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By ANDREAS HALLBRUCKER and ERWIN MAYER

Institut für Anorganische und Analytische Chemie, Universität Innsbruck,
A-6020 Innsbruck, Austria

and G. P. JOHARI

Department of Materials Science and Engineering, McMaster University,
Hamilton, Ontario, Canada L8S 4L7

ABSTRACT

The glass transition and heat capacity of hyperquenched glassy water have been studied by differential scanning calorimetry and by isothermal measurements from 103 K to a temperature where its crystallization to cubic ice is complete. Glassy water shows a thermally reversible glass–liquid transition and has a T_g of 136 ± 1 K. The activation energy of structural relaxation in the transition range is $\sim 55\,\text{kJ mol}^{-1}$ and is a reflection of the energy required to break two hydrogen bonds before a rotational–translational diffusion of a water molecule in the H-bonded network can occur. The temperature width of the transition is $\sim 12°$, and the increase in the heat capacity is $1\cdot6 \pm 0\cdot1\,\text{J K}^{-1}\,\text{mol}^{-1}$. Liquid water formed on heating the glassy water to 146 K is more stable against crystallization than that which exists near 232 K. The hyperquenched glassy form of water can be thermodynamically continuous with liquid water, but whether or not it has the same structure as water above 273 K or supercooled water near the postulated λ-type transition is not known.

§ 1. INTRODUCTION

Amongst the several forms of amorphous solid water which have been prepared during the last decade, only that which is obtained by supercooling the liquid is truly glassy, and its structural state is anticipated to be thermodynamically continuous with the structural state of normal or supercooled water. Glassy water therefore has been prepared by hyperquenching or rapid cooling at rates $> 10^5\,\text{K s}^{-1}$, either in the form of the micrometre sized droplets of pure water in a liquid cryomedium (Brüggeller and Mayer 1980, 1982), or by depositing on a copper substrate, held at ~ 77 K, droplets from an aerosol without the use of a liquid cryomedium (Mayer 1985 a, b, c 1986). It has also been prepared as $\sim 0\cdot1$ µm thick films on a hydrophilic carbon surface of electron microscope screens by cooling in a cryomedium such as liquid ethane and propane (Dubochet and McDowell 1981).

Hyperquenched glassy water samples have shown a glass→liquid transition (Johari, Hallbrucker and Mayer 1987), but the vapour-deposited amorphous ice in the new experiments of MacFarlane and Angell (1984) has not. Our recent experiments (Hallbrucker, Mayer and Johari 1989) have shown that a careful procedure can reveal an endothermic feature that is attributable to the glass–liquid transition of the latter

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solid. The low- and high-density forms of amorphous ice obtained by squeezing hexagonal ice (Mishima, Calvert and Whalley 1984, 1985) also do not show a glass→liquid transition (Handa, Mishima and Whalley 1986). Part of the difficulty in observing a glass→liquid transition in these solids is caused by the spontaneous exothermic structural relaxation that occurs at temperatures below the transition. This difficulty can be eliminated in careful experiments. We report the results of experiments on the thermal behaviour of hyperquenched glassy water, designed to investigate the reversibility of its glass transition, and its heat capacity. We further examine whether a thermodynamic continuity of states (Johari 1977) between the glassy and normal liquid water exists. A brief report on the glass transition of water has already appeared (Johari *et al.* 1987).

§ 2. Experimental section

De-ionized water droplets of $\leqslant 3 \, \mu m$ size, made by means of an ultrasonic nebulizer, were suspended as an aerosol in N_2 gas and allowed to enter a high vacuum cryostat through a $200 \, \mu m$ circular aperture in one case and $300 \, \mu m$ aperture in the second. When inside the cryostat, the droplets moved with supersonic speed towards a copper substrate held at $\sim 77 \, K$ and deposited on it. This produced a 2–3 mm thick disc-shaped sample layer in 2 h with a $200 \, \mu m$ aperture and in 1 h with a $300 \, \mu m$ aperture. The estimated rate of cooling in this procedure of hyperquenching is $> 10^5 \, K \, s^{-1}$ (Mayer 1985c), which is comparable with the melt-spinning or splat-quenching processes. The details of the apparatus are given earlier (Mayer 1985a, b, c, 1986, Hallbrucker and Mayer 1987). The glassy water was handled while submerged in liquid N_2 to prevent devitrification due to accidental heating. Several batches of glassy water were made. None contained more than 5% cubic ice as characterized by the calorimetric and X-ray measurements (Mayer 1986, Hallbrucker and Mayer 1987). The mass of the samples obtained in one deposition was 1 to 2 g, and it had a porcelain-like appearance and texture.

