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QUASI-STATIC STUDY OF THE GLASS TRANSITION OF GLYCEROL BY DSC

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ABSTRACT

The glass transition of glycerol has been studied using a DSC apparatus in step heating mode, on cooling and warming. Using the electrical model of the calorimeter, the supposed thermal behavior of the sample is computed, and compared with the experimental results. The glass transition of glycerol appears to be reversible, with a slow endothermic effect (5 J g^{-1}) and a change in thermal capacity.

INTRODUCTION

Glass transition has been studied by many workers and a number of results have been published. However, precise calorimetric measurements of the glass transition during warming are scarce [1–4] and, to our knowledge, no data exist for this transition on cooling. By contrast differential scanning calorimetry (DSC) with linear temperature scanning has been widely used. Since unusually high heating rates are required, the interesting question of the thermal behavior of an "equilibrium" glass [5] on cooling and warming is still open. In a previous DSC work [6] on the glass $0.23LiCl,0.77H_2O$, overshoot of specific heat versus temperature was observed on cooling, as if the liquid were "relaxing" to the glass. However, to study the glass transition at equilibrium, it is important to decrease the heating rate to nearly zero and to compare specific heats as measured on cooling and on warming.

Use of DSC is not limited to linear temperature scanning. Several previous papers used step programming techniques [7–10]. The measurement of the specific heat is reported to have good precision [7,10], and a thermodynamic steady state can be reached.

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MATERIALS AND METHODS

A Mettler TA 2000 B heat flow DSC apparatus was used. It was controlled by an H.P.85 microcomputer, which measured the calorimetric signal via an H.P.3455 A digital voltmeter.

The apparatus was standardized for temperature and heat flow using temperatures and heats of melting of high purity metals or compounds as described elsewhere [11], giving a relation between the calorimetric signal Δ and the thermal power $\mathrm{d}Q/\mathrm{d}t$

$$\mathrm{d}Q/\mathrm{d}t = K_c\,\Delta$$

where K_c is the standardization factor of the calorimeter.

Glycerol purchased from PROLABO with a purity better than 99.5% was used in this study, in place of a more complex water–salt glass. The sample was sealed in an aluminum crucible and weighed. The masses of the glycerol samples were in the range 30–55 mg.

An acquisition program was written to control the experiment automatically.

Step heating with a heat-flow DSC

The apparatus is set at a temperature $T1$. When heat flow is zero, a step is started with a heating rate $\mathrm{d}T/\mathrm{d}t$ up to temperature $T2$. When heat flow returns to zero, meaning that a new thermal equilibrium has been reached, a new step is begun. The procedure is applicable for warming or cooling, and the duration or amplitude of each step can be controlled within a wide range.

Each temperature step ΔT (up to 5 K) lasts about 1 min. The computer sets the DSC at a constant temperature when the limit of the step is reached. The calorimetric signal is read every 5 s, and a step is finished when the change in thermal power is less than 0.2 $\mu\mathrm{W\ s^{-1}}$ and the difference between the average of the calorimetric signal before and after the step is less than 40 μW during twenty-four consecutive measurements, so as to take into account the thermal dissymetry of the furnace.

Every experiment was run with the same reference crucible. Its mass was chosen so that the calorimetric signal would always deviate in the same direction during a run. One experiment generates a series of peaks. Each peak's area is proportional to the difference in enthalpy change between the sample and the reference, while heating or cooling from the initial to the final temperature for that step.

In order to minimize the error arising from the determination of K_c, it is more accurate to run an experiment with a known product and compute only the difference between the sample and the standard for the same step. Aluminum was used as the standard. Its molar specific heat has been determined by Downie [12]. Within the temperature range of these experiments (160–210 K), the following equation was used

$$C_p(\mathrm{Al}) = 6.30736 + 0.128372T - 2.43066 \times 10^{4}T^{-2} - 2.43066 \times 10^{-4}T^{2}$$

With the assumption that the specific heat of glycerol (C_p) is constant in the small temperature range ΔT, it follows that

$$C_p = \left((m_1' + m_2' - m_2)\int_{T1}^{T2} C_p(\mathrm{Al})\,\mathrm{d}T + (S_1 - S_1')K_c\right)/(m_1\,\Delta T)$$

where S_1 is the area of the peak observed for the mass m_1 of glycerol contained in an aluminum crucible of mass m_2, and S_1' is the area of the peak for mass m_1' of aluminum contained in another crucible of mass m_2'.

