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ENTHALPY RELAXATION IN VAPOR-DEPOSITED BUTYRONITRILE *

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ABSTRACT

Spontaneous enthalpy-evolution processes reported previously for vapor-deposited non-crystalline samples of solid butyronitrile were analyzed in terms of the equations of Kohlrausch, Williams and Watts (KWW), and of Adam and Gibbs (AG). The application of the KWW equation showed that the enthalpy relaxation deviated significantly from exponential behavior. The fractional exponent β characterizing the non-exponential nature was found to be 0.07 at 83.8 K, 0.11 at 89.7 K and 0.21 at 95.0 K. The significant deviation of β from unity reflects the extremely high fictive temperature of the specimen. The AG equation fitted the relaxation data well suggesting that the chemical potential $\Delta\mu$ hindering the cooperative rearrangement of molecules at each temperature was almost constant. The results were compared with other data derived from glasses prepared by conventional cooling of liquids.

INTRODUCTION

It is not unusual during the continuous cooling of a disordered system for some aspects of the system to fail to maintain thermal equilibrium [1]. The most dramatic examples of such freezing transitions are found in glass-forming materials [2,3]. Real glass-forming liquids of molecular, ionic, and polymeric origins exhibit some common properties around their glass transition temperatures, such as sudden decreases in the heat capacity and associated thermodynamic quantities, non-exponential relaxations of various properties, and a temperature-dependent activation enthalpy for structural relaxation [4]. A central problem in the study of glasses is that of understanding the nature of the relaxation processes in the liquid and glassy states [5].

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It is now recognized that glass-forming ability is almost a general property of condensable matter. Vapor deposition [6] is a powerful technique for producing non-crystalline solids. The method extracts rapidly the thermal energy of molecules and produces a non-crystalline solid in a molecule-by-molecule fashion.

In a previous paper [7], we reported a new type of adiabatic calorimeter for producing vapor-deposited material and the successful production of non-crystalline samples of solid butyronitrile. The following is a brief synopsis of the experimental results. (a) Both the vapor-quenched (VQ) and the liquid-quenched (LQ) samples of butyronitrile exhibit heat capacity jumps characteristic of the glass transition at the same temperature 97 K. (b) The excess configurational enthalpy of the VQ sample is much higher than that of the LQ sample. For the VQ sample deposited at 40 K, the configurational enthalpy was 1.33 kJ mol^{-1}, compared with 0.08 kJ mol^{-1} for the LQ sample, indicating the formation of a non-crystalline solid with high fictive temperature [8]. (c) Enthalpy stabilization began to occur at much lower temperatures for the VQ samples than that for the LQ sample. The rate of enthalpy relaxation of the VQ sample observed at three different temperatures showed highly non-exponential behavior.

Such a non-exponential relaxation is known to be a characteristic feature of conventional glasses prepared by cooling liquids around and below their glass transition range. Many empirical and theoretical equations have been proposed to reproduce the experimental data for various kinds of liquid. It is the purpose of the present paper to examine whether these equations can be applied to a vapor-deposited non-crystalline solid far from equilibrium.

SOME PROPOSED EQUATIONS FOR RELAXATION

The temperature dependence of the structural relaxation time when there is a marked deviation from the classical Arrhenius behavior is well expressed by the following empirical relation, known as the Vogel, Tammann and Fulcher (VTF) equation [9,10]

$$\ln \tau = A + B/(T - T_\infty) \tag{1}$$

where T_∞ is the temperature at which the relaxation time becomes infinity and may be replaced by the Kauzmann temperature T_0 [11]. The Kauzmann temperature is defined as the temperature at which the excess configurational entropy of the liquid vanishes [12]. This equation, however, holds only in a state close to equilibrium near the glass transition temperature. In fact, spontaneous heat evolution in the VQ sample of butyronitrile was observed far below the Kauzmann temperature T_0, which was calculated later to be 81.2 K. This provides evidence that the VTF equation cannot be applied directly to relaxation processes occurring in a state far from equilibrium.