A differential scanning calorimeter model DSC 4 made by Perkin Elmer corporation with a TADS computerized data acquisition facility was used. The baseline obtained with empty sample pans was subtracted during each scan made with 15 to 27 mg of glassy water. The change in heat capacity at T_g was determined from scans with a heating rate of $30 \, K \, min^{-1}$.

§ 3. Results

During reheating of the glassy water by differential scanning calorimetry (DSC) without any previous annealing treatment, a broad exotherm is observed starting at $\sim 125 \, K$ which extends into the devitrification region. This broad exotherm, which is characteristic of the glassy state of materials, arises from the rapid and spontaneous enthalpy relaxation to a structural state of lower enthalpy and free energy at $T < T_g$. It partly obscures any endothermic step due to a glass→liquid transition, and had to be eliminated by annealing. The glassy water samples were annealed while inside the instrument at several temperatures near $130 \, K$ for periods extending up to 4 h, thereafter cooled to 103 K and finally scanned. Glassy water samples annealed this way showed for the usual heating rate of $10 \, K \, min^{-1}$ a small endotherm at $\sim 15°$ below the crystallization temperature. To accentuate this endotherm, the heating rate was increased to $30 \, K \, min^{-1}$. The endotherm became more resolved and had the characteristic shape of a glass→liquid transition at a temperature prior to that of the exothermic peak caused by the irreversible crystallization to cubic ice. All samples

annealed by this procedure lacked the broad exotherm in their DSC scans and showed a glass→liquid endotherm.

The above steps of the DSC scans of the glassy water are shown in fig. 1. All are for a heating rate of $30\,\mathrm{K\,min^{-1}}$. On initial heating from 103 to 130 K, a pronounced decrease in the heat output occurs (curve 1). This is due largely to enthalpy relaxation. The DSC scan of the same sample showed on reheating a positive slope, which is due to the steady increase of the heat capacity of the sample with rising temperature (curve 2). After annealing at 130 K the beginning of the glass transition endotherm at 138 K was observed on third heating (curve 3). The reversibility through T_g was checked by curve 4 (for details see the caption). Several samples showed similar behaviour. A comparison of crystallization exotherms with melting endotherms ascertained that no significant crystallization occurred during this procedure (Hallbrucker and Mayer 1987). The onset temperature of the endothermic step in the DSC scan is taken as T_g, which is 138 $\pm\,1$ K, the midpoint temperature of the transition endotherm is 144 ± 1 K and the crystallization to cubic ice begins at 152 ± 1 K. After correction for the instruments'

Fig. 1
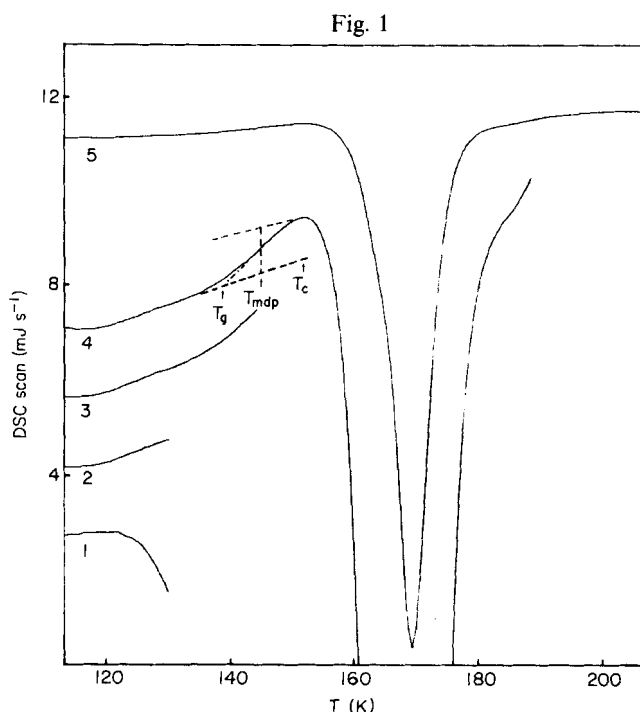
The glass→liquid transition of hyperquenched water as seen in a DSC scan. The sample was heated or cooled at a rate of $30\,\mathrm{K\,min^{-1}}$ in all cases. Curve (1) is for a 20·4 mg sample (prepared by using a 200 µm aperture) heated to 130 K. Curve (2) the same sample but which was cooled to 103 K and reheated to 130 K. Curve (3) the same sample annealed at 130 K for 90 min, cooled from 130 to 103 K, and thereafter heated to 148 K. Curve (4) the same sample but now cooled immediately from 148 to 130 K, annealed at 130 K for 90 min, cooled to 103 K and then heated to 220 K. Curve (5) is a plot on a reduced scale ($\times 1/8$) to show the crystallization of glassy water. T_g is the glass transition temperature, T_{mdp} the midpoint temperature of the glass–liquid transition endotherm. T_c is the crystallization temperature. The temperature scale is not corrected for the thermal lag of the calorimeter. ΔC_P at T_g was evaluated as shown in curve 4 (broken lines).

