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PHASE TRANSITIONS OF ADSORBATES
PART 2 - VAPOUR PRESSURE AND EXTENSION ISOTHERMS
OF THE POROUS - GLASS + WATER SYSTEM BELOW 0 °C

BY

E. W. SIDEBOTTOM AND G. G. LITVAN

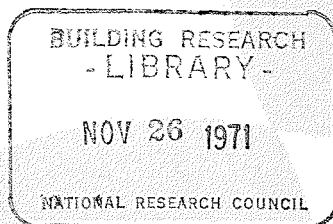
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TRANSITION DANS LES PHASES DES PRODUITS ADSORBES

II. PRESSION DE VAPEUR ET ISOTHERMES D'EXTENSION SOUS 0°C DU SYSTEME VERRE POREUX-EAU

SOMMAIRE

La pression de vapeur et les isothermes d'extension du système eau -- verre poreux (96% de silice) ont été déterminés à +1.5, -6.4, -14.6, -25.4 et -35.3°C. Les isothermes obtenus à ces températures coïncident si la quantité d'eau adsorbée, a , est tracée en fonction de la pression relative par rapport à celle de l'eau surfondue. Ceci démontre que l'eau adsorbée isothermiquement est dans un état semblable à un liquide et confirme que la réduction importante de a avec une baisse de température est attribuable à une diminution de la pression relative maximale qui peut être réalisée expérimentalement. Contrairement aux résultats d'études précédentes, on a trouvé un minimum à l'isotherme d'extension pour de faibles concentrations, ce qui indique que les groupes adjacents de silanes à liaison avec l'hydrogène ne sont peut-être pas le lieu d'adsorption de l'eau comme on l'a supposé par le passé. Une revue de la littérature technique appropriée semble indiquer que le minimum de l'isotherme d'extension s'obtient par l'adsorption de la plupart des substances à condition que la température expérimentale ne soit pas plus élevée que le point d'ébullition de masse. On suppose que l'effet de contraction et l'hystérèse secondaire pour des faibles concentrations d'adsorption sont causées par micro-porosités.

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PHASE TRANSITIONS OF ADSORBATES

PART 2.—VAPOUR PRESSURE AND EXTENSION ISOTHERMS OF THE POROUS-GLASS + WATER SYSTEM BELOW 0°C

Phase Transitions of Adsorbates

Part 2.—Vapour Pressure and Extension Isotherms of the Porous-Glass + Water System Below 0°C

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The vapour pressure and extension isotherms of the water-porous 96 % silica glass were determined at +1.5, -6.4, -14.6, -25.4 and -35.3°C. Isotherms obtained at these temperatures coincided if the amount of adsorbed water, a , was plotted against the relative pressure with reference to that of undercooled water. This demonstrates that the isothermally adsorbed water is in a liquid-like state and confirms that the drastic reduction of a with declining temperature is due to a decrease of the maximum relative pressure that can be realized experimentally. In contrast to previous studies, a minimum in the extension isotherm at low concentration was found, indicating that adjacent hydrogen-bonded silanol groups of the glass may not be the site of water adsorption as has been assumed in the past.

Examination of the pertinent literature suggests that a minimum of the extension isotherm is obtained on the adsorption of most substances if the experimental temperature is not higher than the bulk boiling point. The contraction effect and the secondary hysteresis at low coverages are assumed to be caused by microporosity.

Phase transitions of water adsorbed in porous materials are of great technical and economic importance. In the continuing project aiming to clarify the mechanism of frost action in porous materials the heat of fusion of adsorbed ice was determined.¹ It became evident that thorough knowledge of the adsorption characteristics of the systems below the triple point of the adsorbate would greatly facilitate further progress and the present work was undertaken.

Several studies have been made in this field.²⁻⁸ The most important finding reported is that for a relative pressure, p/p° , the amount of the adsorbate, a , decreases with decreasing temperature if p/p° is based on the vapour pressure of the crystalline solid, p_s° .

