NRC Publications Archive
Archives des publications du CNRC

Phase transformations of water in porous glass
Antoniou, A. A.

This publication could be one of several versions: author’s original, accepted manuscript or the publisher’s version. / La version de cette publication peut être l’une des suivantes : la version prépublication de l’auteur, la version acceptée du manuscrit ou la version de l’éditeur.
For the publisher’s version, please access the DOI link below./ Pour consulter la version de l’éditeur, utilisez le lien DOI ci-dessous.

Publisher’s version / Version de l'éditeur:
https://doi.org/10.1021/j100792a004
The Journal of Physical Chemistry, 68, 10, pp. 2754-2764, 1964-12-01

NRC Publications Record / Notice d'Archives des publications de CNRC:
https://nrc-publications.canada.ca/eng/view/object/?id=421eccdf-3c4f-47ce-bf4f-6dc33058fdad
https://publications-cnrc.canada.ca/fra/voir/objet/?id=421eccdf-3c4f-47ce-bf4f-6dc33058fdad

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at
https://nrc-publications.canada.ca/eng/copyright
READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L’accès à ce site Web et l’utilisation de son contenu sont assujettis aux conditions présentées dans le site
https://publications-cnrc.canada.ca/fra/droits
LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D’UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n’arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

National Research Council Canada
Conseil national de recherches Canada

18 115

NATIONAL RESEARCH COUNCIL
CANADA

DIVISION OF BUILDING RESEARCH

PHASE TRANSFORMATIONS OF WATER IN POROUS GLASS

BY

A. A. ANTONIOU

REPRINTED FROM
JOURNAL OF PHYSICAL CHEMISTRY, VOL. 68, NO. 10, OCTOBER 1964,
P. 2754 - 2764

RESEARCH PAPER NO. 234
OF THE
DIVISION OF BUILDING RESEARCH

OTTAWA

PRICE 25 CENTS DECEMBER 1964 NRC 8270

Sommaire

Le verre poreux du systeme saturé a été étudié en ce qui concerne l'eau, dans l'intervalle des températures allant de +2 à -40°. Des mesures calorimétriques accompagnées d'observations simultanées sur les changements de longueur ont révélé que deux genres de transformations ont lieu à différentes températures sous le point de fusion normal de la masse d'eau. La quantité d'eau qui ne s'est pas transformée lorsque le système a été refroidi jusqu'à environ -40° correspond à environ 3 monocouches. On déduit des résultats expérimentaux que l'eau absorbée dans le verre poreux, même au milieu des capillaires, a un état différent de celui de la masse d'eau et on conclut que la dépression observée du point de gel doit être considérée en fonction de la structure différente que le produit d'absorption reçoit de l'état de masse.

[Reprinted from the Journal of Physical Chemistry, **68**, 2754 (1964).]

Phase Transformations of Water in Porous Glass

by A. A. Antoniou[1]

Division of Applied Chemistry, National Research Council, Ottawa, Canada *(Received February 26, 1964)*

The system porous glass saturated with respect to water was studied in the temperature range +2 to −40°. Calorimetric measurements with simultaneous observations on length changes revealed that two kinds of transformations took place at different temperatures below the normal melting point of bulk water. The amount of water that did not transform when this system was cooled to about −40° is shown to correspond to approximately three monolayers. The experimental results suggest that the adsorbed water in porous glass even in the middle of the capillaries has a different state from that of bulk water, and it is concluded that the observed depression of the freezing point should be considered in terms of the different structure the adsorbate acquires from that of the bulk state.

Introduction

One of the interests of the Division of Building Research, National Research Council, Canada, is the action of frost in porous building materials, such as concrete, which is a consequence of the climatic conditions prevailing in this country. This problem is in essence the behavior of adsorbed water in porous materials at temperatures below the normal freezing point of bulk water. It is well known that the adsorbed water behaves differently from bulk water in that it shows a depression of its freezing point. Other adsorbates besides water also exhibit a similar behavior; such a study, therefore, could throw some light on the state of the adsorbed phase.

A variety of techniques have been used to study the phase changes occurring in the adsorbates: vapor pressure measurements,[2] dilatometric techniques,[3a] calorimetric methods,[3b,4] and observance of dielectric behavior.[5] In most of this work the depression of the freezing point below the normal one has been related to the existence of menisci, and thus the Kelvin equation has been used in combination with the Clausius–Clapeyron equation, pointing to a unique freezing point depending on the radius of the capillaries. The calorimetric methods used were based on the observance of the temperature change of the system under investigation, while a constant rate of heating was maintained. It is shown in the present work, however, that with this type of calorimetric method equilibrium conditions cannot be achieved.

Hodgson and McIntosh[6] studied the phase changes of water and benzene in porous glass at different degrees of saturation and found the existence of a range of temperatures at which water transforms from one state to another. At about −22° they observed an increase in volume when the system porous glass–water was cooled, and they concluded that a phase transformation occurs at about this temperature.

Since the system porous glass–water has been most extensively studied and since the results obtained by Hodgson and McIntosh were not conclusive, it was decided to study the same system, but at a state at which it is saturated with respect to water. Two parameters, length changes and heat measurements, have been measured, both at the same time. To the writer's knowledge simultaneous measurement of these two parameters has not been reported until now.

Two samples of porous glass have been studied. Although they belonged to the same batch of glass supplied by the Corning Glass Works, they exhibited different B.E.T. surface areas, and showed similarities as well as differences in their behavior. These are

---

[1] Formerly Inorganic Materials Section, Division of Building Research, National Research Council, Ottawa, Canada.

[2] B. R. Puri, Y. P. Myer, and D. D. Singh, *Trans. Faraday Soc.*, **53**, 530 (1957).

[3] (a) I. D. Jones and R. A. Gortner, *J. Phys. Chem.*, **36**, 387 (1932); (b) W. A. Patrick and W. A. Kemper, *ibid.*, **42**, 369 (1938).

[4] Y. J. Iwakami, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **80**, 1094 (1959).

[5] I. Higuti and M. Shimizu, *J. Phys. Chem.*, **56**, 198 (1952).

[6] C. Hodgson and R. McIntosh, *Can. J. Chem.*, **38**, 958 (1960).

described and the information derived is discussed below.