A variety of experiments have shown that the decay of density or enthalpy in a liquid can be expressed over a period of time by the Kohlrausch–Williams–Watts (KWW) empirical equation [13],

$$\phi(t) = \exp\left[-(t/\tau)^{\beta}\right] \qquad 0 < \beta \leq 1 \tag{2}$$

where $\phi(t)$ is the relaxation function, τ is the relaxation time and β is a constant characteristic of the distribution of the relaxation times. Obviously $\beta = 1$ corresponds to exponential decay. Therefore, β reflects the non-exponential nature of the relaxation and is called the fractional exponent. The equation was introduced in 1847 by Kohlrausch [14] for describing the viscoelastic property of plastics. Williams and Watts [15] showed later that this function can be transformed analytically to give the frequency-dependent dielectric permittivity if β is chosen to be 0.5. A numerical calculation has been performed to find the distribution for $\beta = 0.1$ to 0.9 [16]. In the glass transition region, there exists a wide distribution of the relaxation times [16,17]. In this respect, the equation has the advantage of replacing a complicated distribution of the relaxation times by the single parameter β. This exponent is usually, but not always, close to 0.5 but may differ for different relaxing quantities in the same material [18]. It cannot be stressed enough that this is a response to an infinitesimal perturbation [19], like a small temperature jump or pressure jump applied to an equilibrated liquid. For most materials, it is found that the average relaxation time τ has non-Arrhenius behavior with an activation enthalpy that increases rapidly as the temperature is lowered.

Another commonly used expression to describe the temperature dependence of the average relaxation time is that proposed by Adam and Gibbs (AG) [20],

$$\tau = A \exp\left[\Delta\mu s_c^{\star}/kTS_c\right] \tag{3}$$

where S_c is the macroscopic configurational entropy which reflects the actual structure of the liquid. The quantity $\Delta\mu$ is the chemical potential per molecule hindering the cooperative rearrangement of a group of molecules (namely a cluster), and $s_c^{\star}$ is the configurational entropy of the smallest cluster that can undergo a rearrangement. The configurational entropy S_c is defined as the entropy of the metastable liquid relative to that of the stable crystal at the same temperature. Often, it is found that extrapolations of entropy data to temperatures below the experimental glass transition temperature T_g predict that the configurational entropy vanishes at the Kauzmann temperature T_0 at which point the constituent molecules take the amorphous ground-state configuration [20]. Controversy remains as to what may occur at T_0. The AG entropy theory suggests that the dramatic increase in the structural relaxation time of a liquid at low temperatures is caused by a thermodynamic singularity at T_0. The temperature is related to the heat capacity jump ΔC_p at T_g, the difference in the heat capacities of the liquid and crystal at T_g, by the following equation,

$$\int_{T_0}^{T_{\text{fus}}} \frac{\Delta C_p}{T}\,dT = \Delta_{\text{fus}}S \tag{4}$$

where $\Delta_{\text{fus}}S$ is the entropy of fusion at T_{fus}. Integration shows that the Kauzmann temperature T_0 of butyronitrile is 81.2 K. Naturally the difference between the temperatures T_0 and T_g depends on the magnitude of ΔC_p and $\Delta_{\text{fus}}S$. Liquids with high ΔC_p values, as in the present case, were called "fragile" by Angell [21] because they have structures which degrade rapidly on warming around T_g. Equation (3) has been applied successfully to many monomeric and polymeric glasses both near equilibrium [20] and far from equilibrium [22].

