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# Specific heats of hydrogen, deuterium, and neon in porous Vycor glass

J. L. Tell and H. J. Maris
*Physics Department, Brown University, Providence, Rhode Island 02912*
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The specific heats of hydrogen, deuterium, and neon in porous Vycor glass have been measured. The freezing and melting temperatures have been determined, and a lower limit has been placed on the values of the liquid-solid surface energy.

## I. INTRODUCTION

It has been known for a long time that when a liquid is in a porous medium the freezing temperature is usually depressed.[1] Recently, this effect has attracted renewed attention as a result of several experiments with liquid helium. Bulk helium under its saturated vapor pressure remains a liquid down to $T=0$ K, and can only be solidified by the application of pressure (25 bars for $^4$He). Helium in porous Vycor glass has been found to remain liquid up to pressures in excess of 40 bars[2–5]. This has made possible the study of superfluid helium up to these high pressures. In this paper, we report measurements of the specific heat and the depression of the freezing temperature for hydrogen, deuterium, and neon in Vycor. Studies of these materials are of interest because, except for helium, these are the elements for which quantum-mechanical effects are the most important. Earlier work on Vycor has included studies of classical materials such as water,[6,7] benzene,[8] and xenon.[6]

## II. EXPERIMENTAL METHOD

The porous Vycor glass (Corning code 7930) was a rod 0.353 cm diam. and 2.16 cm long. A measurement of the amount of water required to fill the pores indicated a porosity of 28%. The average pore radius was estimated[9] to be 27 Å. The glass was cleaned by boiling in hydrogen peroxide. It was rinsed in isopropyl alcohol, acetone, and distilled water, and then dried for several hours at 100 °C. This procedure was suggested by Corning.

The glass was contained in a closely fitting oxygen-free high-conductivity copper can with walls 0.13 cm thick. A stainless-steel filling capillary approximately 100 cm long and 0.025-cm i.d. entered through one end cap of the can. The capillary ran to a valve at room temperature. Attached to the copper can was a wire-wound heater and a carbon-resistor thermometer. The carbon resistor was calibrated against the bulk triple points of neon and *n*-hydrogen, the superconducting transitions of lead and indium, and the vapor pressure of liquid $^4$He. The can was thermally linked to a variable-temperature heat sink at approximately the same temperature as the cell (typically ±0.1 K). The link was a brass strip chosen to produce a time constant for the cell of the order of 1000 sec. Thus, by changing the temperature of the heat sink it was possible to change and control the temperature of the cell. The can was surrounded by a heat shield at the same temperature as the heat sink.

To measure the specific heat the following procedure was used. The temperature of the cell thermometer was recorded for several seconds to measure the temperature drift. This drift was due to the difference between the cell and heat-sink temperatures. A voltage pulse was then applied to the heater for a short time (0.4 sec). The cell temperature $T_c$ was recorded for about 2 min after the application of the pulse. Usually $T_c$ increased for a few seconds during the time taken for the heat to flow from the heater to the thermometer and into the Vycor, and then decayed exponentially as the heat flowed out to the heat sink through the thermal link. From the recorded $T_c$ the background drift was first subtracted. An exponential was then fitted to this corrected $T_c$ in the time range where the heat was flowing out of the cell into the sink. This exponential was extrapolated back to the time at which the pulse was applied, in order to obtain a better estimate of the rise in temperature which would have occurred in the absence of any external thermal coupling.

A set of specific-heat data $C(T)$ was obtained by monotonically varying the temperature of the heat sink over a period of several hours. For each substance studied the Vycor was filled from a gas-handling system, initially at 750 Torr. The temperature of the cell was such that the saturated vapor pressure for bulk liquid was 730 Torr. When the cell was full, the valve at the room-temperature end of the filling line was closed. This presumably left a few cm of liquid in the filling capillary immediately above the cell. The volume of this liquid was only a few percent of the liquid volume in the cell. When the cell temperature was lowered, the thermal contraction of the liquid in the cell probably pulled the liquid from the capillary into the cell. By the time the bulk triple point was reached the capillary was empty, as confirmed by the absence of any indication in the specific-heat measurements of a latent heat at the bulk triple point.