Experimental

Calorimeter Assembly. The calorimeter used in this investigation is of an adiabatic type and is shown schematically in Fig. 1. It will be described in more detail later. The two principles upon which adiabatic calorimeters are constructed have been employed, *i.e.*, the space surrounding the container in which the sample under investigation is enclosed is evacuated and the container is surrounded by an adiabatic shield which is kept at all times at the same temperature as the calorimeter, within a few thousandths of a degree. The container in which the sample is placed will be referred to in this paper as "the calorimeter" and the shields, together with the calorimeter, "the calorimeter assembly." It is not strictly adiabatic because during measurements taken when heating the sample, the whole assembly had a constant rate of cooling. This was achieved by maintaining the temperature of the bath in which the calorimeter assembly is immersed, lower by 3° than the temperature of the calorimeter. This rate of cooling was found necessary because the process occurring during the heating of the sample is an endothermic one. The novel feature of this calorimeter is the incorporation of a window to allow length measurements to be taken together with heat measurements, using an extensometer which will be described later. The same calorimeter assembly but with a thermal shunt of copper turnings between the shield and the outer vessel was also used to measure heat capacities while cooling the sample.

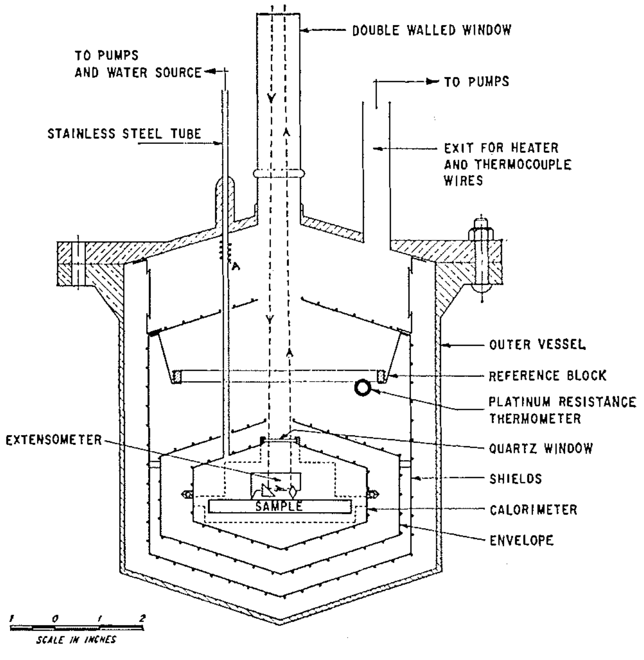

Figure 1. The calorimeter assembly.

The temperature was measured with a platinum resistance thermometer, capsule type, made by Leeds and Northrup Inc., No. 1531634, and was calibrated by the National Research Council, Canada. This capsule was attached thermally to the reference block. The resistance of the platinum resistance thermometer was measured with a G-2 Mueller bridge. The temperature difference between this block and the calorimeter was detected by a five-junction thermopile, which integrated the temperature of the surface of the calorimeter. This temperature difference was read by a Keithley millimicrovolt meter to $1 \times 10^{-3\circ}$.

The reference block where the platinum resistance thermometer is attached, the upper end "A" of the stainless steel tube, and the adiabatic shield were kept at the same temperature as the surface of the calorimeter within a few thousandths of a degree. This temperature control was achieved by a system of differential thermopiles, which transmitted the effects of any imbalance of temperature between the two surfaces concerned to a sensitive galvanometer, which in turn activated a system of phototubes and relays. The existing temperature difference was recorded and was integrated with respect to time, and the heat exchanged between the two surfaces was thus calculated. Between runs, the temperature of the upper part of the stainless steel tube was kept higher than that of the calorimeter to avoid cold spots; the temperature of the calorimeter was kept constant within 0.1° by proper adjustment of the bath temperature and that of the adiabatic shield.

Extensometer. The extensometer used in this investigation, called the Tuckerman gage, was manufactured by the American Instrument Co., Inc. Its construction is based on the principle of the optical lever and has approximate dimensions of 2.5 cm. × 1.3 cm. × 1.3 cm. It was attached firmly to the sample by a stainless steel spring.

The extensometer's sensitivity, $(\Delta l)/l$, is 4×10^{-6} as calibrated by the manufacturer. This was reduced by a factor of two through loss of clarity due to the calorimeter windows in the light path.

The thermal coefficient of expansion of the extensometer was determined by calibrating it against a copper–tellurium alloy bar whose thermal coefficient of expansion was measured by the National Research Council, Division of Applied Physics.

To ensure firm attachment of the extensometer to the sample, the surface of the sample was roughened where the extensometer came in contact with it. It is believed that no accidental displacement of the extensometer relative to the sample occurred during measurements, because readings were consistent when the temperature remained constant overnight or during longer periods of a few days. Furthermore, the information obtained does not show any erratic behavior.

Gravimetric Balance. The sample was saturated with respect to water in a McBain type quartz balance, which was suspended in a long glass tube tapered at the lower end a little above the position where the sample was suspended. The part of the tube where the sample was suspended was immersed in a cold bath. In order to maintain the same temperature inside the part of the tube where the sample was suspended as that of the outside cold bath, helium was introduced and a platinum foil in the shape of a frustrum of a cone was placed on the tapered sides of the tube. This cone prevented convection currents from the lower to the upper part of the gravimetric tube which was at room temperature. The temperature of the cold bath was regulated with a Precision temperature controller manufactured by the Bayley Instrument Co. As a refrigerant, precooled glycol solution was circulated in a copper coil placed in the outer part of the cold bath, which was filled with acetone. The bath could be removed so that a heater could be placed around the glass at the height where the sample rested, and the latter could be heated to about 300° in an oxygen atmosphere to burn out any contaminants. The cathetometer was manufactured by the Precision Tool and Instrument Co. Ltd.

To avoid contamination of the surface of porous glass with grease, the top of the gravimetric tube was sealed with a neoprene O-ring. Hoke valves were also used instead of stopcocks. The gravimetric assembly, together with the cold bath surrounding it, could be disconnected from the evacuating train and rolled into a cold room kept at −10° where the sample was demounted from the quartz balance and placed in the calorimeter.

The System Porous Glass–Water. The adsorbent was porous glass (Vycor brand) No. 7930 manufactured by the Corning Glass Works. It was 96% SiO_2 with 3% B_2O_3. The glass was first evacuated in the gravimetric apparatus to a pressure of 1×10^{-4} mm., and was treated with oxygen at about 300°. During this treatment the glass changed color to dark brown and became clear when the organic contaminants were burned off. The samples were cut out of 0.5-cm. thick porous glass plate. Their approximate dimensions were 8 cm. × 1 cm. × 0.5 cm. The adsorbate was distilled water, degassed by repeated freezing and melting.