RESULTS AND DISCUSSIONS

Evaluation of effective relaxation times

Figure 1 reproduces from ref. 7 the heat capacities of butyronitrile in various states of aggregation. The measurement is based on a discontinuous heating mode under adiabatic conditions. Solid circles stand for the values

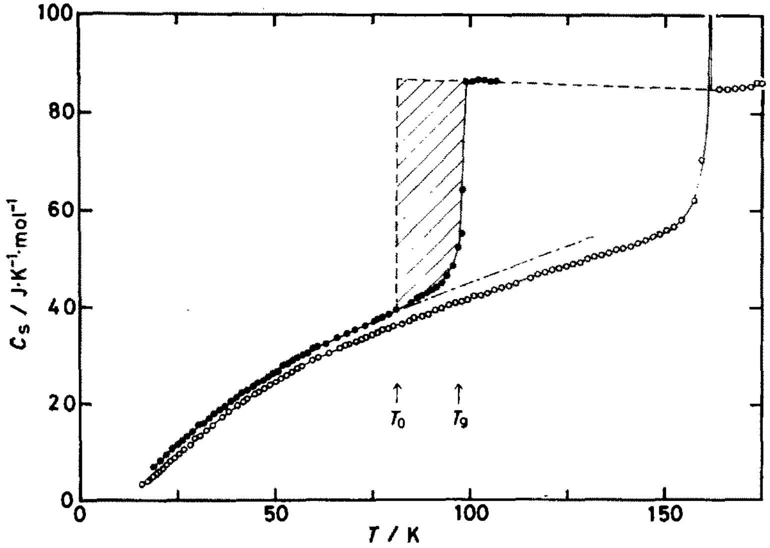

Fig. 1. Molar heat capacities of butyronitrile reproduced from a previous paper [7]. Open circles stand for the data of crystal and liquid, solid circles for those of glass and undercooled liquid, and a broken line for the assumed temperature dependence of heat capacity of the undercooled liquid at equilibrium. T_g and T_0 denote the glass transition and the Kauzmann temperatures, respectively.

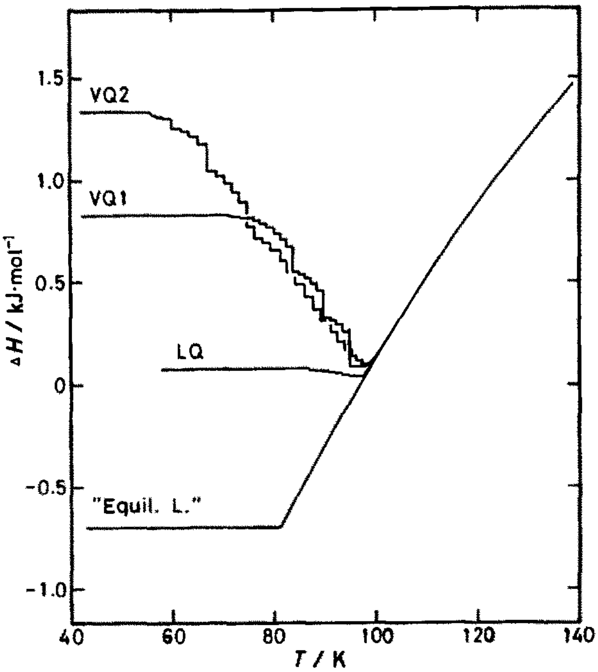

Fig. 2. Configurational enthalpy versus temperature followed in the measurements. The "Equil. L." line was derived from the assumed equilibrium heat capacities shown by the broken line in Fig. 1.

of the undercooled liquid and non-crystalline solid, and open circles for those of the equilibrium liquid and crystal. Owing to the small size of the sample (about 0.02 mol), the accuracy of the results is inferior to that obtained by standard calorimetry with a large amount of sample. To overcome the lack of heat capacity data in the wide 'crystallization-dangerous' temperature range of this material, we assumed that the hypothetical equilibrium heat capacity of the undercooled liquid could be found by joining smoothly the values immediately above the glass transition and fusion temperatures (broken line in Fig. 1). The dot-dash line approximates the heat capacities of the glass without the glass transition and represents the contribution from the relevant vibrational degrees of freedom in the non-crystalline state, as assessed from the crystal heat capacity multiplied by an appropriate factor.