Amberg *et al.*² and Kiselev and Kulichenko³ suggested that the decrease in the adsorptive capacity is only apparent. They argued that because the adsorbate is known to be in a liquid-like state the adsorption is governed by the magnitude of p relative to p_l° (the pressure of the undercooled liquid), and not p_s° . Since the upper limit of the experimentally realizable pressure is p_s° , p_l° can never be achieved except at the bulk freezing point. As p_l° exceeds p_s° by an increasing margin as the temperature is lowered, the isotherms are terminated at values of p/p_l° which become progressively lower and which are always less than unity. If a is expressed in terms of p/p_s° the limiting pressure value equals unity and complete saturation is implied. This results in distortion of the constructed isotherm and an apparent reduction of a for a given p/p_s° . Accordingly, when a is plotted against p/p_l° the isotherms superimpose.³

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In those cases in which $p/p_i^\circ = 1$ could not be achieved the desorption branch followed the "scanning" path.

Certain points, however, remained in need of clarification. First, according to this explanation, the lower closure point of the hysteresis loop should shift to higher relative pressures with decreasing temperature if a is expressed as a function of p/p_s° because of the distortion of the isotherm.⁴ No indication of this could be found in the literature. Secondly, no explanation was offered for a startling, and from the frost mechanism point of view important, observation^{4, 9} that porous bodies appear to have a higher adsorptive capacity below the triple point, if an isosteric rather than an isothermal path is followed. Thirdly, no prediction could be made regarding the behaviour of water as adsorbate because of its tendency to be irregular, necessitating the study of the actual system.

For these reasons the present investigation of the previously studied^{1, 10} water-porous 96 % silica glass system has been undertaken. Both the vapour pressure and extension isotherms were determined at temperatures below 0°C.

EXPERIMENTAL

APPARATUS

The apparatus, free of grease and mercury vapour, was constructed of stainless steel and glass, and could be pumped down to 10^{-7} N m⁻² pressure. The weight of the adsorbate ($\pm 1 \times 10^{-4}$ g) was determined gravimetrically with the aid of a quartz helical spring (sensitivity: 30.68 cm/g) and the length changes of a companion sample with a Tuckerman-type optical extensometer¹¹ (2.0×10^{-5} cm/cm). An insulating evacuable jacket surrounded the stainless steel sample cell. The assembly was immersed in an alcohol bath contained in a Dewar vessel.

The temperature of the cell was controlled to $\pm 0.03^\circ\text{C}$ with the aid of a saturable reactor-type instrument which governed the heater wound around the cell. By varying the output of two auxiliary heaters the temperature gradient did not exceed $0.02^\circ\text{C}/\text{cm}$. The alcohol bath was cooled by the regulated flow of liquid nitrogen through an immersed coil and stirred by bubbling air.

The pressure of the water vapour was measured with an Atlas diaphragm gauge in the range between 10^{-2} and 10 N m⁻² and by a Texas Instrument quartz Bourdon gauge above this value. An auxiliary pumping system provided the 10^{-5} N m⁻² reference pressure. An ionization gauge was used to measure very low pressures.

The temperature of the cell was measured with the aid of six copper-constantan thermocouples and a Leeds and Northrup model K-3 potentiometer.

MATERIALS

The porous 96 per cent silica glass¹² (Corning 7930) adsorbent was in the form of a 1-mm-thick plate. Burning off the adsorbed impurities at 400°C in air required 14 days. The dry weight of the gravimetric sample was 0.9144 g and the nitrogen BET area $221 \text{ m}^2/\text{g}$.

The water was purified by vacuum distillation and repeated freezing and thawing.

PROCEDURES

After placing the samples in the cell the apparatus was baked at 200°C for 24 hours. In order to restore the original concentration of the hydroxyl groups on the glass surface, which was reduced during baking, saturation water vapour pressure was maintained in the cell for 48 h. This procedure proved to be inadequate as manifested by the large secondary hysteresis loop exhibited by the first isotherm that was obtained. The separation between the two branches was equivalent to 0.016 g water per g glass at zero relative pressure. Although on the repeated and subsequent runs irreversibility was still apparent (to be discussed later), no weight gain was detected at 10^{-6} N m⁻² pressures. In order to avoid dehydroxylation this pressure was achieved between runs by pumping only at room temperature.