## III. RESULTS

The specific heat of the empty cell was measured first. Owing to poor thermal contact between the Vycor and the cell wall, some overshoot of the thermometer was observed immediately after the pulse was applied. In the temperature range 6–25 K the results could be fitted to an accuracy of ±2% (roughly the scatter in the data) by

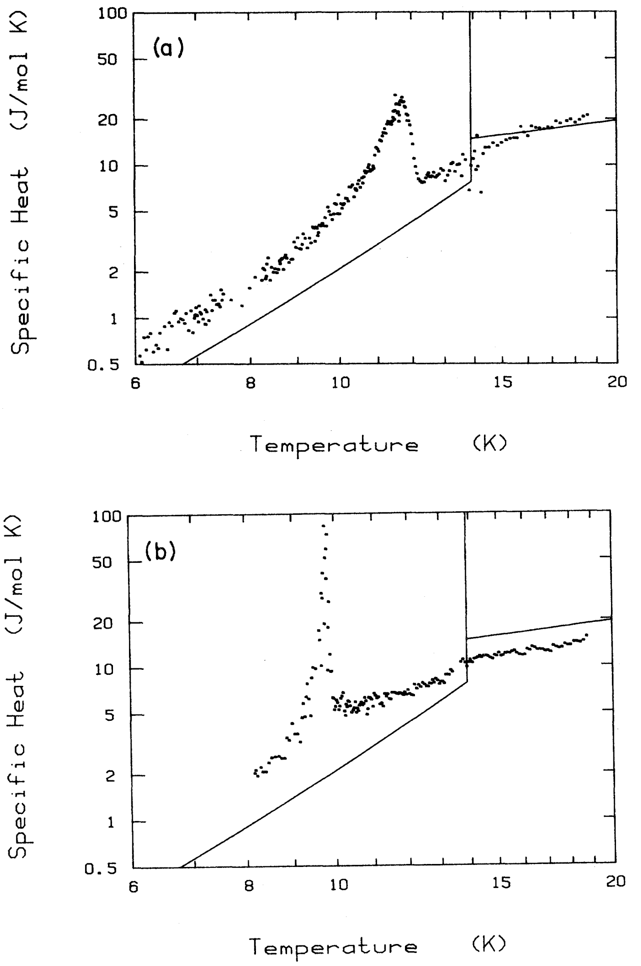

FIG. 1. Specific heat of hydrogen in Vycor. (a) Temperature increasing. (b) Temperature decreasing. Solid line shows the specific heat of bulk hydrogen.

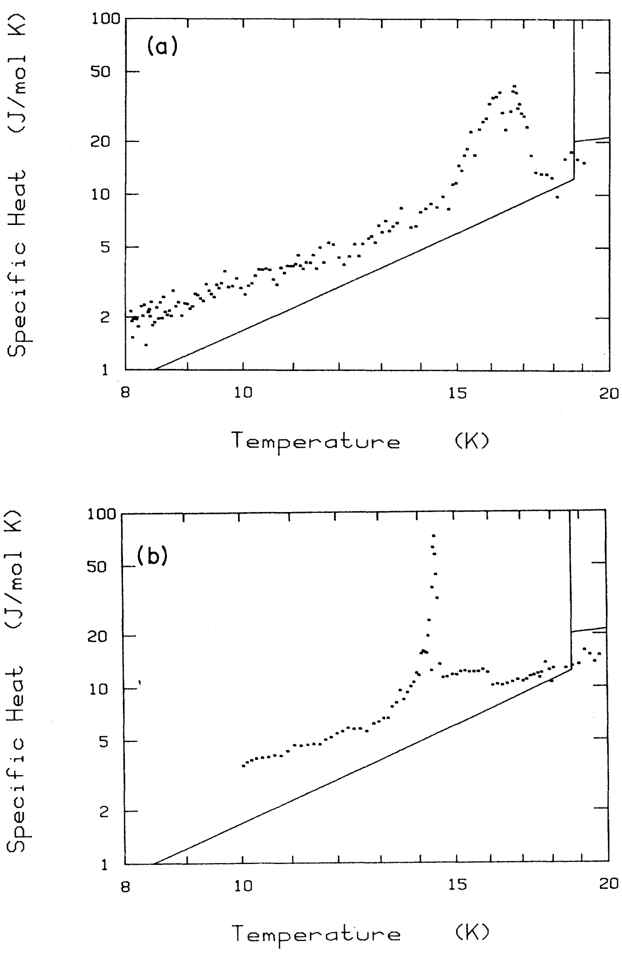

FIG. 2. Specific heat of deuterium in Vycor. (a) Temperature increasing. (b) Temperature decreasing. Solid line shows the specific heat of bulk deuterium.

the function

$$C=5.2\times10^{-5}T^{2.55}\ , \tag{1}$$

in units of $\mathrm{J\,K}^{-1}$. This fit was used as the background specific heat of the empty cell and was subtracted from the total specific heat measured to find the specific heat of the enclosed material.