Figure 2 shows the configurational enthalpies of various states of butyronitrile based on the corresponding heat capacity data. Adiabatic calorimetry was used to measure the enthalpy of the material as a function of temperature. From this, the heat capacity was calculated after correcting for temperature drift arising from residual heat leakage and enthalpy relaxation [23]. If the enthalpy of a sample in a non-equilibrium state relaxes towards the equilibrium value, the process can be monitored by observing the spontaneous change of calorimetric temperature in the equilibrium period under adiabatic conditions. A decrease of sample enthalpy reveals itself as a spontaneous temperature rise and vice versa. In this study, the temperature drifts were treated in the heat capacity calculations as if they arise solely from heat leakage, so that the obtained result is equivalent to the 'instantaneous' heat capacity and contains no contribution from the relaxational degrees of freedom. The enthalpy of the equilibrium liquid is denoted in Fig. 2 as Equil. L. and that of liquid-quenched sample as LQ. Two kinds of vapor-deposited samples were measured: VQ1 was prepared at a substrate temperature of 67 K and VQ2 at 40 K. The reference value for the configurational enthalpy was taken to be the value for the LQ sample at the temperature at which the spontaneous temperature drifts change from being positive to being negative. This occurs when the enthalpy curves of the actual and equilibrium states cross each other.

The enthalpy–temperature relation of each non-equilibrium state was calculated using successive backward integrals of the temperature drift rate with respect to time, and addition of the supplied electric energy in each heating period from the temperature of the equilibrium liquid to the point being determined. The curves give the thermodynamic paths which the respective samples followed in the actual heat capacity measurements. The horizontal segments of each curve correspond to the temperature rise owing to Joule heating with quasi-isoconfiguration, while the vertical segments correspond to the quasi-isothermal enthalpy relaxation toward the equilibrium liquid. The rather long vertical segments in the VQ1 and VQ2 samples indicate that the spontaneous temperature drifts of the samples were followed over a long period.

Figure 2 enabled us to estimate the fictive temperature T_{fic} [8] of each non-crystalline sample. This quantity is a measure of the deviation of a system from equilibrium and is a single-order parameter. It is defined as the temperature at which the configuration of the liquid would be at equilibrium. Thus the value of T_{fic} of the VQ2 sample is 134 K, that of VQ1 is 119 K, and that of LQ is 100 K. These values can be compared with the conventionally defined T_g, 97 K. The results indicate that the vapor-deposition technique produces a non-crystalline state which deviates farther from the equilibrium liquid produced by the liquid-cooling method.

The rate of enthalpy relaxation was analyzed by the following equation with an effective relaxation time τ_{eff}

$$\mathrm{d}\Delta H(t)/\mathrm{d}t = -\Delta H(t)/\tau_{\mathrm{eff}}(t) \tag{5}$$

where ΔH(t) is the excess enthalpy at time t that can relax toward the equilibrium value. The left-hand side of the equation, $\mathrm{d}\Delta H(t)/\mathrm{d}t$, can be calculated by multiplying the experimental heat capacity with the temperature drift rate at each time. As an example, the decay of the configurational enthalpy observed at 95 K for the VQ1 sample is shown in Fig. 3 as a

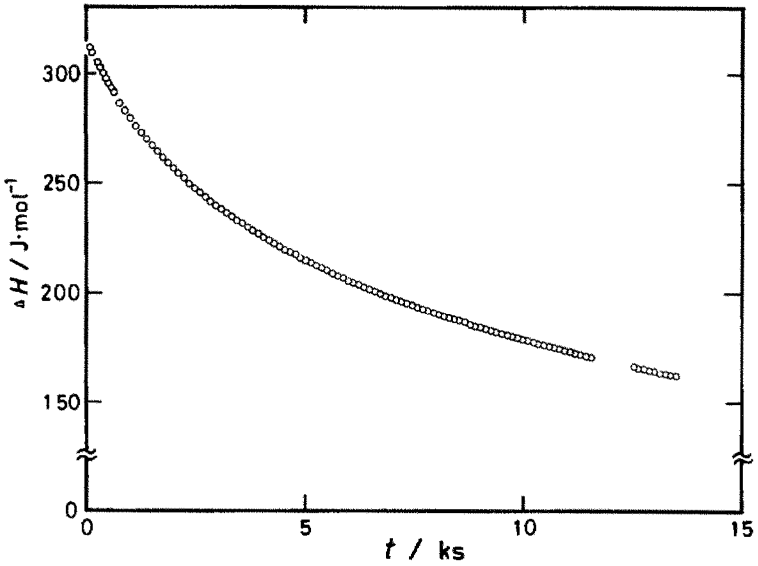

Fig. 3. Enthalpy relaxation rate observed at 95.0 K.