Results for an experiment run on cooling and warming in 2 K steps are shown in Fig 1. The shapes of the peaks change with temperature, giving dynamic information on the changes occurring in the sample.

The following two parameters are of particular interest: (i) slope P of the peak at the beginning of the temperature step. One can use an elementary calorimeter model to show that P is proportional to the difference of the thermal capacity of the reference and that of the product. (ii) The time constant τ of the trailing edge of the peak after the end of the temperature step. It depends on the thermal capacities. Any variation in τ not related to a heat capacity change must be caused by a time-dependent thermal effect occurring in the product.

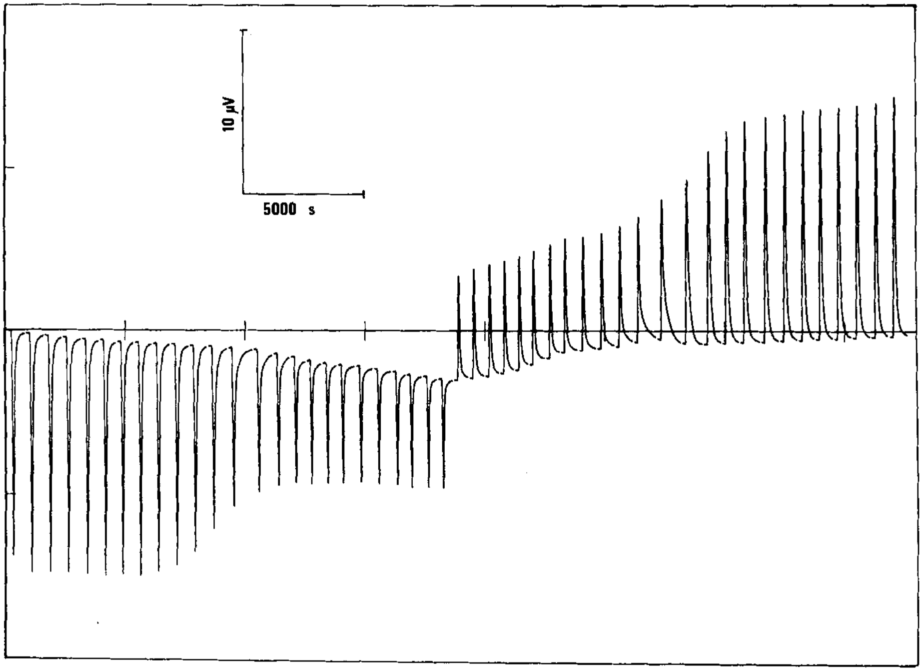

Fig. 1. Glycerol: Experimental trace. Warming from 163 to 213 K, then cooling from 213 to 163 K, $\Delta T = 2$ K; heating rate 0.033 K s^{-1}.

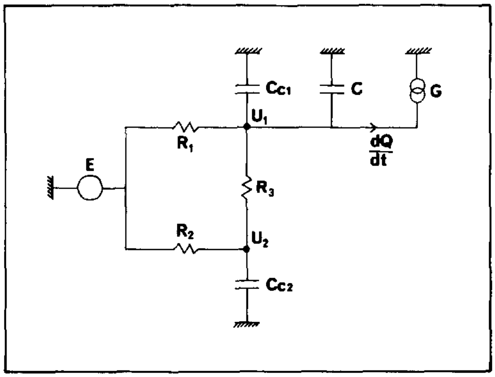

Fig. 2. Electrical representation of a disk-type DSC apparatus. E = temperature of the furnace; R_1 = Furnace–sample thermal resistor; R_2 = furnace–reference thermal resistor; R_3 = sample–reference thermal resistor; C_{c1} = thermal capacity of the detector (sample side); C_{c2} = thermal capacity of the detector (reference side); C = thermal capacity of the sample at T; G = thermal effect in the sample; U_1 = temperature of the sample; U_2 = temperature of the reference; $R_1 = R_2 = 0.306$ K mW^{-1}; $R_3 = 0.826$ K mW^{-1}; $C_{c1} = C_{c2} = 100$ mJ K^{-1}; mass of sample = 40 mg.