RESULTS AND DISCUSSION

VAPOUR PRESSURE ISOTHERMS

Fig. 1 and 2 show plots of a against p/p_i° and p/p_s° . The results support the explanation put forward by Amberg *et al.*¹ and by Kiselev and Kulichenko.² The isotherms obtained at various low temperatures can be superimposed if the relative pressures are based on p_i° . The deviation at low temperatures is believed to be due to uncertainty in the temperature measurement and the application of improper reference pressure. It is also apparent that the lower closure point of the hysteresis loop shifts to higher p/p_s° values with decreasing temperature.

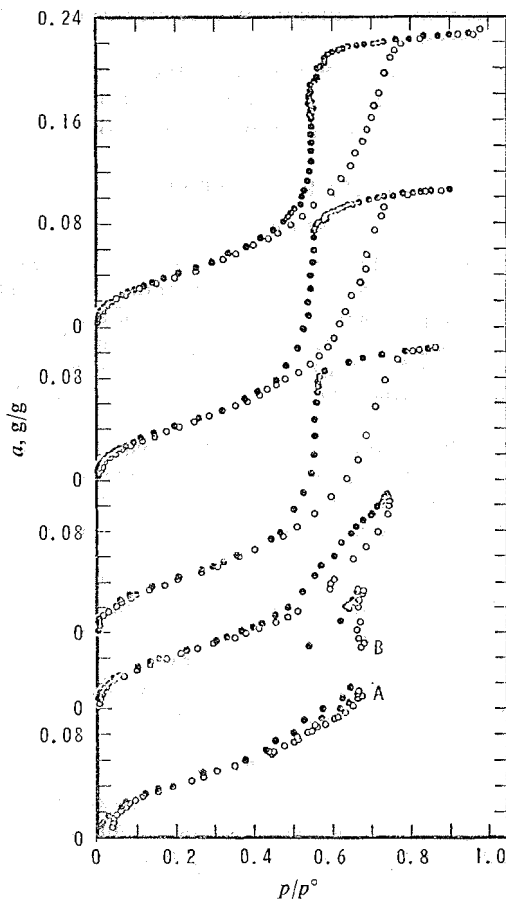


Fig. 1.—Vapour pressure isotherms, a against p/p° at temperatures of $+1.5$, -6.4 , -14.6 , -25.4 and -35.3°C (from top to bottom). Adsorption $\circ$, desorption $\bullet$.

The isotherm of -35.3°C (fig. 1) is of special interest. In this case after having obtained by isothermal adsorption the point marked A with excess water in the cell walls, the temperature was raised ($\sim 2^\circ$) which resulted, as expected, in further adsorption. Restoring the original temperature caused desorption but at the original pressure a net increase of a was found (point B). By repeating this warming/cooling process successive increments of water were transferred to the specimen. In this work the upper limit of the hysteresis loop, as established by the isotherm at $+1.5^\circ\text{C}$,

was not attained but in theory there is no reason why this should not be achieved if sufficient warming-cooling cycles are carried out. The desorption points obtained subsequently were all in stable equilibrium (at -35.3°) and were above those obtained on adsorption. Under these conditions the adsorption isotherm is a vertical line at the maximum relative pressure that can be realized experimentally.