function of time. The slope of the curve at each moment corresponds to the left-hand side of eqn. (5), $d\Delta H(t)/dt$. The relation of the effective relaxation time to the temperature for each sample thus determined is shown in Fig. 4. All the values of τ_{eff} range from 10^3 to 10^7 s, conforming to the time-scale of the calorimetric observation. Open and solid circles represent the results of two series of measurements for the LQ sample. Since the samples in both series approach the equilibrium state with increasing short-range order on heating, the curves are convex. Such an observation cannot

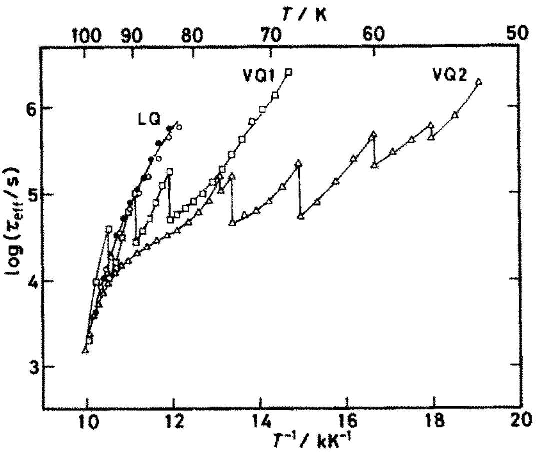

Fig. 4. Temperature dependences of effective relaxation times which LQ, VQ1 and VQ2 samples followed on heating.

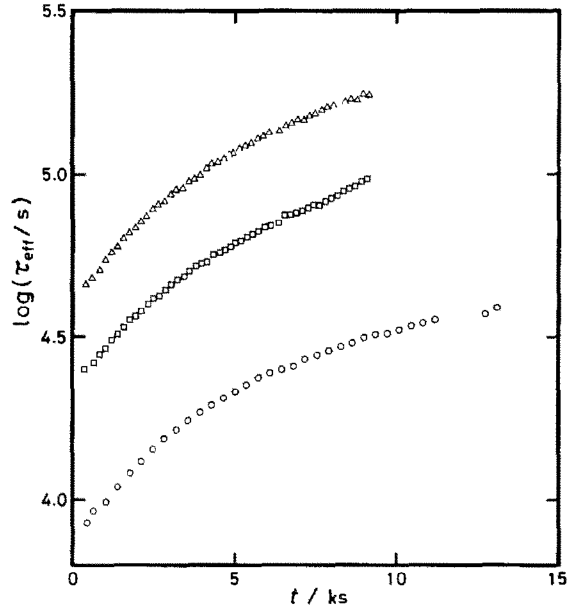

Fig. 5. Changes of the effective relaxation times at 83.8 (△), 89.7 (□) and 95.0 K (○) with time, indicating non-exponential enthalpy relaxations of vapor-deposited butyronitrile.

be explained simply using equilibrium properties as in the VTF equation (eqn. (1)).

Nearly vertical segments in the plots of VQ1 and VQ2 show that the τ_{eff} becomes long during annealing at these points. Figure 5 shows details of changes in the relaxation times when the temperature of the VQ1 sample was maintained quasi-isothermally for a long period at 83.8 K, 89.7 K and 95.0 K. Obviously, the relaxation time is not constant, with relaxation taking place faster than the exponential relaxation in the initial stages and slower than it in the final stages. These data correspond to Kohlrausch's observation [14] that the relaxation time changes with time. Hereafter, only the data for the enthalpy relaxation of the VQ1 sample measured at these three temperatures are used in the analysis.