The behavior of two samples of porous glass cut from the same batch, but not from the same plate, is reported. At saturation the first sample adsorbed 21 weight % of water; the second, 24%. The total amount of water adsorbed in the first sample was 1.53 g. and 1.82 g. in the second.

Precision and Accuracy of Calorimetric Results. The precision of the calorimetric measurements taken during heating was 0.3% of the total heat capacity of the calorimeter with porous glass saturated with respect to water. The heat capacity of the adsorbed water amounted to only 5% of the above amount, and therefore the precision with which the adsorbed water was measured was 6%. To determine the accuracy of these measurements the heat capacity of an amount of sodium chloride equivalent in calories to the amount of absorbed water present in the system was determined under similar conditions; these values were found to be 5% higher than the ones reported by Morrison, *et al.*[7]

Procedure

Saturation of the Porous Glass with Respect to Water. Calorimeter Assembly. The saturation of the porous glass took place in the gravimetric tube at a temperature just above 0° after it had been evacuated and heat treated at 300°. When the weight of the adsorbed water reached a constant value within $\pm 5 \times 10^{-4}$ g./g. of glass, saturation was taken to be complete.

To prevent distillation of the water from the sample when its temperature was lowered, helium was introduced into the gravimetric tube to a pressure of 25 mm. and the temperature of the bath was lowered to about −10° at a rate of less than 2°/hr. Separate experiments were carried out with other samples saturated with respect to water in which the temperature was lowered to −25°. The purpose of these experiments was to find out the conditions under which the temperature of the sample could be lowered without any appreciable loss of water. This was important because the sample in the calorimeter had to be cooled to −40°. It was found that when exchange gas was present at the above-mentioned pressure and the above rate of cooling was not exceeded, the weight of the sample remained constant within ±0.3%.

The transfer of the sample from the gravimetric tube to the calorimeter, the mounting of the extensometer, and the assembly of the calorimeter were done in a cold chamber kept at about −10°. It was considered acceptable to expose the sample to the atmos-

---

[7] J. A. Morrison and D. Patterson, *Trans. Faraday Soc.*, **52**, 764 (1956).

phere at this temperature after it was saturated with water since diffusion of any gases into the adsorbate at this state would be extremely difficult. The assembled calorimeter was placed in its bath which was kept at −10° and was connected to the evacuating train.

To remove the air from the calorimeter, it was evacuated to a pressure corresponding to a relative humidity of approximately 0.7. Resaturation of the sample took place at the triple point of water using a degassed water source at the same temperature. Saturation was considered complete when no more heat of adsorption was evolved, when the vapor pressure of the sample measured on a butyl phthalate manometer corresponded to the vapor pressure of the bulk water at +0.01°, and when no more length changes occurred. During this process, the calorimeter was kept at a temperature not lower than +0.01° in order to ensure that no condensation of bulk water occurred in it. Also to avoid cold spots along the stainless steel tube, its upper part was kept warmer than the calorimeter. Finally, dry helium was passed into the calorimeter, which was isolated from the rest of the evacuating train by closing the valve situated immediately after the stainless steel tube.

Length Changes. These measurements were taken with the extensometer as described in the temperature range of +20 to −40°. The change of temperature after each measurement was less than 1°, especially when transformations were observed. The rate of change of temperature was less than 4°/day, and even smaller at the temperatures at which transformations were accompanied by evolution or absorption of heat.

Calorimetric Measurements Obtained When Heating the System. Calorimetric measurements obtained when heating the system were taken at increments of temperature of less than 1° and at a rate of less than 2°/day, especially in the transformation range of temperature. The temperature increase after a certain heat input was determined by extrapolating the fore and after drifts, to the middle of the heating period. Particular attention was given to the rate of cooling in order that the fore-period would be exactly the same as the after-period. The time required for the calorimeter to obtain this predetermined rate of cooling, after a heat input, was found to vary from a few minutes, when no transformations took place, up to more than 4 hr. when transformations occurred and for an increment of temperature of only 0.5°. The rate of cooling was of the order of 15×10^{-3}°/hr. During these measurements, the temperatures of the upper part of the stainless steel tube, reference block, and adiabatic shield were controlled and the heat exchanged was determined so that the necessary corrections could be applied to the heat capacity information. In most cases, these corrections were smaller than the accuracy of the measurements.

Calorimetric Measurements Obtained when Cooling the System. In order to detect the range of temperatures when evolution of heat takes place while cooling the system, use was made of the first-order rate law

$$\frac{\mathrm{d}T}{\mathrm{d}t} = K(T_{\mathrm{as}} - T) = \frac{k}{C}(T_{\mathrm{as}} - T) \qquad (1)$$

where T is the temperature of the calorimeter at time t, T_{as} is the temperature of the adiabatic shield, k is a cooling constant, C is the heat capacity of the system together with the calorimeter, and $K = k/C$. T_{as} was kept lower than T by about 0.8° and was of course different for each run. During the measurements it was kept constant within ± 0.02°. Besides employing the thermal shunt made of copper turnings it was also found necessary to increase the pressure to a fixed value in the space surrounding the calorimeter in order to increase the rate at which heat was removed from the calorimeter.

The K value in (1) was determined experimentally at a temperature above the normal melting point of water when no transformations take place. The heat capacity of the calorimeter and the system C was calculated from data already determined during the heating of the system, and thus the k value was obtained. This constant was used to obtain the heat capacity data in the temperature range where transformations take place. Between runs the temperature of the calorimeter was maintained constant within 0.02°.

Results

Length Changes. Figure 2 shows the behavior of the first sample during a temperature cycle from −40 to 0°. Repetition with the same sample gave essentially the same results after the water had been partly desorbed by degassing and the sample was resaturated according to the procedure mentioned above. Figure 3 shows the behavior of the second sample cut from the same batch of porous glass, but at temperatures extending from −40 to +20°.

These two samples are distinguished by different B.E.T. surface areas, 94.5 m.^{2}/g. in the first and 82.5 m.^{2}/g. in the second. Both samples showed essentially the same behavior during warming as well as during the cooling process. The four sections distinguishable in the cooling process and the four sections observed during the warming process will be dealt with separately.

