heating eliminates it. The dispersoid in this case is even too fine to show appreciably in the Tyndall beam which we use, but we have been able to determine its rate of coagulation with Mr. Green's condensation apparatus."

Likewise, the electrification produced upon the disruption of materials and surfaces is well known.[7]

Summary

1. When various gases are passed over a metal that is cooling during sorption and desorption, the gas stream on the outward side becomes electrified. It causes a luminescence on the walls of a silica tube.

2. The effect is ascribed to very fine electrified ultramicroscopic particles released from the metal.

STANFORD UNIVERSITY, CALIF. RECEIVED APRIL 29, 1943

[7] Obreimoff, *Proc. Roy. Soc.* (London), **127A**, 294 (1930); J. Strachan, *Nature*, **139**, 803 (1937); E. Newton Harvey, *Science*, **89**, 460–461 (1939); S. C. Blacktin, *Nature*, **140**, 280 (1937).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

Sorption and Surface Area in Silica Aerogel

BY S. S. KISTLER,[1] E. A. FISCHER[1] AND I. R. FREEMAN[2]

Introduction

The discovery of a process[3] by which water can be removed from a hydrogel without the collapse of its structure has made it possible to learn facts about that structure that were formerly obscure. The present work was undertaken in 1935 as a part of a comprehensive program on the properties of gels but was interrupted after preliminary data had been taken by the departure of all three authors from the University. It had been hoped that a more complete study could be made before publication, but since no opportunity is before us, the information is here offered in its fragmentary state, since definite conclusions on some moot questions have already been attained.

Attention will be confined to silica aerogel and silica gel.

Several facts are known that should have a bearing on our conclusions. As silica gel sets, its mechanical properties strongly indicate a fibrillar nature to the elements of structure. Diffusion and electrical conductivity in the hydrogels indicate extremely free passage of particles the size of molecules through the solid framework, as does the fact that the liquid in a lump of gel at the critical temperature of the liquid can be released very rapidly without the outward rush of gas disrupting it.

Ultramicroscopic observations[4] that silica aerogel is optically empty would seem to eliminate a predominance of platelike elements of structure due to the fact that platelets with the solid volume and surface area of silica aerogel would certainly be large enough to produce visible reflections.

Some hollow structures, *e. g.*, tubules, are not excluded but probably must compose a minor fraction of the gel. Heat conductivity data[5] show that gas molecules can move freely within the structure of silica aerogel, and in flying from surface to surface travel on the average approximately 7×10^{-6} cm. between impacts. If the major portion of the structure were tubules with diameters of this magnitude they would almost certainly be visible in the ultramicroscope. In addition, they would have a combined area too small to account for the area as calculated from the heat conductivity data or as calculated from adsorption.[6]

The probable structure of silica aerogel is, therefore, a mat or felt of filaments, needles, etc., forming a three dimensional network. It can be much more accurately visualized as like a felt of glass wool in which many fibers are attached to each other at their points of contact, rather than as a system of capillaries. This picture would lead to the conclusion that the total surface area will not be much affected by compression of the aerogel to a smaller volume. References (3) and (4) show that the area of silica aerogel is of the same magnitude as that of some samples of silica xerogel (the gel prepared by drying in the usual manner).

[1] Present address, the Norton Company, Worcester, Massachusetts.

[2] Present address, U. S. Reduction Company, East Chicago, Indiana.

[3] Kistler, *J. Phys. Chem.*, **36**, 52 (1932).

[4] E. R. Riegel, private communication.

[5] Kistler, *J. Phys. Chem.*, **46**, 19 (1942); **39**, 79 (1935); *Ind. Eng. Chem.*, **26**, 658 (1934).

[6] Harvey, Dissertation, Princeton University, 1941.

Apparatus and Methods

The apparatus consisted of McBain–Bakr balances sealed into glass tubes with side arms. These tubes were held at constant temperature to ±0.01° in a large air thermostat. The side arms dipped into a water thermostat within the air cabinet. In the experiments where water alone was used, conductivity water was placed in the side arm and boiled under reduced pressure while heating the arm with the gel in it to 300 ± 15°. After at least half of the water was boiled away, it was frozen in solid carbon dioxide while the heating of the gel continued and the pressure was reduced to less than 10^{-4} mm. The pump was then closed off by a stopcock, the water allowed to thaw and the gel to cool until a moderate amount of sorption had taken place. The water was again frozen, the gel heated and the pumping repeated. After four such cycles, the apparatus was sealed while on the pump. It is felt that residual air was reduced to a small value by this procedure.

