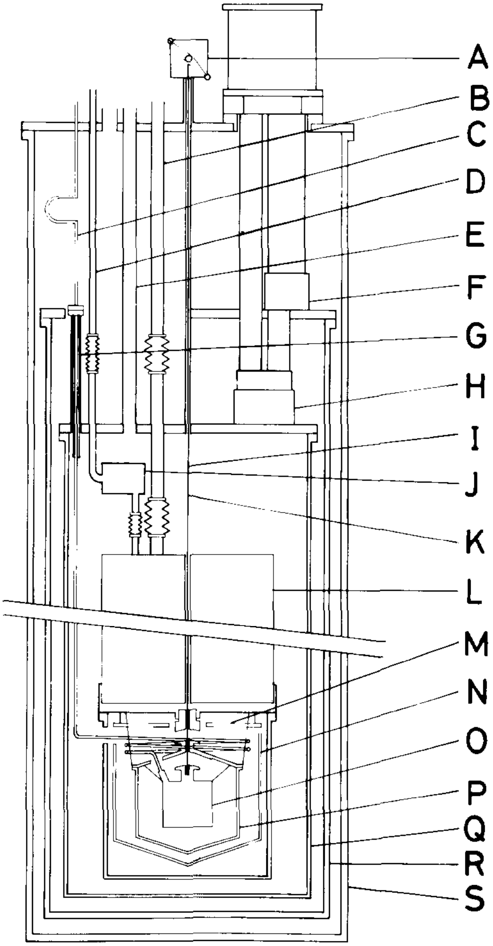

Fig. 1. Schematic drawing of an adiabatic calorimeter for vapor-deposited sample: A, windlass; B and D, inlet and outlet tubes of coolant; C, sample filling tube; E, evacuation; F, first stage of refrigerator; G, multi-folded steel tube; H, second stage of refrigerator; I, nylon thread; J, heat exchanger; K, nylon thread; L, coolant tank; M, copper plate; N, outer adiabatic shield; O, calorimeter cell; P, inner adiabatic shield; Q, inner jacket; R, radiation shield; S, outer jacket.

N and of five portions of the filling tube under high vacuum. A thermal contact between the top part of the cell and a coolant tank L is made by operating a windlass A to lift the cell with a braided nylon thread I.

A large temperature difference between the sample cell and the filling tube must be maintained during sampling in order to avoid condensation of the sample vapor inside the filling tube. Minimization of heat leak through the sample filling tube is important for obtaining accurate heat capacity data. To this end, a special connector between the cell and filling tube was developed by using a thin stainless steel tubing. The heat flux through this connector was estimated to be 50 mW in the situation where the cell temperature is 20 K while that of the filling tube is 300 K. The heat capacity data are necessarily inferior to those obtained by conventional adiabatic calorimeters by two factors; the small amount of deposited sample and the additional heat leakage through the filling tube.

Two samples, butyronitrile and 1-pentene, were vitrified by vapor-deposition (VQ) and liquid cooling (LQ), respectively. For butyronitrile, the vapor was condensed into the cell kept at around 40 K (VQ1) and 67 K (VQ2), in order to examine how the substrate temperature affects the thermodynamic properties of the amorphous solid. For 1-pentene, only one VQ sample was produced in the cell controlled at temperatures between 38 and 47 K. The sample thickness can be calculated to be approximately 100 μm by assuming uniform deposition. The LQ sample for each compound was produced by cooling their liquids at a rate of 2-3 K min^{-1}.

3. Results and discussion

Fig. 2 displays the molar heat capacities of butyronitrile for its crystalline, amorphous (LQ), and liquid states as a typical example. The heat capacities of the VQ sample are essentially the same as those of the LQ sample. Both the LQ and VQ samples exhibit large heat capacity jumps due to the glass transition at nearly the same temperature, 77 K. Large exothermic temperature drifts followed by endothermic ones arising from the enthalpy relaxation were observed for both samples [10]. The temperatures at which the turnover of the exothermic to endothermic temperature drifts took place did not differ significantly from each other. This turnover temperature can be taken operationally as the glass transition temperature T_g.