thermal lag, these values are 136, 142 and 150 K respectively, and are accurate to within $\pm 1°$.

From DSC scans of ten different samples the change of heat capacity at T_g, ΔC_P, was determined as $1·6 \pm 0·1$ J K^{-1} mol^{-1}. This value is corrected for a possible 5% impurity due to the presence of crystalline ice. This ΔC_p value is a lower limit because the glass→liquid transition could be partially masked by the onset of the crystallization exotherm, as the evaluation from curve 4 in fig. 1 indicates.

We also determined the heat capacity of glassy water after annealing at 130 K, by using the heat capacity measurement procedure developed by Perkin-Elmer for the DSC-4 instrument. Several samples gave C_P values for glassy water which were about 10% lower than those for cubic ice, and the values for cubic ice were in turn about 5% lower than those for hexagonal ice. This order of values for the different ices is in contrast with the measurment of Sugisaki, Suga and Seki (1968) on vapour-deposited amorphous solid water, $H_2O(as)$. The order of measured C_P remained unaltered on varying the time and temperature of annealing, scan rate and sample's mass. Holding the samples for several hours in the instrument also did not cause the measured C_P values of cubic and hexagonal ice to change, and therefore we conclude that this order of C_P values was not caused by a drift in the instrument's response with time. The same order of C_P values was also obtained with a sample of $H_2O(as)$, that is, C_P of $H_2O(as)$ lower than that of cubic ice by $\sim 10\%$, and C_P of cubic ice lower than that of hexagonal ice by $\sim 5\%$. We surmise that the unexpected order of C_P values may be associated with problems in measuring C_P of the metastable state of substances by DSC, as pointed out by Suzuki and Wunderlich (1984). Nevertheless, the relative values of C_P for crystalline ices do not affect our discussion on the thermal behaviour of glassy water.

§4. DISCUSSION

4.1. *The glass liquid transition region*

The reversibility of the glass⇌liquid transition of water is seen in fig. 1, where the sample could be thermally cycled between its glassy state at $T < 136$ K and its relatively fluid state at 146 K. This means that in the glass transition range, the structural states of glassy and liquid water are thermodynamically continuous and crystallization to cubic ice does not appreciably occur; this is an observation that has eluded all previous studies. Clearly, fluid water at 146 K is more stable against crystallization to cubic ice than bulk water is at a temperature near its inferred λ-type anomaly (Angell, Shuppert and Tucker 1973, Angell 1983).

In fig. 1, the temperature width of the glass transition endotherm is 12 ± 1 K. It is conceivable that the endotherm is even wider in temperature, if partially masked by the exotherm of crystallization to cubic ice, which could not be prevented. So, the temperature width of ~ 12 K may be a lower limit. It is not likely to be much greater than this, since no crystallization in the sample occurred up to 146 K, that is, nearly 10° above the T_g, where the maximum in the endotherm is almost reached. This width is much greater for glassy water than for other substances such as aqueous LiCl solution (~ 5 K, MacFarlane and Angell (1984)), Se (~ 5 K, Stephens (1976)), 1,2-propanediol (~ 7 K) and other alcohols (unpublished data).