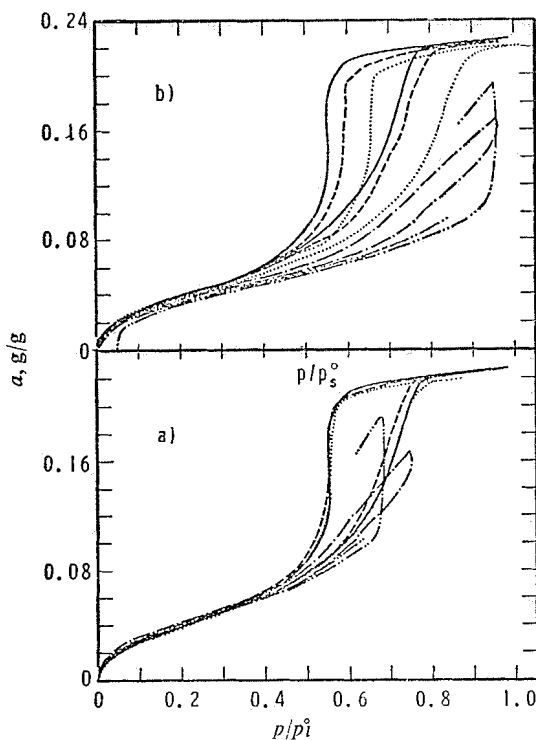


FIG. 2.—Vapour pressure isotherms superimposed (a) a against p/p_i^0 (b) a against p/p_s^0 . —, $+1.5^\circ$; ---, -6.4° ; ···, -14.6° ; - · -, -25.4° and - - - - -, -35.3°C .

The behaviour leading to the vertical portion of the -35.3°C isotherm is similar to that described in ref. (8) and can be explained in the following way. With increasing temperature, p_s^0/p_i^0 increases, eventually becoming unity at 0°C . Warming of the cell that contains bulk ice causes an increase of a . On cooling, a decreases but if the system is in the hysteresis region, on desorption it will follow a scanning curve that lies above the adsorption boundary curve. Thus a warming cycle results in an increase of a , and a cooling cycle in a decrease.

Similar reasoning can be used to explain the observation that, below the triple point, a is found to be greater if the state has been realized by isosteric cooling rather than by isothermal adsorption. If the adsorbent is saturated above the triple point and subsequently cooled below this temperature, the system follows essentially the upper boundary desorption curve of the isotherm.* Isothermally the system can get onto this path only at a pressure greater than that of the upper closure point of the hysteresis loop. Because such pressures cannot be generated even at temperatures only a few degrees below the triple point these states cannot be realized isothermally. The implications of this fact on the mechanism of frost action will be discussed in a subsequent paper.

* the isotherms change very little with temperature (see fig. 2a)

ISOSTERES AND ISOSTERIC HEATS OF ADSORPTION

Isosteres for selected concentrations were constructed from the isotherms and are shown in fig. 3. No break point, which is an indication for a phase change of the adsorbate, can be detected in the isosteres. The slope of the regression line has a 95 % confidence interval of 0.8 K J mol^{-1} or 4 %; the isostere for 0.025 g/g concentration was disregarded because of the errors due to the low absolute pressures.

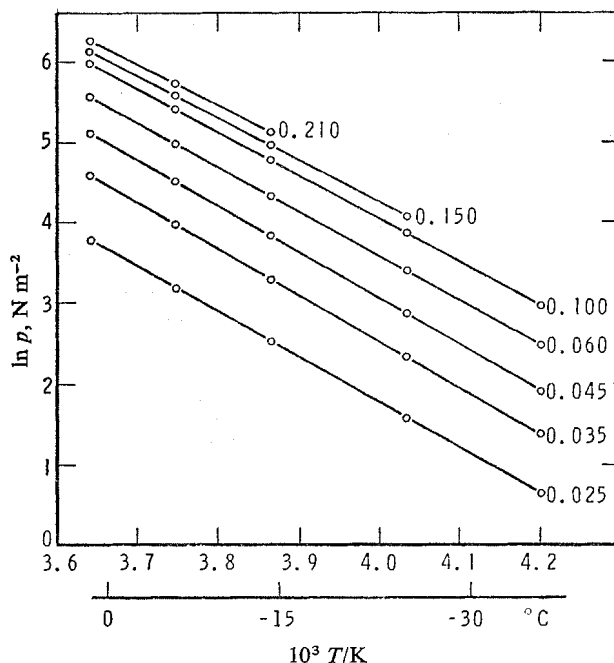


FIG. 3.—Isosteres constructed from the isotherms. Coverages, in g/g, are indicated at the right-hand side of the curves.