The heat capacities of both VQ and LQ samples were definitely larger than those of the crystal over the whole range of temperatures below T_g, as is usually observed in many glasses. It should be mentioned that the sample temperature undergoing spontaneous change due to enthalpy relaxation was extrapolated to the mid-point of each energizing period to determine the temperature increment. The heat capacity thus determined, therefore, corresponded to the vibrational part of the heat capacity of the system keeping a quasi-constant disordered configuration.

As far as the heat capacities determined in this way are concerned, there seems to be no significant difference between the VQ and LQ solids. If the configurational

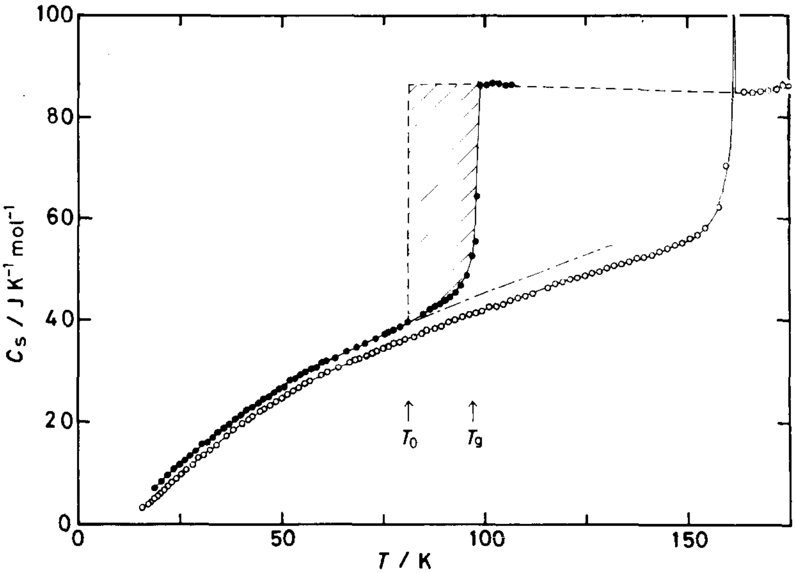

Fig. 2. Molar heat capacity of butyronitrile. Open circles stand for the data of crystal and liquid, and solid circles for those of glassy and undercooled liquids. The heat capacities of the VQ sample are essentially the same as those of the LQ sample. T_g and T_0 denote the glass transition and the Kauzmann temperatures, respectively.

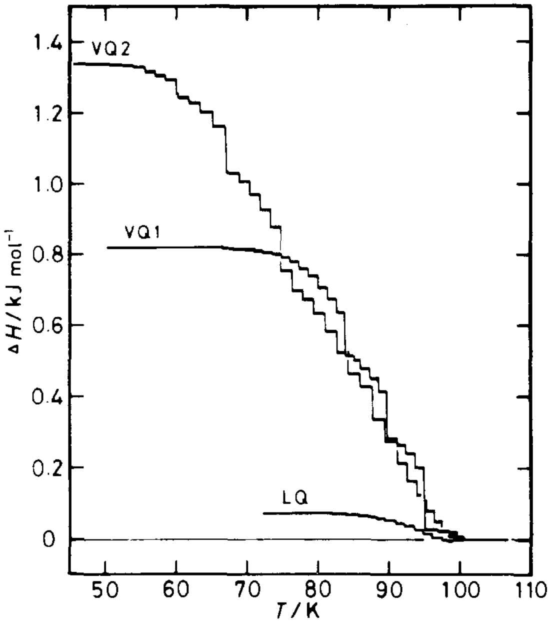

Fig. 3. Configurational enthalpy of butyronitrile liquid plotted against temperature for the VQ and LQ samples. The value at T_g is taken arbitrarily to be zero.

enthalpies of both solids are compared, however, a large distinction can be observed. The amount of configurational enthalpy evolved during warming from 11 K can be calculated from the spontaneous temperature drift rates by integrating them with respect to time for the heating and equilibration periods, along with the heat capacity data. The results are summarized in Fig. 3. Here, the configurational enthalpy at T_g is taken arbitrarily to be zero.