The structural relaxation time calculated from a DSC scan (Angell and Torrel 1983) obtained by heating at a rate of 30 K min^{-1} is ~ 70 s at the onset temperature, or T_g(136 K), and ~ 7 s at the midpoint (142 K) of the glass transition endotherm. Since crystallization does not occur, this implies that nucleation and/or crystal growth of

cubic ice in the liquid is slower than the structural relaxation of the liquid. By assuming that the structural relaxation time increases exponentially with reciprocal temperature in the narrow range 136–150 K, we calculated an activation energy of $55 \pm 5 \, \text{kJ mol}^{-1}$. This value is substantially less than that observed by viscosity measurements for SiO_2, silicates and other network glasses (Wong and Angell 1976), but is comparable to that of several H-bonded liquids which show nearly an Arrhenius behaviour at temperatures near their T_g (Johari and Goldstein 1971) and further with that of hexagonal ice (Hobbs 1974).

In a fully H-bonded structure, rotational and translational diffusion of a molecule is possible only if thermal excitation is high enough to break an H-bond. For a tetrahedrally bonded network of glassy water, at least two hydrogen bonds need be broken before a water molecule can change its position and orientation. Therefore, the observed low value of the activation energy of $\sim 55 \, \text{kJ mol}^{-1}$ is consistent with our general understanding of structural relaxation in an H-bonded liquid. The structural relaxation times of 70 and 7 s of liquid water at 136 and 142 K respectively thus represent the life-time of a hydrogen bond at these temperatures.

The extrapolated structural relaxation time at the onset of crystallization at 150 K is $\sim 0.4 \, \text{s}$. This is useful as a high-temperature and time limit for the handling of cryofixed biological materials in pure water, a subject of much current interest (Plattner and Bachmann 1982, Robards and Sleytr 1985, Steinbrecht and Zierold 1987).

4.2. *The heat capacity of glassy water*

Owing to the limitations of the instrument, we have not been able to determine reliable values for the heat capacity of glassy water. Only the increase at T_g could be accurately measured. Nevertheless, an estimate for the percentage increase at T_g is obtained from a comparison with crystalline ice. The ΔC_P of glassy water of $1.6 \, \text{J K}^{-1} \text{mol}^{-1}$ is $\sim 8\%$ of the C_P value of cubic or hexagonal ice at 136 K ($\sim 21 \, \text{J K}^{-1} \text{mol}^{-1}$, Sugisaki *et al.* (1968)). Since the values of the ices are expected to be only slightly smaller than that of glassy water at $T < T_g$ (Sugisaki *et al.* 1968, Johari 1977), the estimated ΔC_P at T_g of $\sim 8\%$ is an upper limit. This change in C_P at the glass→liquid transition is much less than that observed for most glasses, but is comparable with the values of $\sim 8\%$ observed for GeO_2, $\sim 6\%$ for SiO_2 (read from Wong and Angell (1976), fig. 6 p. 39) and 13–17% observed for polystyrenes of molecular weight 2300–3650 (Wunderlich 1960), all with much higher values of T_g than glassy water.

The small increase in C_P at T_g implies that the configurational contribution from changes in both the average coordination of a water molecule and the extent of short range order to the C_P of liquid water is small and/or the vibrational contribution to the C_P of water rapidly decreases at its glass–liquid transition. The estimated increase in C_P (Kamb 1968) owing to the changes in the intermolecular vibration frequencies that occur at hexagonal ice→water transformation at 273 K is $2.5 \, \text{J K}^{-1} \text{mol}^{-1}$. Since a change in volume generally does not occur at the glass→liquid transition temperature (Elliott 1984), the ΔC_P of $1.6 \, \text{J K}^{-1} \text{mol}^{-1}$ at T_g of 136 K of glassy water represents the energy involved in configurational changes of the liquid. Quantitative interpretations of the C_P of liquid water at 273 K by Davies and Jarzynski (1967–68), Kamb (1968) and Eisenberg and Kauzmann (1969) show that the configurational and vibrational contributions to C_P are about the same for water at 273 K. The observed ΔC_P at T_g is of course much smaller and is presumably a reflection of the possibility that increase in either both the configurational and vibrational contributions on glass→liquid transition

are small, or that the increase in configurational C_P is largely compensated by a decrease in the vibrational C_P. This situation cannot be resolved by the available data.

The measured ΔC_P value of glassy water at T_g is lower by more than an order of magnitude than the estimated value of between $19–25 \, \mathrm{J \, K^{-1} \, mol^{-1}}$ obtained from an extrapolation of the values for concentrated aqueous solution glasses (Angell and Tucker 1980). The results given here suggest that an extrapolation of C_P from solution studies is not as generally useful as was originally believed.