In the one series in which sorption of water was followed by sorption of silicon tetrachloride, carbon tetrachloride and benzene in succession, a plurality of side arms was employed, each containing a bulb of carefully purified liquid and an iron armature sealed into a tube. When the apparatus and gel samples had been flushed and evacuated as above, the sorption curve was determined for water. The water was then frozen out in its side arm while heating the gel, following which the side arm was sealed off. The pump was not sealed off in this experiment, a mercury seal being used. Following removal of the water, a bulb of silicon tetrachloride was broken in the system and allowed to sorb on the gel, with alternate heating and cooling. After forty-eight hours of this treatment, the silicon tetrachloride and evolved hydrogen chloride were pumped down to less than 10^{-4} mm., the mercury seal closed and a second bulb of silicon tetrachloride broken. The sorption curve was then determined. Subsequent procedures with carbon tetrachloride and benzene were similar.

The vapor pressures during the sorption operation were measured directly on a mercury manometer.

Objectives and Results

Influence of Density upon Sorption.—One of us had already measured roughly the extent of sorption on aerogels of different density and observed that the partial pressure at which the sorption curve was the steepest was lower, the greater the density. This observation looked like confirmation of capillary condensation, and one series in the sealed tubes was planned to obtain quantitative data.

The aerogels were prepared as follows: 500 ml. of Philadelphia Quartz Company E Brand water glass, diluted to a specific gravity of 1.18, was poured into an equal volume of 4 *N* acetic acid with vigorous stirring. The sol was filtered quickly and one portion poured into several paraffined crystallizing dishes to a depth of about 2 cm. and allowed to gel. The remainder was gelled over mercury in crystallizing dishes to a depth of 1 cm. These latter cakes with accurately parallel surfaces subsequently were used for heat conductivity measurements, the results of which are reported in ref. 5, first paper, page 28.

After twenty-four hours, the cakes to be used for sorption were removed from the dishes and washed free of soluble salts, after which they were divided into three parts. The first part was placed in water; the second and third parts were weighed and set on edge on blotting paper to dry. When part II had dried to one-third of its original weight and part III to one-sixth, they were placed in water along with part I. They were then transferred to alcohol and eventually autoclaved, as formerly described.[3] The densities, as measured by the displacement of fine sand were:

I, 0.154 g./cc.; II, 0.44 g./cc.; III, 0.92 g./cc.

Before using, the three samples of gel were freed from organic matter by oxidation with nitric acid vapor and air at 200°.

Sorption measurements were made with the gels at 35.4°, varying the temperature of the water tubes. The results are plotted in Fig. 1. At this temperature the vapor pressure of water is 43.1 mm. The points do not fall on as smooth curves as one would wish, due partially to trouble with the thermostat regulators and partially to an aging effect, particularly noticeable in I. This aging effect, observed also by Harvey,[6] consists of a shrinkage of the aerogel and a reduction in its sorption capacity when allowed to stand at constant partial pressure. In spite of the lack of smoothness to the curves, the differences between the gels are so large compared to these irregularities as to permit no question of experimental error as an explanation.

It will be observed that gel I was not nearly full at 98.1% relative humidity in spite of its containing 2.13 g. of water per gram of silica. Had no shrinkage occurred, it could have picked up 6.4 g. of water per gram of silica. The shrinkage reduced this figure some but certainly not to 2.13 g. Undoubtedly if it could have been held within a few tenths of a per cent. of saturation for weeks, it would have sorbed much more water.

Gel II showed no visible signs of shrinking during the sorption process. It could have held 2.05 g. water, although it seemed to level off at 0.76 g., approximately the same fraction of its capacity being used as with gel I. On the other hand, gel

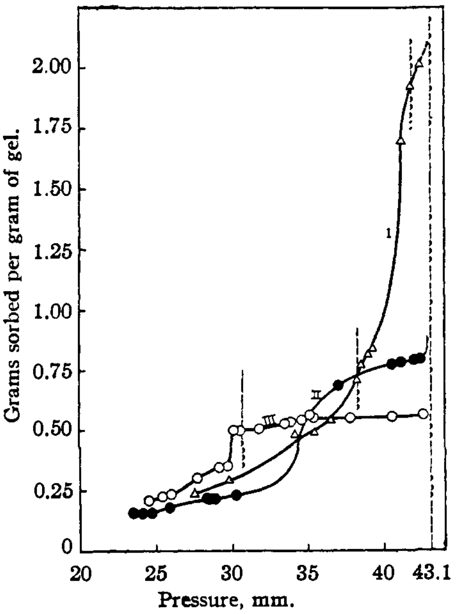

Fig. 1.—The sorption of water at 35.4° by aerogels of similar origin with densities of 0.154, 0.44 and 0.92. The curves are numbered in this order.