The curves give only the thermodynamic paths of the respective samples followed during the actual heat capacity measurement. The vertical segments of the VQ1 and VQ2 samples indicate that the sample temperatures were followed over a relatively long period for the determination of the rate of the enthalpy relaxation. The effect of residual heat leakage was corrected for in the calculation. The most remarkable fact is that the configurational enthalpy of the VQ2 sample amounts to more than 1.3 kJ mol^{-1} at the initial deposited state. The corresponding value of the VQ1 solid is about 0.8 kJ mol^{-1} and that of the LQ solid is less than 0.1 kJ mol^{-1}. The value for the VQ2 solid corresponds roughly to 40% of the enthalpy of crystallization at 110 K. The lower the substrate temperature, the higher the configurational enthalpy. In terms of the concept of fictive temperature T_{fic} [11], it can be concluded that the VQ solid has a T_{fic} value higher than that of the LQ solid. The concept introduced by Tool [11] is based on the assumption that each non-equilibrium state at a temperature T exhibits the same structure as that of the equilibrium liquid at a T_{fic} possessing the same configurational enthalpy. Also it can be said that the sample deposited on substrate with lower temperature gives amorphous solid with higher T_{fic}.

Another significant fact is that the enthalpy relaxation for the VQ samples starts to occur just above the deposition temperature. The enthalpy relaxation can be observed generally at temperatures 10–20 K lower than T_g for many classical glass-forming liquids [12]. Butyronitrile is not an exceptional case. In glass science, a particular temperature designated the Kauzmann temperature T_K (or T_0) with singular nature is defined [1]. This is the temperature at which the configurational entropy of the equilibrium liquid vanishes with decreasing temperature. For butyronitrile, T_K is calculated to be 81.2 K. Thus the enthalpy relaxation occurs in the VQ solid in the temperatures far below T_K depending on the substrate temperature. The low temperature enthalpy relaxation is one of the characteristic features of the VQ amorphous solids that has never been observed in ordinary glasses.

Essentially the same results were obtained for 1-pentene, which again is known as a good glass-former. The molar heat capacity for its crystalline, amorphous (VQ and LQ), and liquid states is given in Fig. 4. In this case, only one type of VQ sample was prepared in the calorimetric cell kept at temperatures between 38 and 47 K. The crystalline sample was produced inside the cell by annealing the undercooled liquid at several temperatures between the glass transition temperature of 70 K and the fusion temperature of 107.8 K. Large heat capacity jumps associated with the glass transition appeared at essentially the same temperature for both types of amorphous solid. The configurational enthalpy relaxation of the VQ solid occurred at temperatures much lower than those for the LQ solid. The configurational enthalpy traced during the actual measurement is shown in Fig. 5 as