4.3. *The structure–continuity paradox*

Since the suggestion of the lack of structural and thermodynamic continuity between the vapour-deposited amorphous solid and liquid water and of the possibility of the polymorphism in the amorphous state of solid water (Johari 1977, Mayer and Pletzer 1984), several forms of amorphous solid water have been prepared by additional and different procedures. These are: (i) rapid-quenching of jet-produced micrometre-sized droplets in a cryomedium (Brüggeller and Mayer 1980, 1982), (ii) rapid-quenching of water as $\sim 1 \, \mu\mathrm{m}$ thick film contained in electron microscope grade carbon grids in a cryomedium (Dubochet and McDowell 1981, Dubochet, Lepault and Freeman 1982), (iii) hyperquenching of micrometre-sized droplets on a cryoplate (Mayer 1985a, b, c, 1986), (iv) uniaxial compression of hexagonal ice (Mishima, Calvert and Whalley 1984, 1985), and (v) supercooling of emulsified water in a ternary system with octane after a special thermal treatment (Angell and Choi 1986). None of these, possibly different, forms seem interconvertible *via* a single thermodynamic path by varying either pressure or temperature, and it is not certain whether or not any one of these forms is structurally and thermodynamically continuous with the state of water above 273 K.

Since the amorphous state of a material allows one to study the static or spatial disorder in the absence of a dynamic or temporal disorder, a study of the amorphous solid forms of, in particular, water has been considered quite useful for understanding the structure of liquid water (Sceats and Rice 1982). The existence of polymorphism in the amorphous state makes the assumed structural similarity between the amorphous solid and liquid forms less convincing and any conclusions from studies based upon such a continuity precarious. A crucial test for such a continuity of states is a demonstration that the glass⇌liquid transition is thermally reversible, namely that the progressively increasing configurational restriction on cooling a liquid has produced a solid-like rigidity over the experimental time scale (100–1000 s). Even when this is done, the structure of the glass thus formed would be representative of the spatial disorder in a liquid at the temperature where it appeared to have become rigid, and not at some higher temperature. Amongst the five amorphous solids produced by the procedures given above, and the sixth produced by heating the high-density form (Mishima *et al.* 1985), only hyperquenched glassy water (method (iii)) successfully meets this requirement.

Regardless of these difficulties in seeking a structural similarity between the hyperquenched water (both as a glass below 136 K and, more importantly, as a liquid at 146 K) and liquid water above 273 K, it is important to consider whether or not hyperquenched water is thermodynamically connected with bulk water at 273 K. To allow this discussion fig. 4 from Johari (1977) is redrawn here. As discussed in the preceding section, C_P of hyperquenched glassy water at 147 K (i.e. the end of the endothermic step with $\Delta C_P = 1·6 \, \mathrm{J \, K^{-1} \, mol^{-1}}$ at 147 K) is $\sim 8\%$ higher than that of ice. This value is indicated by a cross in fig. 2. All notations and source of data refer to the

Fig. 2
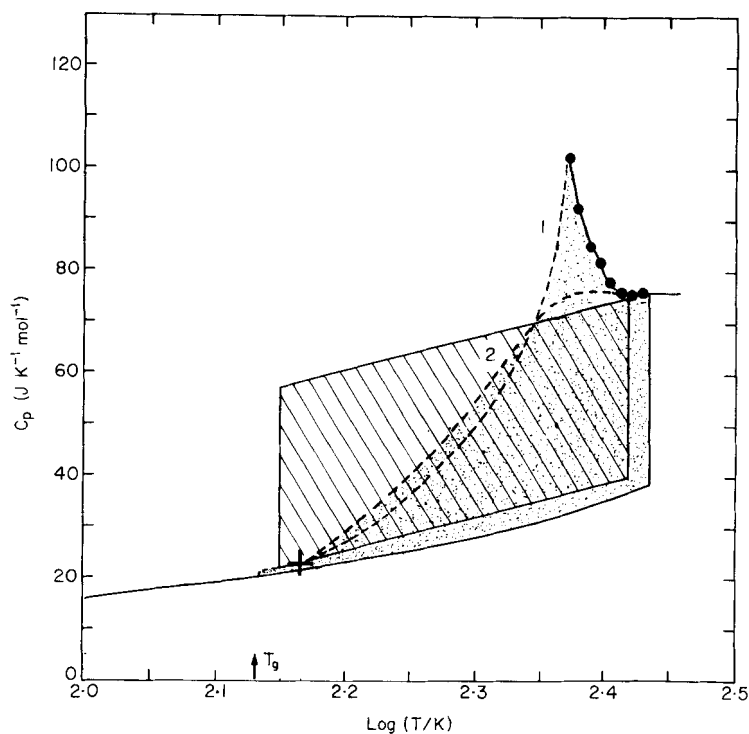
The heat capacity, C_P, of ($+$), hyperquenched glassy water at 147 K; ($-$), hexagonal ice; and ($\bullet$), supercooled emulsified water and bulk water (with the new values from Angell, Oguni and Sichina (1982)) plotted against the logarithm of temperature. The cross-hatched area represents the magnitude of the entropy of fusion ΔS_f of ice at 273 K ($21 \cdot 88$ J K^{-1} mol^{-1}). Dashed lines 1 and 2 indicate two possible supercooling paths that fulfill the requirements for the entropy loss based on the applicability of third law of thermodynamics and of a maximum residual entropy of $9 \cdot 2$ J K^{-1} mol^{-1}, that is, the dotted area represents $21 \cdot 88 - (9 \cdot 2 - 3 \cdot 4) = 16 \cdot 1$ J K^{-1} mol^{-1}.