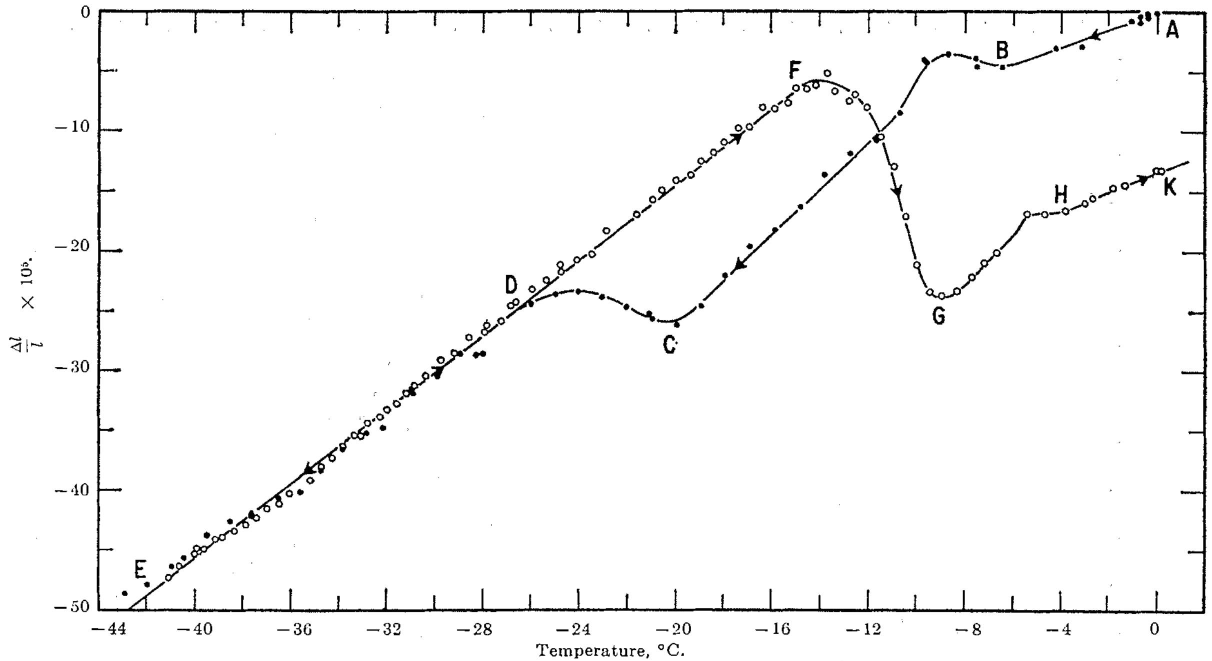

Figure 2. Porous glass saturated with respect to water, first sample. Length changes: ●, data obtained during cooling; ○, data obtained during warming.

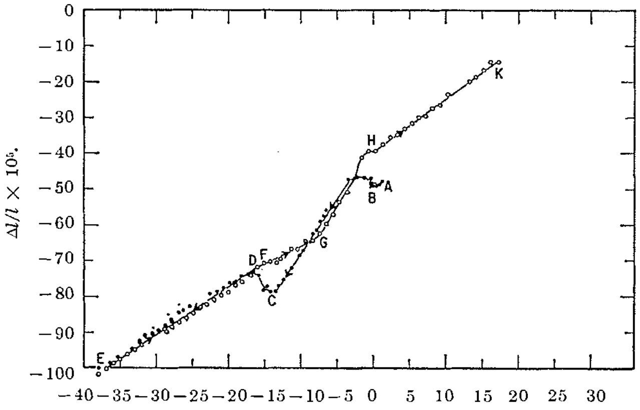

Figure 3. Porous glass saturated with respect to water, second sample. Length changes: ●, data obtained during cooling; ○, data obtained during warming.

Section A–B. In Fig. 2 the sample contracts with a linear thermal coefficient of 7×10^{-6} deg.$^{-1}$ until it reaches −7°. In Fig. 3 measurements start just above 0° and the thermal coefficient cannot be determined. This cycle was repeated and a thermal coefficient of contraction of 5×10^{-6} deg.$^{-1}$ was found. These figures compare well with the linear thermal coefficient of expansion of porous glass evacuated with respect to water to a pressure of 1×10^{-4} mm., which was found to be 5×10^{-6} deg.$^{-1}$.

Section B–C. At approximately −7° (Fig. 2) and at −1° (Fig. 3) a small expansion occurs. This hump is not accidental. Litvan and McIntosh,[8] studying the behavior of porous glass partly saturated with respect to water by observing length changes, have noticed even more pronounced humps (expansions followed by contraction) in the same range of temperatures. The magnitude of these humps decreased with increasing water content the more saturated the porous glass was with respect to water. Following this small expansion the porous glass contracts with a higher linear coefficient of contraction, about three times the former value.

Section C–D. Between −20 and −26° (Fig. 2) and between −14 and −16° (Fig. 3), respectively, the two samples expand. The temperature range at which each sample expands was found to be reproducible when the temperature cycles were repeated. These expansions were studied for decrements of 0.5° or less and they were found to be gradual. In no case was a sudden expansion observed similar to the one which would be expected if a supercooled liquid transformed into a solid state.

Section D–E. The two samples contract below −26° (Fig. 2) and below −16° (Fig. 3), respectively, with a linear thermal coefficient of $15 \pm 1 \times 10^{-6}$ deg.$^{-1}$ in both cases.

Section E–F. Both samples expand when increasing the temperature from −40 to −15° with approximately the same linear coefficient as for contraction.

---

[8] G. G. Litvan and R. McIntosh, *Can. J. Chem.*, **41**, 3095 (1963).

