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PHASE TRANSITIONS OF ADSORBATES

III. Heat Effects and Dimensional Changes in Nonequilibrium Temperature Cycles

by
G. G. Litvan

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Transition dans les Phases des Produits Absorbés

III. Effets de la Chaleur et Changements Dimensionnels au Cours de Cycles de Temperature Non-Equilibres

Les changements dimensionnels et la quantité de chaleur du système eau-verre poreux (96% de silice) ont été déterminés au cours de cycles de température variant entre $+5$ et -40°C au taux de $0.33^{\circ}\text{C}/\text{min}$. Les résultats s'expliquent par le fait que la pression relative maximale réalisable expérimentalement, basée sur celle de l'eau surfondue, devient plus faible que l'unité sous 0°C et diminue avec un abaissement de température. Comme résultat, la teneur en produits adsorbés diminue par une migration de l'eau à la surface où elle gèle entre 0 et -8°C . A de plus faibles températures (-20°C) l'eau s'écoule hors des plus petits passages capillaires, s'accumule dans les vides plus importants et se solidifie. On donne un compte rendu des anomalies des isostères d'extension, y compris l'hystérèse. Contrairement aux études précédentes, les résultats obtenus avec le verre poreux et les produits organiques adsorbés sont semblables à ceux obtenus avec le verre poreux et les produits inorganiques adsorbés.

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Phase Transitions of Adsorbates

III. Heat Effects and Dimensional Changes in Nonequilibrium Temperature Cycles

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Changes in the dimensions and heat content of the porous, 96% silica glass-water system were determined as temperature was cycled between $+5^{\circ}$ and -40°C at a rate of $0.33^{\circ}\text{C}/\text{min}$. The results are explained by the fact that the maximum experimentally realizable relative pressure, based on that of undercooled water, becomes less than unity below 0°C and diminishes with declining temperature. As a result, the adsorbate content decreases by migration of water to the outer surface, where it freezes between 0° and -8°C . At lower temperatures (-20°C) water drains from the smaller capillaries into larger voids and solidifies. An account is given of the anomalies of the extension isosteres, including hysteresis. In contrast with previous studies, the results obtained with porous glass and organic adsorbates are similar to those of the glass-water system and can be explained by the same theory.

The porous, 96 % silica glass-water system has in several temperature regions below 0°C anomalous coefficient of thermal expansion values assumed to be due to phase changes of the adsorbate (1-3). Evidence to this effect has been obtained for only one anomaly, that occurring on warming around -10°C and proved by calorimetric means to be caused by melting (4, 5).

Other points of past studies may be summarized as follows: No anomaly is observable with an amount of water less than the equivalent of two layers (3, 5), but at higher concentrations abnormal behavior is exhibited, on cooling, at approximately -7° and -22°C and, on warming, at approximately -11°C . Melting is of the anomalous first-order type and the latent heat of fusion approximately two-thirds the bulk value (5). The freezing point at -22°C and the melting point at -11°C appear to be, above the critical value, independent of concentration. Study of the behavior of other adsorbates (2, 3) showed differences with respect to that of water; on cooling only one length anomaly

was observed and it depended on concentration.

Only limited success has been achieved in relating peculiarities (expansions, change in slope, hysteresis) to physical processes. The present investigations were undertaken because the results of the low-temperature, isothermal adsorption studies of the porous glass-water system (6) suggested that non-equilibrium experiments might be of value toward this end.

EXPERIMENTAL

Apparatus. The extension isosteres and differential thermograms were determined simultaneously. A specimen approximately 3.0 cm long was held between the clamp of the invar framework and that of the movable iron core of a differential linear transformer. The transformer was as temperature-controlled ($\pm 0.05^{\circ}\text{C}$) and supplied with constant voltage ($\pm 0.002\%$). Biasing the output made it possible to measure the changes in the 50-mV range of a recording potentiometer with a precision of $\Delta L/L = 1 \times 10^{-5}$.