original fig. 4. In fig. 2, at least two qualitatively different (almost infinitely quantitatively different) thermodynamic paths can be followed by the heat capacity of water between 273 and 136 K. These are shown by dashed lines (1) and (2). Both paths fulfill the requirement of the third law of thermodynamics, namely that the entropy given by the area of the C_P of supercooled water does not exceed the entropy of fusion of hexagonal ice. These two paths also fulfill the requirement placed by the maximum residual entropy of glassy water, calculated from Bell and Dean's (1968, 1969) model, of $9 \cdot 2$ J K^{-1} mol^{-1} as discussed before (Johari 1977). This requirement is that the total entropy loss is $5 \cdot 8$ ($9 \cdot 2 - 3 \cdot 4$) J K^{-1} mol^{-1} less than the entropy of fusion where $3 \cdot 4$ J K^{-1} mol^{-1} is the residual entropy of hexagonal ice or the residual entropy of glassy water due to orientational disorder alone. Which one of the two paths is qualitatively more likely cannot be conclusively determined by our present experiment.

An important difference between the characteristics of the two paths is that path (1) postulates the existence of a λ-type transition on the basis of C_P and expansivity data of supercooled emulsified water (Angell and Tucker 1980, Speedy 1982) and the second

assumes that the approach towards a λ-type anomaly in supercooled water may be associated with either the increasing size and concentration of embryo ice crystals (Rasmussen and MacKenzie 1973) and/or the surface effects induced by the hydrophobic interaction of emulsifying agents. Once water is attained as liquid at 146 K and lasts without crystallization for a few seconds, a variety of spectroscopic and kinetic experiments can be made during the duration of its stability. In particular fast Fourier-transform infrared and dielectric spectroscopy could reveal its approximate structural similarity with either the bulk water above 273 K or with the existence of pentagonal rings, characteristic of clathrate-like structures which are presumed to form near the temperature of the λ-type anomaly.

Recent discussion by Angell (1988) on the relevance of instability and its removal by the slowness of fluctuations, (or molecular motions), implies that the liquid-to-glass transition has occurred at $T > 228$ K and/or that the rapid cooling has completely eliminated the instability described by Prielmeyer, Lang, Lüdemann and Speedy (1987). This too becomes debatable in the light of our observation in that glassy water does become fluid at 146 K (10 K above its T_g) and is stable for appreciably long times.

§5. CONCLUSION

The glassy state of water obtained by hyperquenching micrometre-sized liquid droplets undergoes a glass⇌liquid endothermic transition at 136 ± 1 K. The increase in C_P at the transition is comparable with that observed for SiO_2 and GeO_2 and is a reflection of the small amount of energy required for the thermally induced configurational changes that occur in the viscous liquid and not in the rigid glass. The structural relaxation has an activation energy of ~ 55 kJ mol^{-1} and is associated with the breaking and reforming of two hydrogen bonds required for the rotational–translational diffusion. The results suggest that there is a continuity of structural states between water at 273 K and that at 136 K, with or without the inferred presence of a λ-type transition.

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