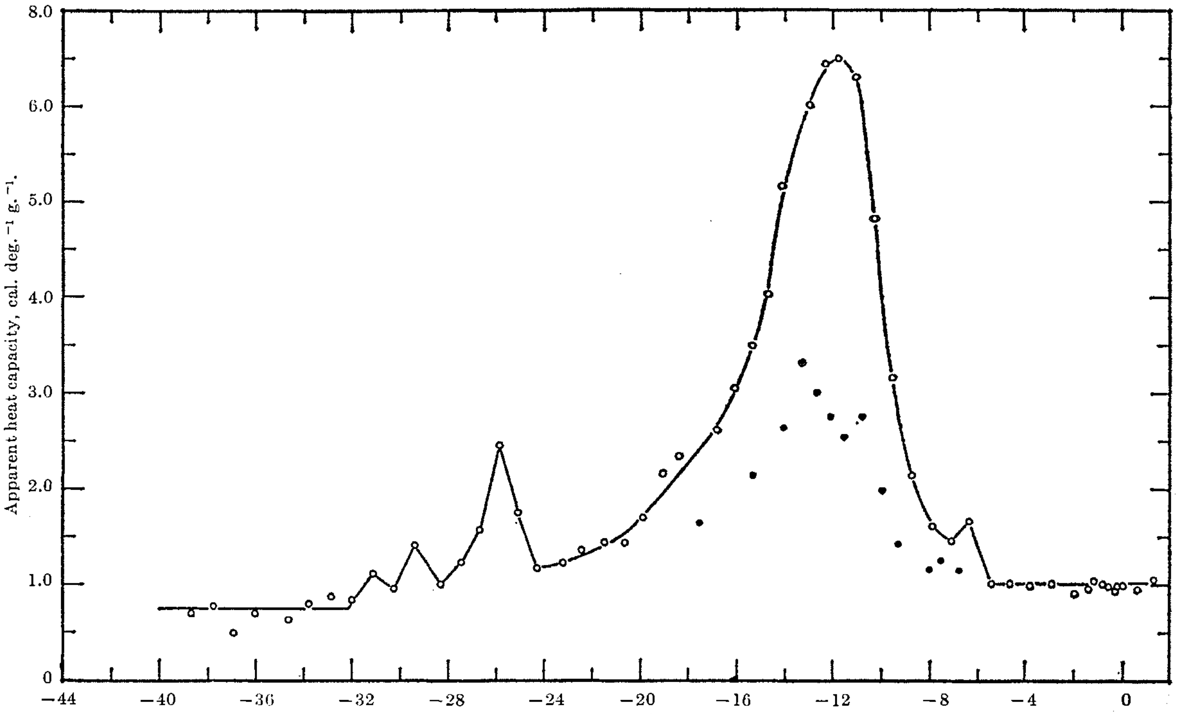

Figure 4. Porous glass saturated with respect to water, first sample. Apparent heat capacity of adsorbed water. For explanation of open and full circles refer to text.

Section F–G. A contraction is observed between −15 and −9° (Fig. 2) and a probable contraction superimposed on DG in Fig. 3 in the same temperature range. In the first case the absolute length of the sample after contraction was smaller than its length at the same temperature while cooling. In the second case, the contraction is more gradual, extends to a wider temperature range, and the absolute length of the sample after contraction is approximately the same as it was at the same temperature while cooling.

Section G–H. Upon further increase of temperature an expansion is observed (Fig. 2) for a short interval of temperatures up to −6° and for a wider range (Fig. 3) up to −1°. The slopes give 21×10^{-6} deg.$^{-1}$ for the first sample and 30×10^{-6} deg.$^{-1}$ for the second.

Section H–K. Above −5° (Fig. 2) and −1° (Fig. 3) the samples continue to expand but with a linear coefficient of expansion of 8×10^{-6} deg.$^{-1}$ in the first case and 15×10^{-6} deg.$^{-1}$ in the second.

Calorimetric Measurements Obtained when Heating the System. These were taken in the temperature range −38 to +2°. Three series of runs were obtained with the first sample of which the first one was of an exploratory nature; the other two were taken in more detail and accuracy and were accompanied by measurements of length changes. Nevertheless, all three depict the same general behavior, *i.e.*, an increase in the apparent heat capacity of the system in the same temperature range.

Figure 4 shows the observed "apparent heat capacities" for 1 g. of adsorbed water in porous glass, at saturation. The term apparent heat capacity is used because this quantity was calculated by subtracting from the total heat capacity observed, the heat capacity of the calorimeter and porous glass degassed to 1×10^{-4} mm. at room temperature. Under these conditions, of course, the glass was not completely degassed with respect to water.

Above −5° the points (open circles) fall on a straight line within the accuracy of measurements. It is reasonable to assume that no transformations take place in this region since the apparent heat capacity is constant and very close to unity. In all three sets of runs the heat capacity had leveled to this value at about −5°.

Between −32 and −5° the apparent heat capacity of the adsorbed water shows considerable variation and increase. There is a maximum at about −26° and another even more pronounced at about −12°. These two peaks were observed in the last two series of runs at the same temperatures.

Below −32° the heat capacities show values about a mean average of 0.8 cal. deg.$^{-1}$. Since the variation is small, it is not known with certainty whether any transformations are involved in these temperatures.

The calorimetric results also show that the process of freezing and thawing is not reversible in the temperature range where transformations take place. This means that in performing a temperature cycle between two temperatures within the range −32 to −5° the adsorbed water does not regain its initial state. This is seen in the calorimetric measurements during heating, by the smaller heat capacities when the initial temperature of the run was lower than the final temperature of the previous run by at least 0.1°. These measurements are shown in Fig. 4 by full circles. A similar observation has already been reported by Patrick and Kemper[3b] for the system silica and water. The specific heat of porous glass degassed with respect to water, as already mentioned, was found to be 0.16 cal. deg.^{-1} at 0°.

Latent Heat of Transformation. It is assumed that, in the region of the increased apparent heat capacities, transformations take place and the increased value is due to the latent heat of transformation. The accompanying change in volume extending within this temperature range substantiates this assumption.

In order to determine the latent heat of transformation, the area under the curve between −32 and −5° was calculated and the heat capacity of the adsorbed water and ice subtracted. The heat capacity of the ice and adsorbed water was determined by calculating the area under a straight line drawn between the heat capacity at −5° and the heat capacity at −32°. This was considered a good approximation since the error involved would be very small compared with the number of calories representing the latent heat of transformation. Furthermore, the heat capacity of the "adsorbed ice" is not known. This area was found to represent 65.5 ± 0.5 cal. for 1.53 g. of adsorbed water in the two series of runs. In order to determine the amount of water which transformed from some sort of ice to some sort of liquid water, it is necessary to know the latent heat of fusion of "adsorbed ice" in porous glass at different temperatures. Such information is not available at present for water in porous glass or for other adsorbates. For this reason the value for the latent heat of fusion of bulk ice to bulk water was used and this was calculated at different temperatures by using eq. 2.[9]

$$\frac{\mathrm{d}}{\mathrm{d}T}\Delta H = \Delta C_{\mathrm{p}} + \frac{\Delta H}{T} - \Delta H\left(\frac{\partial \ln \Delta V}{\partial T}\right)_{\mathrm{p}} \quad (2)$$

As the last term on the right-hand side of eq. 2 was a very small quantity, it was omitted in the calculation. For the heat capacity of liquid water below 0° an extrapolated value was used and the heat capacity of bulk ice was also used for the "adsorbed ice."