III had a theoretical capacity of 0.63 g. and actually sorbed 0.55 g.

Influence of Surface upon Sorption.—Much has been said in the literature[7] on the influence of the nature of the surface upon the character of the sorption curve, particularly on the role of traces of contamination. The view has been supported that gels with surfaces very free from contamination show sorption curves resembling benzene on charcoal, whereas with normal purification the curves are sigmoid. Since the most active spots on the surface of silica gel are covered with water molecules that can be removed only at high temperature, with accompanying reduction in the activity of the gel,[8] or by powerful reagents like silicon tetrachloride,[9] in which case the activity is not greatly reduced, it was thought that experiments with non-aqueous liquids on water-free gel might decide the question whether or not the so-called "classical" isotherm is typical of clean silica gel surfaces. This "classical" isotherm is the type, shown by benzene on charcoal, in which nearly all of the sorption occurs at low partial pressures. It seems to be incompatible with the concept of capillary condensation. It was thought that a surface stripped of its water by silicon tetrachloride might hold that compound with great vigor, and similarly this surface might, if flushed free of its silicon tetrachloride, hold carbon tetrachloride or benzene strongly. In other words, it might be possible to change the surface from hydrophilic to hydrophobic.

The silica aerogel (IV) and xerogel (V) used were similar to I and III above, respectively, except that the xerogel was not put through the alcohol extraction and autoclaving. These gels were also oxidized free of organic matter with nitric acid vapor.

Sorption of Water.—Figure 2 gives the results for the sorption of water by gels IV and V at 40.9°, at which temperature the saturation pressure is 57.6 mm. Four points on each of the desorption curves also were taken. The xerogel (V) shows a prominent and characteristic loop extending down to about 10% relative humidity. The aerogel (IV) also shows a loop, but with the two branches parallel. In view of its appearance and of the behavior in the subsequent experiments, we believe now that there was some systematic error in reading the cathetometer during desorption, and that actually the desorption points should fall on the ascending curve.

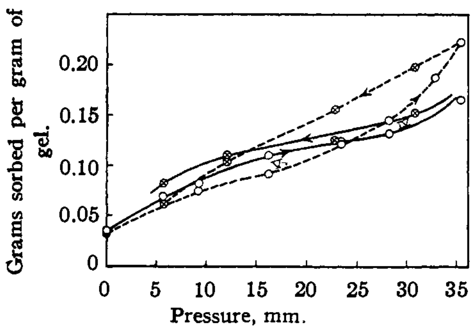

Fig. 2.—The sorption of water at 40.9° by an aerogel, IV. and a xerogel, V: O, sorption; ⊗, desorption.

Sorption of Silicon Tetrachloride.—After evacuation of the water and careful flushing with silicon tetrachloride with intermittent heating to 300°, the sorption curves for this substance on the same gels were obtained. They are plotted in Fig. 3. Here the aerogel shows no hysteresis, within the experimental error, but the xerogel shows distinct hysteresis disappearing at a partial pressure of about 34%. The temperature was again 40.9° and the saturation pressure was 441 mm.

Neither gel shows a strong affinity for the sili-

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(7) McBain, "Sorption of Gases by Solids," Routledge, London, 1932, Chapter VI.

(8) Bartell and Almy, *J. Phys. Chem.*, **36**, 475 (1932).

(9) Kistler and Kearby, *Acta Physicochim. U. S. S. R.*, **1**, 354 (1934).

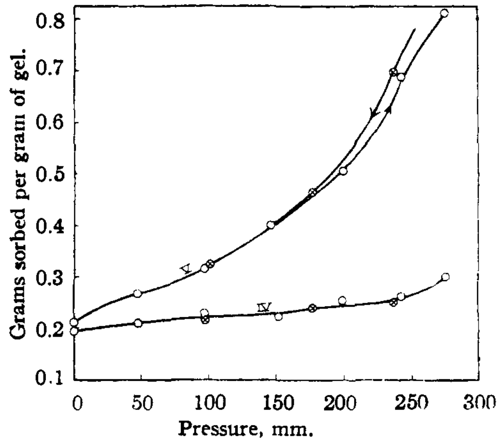

Fig. 3.—The sorption of silicon tetrachloride at 40.9° by aerogel IV and xerogel V: ○, sorption; ⊗, desorption.