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A 28-gauge copper-constantan thermopile and a 0.1-mV full-span potentiometer served for the measurement of the temperature difference between the sample and a non-porous glass reference block. The absolute value of the temperature was determined with the aid of a thermocouple soldered onto a copper band fitted around the specimen.

The assembly was hermetically sealed in a brass cell and placed in a 50 cm deep Dewar vessel above liquid nitrogen. Constant rate of temperature change was achieved by programmed compensation of the cooling effect. The adsorption and extension isotherms were determined concurrently on companion samples in a conventional gravimetric adsorption apparatus incorporating a Tuckerman optical extensometer.

Materials. Porous 96 per cent silica glass (Corning 7930) was in the form of plate 2 and 5 mm thick; BET nitrogen surface areas were 191.2 and 100.0 m²/gm, respectively. The large difference in surface area is surprising and contrary to the present view, according to which little variation in structure exists in specimens of this type of glass. It has been found (7) that the surface area of porous glass plates is a function of thickness, presumably a result of incomplete leaching during the manufacturing process. Adsorbates were of spectroscopic purity grade chemicals.

Procedures. The specimen was vacuum saturated in a glass cell and transferred to the extensometer. Care was taken to avoid desiccation during the mounting operation. In some runs (so indicated) the specimen was almost completely immersed in the liquid, but to avoid interference with the movement of the extensometer the portion of the solid held in the upper clamp was left in the vapor phase. Length-change readings have been corrected for the thermal expansion of the assembly (2.0×10^{-4} mm/°C).

RESULTS AND DISCUSSION

Length Anomaly in the Vicinity of 0°C. The extension isotherms and thermograms of the saturated samples (Fig. 1) show that an anomalous change in the dimensions, occurring in the region between -0.2 and

FIG. 1. Dimensional changes and thermogram of the porous glass-water system: (a) 2 mm thick glass, water saturated, cooling rate 0.25°C/min; (b) 5 mm thick glass, water saturated, 0.25°C/min; (c) 5 mm thick glass, water saturated, 0.33°C/min.

-8°C, was accompanied by a sudden release of heat. This proves the solidification of at least a portion of the adsorbed water.

Because (a) on visual inspection at -10°C the sample was covered with ice, (b) the established melting point of the ice formed at -8.6°C was 0°C (Fig. 2), and (c) on freezing the released heat warmed the system to about 0°C, it may be concluded that ice forms on the outside surface of the specimen and is in the bulk state.

When the glass was cooled while immersed in water, the surrounding water froze at 0°C although the surface water solidified only at -0.4°C, as indicated by the sudden change in the length (Fig. 3). As the glass was in contact with ice crystals, this indi-

cates that the lower freezing point cannot be attributed to undercooling.

The experimentally established facts that ice formed (a) on the outer surface, (b) below 0°C temperature, and (c) in the absence of undercooling suggest that water failed to solidify at 0°C because it was contained in pores where it could not freeze; and that as the temperature became colder than 0°C the water migrated to the surface, where

it formed ice. The causes for this mechanism can be given by examining the adsorption characteristics of porous systems below the bulk triple point of the adsorbate.

Adsorbed water remains in a liquid-like state well below 0°C, and the amount adsorbed a is consequently a function of p/p_i^0 , the relative pressure based on the vapor pressure of undercooled water (p_i^0) rather than on that of ice (p_s^0) (6). Because p_i^0 exceeds p_s^0 by an increasing margin as the temperature decreases, and because in equilibrium the prevailing pressure p cannot be greater than p_s^0 , the system is exposed, on cooling, to relative pressures of less than unity. Figure 4 shows the limiting p/p_i^0 values as a function of temperature T . From this it follows that at temperatures below 0°C $a_{\max}$, the maximum amount adsorbed, decreases and leads to the exudation of water.