The amount of water which transformed at each temperature was calculated by dividing the latent heat of transformation per increment of temperature, as determined experimentally, by the latent heat of fusion for the same temperature, calculated by the use of the eq. 2. The result is shown in Fig. 5. The amount of adsorbed water which transformed between −32 and −5° is found thus to be about 55% of the total amount of adsorbed water. A simple calculation of the amount of water held by a monolayer in the porous glass reveals that, if the above assumptions are correct, the water which does not transform until −40° is that held in approximately three monolayers on the surface of the porous glass.

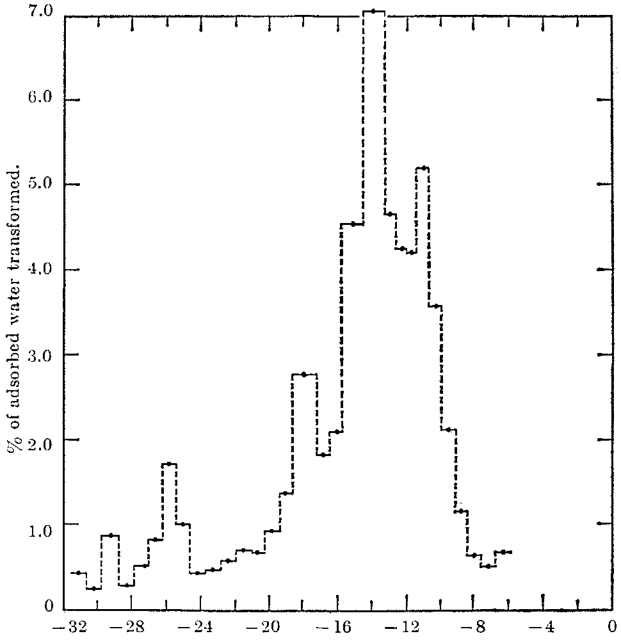

Figure 5. Porous glass saturated with respect to water, first sample. The per cent of adsorbed water transformed during heating per increment of temperature. Lines parallel to abscissa indicate temperature increment.

Calorimetric Measurements Obtained when Cooling the System. Figure 6 shows the calorimetric information obtained with the second sample when cooling the system. Only one series of runs was obtained and length measurements taken at the same time are shown in Fig. 3. They are the ones starting at +1.5° and ending at −38°. The heat data are reported in this case as the total apparent heat capacity

---

[9] E. A. Guggenheim, "Thermodynamics," 1959, p. 151.

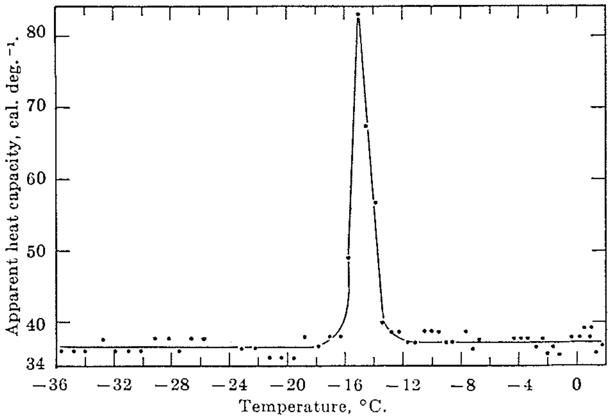

Figure 6. Porous glass saturated with respect to water, second sample. Apparent heat capacity of porous glass saturated with respect to water. The heat capacity of the calorimeter is included. Calorimetric data obtained during cooling.

of the system together with the calorimeter, because the accuracy is considerably lower than in the heating runs. It is seen that heat is evolved between −14 and −16° when at the same time the sample expands. No heat evolution which could be related to the latent heat of transformation is observed between 0 and −14° within the accuracy of these measurements. Again the area under the hump was calculated as before and this corresponded to an evolution of approximately 36 ± 5 cal./g. of adsorbed water. Water transformed was calculated as before using the $\Delta H(T)$ equation and it was found that 45 ± 7% of the adsorbed water was frozen.

Discussion

The phase transformations of water in porous glass have been observed during the process of cooling and heating in the temperature range from room temperature to −40° by observing length changes together with heat effects. This work shows that two kinds of transformations occur in this temperature region. The first one is not accompanied by a heat effect, occurs at temperatures just below the normal melting point of water, and becomes evident by the change of the linear coefficient of expansion. In this transformation the thermal coefficient of contraction or expansion passes through a maximum before returning to a normal value within a small range from 2 to 3°. Similar observations on the thermal coefficients have been observed for crystals which show a continuous transformation through a temperature range rather than a sharp transition. These transformations have been attributed to the coexistence of two different structures in the crystals.[10] Whether this explanation is a plausible one for the adsorbed water in porous glass remains to be seen.

The second kind of transformation occurs at lower temperatures than the one previously described, and extends over a range of temperatures. During freezing, the evolution of heat is accompanied by expansion; during thawing, there is an absorption of heat together with contraction. It is also observed that the length changes do not constitute the most reliable parameter for detecting phase changes occurring in porous materials. This is especially true during the thawing process. The same system, porous glass–water, but at relative humidities less than unity, has been studied by Hodgson and McIntosh[6] by observing the length changes with change of temperature. They showed that transformations occurred in a range of temperatures, and the general behavior of the system was the same as is reported here. The expansion during freezing was shown to occur at about −22°, but this temperature is not characteristic of this system as shown in the present paper. In addition, the first kind of transformations described above were not detected by them. Since there is no general agreement as to the nomenclature of the order or types of transformations,[10,11] and no information on compressibility for this system is available, no attempt is made here to classify these transformations.