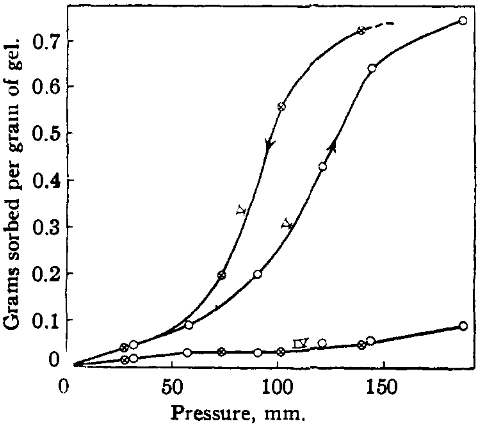

Fig. 4.—The sorption of carbon tetrachloride at 40.9° by gels IV and V after careful dehydration: ○, sorption; ⊗, desorption.

con tetrachloride after the initial irreversible adsorption. The shapes of the curves would indicate that a monomolecular layer is formed only with difficulty and then only at relatively high pressures. Capillary condensation apparently accounts for most of the increase in weight in gel V, since the total surface areas of the two gels are nearly the same.

Both gels initially contained approximately 3.4% of water unremoved by the heating and evacuation. On removal of this water, a residue of hydrolyzed silicon tetrachloride has been left behind. It can be argued that the most active spots on the gel have been covered up by this residue. However, the surface that this residue exposes to the vapors must be either anhydrous or partially chlorinated anhydrous silica. In neither case can a contamination with water be held responsible for the behavior. In addition, only a fraction of the surface of the gel can be covered with this hydrolyzed deposit. It is interesting to note here that such a dehydrated gel has practically the same heat of wetting with water as the activated gel before treatment with silicon tetrachloride,[9] and this rewet gel again holds irreversibly nearly the same amount of water as before, showing that the active spots have probably not been covered up so effectively that a liquid molecule cannot again reach them.

Sorption of Carbon Tetrachloride.—The heating and flushing procedure was again followed using carbon tetrachloride, followed by sorption measurements. Figure 4 gives the results. The temperature was 40.9 and the saturation pressure was 224 mm. Here again it will be seen that the affinity of the gel for this compound is very low, agreeing in this respect qualitatively with the findings of Foster,[10] for a gel that had not been subjected to the action of carbon tetrachloride vapor at an elevated temperature. He believes that at a temperature of 100–120° the reaction

$$CCl_4 + 2H_2O \longrightarrow COCl_2 + 2HCl$$

occurs, which reduces the amount of water on the surface of the gel. After four flushings, he reports having obtained a very different sorption curve with very high sorption at low partial pressures. Three flushings did not produce this change. If the results obtained were real and not due to some unrecognized error, they can scarcely be attributed solely to the dehydration effected by the above reaction, since silicon tetrachloride is an immensely stronger dehydrating agent than carbon tetrachloride and must have effected a much more complete dehydration without, as pointed out before, reducing the surface activity. A striking difference will be observed between the hysteresis loops for carbon tetrachloride and silicon tetrachloride.

Sorption of Benzene.—Figure 5 portrays the results for benzene on the same two gels at 40.9°, and for gel V also at 28.5°, at which temperatures the saturation pressures were 191 and 113 mm., respectively. No desorption curve was obtained at the lower temperature. Here again there is no evidence for strong attraction between the surface and the sorbate. Capillary condensation accounts for nearly all of the sorption by gel V. This gel gives a hysteresis loop much resembling that for carbon tetrachloride.

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(10) Foster, *Trans. Faraday Soc.*, **32**, 1559 (1936).

Applying the van't Hoff equation to the two isotherms for gel V, one finds the heats of condensation given in Table I. The heat of vaporization of benzene at its boiling point is 94 cal./g. As will be shown later, neither the sorption nor desorption curve represents true equilibrium when hysteresis is present; therefore, these calculations should not be taken too seriously, but qualitatively they show that the heat of sorption of benzene vapor in the gel is not much more than the heat of vaporization, and that this heat likely diminishes as the amount of sorbed benzene increases.