The isosteric heats of adsorption, against a plots are of the usual shape: large initial q value at high concentrations rapidly decreases to approximately the heat of condensation. The over-all proximity of the heats above monolayer coverage to that of the heat of condensation is indicative of a liquid-like state.

DIMENSIONAL CHANGES

The extension isotherms shown in fig. 4 are similar to those of Amberg and McIntosh¹⁰ but there are certain points of difference. Instead of expansion in a linear fashion small but definite contraction was found at point A. With increasing concentration the specimen expanded up to point B but only half as much as did the previously studied system. The section between points B and C is not horizontal but sigmoid-shaped.¹⁰ A similar observation was made with the porous-glass—benzene¹³ and the charcoal—water systems.¹⁴ In the present study a very large expansion took place beyond point C so that the total expansion at D is comparable to that previously reported.¹⁰ Since, on desorption, a contraction below the initial length occurs, the similarity between the present extension isotherm and that for the benzene-glass system extends even further.

In fig. 5 the extension isotherms are superimposed. The good fit is further evidence that the decreased adsorption capacity is an artefact of applying the improper reference pressure. If the adsorbate were in a solid-like state and the decrease of the adsorption capacity were real, the dimensional isotherms would not remain unaltered. The spread at higher coverages is caused by the fact that the desorption branches follow a "scanning path" not the boundary curve due to the decreased ultimate uptake.

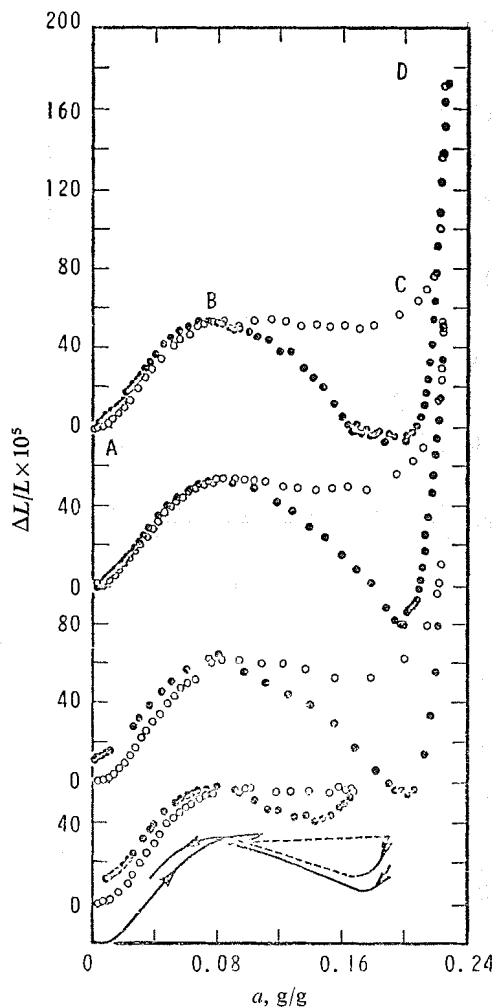


FIG. 4.—Extension isotherms at temperatures of $+1.5$, -6.4 , -14.6 , -25.4 and -35.3°C (from top to bottom). Adsorption $\circ$, desorption $\bullet$. For the sake of clarity of presentation the measured points of the isotherm at -35.3°C are not shown. Arrows indicate direction of adsorption path, broken lines presumed path measured between points.

INITIAL CONTRACTION OF THE ADSORBENT

It has been observed that a number of activated charcoals contract on the adsorption of various substances in low concentrations.¹⁴⁻¹⁶ Subsequently, a similar effect was found with the porous 96 per cent silica glass adsorbent.¹⁷⁻²¹ Haines and

McIntosh¹⁴ suggested that the initial contraction in charcoals is associated with the adsorption of molecules in narrow crevices where the field of attractive forces equals the crevice diameter. Lakhanpal and Flood¹⁵ listed the following possible causes for the phenomenon: (i) polar character of the adsorbate molecule, (ii) hydrogen bonding, (iii) cooperative van der Waals forces between neighbouring adsorbate molecules, and (iv) bridging of the neighbouring sites by single adsorbate molecules. They concluded that, in the case of carbon, (iv) is the most probable cause.

