[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE RICE INSTITUTE]

The Sorption–Desorption Hysteresis Characteristics of the System SiO_2–H_2O Below the Bulk Freezing Point of Water[1]

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The properties of sorbed materials may be in general quite different from those associated with the same materials under bulk conditions. This fact is of especial significance when sorption is considered to result from capillary condensation, since condensate in the pores might be expected to resemble closely a three-dimensional liquid. However, experimental observations indicate that even in such a system, differences between the capillary phase and the bulk phase are pronounced. The most striking differences appear to be (a) an abnormally low vapor pressure, (b) the absence of irregularities at the critical temperature and (c) a depressed freezing point.

There are reported in the literature[4–10] a number of investigations designed to determine the effect of capillary condensation on sorbate properties. In no case were there detected discontinuities or irregularities in the isotherms at the critical temperature. More recently Brunauer and Emmett in unpublished work (*cf.* ref. 8) found "that acetylene adsorption curves on iron catalyst for the synthesis of ammonia are the same over the range −78° to −100° when plotted on a relative pressure basis (using the extrapolated vapor pressure curve of liquid acetylene for p_0), even though the melting point of acetylene is −81.5°." Other investigators deduced from dilatometric measurements[11,12] and heats of fusion[13] that sorbed liquids behave abnormally below their bulk freezing point.

A different point of view was developed by Kubelka.[14] By combining the expression developed by Rie[15] and others for the lowering of melting points of finely divided crystalline solids with well known properties of gels, Kubelka derived an expression

$$(T_m - T)/T_m = (2V\sigma/rq)\cos\phi$$

where T_m is the normal melting point of the sorbate, T the melting point of the sorbed material, V the molal volume of the liquid, r the capillary radius, q the heat of fusion, σ the solid–liquid interfacial energy, and ϕ the angle of contact of the liquid with the gel material.

Experimental

In view of the evidence that materials in the sorbed condition may not undergo phase transitions at or near the bulk freezing point, it was believed that further observations to compare certain properties of the sorbate with those of the solid and liquid forms would be useful. For this study there was selected a series of silica gels whose sorption characteristics above the normal melting point of the sorbate had already been investigated in some detail.[16] In the present work, the water sorption–desorption isotherms for these gels were studied at −5° for comparison with results of the similar measurements carried out previously at 12°.

Preparation of Samples.—A detailed description of the samples has been given in a previous paper.[16] The sorbent consisted of an air-dry silica gel heated in air for two hours at the following temperatures, respectively: 450, 500, 650, 725 and 880°. Following the heat treatment the samples were placed in an air stream saturated with water vapor at room temperature (30°), and finally sorption–desorption isotherms were obtained at 12°.[16] These identical gels were then examined at −5° as described below.

Apparatus.—The isotherms for the five samples were measured at −5° in a multiple apparatus described in a previous report from this Laboratory.[17] The temperature was held constant to better than ±0.005°. During the initial degassing period of twenty-four hours, the samples came to equilibrium at a pressure not exceeding 10^{-6} mm. At the end of the evacuation period the vacuum system was closed off and air-free water vapor (from the thermal decomposition of degassed $BaCl_2 \cdot 2H_2O$) was pumped intermittently into the manifold containing the gels; sufficient time was allowed after each pressure increase to ensure that the system attained equilibrium. The weight of water sorbed on 100-mg. samples of dry gel was determined with a precision of 0.01 mg. by the change in deflection of McBain–Bakr silica spring balances. The prevailing pressure was read by means of an oil manometer to within 0.01 cm. of oil, corresponding to 0.004 p/p_0 unit. The isotherms (x/m *versus* p/p_0) taking p_0 equal to the saturated vapor pressure of supercooled water, are shown in Figs. 1–5. In the same figures are plotted the corresponding uncorrected frequency distribution curves, $(\partial V/\partial r)_T$, *versus* r (V is the volume of sorbate, referred to liquid conditions, and r is the capillary radius).

Discussion

A comparison of the isotherms at −5° with those at 12° reveals that the curves are almost identical if the saturated vapor pressure of supercooled water rather than that of ice is used in plotting. Of necessity p can never reach p_0 because of the intervening condensation pressure of ice, hence there is a variation in behavior at values above p/p_0 equal to 0.9.