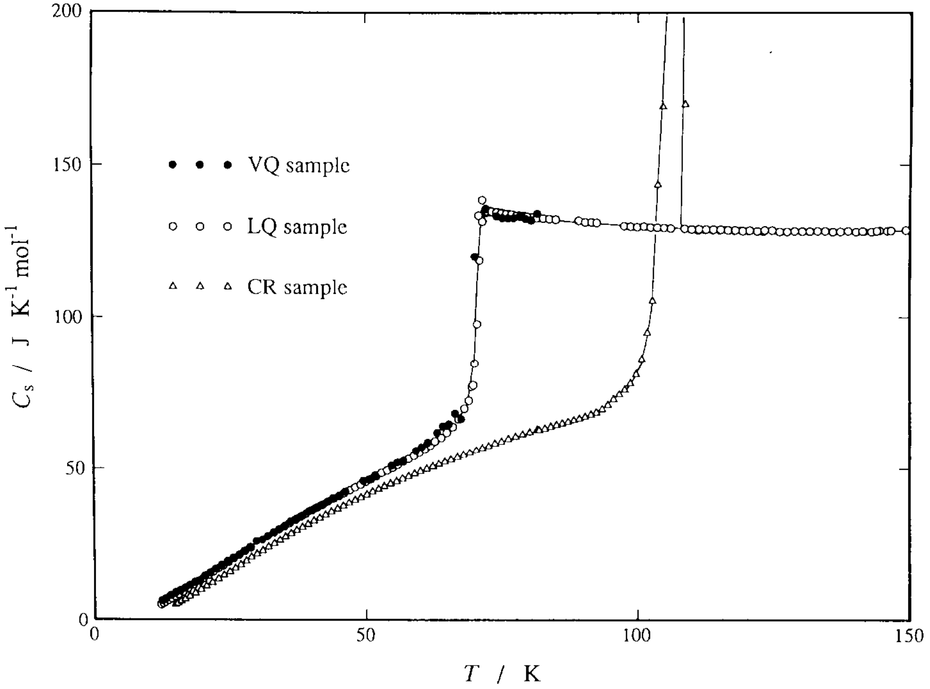

Fig. 4. Molar heat capacity of 1-pentene.

a function of temperature for both the VQ and LQ solids. The effect of residual heat leakage was also corrected for. The total enthalpy of the VQ solid relaxed below T_g was more than 1 kJ mol^{-1}, while that of the LQ solid was about 0.15 kJ mol^{-1}.

The residual entropy of non-equilibrium disordered liquid can be obtained by a loop calculation of the quantity C_p/T by integrating it with respect to temperature along the path

$$\text{Crystal (0 K)} \rightarrow \text{Crystal } (T_{\text{fus}}) \rightarrow \text{Liquid } (T_{\text{fus}}) \rightarrow \text{Liquid (0 K)} \qquad (1)$$

In the last step, the glass transition process is involved. The residual entropies of the VQ and LQ solids can be calculated to be 17.75 J K^{-1} mol^{-1}. Because the heat capacities of the VQ and LQ solids are essentially the same, the residual entropies evaluated from these data should coincide with each other. However, this value is an apparent residual entropy because the configurational entropy relaxed during the heat capacity measurement. As has been stated earlier, the experimental heat capacity corresponds to the contribution from vibrational degrees of freedom that can respond quickly to the Joule heating. Also it should be noted that the vibrational heat capacities of the crystal and liquid are not identical over the whole temperature range. The above calculation does not take into account this effect.

If we want to determine the residual entropy associated with frozen-in configurational disorder, we must calculate first the configurational heat capacity C_c by the equation

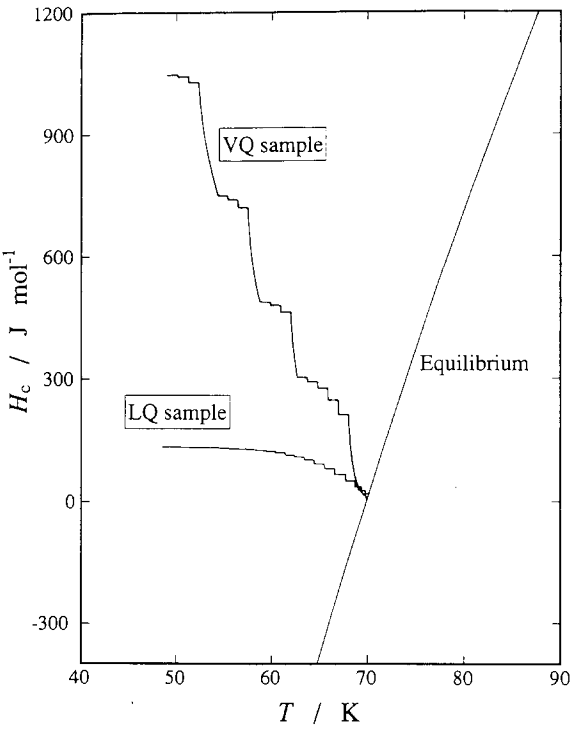

Fig. 5. Configurational enthalpy of 1-pentene plotted against temperature for the VQ and LQ samples.