The temperature at which the water on the external surface freezes depends essentially on two factors: the temperature at which a becomes equal to $a_{\max}$, i.e., the shape of the isotherm, and the rate of nucleation. If $a = a_{\max}$ at 0°C, then migration of water starts immediately below this temperature; if not undercooled, it promptly freezes (Fig. 3). On the other hand, if the specimen is saturated at $T > 0^\circ\text{C}$, then at

FIG. 2. Dimensional changes and thermogram of 5 mm thick porous glass saturated with water during a +5° to -15°C temperature cycle (0.33°C/min).

FIG. 3. Dimensional changes of a 5 mm thick porous glass sample immersed in water.

FIG. 4. (a) Maximum realizable vapor pressure of water as a function of temperature; (b) $\Delta a/\Delta T$ vs. T for 5 mm thick porous glass-water system based on the isotherm of $+0.5^\circ\text{C}$. Ordinate label should correctly read $\Delta a/\Delta T \times 100$.

FIG. 5. Dimensional changes and thermograms of (a) 2 mm and (b) 5 mm thick glass sample partly saturated with water.

FIG. 6. Adsorption isotherm of a 5 mm thick porous glass-water system at $+0.5^\circ\text{C}$.

$T = 0$, we have $a < a_{\max}$ and a becomes equal to $a_{\max}$ only when $T < 0^\circ\text{C}$. If $a \ll a_{\max}$ at 0°C , we have $a \neq a_{\max}$ in the region between 0° and -20°C and no freezing on the surface occurs (Fig. 5).

Figure 4(a) shows values of the limiting p/p_i^0 as a function of T and the isotherm (Fig. 6) links a to p/p_i^0 so that $a_{\max}$ can be related to T for this system. The derivative of a with respect to T is also given (Fig. 4(b)), and it can be seen that because of the shape of the isotherm a significant amount of water is exuded only below -5°C . This agrees well with the previously observed freezing temperature of -7°C .

In view of the dynamic nature of the factors causing expansion, it is to be expected that if the cooling rate is very slow no anomalous dimensional changes can be observed. This, in fact, was found with the cement-water system (8) at $0.0417^\circ\text{C}/\text{min}$ cooling rate.

The suggested explanation is not specific to water as adsorbate. The extension "isosteres" of porous glass containing adsorbates such as cyclohexane, chloroform, xylene, carbon tetrachloride, benzene, and octanol exhibit similar features (Fig. 7). It can be

seen that in every system there are at least two freezing ranges. The existence of the anomaly at high temperature remained undetected in most former studies, either because of insufficiently low experimental temperature (2) or because of erroneous interpretation (3).

A remarkably uniform behavior is exhibited by the values given in Table I. It appears that the first freezing occurs between

FIG. 7. Dimensional changes and thermograms of 5 mm thick porous glass with various adsorbates: (a) chloroform, mp -63.5°C ; (b) *m*-xylene, mp -47.9°C ; (c) carbon tetrachloride, mp -22.96°C ; (d) octanol, mp -16.7°C ; (e) benzene, mp $+5.5^{\circ}\text{C}$; (f) cyclohexane, mp $+6.5^{\circ}\text{C}$; and (g) benzene immersed.

0.92 and $0.98 T_{f,b}$, where $T_{f,b}$ is the bulk freezing point of the adsorbate in degrees Kelvin. The suggested mechanism is supported also by the fact that melting of the adsorbate occurs always at $T_{f,b}$.

Freezing at Low Temperatures. In the transition occurring at lower temperatures the adsorbate solidifies in the pores. The process is associated with an exothermic heat effect and expansion, both extending over a temperature range of approximately 15 degrees. Despite the gradual nature of the transition for a given type of specimen (*e.g.*, 5 mm thick porous glass) the inception temperature of the process is constant ($\pm 0.3^{\circ}\text{C}$).

The sign of the specific volume change on freezing in the bulk state has no bearing on the dimensional changes of the adsorbent-adsorbate system. Expansion occurred with all systems (Fig. 7), although water is the only substance in the group that expands on freezing in the bulk state.