The initial slope P at the onset of the peak is determined by least-squares analysis. Assuming a simple first-order dependence, the time constant τ is the slope of a line on a plot of Δ vs. $d\Delta/dt$ and this parameter is also found by least-squares analysis. Three curves are obtained: C_p, P and τ versus temperature.

Computer simulation

It is assumed that the calorimeter behaves according to the simplified electrical representation shown in Fig. 2, as previously established [13,14]. The calorimetric signal Δ is determined by solving the equations

$$(C_{c1} + C)\, dU_1/dt = (E - U_1)/R_1 + (U_2 - U_1)/R_3 - dQ/dT$$

$$C_{c2}\, dU_2/dt = (E - U_2)/R_2 + (U_1 - U_2)/R_3$$

$$\Delta = U_2 - U_1$$

By using this calorimeter model, and assuming the thermal behavior of the sample, it is possible to simulate an experiment of n steps for comparison with experimental results. The computed values of Δ are then fed to the program described above to obtain C_p, P and τ. For the models of the behavior of the sample, relationships $C = f(T)$ and $Q = f(t,T)$ are assumed, using reasonable equilibrium and kinetic equations. The supposed equilibrium for the simulation is

$$A_n \rightleftharpoons nA \qquad (1)$$

where A_n and A are miscible and have ideal behavior. Calling α the ratio of the number of dissociated A_n to the initial number of A_n and ΔH, ΔS the enthalpy and entropy change of eqn. (1), it follows assuming constant ΔH and ΔS versus temperature

$$\exp\left(-\frac{\Delta H}{RT}+\frac{\Delta S}{R}\right)=\frac{(n\alpha)^n}{(1-\alpha)[1+(n-1)\alpha]^{n-1}} \tag{2}$$

At each temperature the excess heat capacity $\mathrm{d}Q/\mathrm{d}T$ due to the thermal effect occurring in the sample is

$$\mathrm{d}Q/\mathrm{d}T=\mathrm{d}\alpha/\mathrm{d}T\,\Delta H \tag{3}$$

The thermal capacities of A_n and A are respectively C_I and C_F. The thermal capacity C at temperature T is

$$C=C_I(1-\alpha)+\alpha C_F \tag{4}$$

The heat capacity C_p of the sample is $C_p=C+\mathrm{d}Q/\mathrm{d}T$. The most simple kinetic equation is assumed for α versus time