$$C_c(T) = C_p^{eq}(T) - C_{vib}^{l}(T) \tag{2}$$

where C_p^{eq} denotes the heat capacity of the equilibrium liquid, and $C_{vib}^{l}(T)$ is the vibrational heat capacity of the actual liquid. The latter quantity is just the experimental heat capacity value of the amorphous solids. The configurational entropy S_c of amorphous solid with fictive temperature T_{fic} can be determined by

$$S_c = \int_{T_K}^{T_{fic}} C_c(T)\, \mathrm{dln}\, T \tag{3}$$

Here, T_K is the temperature at which the configurational entropy becomes zero. Taking into account the heat capacity difference between the crystal and liquid, the above equation can be rewritten as

$$\begin{aligned} S_c &= S_c(T_{fus}) - \int_{T_{fic}}^{T_{fus}} C_c(T)\, \mathrm{dln}\, T \\ &= \Delta_{fus}S - \int_{0}^{T_{fus}} [C_{vib}^{l}(T) - C_{vib}^{cr}(T)]\, \mathrm{dln}\, T - \int_{T_{fic}}^{T_{fus}} C_c(T)\, \mathrm{dln}\, T \end{aligned} \tag{4}$$

where $\Delta_{fus}S$ respresents the entropy of fusion, and $C_{vib}^{cr}(T)$ the heat capacity of crystal. The entropy of fusion is not exactly identical with $S_c(T_{fus})$ because of the

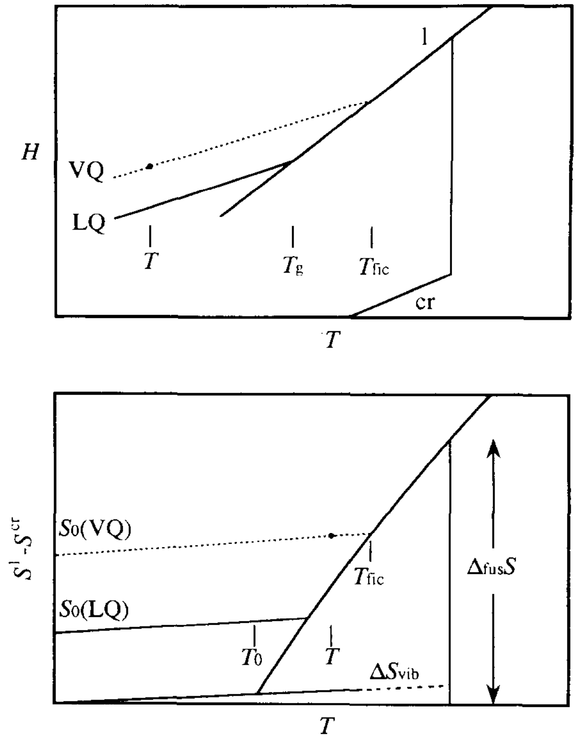

Fig. 6. Schematic drawing for the determination of fictive temperature and residual entropy of vapor-deposited 1-pentene sample initially produced. The Kauzmann temperature is denoted as T_0. The value of T_{fic} for LQ 1-pentene initially produced was determined in the same way.

slight difference in vibrational heat capacities between the crystal and liquid. The fictive temperatures of the VQ and LQ solids at the initial frozen state were determined to be 85.2 and 71.4 K, respectively. The situation is drawn schematically in Fig. 6. By combining these numerical values, the corrected residual entropies of the VQ and LQ solids referred to the initial states were determined to be 31.7 and 19.7 $\mathrm{J\ K^{-1}\ mol^{-1}}$, respectively. These quantities are graphically shown on the ordinate of Fig. 7, in which the entropies of various states of 1-pentene are drawn as a function of temperature.