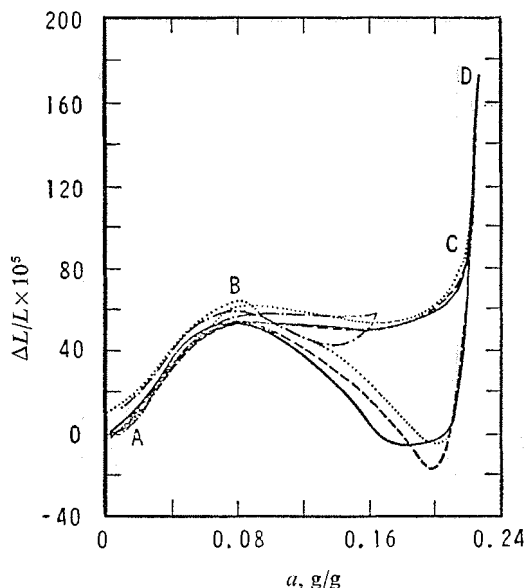


FIG. 5.—Extension isotherms superimposed. Legends of symbols same as in fig. 2.

The study of the contraction effect in porous glass by Folman and Yates¹⁹ showed that: (i) the adsorption only of polar molecules gives rise to the phenomenon, (ii) if the hydroxyl groups are blocked, e.g., by methylation, no irregular behaviour is observed, (iii) a shift in the infra-red vibrational frequency of the surface hydroxyl groups occurs concomitant with the contraction and (iv) the effect vanishes at moderately elevated temperatures. On this basis, they concluded that the contraction effect was caused by hydrogen bonding between the hydroxyl groups and the adsorbate molecules. Surprisingly, however, the adsorption of water failed to give rise to the phenomenon²⁰ although it readily forms hydrogen bonds. This irregular behaviour and certain spectroscopic results suggested that the adsorption site of water is other than the "free" hydroxyl group. The minimum exhibited by the water extension isotherms of this study (fig. 6) is, therefore, of interest.

The characteristic features may be described as follows: (i) more pronounced contraction is exhibited on adsorption than on desorption, (ii) because of strong temperature dependence, above +15°C only a change in slope of the extension isotherm occurs, (iii) marked contraction was found with the baked, partly dehydroxylated specimen, and (iv) the minimum in the curve is not preceded by a maximum as is the case with sulphur dioxide, methyl chloride and acetone.¹⁹

The failure to detect the effect previously may be ascribed to the higher experimental temperature and initial pressure in the past studies. Differences in the glass properties cannot be excluded either. Apparently even minor differences affect

length changes. For example, despite the fact that the phenomenon is well established with this adsorbent, no contraction was found with 18 different charcoals²² nor with Saran charcoal.²³