Analysis of the relaxation by use of the KWW equation

The fractional exponent β of the relaxation function can be evaluated by a direct application of the KWW equation to the enthalpy relaxation curve as shown in Fig. 3. When the equation is transformed into the following form, the exponent β is given explicitly as the slope of the plot of the left-hand side versus $\log(t/\mathrm{s})$.

$$\log\{\log[\Delta H(0)/\Delta H(t)]\} = \beta \log(t/\mathrm{s}) \qquad (6)$$

Results from the analysis of the data are shown in Fig. 6. In the curve fitting, t was replaced by $t - t_0$. Here, t_0 is an adjustable constant, since the

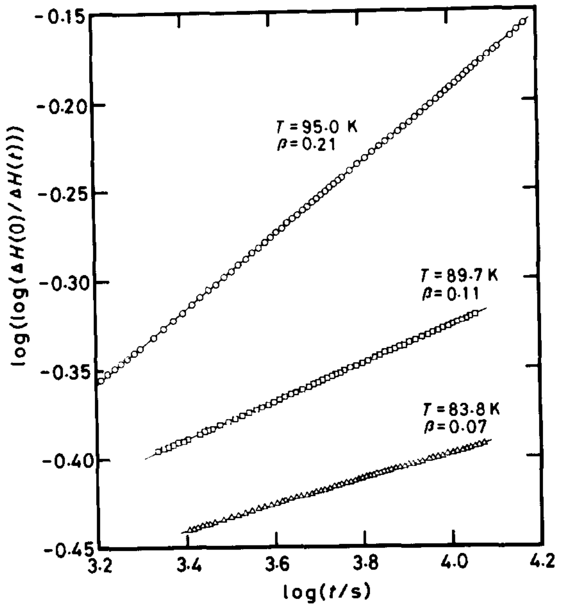

Fig. 6. Fitting of the exothermic enthalpy relaxation process in terms of the KWW equation.

origin of time in the actual experiment is ambiguous in relevance to the application of the exponent. All the data gave straight lines at the temperatures studied. The exponent β at 83.8 K is 0.07, very different from unity. As the temperature is raised, it increases to 0.11 at 89.7 K and 0.21 and 95.0 K.

Analysis of the relaxation by use of the AG equation

Application of the AG equation (eqn. (3)) to the relaxation process requires values for the macroscopic configurational entropy S_c at each moment of relaxation in addition to the effective relaxation times as plotted in Fig. 5. This quantity cannot be measured directly by calorimetry. Thus, the quantity S_c has first to be assessed from the relation of the configurational enthalpy versus the temperature. Figure 7 illustrates the evaluation procedure used in the present work. The upper and lower portions of Fig. 7 show the configurational enthalpy and entropy plotted against temperature, respectively. A dot-and-dash curve in each portion represents the temperature dependences at equilibrium; these were calculated from the undercooled-liquid heat capacity given by the broken line in Fig. 1. Solid arrows in the upper portion of Fig. 7 show the enthalpy relaxations observed in the actual experiment. From this plot, the fictive temperature T_{fic} of the specimen was derived as the temperature at which the equilibrium system would have the same configurational enthalpy as the non-equilibrium state under observation. The equilibrium configurational entropy S_c at T_{fic} can be easily

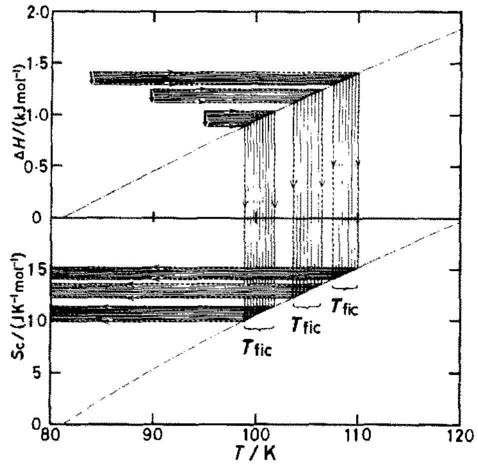

Fig. 7. Diagram showing the procedure for estimating the configurational entropy from the configurational enthalpy.