It is clear that the residual entropy should depend on the manner in which a particular non-equilibrium state was produced. The residual entropy of the LQ solid does not differ much from that obtained by the traditional method ignoring the difference in vibrational heat capacities of the crystal and liquid and the enthalpy relaxed during warming. However, the residual entropy of the VQ solid is much larger than that of the LQ solid, indicating a large-scale frozen disorder with respect to molecular configuration and conformation in the VQ solid. A more detailed description of the thermodynamic behavior of 1-pentene, including a comparison of the nature of enthalpy relaxation of the VQ and LQ amorphous solids will soon be reported [13].

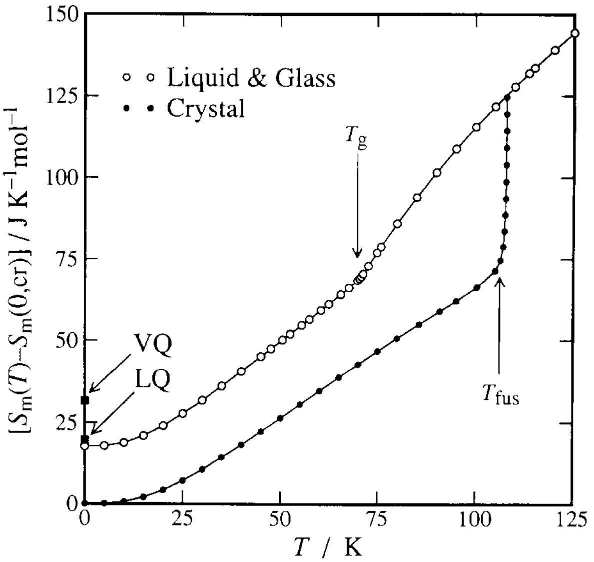

Fig. 7. Third-law entropy of the glassy and equilibrium liquids (open circles) and crystal (closed circles) of 1-pentene. The closed marks on the axis of ordinates denote the estimated residual entropy of the LQ and VQ solids initially prepared.

4. Concluding remarks

Both the butyronitrile and 1-pentene examined here are "fragile" liquids according to the phenomenological classification proposed by Angell [14]. The large magnitude of the heat capacity jump at T_g is taken as a reflection of the degree of melt fragility. Rapid degradation of liquid structure on warming will require extra energy for changing the intermolecular interactions of the system.

The following is a brief synopsis of the experimental results. (a) For butyronitrile and 1-pentene, each VQ and LQ amorphous solid exhibited the glass transition at essentially the same temperature irrespective of the method of preparation. (b) The configurational enthalpy of each VQ solid was much higher than that of the corresponding LQ solid. (c) Enthalpy relaxation began to occur at much lower temperatures for the VQ solid than that for the corresponding LQ solid. This low-temperature relaxation has never been reported in many classical glass-forming liquids. (d) The residual entropy of the VQ solid was much higher than that of the LQ solid, indicating formation of amorphous solid with high T_{fic} for the VQ solid.

A new picture of the vitrification process has emerged [15,16]. It points out the possibility of new kinds of glassy structure composed of clustered pseudophases connected to each other by tissue with disordered structure. If a sample vapor is deposited, various sizes of cluster will be accommodated on the substrate surface. The average size of clusters will be smaller for the VQ solid compared to the LQ solid, because of the rapid condensation of the vapor across a wide temperature difference. The estimated cooling rate is of the order of 10^5 K s^{-1} for the condensation process. The clusters with smaller size in the biphasic structure of the VQ solid will grow first up to the corresponding structure of the LQ solid. This can be considered as an origin of the low-temperature stabilization observed only for the VQ solid. Another possible explanation of the low-temperature behavior is that the extremely high configurational entropy of the VQ solid has a very short relaxation time for the structural change, as has been suggested by Adam and Gibbs [17]. They proposed that the relaxation time is an exponential function of reciprocal TS_c. In any event, it is necessary to characterize thermodynamically the LQ solid prepared in situ by ultra-fast cooling in order to test the validity of these conjectures. Unfortunately, however, this type of experiment is beyond the ability of our present calorimetric system.

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