In the isothermal adsorption studies (6) solidification was found neither at -35°C , $a_{\text{max}} = 0.12$ gm/gm, nor at -25°C , $a_{\text{max}} = 0.17$ gm/gm. This is surprising because even at -35°C , $p/p^0 = 0.7$ was attained and at

TABLE I
ABSOLUTE AND REDUCED TEMPERATURE OF TRANSITIONS OF VARIOUS SUBSTANCES ADSORBED IN POROUS GLASS

	Bulk freezing point ($^{\circ}\text{K}$) $T_{f,b}$	"First" freezing temp ($^{\circ}\text{K}$) $T_{f,1}$	$\frac{T_{f,1}}{T_{f,b}}$	"Second" freezing temp ($^{\circ}\text{K}$) $T_{f,2}$	$\frac{T_{f,2}}{T_{f,b}}$	"Third" freezing temp ($^{\circ}\text{K}$) $T_{f,3}$	$\frac{T_{f,3}}{T_{f,b}}$	$\frac{T_{f,3}}{T_{f,b}}$	"Third" melting temp ($^{\circ}\text{K}$) $T_{m,3}$	$\frac{T_{m,3}}{T_{f,b}}$	"Second" melting temp ($^{\circ}\text{K}$) $T_{m,2}$	$\frac{T_{m,2}}{T_{f,b}}$	"First" melting temp ($^{\circ}\text{K}$) $T_{m,1}$	$\frac{T_{m,1}}{T_{f,b}}$
Chloroform	210	195	0.93	173	0.82				191	0.91	210	1.0		1.0
<i>m</i> -Xylene	225	207	0.92	182	0.81				204	0.91	225	1.0		1.0
Carbon tetra- chloride	250	245	0.98	223	0.89	188	0.75		226	0.90	251	1.0		1.0
<i>n</i> -Octanol	256	252	0.98	225	0.88				235	0.92	257	1.0		1.0
Benzene	278	267	0.96	235	0.84				258	0.93	278	1.0		1.0
Cyclohexane	279	276	0.98	213	0.76	183	0.65		243	0.87	279	1.0		1.0
Water	273	267	0.97	251	0.91				260	0.95	273	1.0		1.0

this value of the relative pressure, according to the Kelvin equation, pores with less than 66 Å diameter are all filled with water which has an estimated freezing point as high as -13.5°C (9). On the other hand, transition took place on "isosteric" cooling with $a = 0.12$ gm/gm (5) and even with $a = 0.084$ gm/gm (3). These findings, if the hypothesis that cooling brings about desorption is correct, imply that freezing takes place only in states defined by the desorption branch of the isotherm. The theory that the meniscus effect is the sole cause of the freezing point lowering, the magnitude of which is assumed to be inversely proportional to the extent of the vapor pressure reduction, appears to be contradicted by this; for a given value of a the adsorbate has a lower vapor pressure on desorption than on adsorption, so that the latter should have a higher freezing point. The opposite, however is found.

The $\Delta a/\Delta T$ curve (Fig. 4(b)) increases its value at about -5°C and -15°C in temperature regions that coincide with the freezing ranges. The causal relation between the two phenomena at the higher temperature has been demonstrated in the preceding section. A similar mechanism may explain the findings related to freezing at low temperatures.

One may argue that because water remains in the liquid state (being unable to freeze in the pores if filled on isothermal adsorption) it drains into the partly filled larger pores when, on cooling, the maximum realizable relative pressure becomes less than its vapor pressure. The sharp rise of the $\Delta a/\Delta T$ curve indicates that below -15°C a large amount of water has to leave the porous system. This is probably seldom possible at this low temperature because of the low vapor pressure, the high viscosity, and the partly blocked pores. Equilibrium can be attained, however, if the trapped water freezes, thus reducing the vapor pressure to that of ice so that equilibrium conditions are attained. The well-established difference between the freezing and melting points of the adsorbate can then be expected because freezing occurs at the temperature at which water is transported to a pore in which it can form ice; the melting point is

determined by the characteristics of the formed ice.