Prediction of the Transition Temperature by the Kelvin Equation. The depression of the freezing point of the adsorbates has been attributed in the past to the different state the adsorbate acquires because of the existence of menisci. With this assumption, the Clausius–Clapeyron equation is combined with the Kelvin equation to yield the relationship[6]

$$\Delta T = 2T_{\mathrm{f}}(\sigma_{\mathrm{lv}}\bar{V}_{\mathrm{l}} - \sigma_{\mathrm{sv}}\bar{V}_{\mathrm{s}})/r\Delta H_{\mathrm{ls}} \qquad (3)$$

Both the Clausius–Clapeyron and the Kelvin equations refer to a one-component system. Combination of the two equations presupposes the existence of equilibrium between vapor–liquid and solid. For a one-component system, there is only one temperature at which the three phases can coexist and this is the triple point of the macroscopic one-component system. If the adsorption forces do contribute in the freezing, in which case the situation is similar to the freezing of a macroscopic two-component system,[6] there is no term in eq. 3 to take care of the contribution of these forces. In addition, it has become certain that transformations occur within a range of temperatures.

Concluding Discussion. It is reasonable to assume

---

[10] A. R. Ubbelohde, *Quart. Rev.* (London), **11**, 246 (1957).

[11] J. Jaffray, *Ann. Phys.* (N. Y.), **3**, 5 (1948).

that the water that transforms during cooling or during warming of the sample is only the water found in the middle of the capillaries and not that adhering closely to the surface. This assumption is supported by the observations of Litvan and McIntosh[8] who studied the same system porous glass–water at different degrees of coverage by following length changes in the same temperature range as this work and they observed anomalies only at coverages higher than two monolayers. Morrison, Drain, and Dugdale[12] also observed increased heat capacities for the system nitrogen on titanium dioxide, again at coverages above the second monolayer. In addition, the observed differential heat of adsorption approaches very closely the heat of liquefaction after the completion of the second monolayer for most systems.

Further, it can be seen from the following observations that the water in the middle of the capillaries is not bulk water, *i.e.*, that it has properties different from bulk water. (1) The amount of water that transformed during heating above $-38°$, as calculated from the calorimetric results obtained during heating, amounts to 55% of the total adsorbed water in porous glass at saturation. This calculation shows that less than three monolayers of adsorbed water were unfrozen below $-38°$. A similar result is obtained from the calorimetric data of the cooling runs (within the accuracy of these results), for the amount of water frozen in the second sample.

On the other hand, the cubical expansion calculated from the observed linear expansion during cooling between -20 and $-26°$ in the first sample and -14 and $-16°$ in the second sample is 1.3×10^{-3} cm.^{3}/g. of adsorbed water, which would correspond to the approximate expansion of 0.014 g. of bulk liquid water when transformed into bulk ice. The observed contraction between -14 and $-9°$ in Fig. 3 during the heating runs will correspond to the melting again of 0.026 g. of bulk ice. Comparing these figures with those calculated from the calorimetric results, it is seen that the ratio of the amount of water transformed as calculated from the heating data to the amount transformed as calculated from the length changes is 40 in the first case and 20 in the second. Even though the assumptions which lead to this argument, *i.e.*, the calculation of ΔH as a function of temperature and the isotropic nature of the sample are not rigorous, the ratio observed is so high that it cannot invalidate the above argument. In addition, a Young's modulus of 1.5×10^{11} dynes cm.$^{-2}$ [13] shows that a pressure of only 40 atm. exerted by the adsorbed phase on the walls of the capillaries could produce the same volume expansion. For the water–ice transformation at these temperatures a pressure up to 2000 atm. is required. (2) The system porous glass saturated with respect to water shows a continuous contraction when the temperature is lowered from $+2$ to about $-7°$ (Fig. 2) with a thermal coefficient of contraction of approximately 6×10^{-6} deg.$^{-1}$ and with an even higher coefficient below $-7°$. When the temperature cycle shown in Fig. 3 was repeated, the sample again contracted from room temperature to about $-2°$ with the same thermal coefficient as shown in Fig. 2. These data are not shown in Fig. 3 for the sake of clarity.

It is seen, therefore, that in the first case the expansion should have been considerably greater if bulk water had been transformed into bulk ice. In the second case the system contracts from room temperature in a different pattern from that expected for bulk water, even in the supercooled state,[14] since no maximum in the density of the adsorbate is observed at $+4°$; and on the contrary the system exhibits a higher thermal coefficient of contraction below 0° at temperatures different in the two samples. It is obvious, therefore, that this state of water differs from that in the bulk state.

There is little doubt that the water adsorbed in the first two monolayers has a completely different structure from that of bulk water. Frohnsdorff and Kington[15] found that the apparent heat capacity of the intracrystalline water in zeolites at low water contents is 20 to 23 cal. deg.$^{-1}$ mole^{-1} at 27°, a value which is considerably greater than that of liquid bulk water. The heat capacity appeared to decrease with increasing water concentration. A possible explanation offered was that the two coordinated water molecules would have a greater vibrational and a greater "flapping" freedom (pendulum motion about surface) than the three or four coordinated molecules, and thus the heat capacity at low water concentrations would be expected to be greater than that of liquid water. Since, therefore, the first monolayers have a different structure than bulk water, and these will necessarily constitute the framework upon which further condensation from the gas phase takes place, it is possible that with further condensation the adsorbate assumes a different structure, a different epitaxy than it has in the bulk state. The conclusion is therefore reached that the change in freezing temperature of the adsorbed

---

[12] J. A. Morrison, L. E. Drain, and J. S. Dugdale, *Can. J. Chem.*, **30**, 890 (1952).

[13] Y. Kozirovski and M. Folman, *Trans. Faraday Soc.*, **58**, 2228 (1962).

[14] J. F. Mohler, *Phys. Rev.*, **35**, 236 (1912).

[15] G. F. C. Frohnsdorff and G. L. Kington, *Proc. Roy. Soc.* (London), **A274**, 469 (1958).

water should be related to the different structure of the water in porous glass. Similar considerations could, very likely, also hold for other adsorbates which exhibit anomalous behavior during cooling. Ubbelohde[16] has suggested that the depression of the freezing point of adsorbates might be associated with the different structure the adsorbent imposes on the adsorbate since there is a preferred orientation in the first monolayer. Perhaps his suggestion has not been sufficiently appreciated because of the lack of additional experimental evidence.