calculated from its dependence on temperature, as illustrated in the lower portion of the figure. The quantity S_c thus obtained at each moment of relaxation process was used in the application of the AG equation. This procedure assumes that systems with the same configurational enthalpy have the same configurational entropy, even if they are at different ambient temperatures and/or they have experienced different thermal histories. In other words, it assumes that the system in a non-equilibrium state relaxes along the dot-and-dash line which represents the temperature dependence of the equilibrium state.

The AG equation (eqn. (3)) can be rearranged into the following form by taking logarithms of both sides

$$\log \tau_{\text{eff}} = \log A + (\Delta \mu s_c^{\star}/TS_c) \tag{7}$$

Figure 8 shows plots of log τ_{eff} versus $(TS_c)^{-1}$ at the three different temperatures. The values of abscissa and ordinate were determined experimentally and a fitting parameter was not used in the analysis. The plots at each temperature are nearly straight lines implying that the numerator of the second term of the right-hand side in eqn. (7), $\Delta \mu s_c^{\star}$, is almost constant during the relaxation at each temperature. Increasing temperature causes the slope and therefore the quantity $\Delta \mu s_c^{\star}$ to reduce.

Comparison with other results

The KWW equation was applied to the relaxation behavior of glassy materials near the equilibrium state. Equation (2) has been shown to provide a good description of mechanical and dielectric relaxations [24], of enthalpy relaxation [25], and of light scattering [26] over a wide variety of materials.

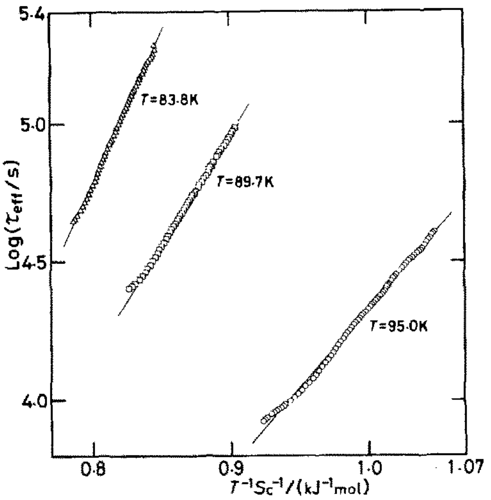

Fig. 8. Application of the AG equation to the exothermic relaxation process.

For nonpolymeric liquids, β usually lies between 0.3 and 0.8, with 0.5 being a typical value.

The same equation was found in the present analysis to describe the enthalpy relaxation of vapor-deposited non-crystalline samples of solid butyronitrile far from equilibrium. The derived fractional exponent revealed the highly non-exponential nature of the relaxation. The samples were deposited at the substrate temperatures of 67 K (VQ1) and 40 K (VQ2), both being lower than the Kauzmann temperature (81.2 K). The large deviation of β from unity indicates that the vapor-deposited sample contains various sizes of clusters with different relaxation times for molecular rearrangement.

The Cole–Davidson parameter β_{CD} of pure liquid is known to deviate gradually from unity in the equilibrium state as the temperature decreases [27]. This is caused by a spread in the distribution of relaxation times owing to inhomogeneity in the structure with different local short-range order. The temperature dependence of parameter the β is considered to show the same trend as that of β_{CD}, as exemplified by a dielectric study on poly(vinyl acetate) [28]. Thus, the extremely small value of β is considered to be evidence that the sample is located far from equilibrium with diverse short-range order. Indeed, Angell [29] observed that the non-exponentiality parameter β depended on the magnitude of the departure from equilibrium for the mechanical relaxation of $3KNO_3 \cdot 2Ca(NO_3)_2$ glass.