For hydrogen, deuterium, and neon, the specific heat was measured for temperatures increasing and decreasing in the range between 7 K and the filling temperature. This procedure was repeated on four consecutive days. Overnight the cell was left at 6 K. It was found that, while the results were the same on each day (within the experimental uncertainty), the specific heat measured during a monotonic decrease in temperature was not the same as that measured while the temperature was increasing. Results are shown in Figs. 1—3. The hydrogen and deuterium used in these experiments had not been converted to the lowest-energy angular-momentum state, i.e., the ortho-para ratio was initially close to the equilibrium value for room temperature. During the course of the experiments significant changes in the ortho-para ratio should occur, but we have seen no effect of this on the specific heat.

The peaks observed in these measurements are assumed to be due to freezing and melting. The measurements indicate that the freezing temperature $T_f$ is less than the melting temperature $T_m$, and values of these quantities are listed in Table I. Notice that one has to interpret these differences rather carefully. For example, we are defining $T_f$ as the temperature at which the specific-heat peak occurs on cooling. But, of course, to make the measurement of $C$ we always put heat into the sample. Thus, in fact the energy absorbed by the sample in the range of the "freezing peak" is associated *with melting*. Nevertheless, it is convenient to continue to refer to these peaks as melting and freezing. The freezing peak is spread over a much smaller range than the melting peak, in each of the three substances studied.

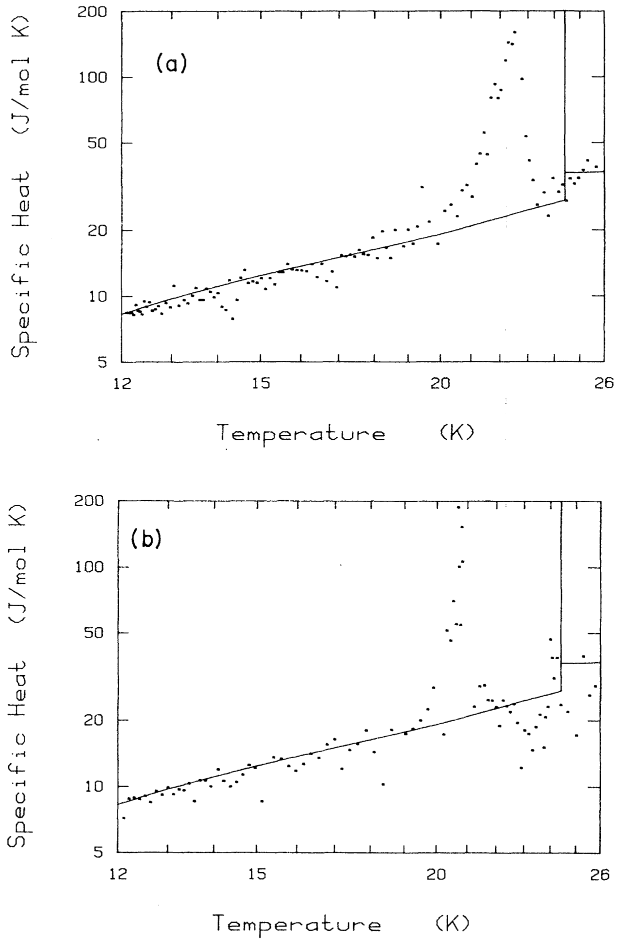

FIG. 3. Specific heat of neon in Vycor. (a) Temperature increasing. (b) Temperature decreasing. Solid line shows the specific heat of bulk neon.