Table I summarizes the behavior of the two different samples of porous glass characterized by two different B.E.T. nitrogen areas. As the chemical composition of the adsorbents and of the adsorbates is the same in both cases, the differences indicated in Table I should be attributed to the different geometry of the pores which results in the different structure of the water in the pores. If the melting temperature is a unique function of the structure of the water and the structure of the water is a unique function of the geometry of the pores, the distribution presented in Fig. 5 should represent a pore-size distribution of the sample. This is compared with the pore-size distribution, Fig. 7, calculated from the desorption part of the isotherm determined for the same sample of porous glass and calculated by using the Kelvin equation, which relates the relative vapor pressure to the radius of the capillary (meniscus). The derivation of the Kelvin equation assumes, nevertheless, that the adsorbate can be treated as bulk water under reduced pressure which is due to the existence of menisci. It is shown in this work that the adsorbate is not bulk water and that there is a series of domains, which are considered to be related to the different structure of the water. Under these circumstances the Kelvin equation should be used with caution. Comparison of Fig. 5 and 7 shows the different distribution one obtains in either case. The relation between the melting point and the radius of the capillary should be based on considerations of the structure of the adsorbate. Such a relationship is not as yet known and in consequence the distribution represented in Fig. 5 cannot be expressed in terms of the radii of the capillaries. More work is required with samples bearing from less than one to more statistical monolayers.

Table I: Differences Observed in the Two Samples

Sample	B.E.T. surface areas, m.²/g.	Amount of water adsorbed at saturation, g./g.	Temp. at which linear thermal coefficient of contraction changes	Temp. range at which samples expand
First	94.5	0.21	−7°	−20 to −24°
Second	82.5	0.24	−1°	−14 to −16°

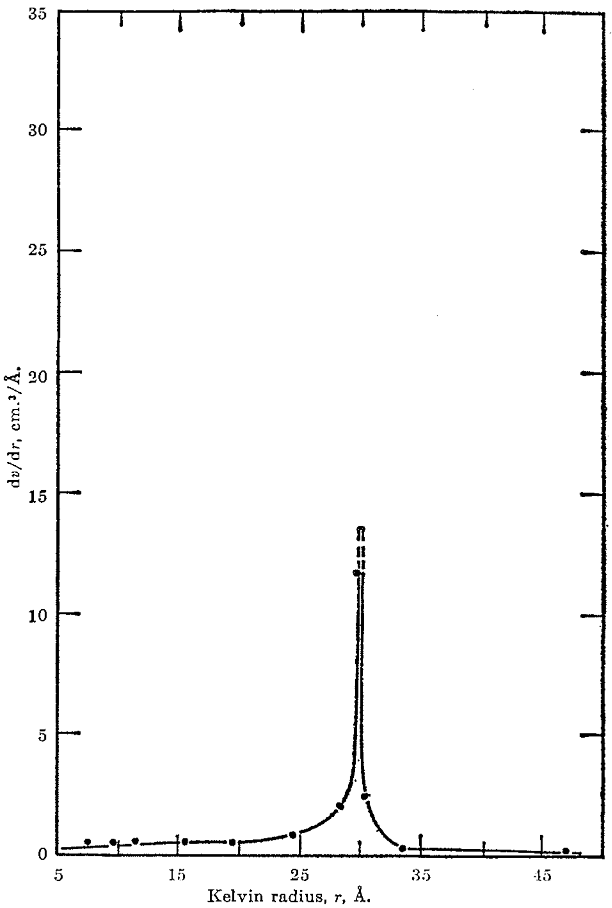

Figure 7. Porous glass saturated with respect to water, first sample. Pore-size distribution calculated from the desorption part of isotherm of same sample.

Acknowledgments. The author wishes to thank Mr. P. J. Sereda for assistance offered during the course of this work, Dr. C. H. Amberg for helpful discussions, Mr. B. Hurley and Mr. W. Cheh for carrying out part of the experimental work and calculations, Mr. H. F. Slade for technical assistance, and Mr. D. Kulawic for obtaining the B.E.T. data.

Discussion

M. L. White (Bell Telephone, Murray Hill). Did you obtain any time effects associated with length changes? That is, were there any supercooling effects that might explain some of the "humps" in your graphs?

---

[16] A. R. Ubbelohde, *Quart. Rev.* (London), **4**, 356 (1950).

A. ANTONIOU. The system was considered to have reached equilibrium only when the rates of change of temperature before and after heat input became identical. Observations on both the dimensional changes and the heat effects were made only at that stage. The time required to attain equilibrium was from 2 to 5 hr. for the range where the transformations took place, in contrast to about 15 min. when no transformations occurred. When the system expanded, the temperature was decreased as little as 0.2° and not more than three observations were taken in the course of 24 hr. The system did not show any sudden changes which could be attributed to supercooling. Under these conditions, one can assume to have reached an equilibrium state after each temperature change.

H. VAN OLPHEN (Shell Development Company, Houston). In the interpretation of your results, long-range effects of the surface on the structure of water are invoked, extending beyond one or two monolayers. My own belief is that a diffuse double layer is formed upon contacting the water with the glass. Therefore, any long-range effects might be discussed by taking into account the diffuse counterion atmosphere. Electroosmosis effects would indicate whether or not the presence of a double layer is important in this problem.

A. ANTONIOU. If we consider the capillaries to be some sort of tubes, we have to assume that this double layer should extend to their center, so that it would influence the properties of the adsorbate. This does not seem to me very likely. One would think that the diffuse double layer will extend only a few statistical monolayers away from the surface, so that the adsorbate in the middle of the capillaries will behave as in the bulk state, which is shown not to be the case. On the other hand, if the adsorbent is in the form of a network and the adsorbate fills the vacancies of this network, it may be that this double layer could extend throughout the bulk of the adsorbate. This would result again in a metastable condition for the adsorbate. Electroosmotic effects could possibly show the extent to which the diffuse double layer influences the orientation of the adsorbate.

T. MARTIN (Massachusetts Institute of Technology, Cambridge). In other systems there have been observations of rhythmic ice band structures. Do such structures have any bearing on your experiments?

A. ANTONIOU. It is doubtful whether one could distinguish ice bands in porous glass, as one can in macroscopic crystals, since the thickness of these bands in the adsorbate will have to be of molecular dimensions. It is apparent, though, that there is a series of domains which could be related to ice bands, though on a molecular scale.

A. C. HALL (Socony Mobil Oil Company, Dallas). In connection with Dr. Van Olphen's point as to the range of adsorption forces, I should like to draw attention to Deryaguin's work in which it was found that isotherms of polar adsorbates on high energy surfaces intercepted the adsorption ordinate whereas isotherms of nonpolar adsorbates did not, and to ask whether you expect to extend your experiments to nonpolar fluids.

A. ANTONIOU. The results which are reported certainly pose many questions which cannot be answered at the present time. Experiments with nonpolar fluids are under way at the Division of Building Research, National Research Council.