$$\mathrm{d}\alpha/\mathrm{d}t=(\alpha_E-\alpha)/\tau_R \tag{5}$$

where α_E is the value of α when the chemical equilibrium is reached at

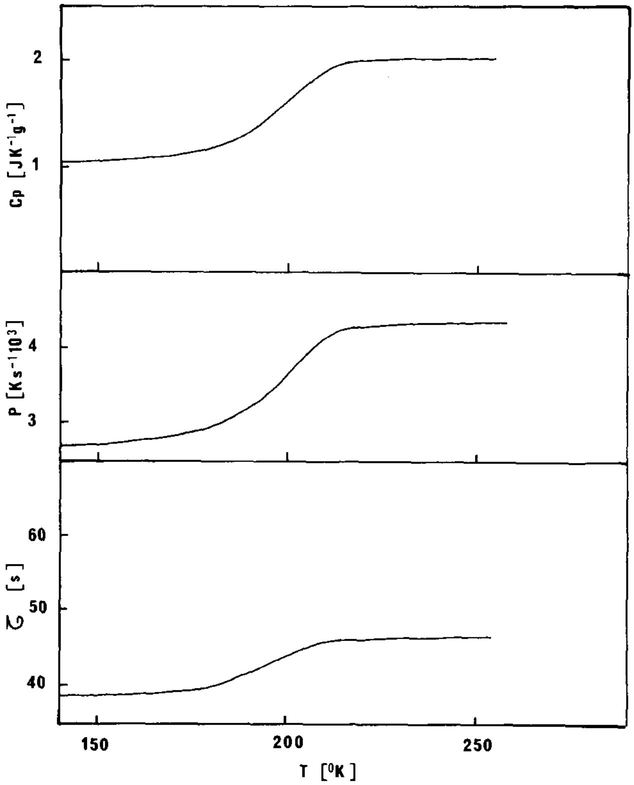

Fig. 3. C_p, P and τ vs. T: C is temperature-dependent.

temperature T. For the computation the following numeric values for eqns. (1) and (5) are assumed: $\Delta H = 80\,000$ J, $\Delta S = 444$ J K^{-1}, $n = 176$, $C_l = 1$ J K^{-1} g^{-1}, $C_F = 2$ J K^{-1} g^{-1}, $\tau_R = 200$ s

Four different examples have been chosen to provide a better understanding of the relationships between the experimental curves C_p, P and τ vs. T and the chemical system. Each one corresponds to a known chemical mode: (a) constant specific heat: the computed curves are straight lines. Similar experimental curves are obtained with the aluminum experiment, used as reference (see above). (b) Change of the specific heat of the sample: C is given by eqn. (4), and $Q = 0$. The curves C_p, P and τ vs. T are similar, as is shown in Fig 3. (c) Change of the specific heat of the sample with a temperature-dependent thermal effect: C is given by eqn. (4) and excess capacity dQ/dT by eqn. (3), $d\alpha/dT$ is given by eqn. (2). The results are plotted in Fig 4. As above, curves C_p and P are similar, while that for τ is only marginally different. (d) Change of the specific heat of the sample with a temperature- and time-dependent thermal effect: C is given by eqn. (4), and dQ/dT by eqn (3) with α computed using eqns. (5) and (2). All the

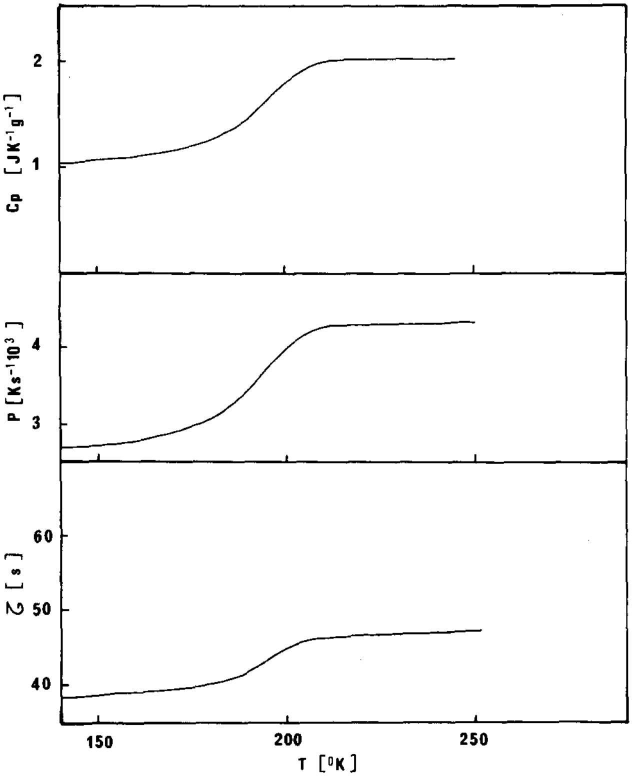

Fig. 4. C_p, P and τ vs. T. C and dQ/dT are temperature-dependent.