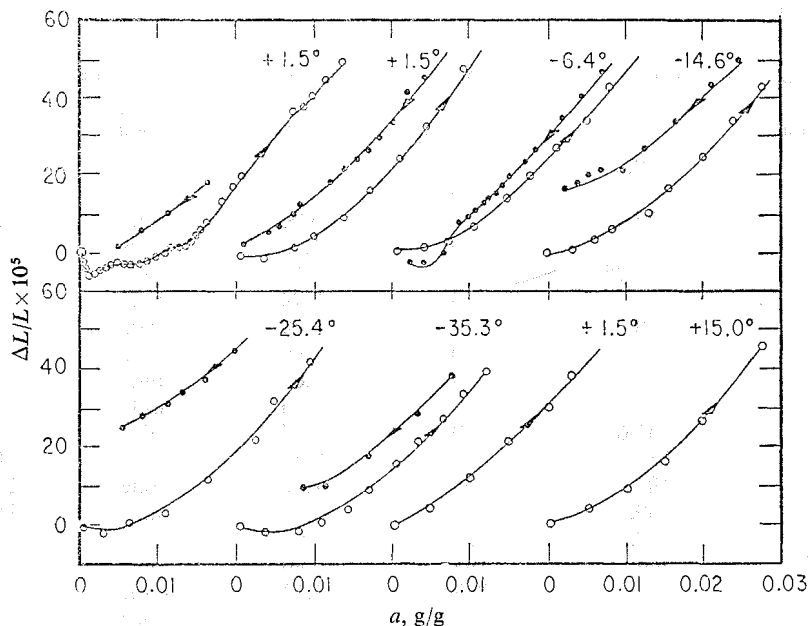


FIG. 6.—Initial section of the extension isotherms at temperatures indicated. For the sake of clarity of presentation curves have been shifted along the concentration axis.

Accepting the contraction observed in this study as real, the theories now obtaining on the nature of the adsorption sites and on the causes of initial contraction must be re-examined.

Although the question of the site of water adsorption cannot be completely clarified without an infra-red study it may be stated that the following two findings are inconsistent with the assumption that the sites are the bound hydroxyl groups: (i) initial contraction, accepted as an indication for hydrogen bonding between the adsorbed molecules and the free hydroxyl groups, was found in the present study and (ii) the most pronounced contraction occurred with the partly dehydroxylated sample in which, one may surmise, the concentration of "bound" hydroxyls is reduced more than that of the "free" hydroxyl groups. Regarding the cause of the contraction, the three suggestions advanced previously: adsorption of polar molecules, adsorption in crevices, and bridging of sites, seem to be feasible. Each mechanism in itself or combined with another can cause the effect.

Folman and Yates demonstrated that good correlation exists between the shift in the vibrational frequency of the surface hydroxyl groups and the net contraction of porous glass.²⁴ Their results, compiled in table I, suggest, however, that the contraction probably occurs on adsorption of any substance if the experimental temperature, T_{exp} , is not much higher than the bulk boiling point of the sorbate T_{bp} . The effect seems to be modified only by the nature of the molecules. This hypothesis is supported by the following: (i) inflexion of the extension isotherms also occurs with inert molecules (H_2 , Ar, Kr), and (ii) the minimum changes to the point of inflexion at moderately elevated temperatures before vanishing at higher temperatures. It

appears that the minimum vanishes at $T_{\text{exp}}/T_{\text{bp}} \simeq 1.0$ in the case of non-polar molecules, and at a value of approximately 1.2 for polar molecules. The exceptionally high value for ammonia (1.76) is probably due to the strong interaction between this molecule and the surface hydroxyl groups.

TABLE 1.—CONTRACTION EFFECT OF POROUS SILICA GLASS AT LOW COVERAGES

adsorbate	boiling point K, $T_{\text{b.p.}}$	experimental temp., K, T_{expt}	$T_{\text{expt}}/T_{\text{b.p.}}$	length anomaly	ref.
H ₂	20.6	79	3.83	inflexion	17
		90		infl.	
Ar	87.4	79	0.90	infl.	17
		90	1.03	none	
Kr	120.85	79	0.65	infl.	17
		90	0.74	infl.	
O ₂	90	79	0.88	infl.	17
		90	1.00	infl.	
N ₂	77.3	79	1.02	infl.	17
		90	1.16	infl.	
CO	81.6	79	0.97	min.	18
CH ₄	111.6	90	0.81	infl.	24
C ₂ H ₆	184.5	195	1.06	none	24
C ₂ H ₄	169.1	195	1.15	min.	24
C ₂ H ₂	189.5	195	1.02	min.	24
CCl ₂ F ₂	244	195	0.80	min.	21
		273	1.12	min.	
		298	1.22	none	
CH ₃ Cl	249.4	195	0.78	min.	21
		273	1.10	min.	
		297	1.19	min.	
		323	1.30	infl.	
SO ₂	263	195	0.74	min.	21
		273	1.04	min.	
		297	1.13	min.	
		323	1.23	infl.	
		348	1.32	infl.	
NH ₃	239.8	373	1.42	none	
		273	1.14	min.	21
		373	1.56	min.	
		423	1.76	min.	
(CH ₃) ₂ CO	329.3	473	1.97	infl.	
		298	0.90	min.	19
		348	1.06	min.	
CH ₃ OH	337.1	293	0.87	min.	20
H ₂ O	373	293	0.79	none	20