## IV. DISCUSSION

Let $\alpha_{\mathrm{LS}}$ be the surface energy between liquid and solid, and let the contact angle between liquid, solid, and the wall of the Vycor pore be $\theta$ (Fig. 4). Then it can be shown[10] that for a liquid in a tube of radius $r$ the melting temperature is lowered from the bulk melting temperature $T_3$ by an amount $\delta T$ given by

$$\frac{\delta T}{T_3}=\frac{2\alpha_{\mathrm{LS}} v_s \cos\theta}{l_{\mathrm{LS}} r}\ , \qquad (2)$$

where $l_{\mathrm{LS}}$ is the latent heat of fusion per molecule and $v_s$ is the volume per molecule in the solid phase. To apply this to our experiment we assume that Vycor can be approximated by a set of tubes with a radius 27 Å, i.e., the mean pore radius. Equation (2) is based upon a free-energy balance including bulk and surface contributions. By comparison of our measurements of the suppression of the melting point $\delta T_m \equiv T_m - T_3$ with $\delta T$ in Eq. (2), we obtain the results for $\alpha_{\mathrm{LS}}\cos\theta$ shown in Table I.

TABLE I. Triple point of bulk material ($T_{\mathrm{bulk}}$) and freezing and melting temperatures ($T_f$ and $T_m$) for material in Vycor. Last column shows $\alpha_{\mathrm{LS}}\cos\theta$ as calculated from Eq. (2).

| Substance | $T_{\mathrm{bulk}}$ (K) | $T_f$ (K) | $T_m$ (K) | $\alpha_{\mathrm{LS}}\cos\theta$ (erg cm$^{-2}$) |
|---|---|---|---|---|
| $H_2$ | 13.9 | 9.9 | 11.7 | 1.0 |
| $D_2$ | 18.7 | 14.5 | 16.6 | 1.4 |
| Ne | 24.5 | 20.7 | 22.5 | 2.6 |

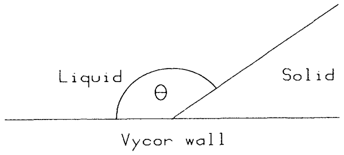

FIG. 4. Definition of the contact angle $\theta$.

The fact that $\delta T_f$ is larger than $\delta T_m$ is presumably due to a problem of nucleation of the solid from the liquid. It is conceivable that there may also be a nucleation problem for nucleation of liquid from solid, and if this is true then the "equilibrium" $\delta T$ given in Eq. (2) is greater than $\delta T_m$. Then the true values of $\alpha_{\mathrm{LS}}\cos\theta$ must actually be larger than those given in Table I.

These results for $\alpha_{\mathrm{LS}}\cos\theta$ are of considerable interest in relation to the possible production of superfluid molecular hydrogen. A recent calculation[11] has shown that, in the absence of heterogeneous nucleation by walls, etc., it should be possible to supercool liquid $H_2$ well below the triple point. An uncertainty in that calculation was the value of $\alpha_{\mathrm{LS}}$. It was found that if $\alpha_{\mathrm{LS}}$ is greater than a critical value $\alpha_c$, which is about 1.2 erg cm$^2$, it should be possible to supercool liquid $H_2$ all the way to $T=0$ K. Our results imply that $\alpha_{\mathrm{LS}}\cos\theta$ is equal to or greater than 1 erg cm$^{-2}$, and thus it does appear that there is a good chance that $\alpha_{\mathrm{LS}} > \alpha_c$. This would mean, provided that heterogeneous nucleation can be avoided, that it will be possible to make superfluid hydrogen. The expected transition temperature is 2 or 3 K.

Earlier experiments with hydrogen in Vycor were performed by Bretz and Thomson.[12] They studied the flow of the liquid through Vycor, and their results seem to indicate that, contrary to expectations, the freezing temperature was *above* the bulk value. Apart from possible differences in the surface condition of the Vycor pores, we do not understand why their experiment gives a different result from ours.

For neon the specific heats of the liquid and the solid in Vycor are close to the corresponding quantities in the bulk phases. For hydrogen and deuterium, the specific heat for the solid in Vycor is significantly increased compared to the bulk value, and for the liquid it is slightly decreased. In the solid phase the specific heat does not show hysteresis, but there is a small amount of hysteresis for liquid hydrogen and deuterium. To understand these effects it is important to know the relative contributions to the specific heat from material close to the surface of the Vycor, and in the interior of the Vycor pores. We are currently investigating this by means of measurements of the specific heat as a function of the fraction of the pore volume which is filled.

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[9] This was calculated from the Brunauer-Emmett-Teller (BET) adsorption isotherm for nitrogen. We would like to thank Dr. D. Johnson of Schlumberger-Doll Research Center for the isotherm measurement.

[10] See, for example, Eq. (15.103) of Ref. 1. In Eq. (2) we have neglected the small difference in density between the liquid and the solid.

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