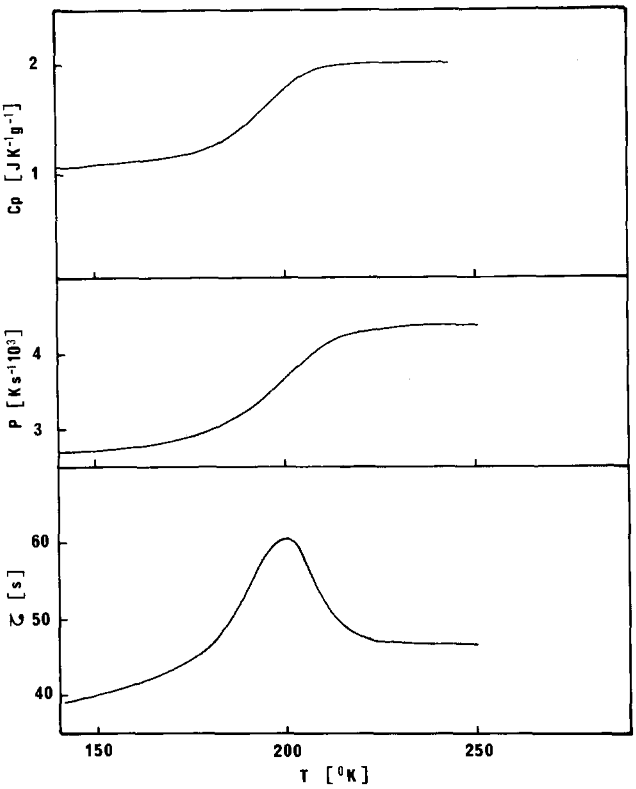

Fig. 5. C_p, P and τ vs. T. C is temperature-dependent; dQ/dT is temperature- and time-dependent

curves (Fig 5) are modified . The principal indicator of the time-dependent thermal effect is a clearly-defined maximum in the τ vs. T curve.

EXPERIMENTAL RESULTS

Numerous laboratory experiments were conducted in heating and cooling modes using various sample masses, step sizes, and glass preparation procedures. A typical experimental curve is shown in Fig 6. There is a clearly-defined peak in the τ vs. T plot. By comparing this experimental result to the computer model, shown in Fig 5, it seems reasonable to conclude that on warming, two different thermal events occur during the glass transition: (a) a slow endothermal effect; (b) a change in specific heat. On cooling, the same thermal behavior is observed. The specific heat measured on cooling is no different than that found on warming. The time constant τ and the slope P are quite reproducible for the heating and cooling runs of the same sample.

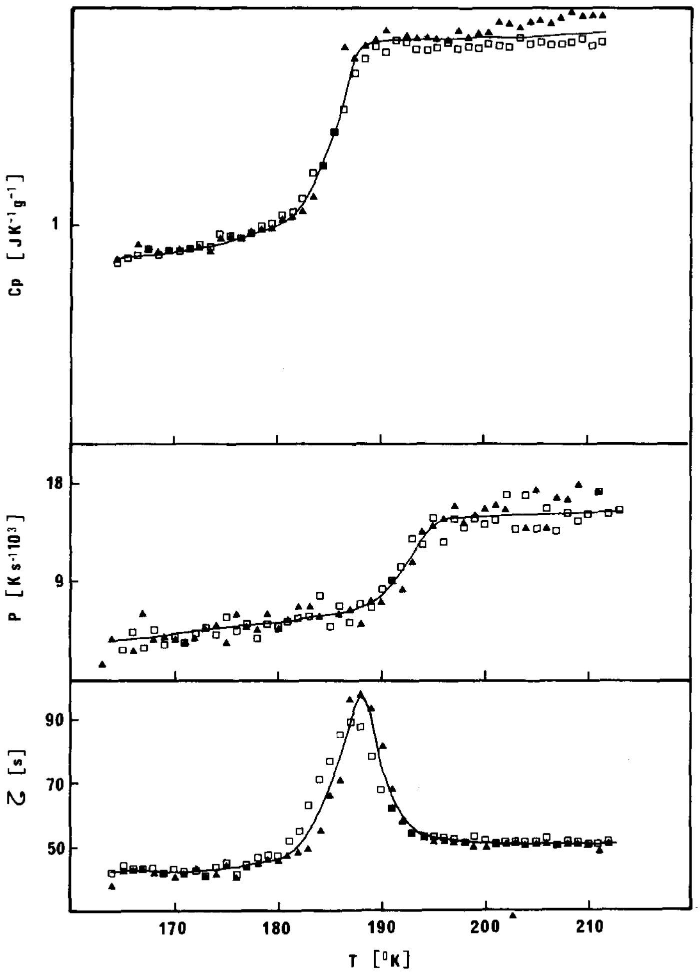

Fig. 6. Glycerol: $\Delta T = 1$ K. ▲, warming; □, cooling.