HYSTERESIS IN THE LOW PRESSURE REGION OF THE VAPOUR PRESSURE AND EXTENSION ISOTHERMS

Every extension isotherm of fig. 4 shows irreversibility at low water concentrations. In the vicinity of the inception point of the primary hysteresis loop the desorption branch of the extension isotherm crosses over the adsorption branch and lies above it at lower concentrations. The separation between the two branches seems to increase with decreasing temperature. Secondary hysteresis effect is also exhibited by the vapour pressure (v.p.) isotherms (fig. 1).

Similar observations were made by Quinn and McIntosh with the butane—porous-glass system^{25, 26} although on re-examination Kershaw and Panckhurst found that the v.p. isotherm was reversible.²⁷ Hysteresis in the low pressure region with the ammonia—porous-silica-glass system detected by Quinn and McIntosh²⁵ was not only confirmed in the case of the v.p. isotherm²⁸ but a similar effect was also found with the extension¹⁹ and even with the dielectric data.²⁸ Secondary hysteresis was exhibited in the vapour pressure isotherm by the following adsorbates on porous glass: ethyl chloride,²⁵ oxygen,^{29, 30} methanol,³¹ ethanol,³¹ n-propanol,³¹ n-butanol³¹ but not with argon,²⁹ carbon dioxide,^{2, 29} water,¹⁰ or benzene.³² Secondary hysteresis in the dimensional plot was found with systems of porous-glass—sulphur dioxide,²¹ methyl chloride,²¹ and xenon.⁴ Kington and Smith³³ reported a difference of 42 J mol^{-1} between the heats of adsorption determined calorimetrically and those calculated by the Clapeyron equation, which is characteristic of irreversible changes. It should be noted that in several studies the desorption branch was not determined in the low pressure regions and perhaps for this reason irreversibilities remained undetected.

Various factors can give rise to the secondary hysteresis phenomenon. Like primary hysteresis, this phenomenon can be attributed to capillary condensation, but it is unlikely that the "Kelvin effect" could be operational in such small pores.

Folman and Yates¹⁹ suggested that on the surface of the glass two types of sites exist, hydroxyl and Si or O, each possessing different adsorption energies and rates. Hysteresis, according to this explanation, is due to the redistribution of the molecules from sites with a fast rate and low energy to those with a high energy and low rate. This theory, however, cannot be accepted without reservation in view of the diverse chemical nature of the molecules associated with the effect. Irreversibility in the low pressure region is common with adsorbents such as carbon black, rubber and cellulose³⁴⁻³⁶ and is considered a result of interlamellar swelling. The corollary of this, that secondary hysteresis is evidence for a layered structure³⁷ cannot be accepted, however, as the case of porous glass demonstrates. It seems possible that the initial contraction of the adsorbent and irreversibility have common cause, perhaps microporosity. If such pores existed in significant number temperature dependence (being a thermally activated process³⁸) would be expected on the adsorption of a wide variety of molecules, particularly those of polar nature.

CONCLUSIONS

Isothermally adsorbed substances remain in a liquid-like state well below the bulk freezing point. Water in this regard is no exception. No indication of solidification could be detected even at -35°C . The decrease of the adsorptive capacity is a consequence of the diminutions of the maximum experimentally realizable vapour pressure below the bulk triple point.

The minimum detected in the low temperature extension isotherms of the porous-glass—water system suggests that the adsorption mechanism in this case is not dissimilar from other systems as it has been assumed.

Secondary hysteresis of both the vapour pressure and extension isotherms is real, and is also an inherent characteristic of this adsorbent. It appears that the contraction and the secondary hysteresis effects are caused by microporosity.

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