It is interesting to note that the KWW equation can be applied to the relaxation that occurs in the KCN–KBr solid solution [30]. In this case, the one component crystal KCN exhibits an orientational order-disorder transition. The replacement of the orientationally anisotropic molecular ions with the isotropic species lowers the temperature of the ordering transition and leads ultimately to a frozen-in state of the orientational degrees of freedom above some threshold concentration [31]. The enthalpy relaxation from the non-equilibrium to the equilibrium state with respect to the CN^- reorientation in the solid solution can be well expressed by the KWW equation with β ranging from 0.57 to 0.71. This value might arise from the distribution of the relaxation times caused by locally non-uniform compositions as well as by different sizes of the cooperative regions. Thus, the KWW equation has proved to be of wide applicability to relaxation processes in non-crystalline as well as crystalline solids.

Most of the structural relaxations have been conducted at modest departures from equilibrium. Scherer [22] has applied the AG equation to the volume relaxation data of an oxide glass located far from equilibrium [32]. The sample glasses were quenched rapidly from high temperatures to far below T_g (816 K). The highest fictive temperature of their samples was 881 K and the observation of volume relaxation was conducted at 773, 723 and 623 K. The estimated T_0 value was 436 K. Scherer concluded that the AG equation is valid for the samples far from equilibrium. These values for their glass samples should be compared with the present vapor-deposited sample; T_{fic} (the highest) = 134 K, $T_g = 97$ K, $T_0 = 81.2$ K and observation temperatures 83.8, 89.7 and 95.0 K. A comparison of the numerical values indicates the high effectiveness of extracting the thermal energy of the molecules during the vapor-deposition.

In Scherer's analysis, the quantity $\Delta\mu$, which is the potential barrier per molecule hindering rearrangement in the cooperative cluster, was treated as a fixed parameter independent of the ambient temperature. The present analysis revealed a weak dependence of $\Delta\mu$ on the ambient temperature. In the AG entropy theory, the average size of the cooperational cluster is inversely proportional to the configurational entropy [33]. The activation energy 'per molecule', $\Delta\mu$, will increase or decrease with the average size of cluster depending on how the potential barrier for the structural relaxation changes with the cluster size.

Summarizing the results, we conclude that the KWW relaxation function and the AG equation can describe the quasi-isothermal enthalpy relaxation of a vapor-deposited non-crystalline sample of solid butyronitrile far from equilibrium.

CONCLUDING REMARKS

Vapor deposition is the most widely successful method of preparing materials in a non-crystalline state. The kinetic energy of the depositing molecules is dissipated so quickly that the molecules do not have sufficient time to organize themselves into ordered arrangements at low temperatures. In spite of the efficiency, however, thermodynamic characterization of vapor-deposited non-crystalline solids has rarely been carried out in the past [34,35]. This may be partly a result of the experimental difficulty of producing even a small quantity of the non-crystalline solid, and partly to the laborious and time-consuming nature of the heat capacity measurements.

We conclude here that the non-crystalline sample of butyronitrile prepared by vapor deposition exhibits essentially the same phenomena as the non-crystalline solid obtained by liquid-cooling. These are the glass transition, residual entropy, enthalpy relaxation and crystallization phenomena. All these common features reflect the metastability and non-equilibrium nature of the non-crystalline solid as compared to the most stable crystalline solid. From a quantitative viewpoint, however, the non-crystalline solids behave differently. The VQ samples show the enthalpy relaxation occurring far below the Kauzmann temperature and have extremely high fictive temperatures compared to that of the LQ sample. The KWW and AG equations have proved to be successful in describing the enthalpy relaxation behavior of the non-crystalline solids near to, as well as far from, equilibrium. It should be stressed that non-crystalline solids have to be characterized by their microscopic structures and by their thermodynamic properties rather than by the method by which they are prepared.

The unique advantage of calorimetry, especially low-temperature adiabatic calorimetry, is that the method provides a wealth of information on the entropy and enthalpy aspects of the non-crystalline solid relative to those of crystalline solid of the same material. Thus, an accurate calorimetric study can be important for the thermodynamic characterization of non-crystalline solids obtained by many unconventional techniques other than the classical liquid cooling.

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