In order to examine more closely the possible

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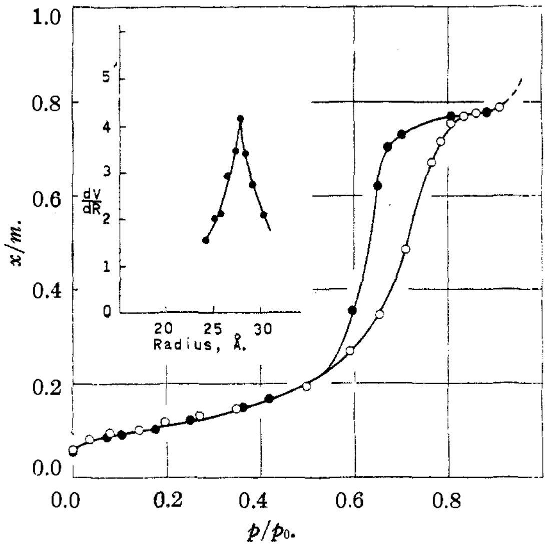

Fig. 1.—Sorption–desorption isotherm at −5° for silica gel heat-treated at 450°.

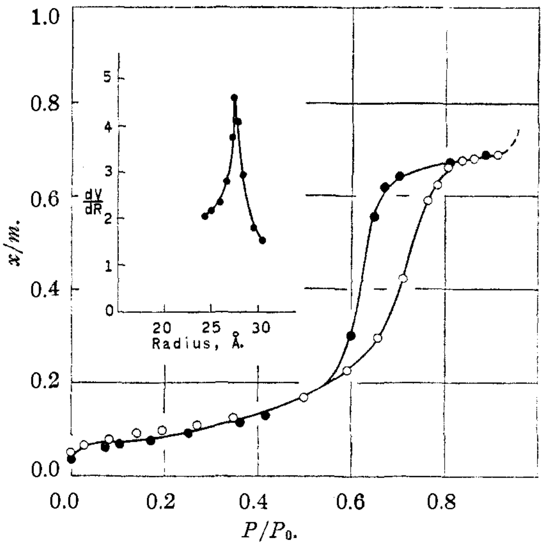

Fig. 3.—Sorption–desorption isotherm at −5° for silica gel heat-treated at 650°.

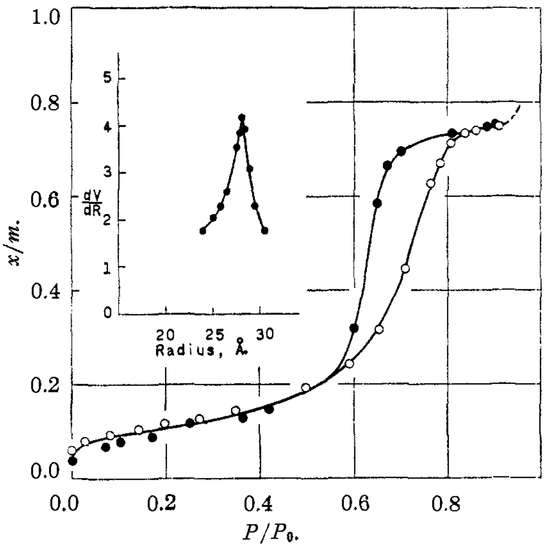

Fig. 2.—Sorption–desorption isotherm at −5° for silica gel heat-treated at 500°.

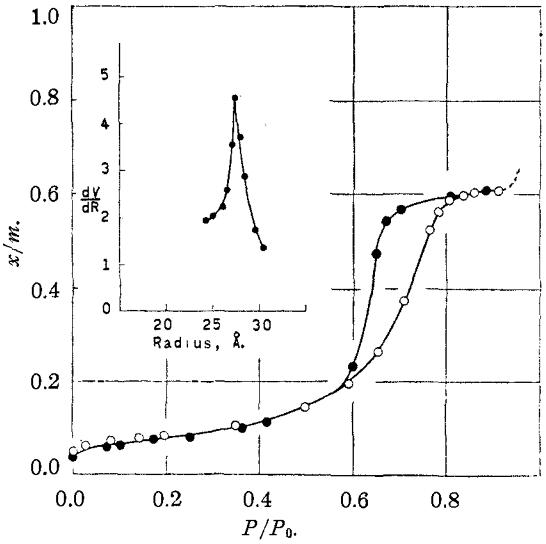

Fig. 4.—Sorption–desorption isotherm at −5° for silica gel heat-treated at 725°.

differences between the isotherms at −5° and 12°, the data were plotted as *V versus r* using the Kelvin equation (15)

$$\ln p - \ln p_0 = -2\gamma V/rRT$$

where γ is the surface tension of supercooled water, V the molal liquid volume, R the gas constant and T the absolute temperature. From this logarithmic relation the frequency distribution curves were derived. The respective peaks in these curves seem to approach very closely those obtained from the 12° isotherms,[16] appearing at virtually the same value of r (*ca.* 28.5 Å) and having strikingly similar shapes.

It is believed that the data obtained in the present set of isotherms constitutes independent verification of the fact that at least in some cases the melting point of sorbed materials may be considerably lower than the bulk value. In addition it is interesting that a close correlation between the frequency distribution curve from isotherms at 12° and −5° results from the use of a saturation pressure corresponding to the experimentally determined vapor pressure of supercooled water at the temperature, while the correlation is poor using p_0 as the vapor pressure of ice.

