ABSTRACTS OF PAPERS PRESENTED AT THE SYMPOSIUM BUT NOT PUBLISHED IN FULL IN THIS VOLUME

ON THE HEAT CAPACITY, ENTROPY, AND "GLASS TRANSITION" OF VITREOUS ICE

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Abstract. An analysis of the thermal properties of vitreous ice shows that both its heat capacity $C_p$ and its entropy above 100 K are partly configurational in origin. The configurational contribution increases with temperature, and the excess $C_p$ and entropy near the solid-liquid transformation temperature are 36.7 and 2.1 J K$^{-1}$ mol$^{-1}$, respectively. The increase is interpreted as indicating the onset of molecular mobility in vitreous ice. The configurational $C_p$ of the melt of vitreous ice at 133.6 K, of $\approx 36.7$ J K$^{-1}$ mol$^{-1}$, is the same as the configurational $C_p$ of water at 273 K. Thus, the short-range order in the melt differs little from that in water at 273 K. The maximum calorimetric residual entropy of vitreous ice is 13.4 J K$^{-1}$ mol$^{-1}$, which is in fair agreement with the maximum value of 9.2 J K$^{-1}$ mol$^{-1}$ anticipated for a tetrahedral random-network model with fully disordered positions of H atoms. Thermodynamic consideration of a glass transition in supercooled liquid water indicates that there is no continuity of state between supercooled water and vitreous ice and, therefore, the structure and thermodynamic properties of a possible glassy state of water should be different from that of vapour-deposited vitreous ice. This paper is published in full in Philosophical Magazine, Eighth Ser., Vol. 35, No. 4, 1977, p. 1077-90.

DISCUSSION

J. Perez: Is it possible to evaluate by extrapolation of your curves, the difference, at 273 K, between the entropy of crystalline ice and that of amorphous ice?

G. P. Johari: No, it is not possible. There seems to be no extrapolation of the entropy of vitreous ice from 135 K to 273 K.

J. W. Glen: Some solutions do cool to a vitreous phase; do you know of any thermal data on these? I suppose they must be true vitreous water.

Johari: Yes, a number of aqueous solutions of organic and inorganic materials supercool to form a glassy state. I am aware of only differential thermal analysis data on most such solutions. Yes, they are a true glassy form of the aqueous solution. I am not certain that the structure of such a solution is the same as that of the anticipated glassy form of water.

J. E. Bertie: In partial response to Dr Perez’ question, Giguère and Harvey (1956) reported making supercooled or vitreous water at $c.$ 100 K by cooling a very thin layer of water between AgCl plates. Their infrared spectra did not prove their claim and no diffraction measurements were made, but this method is perhaps, worth exploring.

S. A. Rice: In the course of other experiments Ms L. Swingle has examined the transmission of very thin films of amorphous solid water $H_2O(as)$ in the OH stretching region. Much to our surprise, she found that very thin films of the $H_2O(as)$ transform to crystalline ice at higher temperatures than 130-135 K, the accepted temperature range established from
studies of thick films. By definition, a metastable substance such as H₂O(as) will transform to a more stable phase on some time scale, though that may be so long as not to be of interest. For films estimated to be c. 1 000 Å thick H₂O(as) appears to be stable for c. 30 min at 160 K. It must be emphasized that the results I have described represent preliminary data—much more must be done to establish the validity of these observations. Accepting them to be correct, my interpretation is that a very thin film of H₂O(as) contains fewer nucleation sites than does a thick film, hence the metastability range is extended, just as supercooling of water in a small capillary is more extensive than in a large capillary by virtue of exclusion of crystallization nuclei. It is conceivable that even thinner films of H₂O(as) can persist for some minutes at still higher temperatures. Assuming the amorphous solid thermodynamic properties remain like those below 135 K, part of the gap between the domains of metastability of supercooled water and H₂O(as) is thereby closed. It remains an open question as to whether H₂O(as) is, or is not, a metastable continuation of liquid water.

Johari: I am not certain whether the thermodynamic properties of c. 1 000 Å thick layers (c. 360 water-molecules thick) would be the same as those of the bulk vitreous ice. I agree with you that more work on the properties of the material you describe is necessary.

J. Hallett: What is the evidence from “splat” (very rapid cooling by impact) studies that vitreous water can be obtained directly by cooling from temperatures about −40°C? It would appear that such experiments on supercooled drops at −30°C might be worth taking.

Johari: I am aware of only one experiment by Professor Uhlmann which succeeded in obtaining vitreous water by splat cooling. His result has not been published in a paper but has appeared in the cited references in several papers on vitreous ice. Yes, I agree with you that the experiment you propose might be worth undertaking.

REFERENCE


THE DIPOLAR CORRELATION FACTOR OF ICE VI

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ABSTRACT. The dipole moment μ of an H₂O molecule in the orientationally disordered ices is greater than the moment of an isolated molecule, 1.84 D, due to two factors: (i) the mutual polarization of molecules, and (ii) the short-range average correlation of the dipole vectors, if the molecules are able to reorient. The magnitude of the average enhancement is given by Kirkwood’s equation,

\[ (\epsilon_0 - \epsilon_\infty) = 2\pi N N_0 \mu^2 / k T, \]

where \( \epsilon_0 \) and \( \epsilon_\infty \) are respectively the limiting low- and high-frequency relative permittivity of orientational polarization, \( N \) is the number density of dipoles, \( k \) is the Boltzmann constant and \( T \) is the temperature. The dipolar correlation factor \( g \) is defined by,

\[ g = \lim_{r \to \infty} \left\langle \sum_{R/r \to \infty} \mu_i \cdot \mu_j / \mu^2 \right\rangle. \]