This hypothesis is supported by the results of X-ray diffraction studies showing that all but two molecular layers of water moved from between the saturated bentonite crystals when cooled to liquid nitrogen temperature (10). In addition, the dynamic aspect of the phenomenon is apparent in the effect of the cooling rate on the magnitude of the expansion at about -20°C : 270×10^{-5} at $0.33^{\circ}\text{C}/\text{min}$ (Fig. 1(c)), 70×10^{-5} at $0.0208^{\circ}\text{C}/\text{min}$ (Fig. 8), and 10×10^{-5} at $2^{\circ}\text{C}/\text{day}$ (5).

In Table I the absolute temperatures of the transitions of various adsorbates occurring at low temperatures are related to $T_{f, b}$; it can be seen that the values range from 0.76 to 0.91 for freezing and from 0.87 to 0.95 for melting. Water appears to be an extreme case.

It may also be significant that for most inert molecules a third freezing range was observed at very low temperature. Only after confirmation of these results, however, can their implications as to the mechanism be considered.

Interpretation of the Extension Isotheres. On the basis of the preceding hypothesis an attempt will be made to specify the physical processes causing the anomalies in the length changes. The specimen saturated at $T > 0^{\circ}\text{C}$, point O (Fig. 1(b)), contracts on cooling owing to thermal effect. At the temperature represented by A (because $a > a_{\text{max}}$), freezing on the surface occurs and the latent heat of freezing warms the system to 0°C . Point B reveals a net contraction for this temperature cycle resulting from loss of water on cooling to A . The system contracts between B and C again because of thermal contraction and continuous loss of water. At C the water in the pores commences to solidify—a process that extends to point D .

The large expansion between C and D is associated with freezing and may be the result of either pressure exerted by the water flow or of the changed interaction between the glass and the solidified adsorbate. This expansion appears to be partly reversible; the system contracts to E on warming, where the low temperature melting

FIG. 8. Dimensional changes and thermogram of 5 mm thick porous glass saturated with water during a $+5^\circ$ to -45°C temperature cycle, $0.0208^\circ\text{C}/\text{min}$ rate.

FIG. 9. Extension isotherm of 5 mm thick porous glass-water system at $+0.5^\circ\text{C}$.

process is completed. The net increase of length at this temperature is a measure of the damage suffered between C and D . It must be recognized, however, that the dimensions of the adsorbent at constant coverage depend also on their being in an adsorption or desorption state, according to the extension isotherms (Fig. 9), and this may well be true for the nonisothermal conditions as was discussed previously (3).

Expansion between E and F is due to adsorption brought about by the increasing relative pressure and the loss of mechanical

strength of the glass. This manifests itself when the ice in the crevices melts.

In a recent publication Feldman¹ concluded that in the porous glass-water system solid menisci exist and freezing of water in the pores involves volumetric expansion in the bulk state. Because our efforts to reproduce these results have remained so far unsuccessful the conclusions of the work were not utilized in the interpretation of the present results.

¹ R. F. Feldman, *Can. J. Chem.* **48**, 287 (1970).

CONCLUSIONS

The inevitable decrease of the maximum realizable relative pressure on cooling adsorption systems below the triple point of the adsorbate leads to desorption. As a result, the adsorbate migrates from the large voids to the outer surface, giving rise to high-temperature freezing, and from the small pores to the larger ones, causing lower temperature freezing. On the basis of the suggested mechanism the features of the extension isosteres can be interpreted in physical terms. The mechanism is valid for all investigated liquids adsorbed on porous glass, and it is expected that it will be applicable to any other system comprising a porous solid and an adsorbed liquid. The mechanism causing mechanical destruction of such systems on cooling, a phenomenon called frost action, will be discussed in a subsequent publication.

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