The facts illustrated by the data suggest a method for estimating the minimum value possible for the sorbate freezing point in the system studied. From the form of the Kubelka equation we may infer that for sufficiently small values of r, or large values of σ there will exist no temperature at

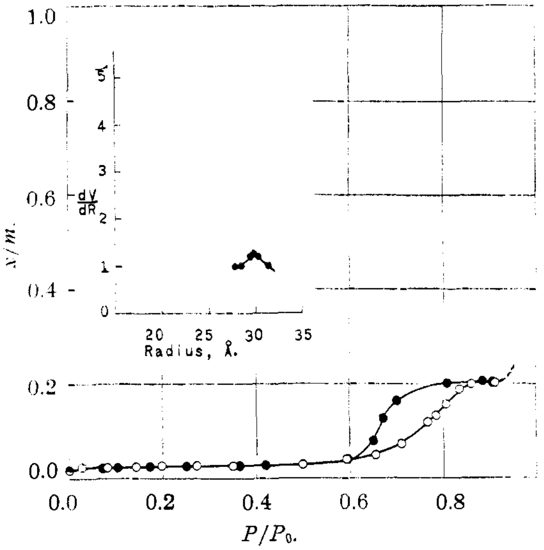

Fig. 5.—Sorption–desorption isotherm at $-5°$ for silica gel heat-treated at 880°.

which the sorbate within the pores will be solid. Inasmuch as there is at hand no reliable means of measuring the interfacial energy between liquid water and ice, it is impossible at present to predict at what apparent pore radius such a condition will obtain. However, since in the present discussion we are estimating the minimum possible "freezing point," a hypothesis will be considered from which the Kubelka equation indicates either a very low, or even non-existent value for T. For the system at hand the validity of such an assumption does not seem unreasonable from a consideration of the relative orders of magnitude of the factors in the equation, taking r as 28.5×10^{-8} cm. These considerations suggest the possibility of freezing the capillary-condensed liquid at a temperature higher than T, the freezing point temperature from the Kubelka equation. This would take place as will be described below by means of a somewhat different mechanism from that associated with the assumptions governing the Kubelka equation. Inasmuch as the vapor pressure of supercooled water is greater than that of ice, the isotherm below 0° is found always to break down with attendant ice formation at some value of p/p_0 (p_0 being based on the value for supercooled water) less than one. As the temperature is decreased, since the divergence between the water and ice vapor pressures increases with decreasing temperature, the p/p_0 value at which the solid bulk sorbate forms in the apparatus also decreases. At some temperature an ice point value of p/p_0 will be reached that corresponds to the vapor pressure of water condensed in the pores of radius r, the radius at which the peak in the frequency distribution curve occurs. Under these circumstances, the vapor pressure of water in the pores will be exactly equal to the vapor pressure of bulk solid ice at the same temperature. Any subsequent lowering of the temperature (solid ice remaining present in equilibrium) would be expected to dehydrate the pores as the vapor condenses in the bulk solid form, which at that temperature is of lower vapor pressure. During melting, the process must be reversed; from the hysteresis in the isotherms it appears evident that a higher p/p_0 (and thus a higher temperature) will be required to recondense water into the pores. This would account for the hysteresis observed by Jones and Gortner.[6]

A comparison of the extrapolated liquid vapor pressure of water with that of ice shows that to obtain ice at p/p_0 of 0.7 (the value corresponding to the pressure exerted by the water condensed in the majority of the pores) the temperature must be $-37°$. This would seem to correspond to a "freezing point." For melting, the p/p_0 value must then be raised to 0.8 (corresponding to the relative pressure at which most of the pores become saturated) with a "required melting point" temperature of $-21°$.

It should be emphasized that the temperatures calculated by this method represent a lower limit for the sorbate freezing or melting point, since the analysis is developed on the assumption that liquid sorbed by capillary condensation in the pores will not freeze.

Summary

Experimental work reported in the literature has shown that substances in the sorbed condition held by so-called capillary condensation forces, may not exhibit anomalous behavior as the temperature is allowed to vary through values at which phase transitions in the bulk condition normally occur. To study further this behavior, a set of sorption-desorption isotherms for water vapor on several silica gels was measured at $-5°$. The sorption characteristics of the same samples had previously been determined at 12° so that a comparison showing the effect of subfreezing temperatures on the isotherm could be made. It was found that when the sorption was plotted against the relative saturation, the isotherms at the two temperatures coincided only if the saturation pressure was taken to be the experimentally determined value for supercooled water at that temperature. On this basis there is suggested a procedure for the estimation of the minimum possible "freezing" and "melting" points, which would yield an explanation of observed freezing–melting hysteresis phenomena consistent with the hysteresis observed in the sorption–desorption isotherms.

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