Under these experimental conditions, heat capacity does not depend upon the thermal amplitude of the step (1 and 2 K), nor does it depend upon the method of glass preparation (slow cooling at 2 K min^{-1} or quenching in liquid nitrogen). The specific heats, determined by the step method agree with the adiabatic calorimetric results reported by Gibson and Giauque [1]. Good reproducibility is obtained. All values are within the error limits of ± 0.05 J K^{-1} g^{-1}. The accuracy of the absolute value is more difficult to evaluate. According to previous experiments, an error limit of 3% seems reasonable.

It is assumed from the results shown in Fig. 5 that the curve $P = f(T)$ represents the true specific heat change of the sample during the glass transition. It is possible to use the specific heat C_p versus temperature relationship to compute the thermal effect at glass transition by integrating

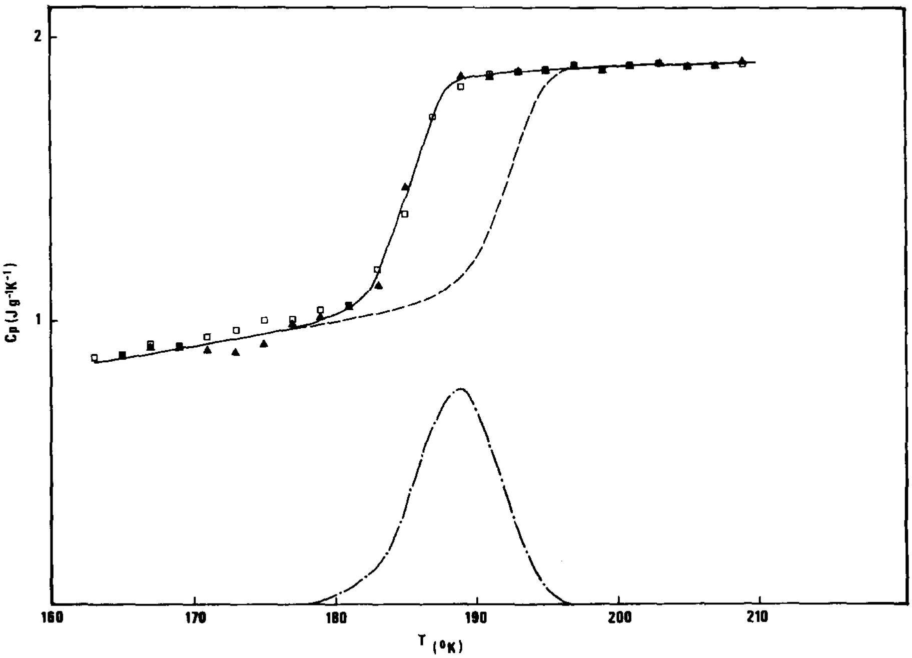

Fig. 7. Glycerol: $\Delta T = 2$ K. ▲, warming; □, cooling. ——— Heat capacity; - - - - - - true heat capacity; ·–·–· excess heat capacity.

the difference $(C_p - P)$ as shown in Fig 7. This thermal effect is 5 J g^{-1} (or 460 J mol^{-1}).

CONCLUSION

The glass transition of glycerol is found to be the sum of two effects: the first is a thermal effect (enthalpy change), and the second is a specific heat change. These thermal data indicate that the glass transition is a reversible phenomenon if the experimental procedure allows for thermal equilibrium.

During a linear temperature scan, an overshoot is observed on the curve $C_p = f(T)$ with the same sample. This is not the case with the quasi-static method described here. Although exhaustive conclusions cannot be drawn from the sole glass studied here, a probable explanation lies in the thermal effect wich governs the glass transition. It is dependent upon temperature, time and possibly even the composition in more complex glasses.

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