TABLE I

HEATS OF CONDENSATION OF BENZENE IN GEL V

Grams benzene sorbed per g. gel	Heat of condensation, cal. per g.
0.07	131
.13	120
.27	100
.35	84

Discussion

Capillary Condensation.—In the data on gels I, II and III, we have an excellent portrayal of the influence of openness of a structure upon the capillary condensation. Here we have three gels made simultaneously, left in contact with water the same length of time and given the same treatment on conversion to the dry gel state. Gel III with a density of 0.92, which is higher than many silica xerogels, can scarcely be called an aerogel, but it had the same treatment as the aerogels and the same precursor. At least the major differences that occur between these three gels must be due to the differences in compression of the structure on drying. Since all three went through the same experiences, it is not likely that large chemical changes occurred in one that were not duplicated in the others.

A glance at the curves of Fig. 1 impresses one with the fact that the major differences lie in the different total capacities of the three gels and the different relative vapor pressures at which each takes up water most rapidly.

Heat conductivity measurements have given a surface area value of 4.1 × 10^6 sq. cm. per gram for aerogel I.[3] Assume that all three gels have this same area. Now, applying the Boltzmann expression, some condensation will occur at a given relative pressure when the surface area in some element of volume is so high that

$$p/p_0 = e^{-ME/RT} \qquad (1)$$

in which p is the partial pressure of vapor, p_0 is its saturation pressure, M is the molecular weight, E is the work required to pump out 1 g. of liquid from this element of volume against surface tension, and R and T have their usual meanings.

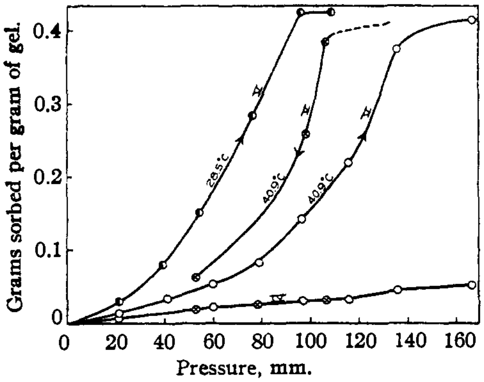

Fig. 5.—The sorption of benzene at 28.5 and 40.9° on gels IV and V.

If V is the total volume of 1 g. of gel, A_g its area, and b is the volume of its solid structure (silica), then the volume of liquid that can be held in 1 g. of gel is $V - b$, and the weight of liquid $= d_e(V - b)$, where d_e is the density of the liquid. The area of surface per gram of liquid is, then, $A_g/d_e(V - b)$. It follows that $E = A_g\sigma/d_e(V - b)$ in which σ is the surface tension, and

$$p/p_0 = e^{-MA_g\sigma/d_e(V - b)RT} \qquad (2)$$

When the liquid is water, the temperature is 35.4°, b is 0.5 and $\sigma = 70.4$ dynes per cm., the exponent $= -4.94 \times 10^{-8} A_g/(V - b)$. Taking $A_g = 4.1 \times 10^6$, exp. $= -0.203/(V - b)$.

The values of p/p_0 have been calculated for the three gels and are given in Table II. These values are also entered in Fig. 1 as vertical broken lines intersecting the graphs.

TABLE II

VALUES OF RELATIVE PRESSURES FOR THE THREE GELS CORRESPONDING TO AN AVERAGE AREA PER G. OF 4.1 × 10^6 SQ. CM.

Gel	Relative pressure	A_g from steepest portion of curve, sq. cm.
I	0.97	6.2 × 10^6
II	.89	8.1 × 10^6
III	.71	4.4 × 10^6

There is evidently a qualitative relationship between the points of intersection of these broken lines with the three curves. It looks as though there may be a quantitative relationship between the steepest portion of each curve and the total area of a gram of gel. Calculation of these areas with equation (2) gives the values in the third column of Table II. The values are the right order of magnitude, and for gels I and III not in bad disagreement with later calculations. The value for gel II seems to be out of line.

In spite of the apparent success of equation (2), it is probably not a fruitful quest to seek a single point on a sorption curve that quantitatively yields the total surface. Such a point has been claimed by Emmett and Brunauer,[11] but its significance is in doubt. When isotherms for small molecules such as nitrogen or carbon monoxide are determined on the same substance, *e. g.*, silica gel, the areas calculated from their point B are in good agreement, but when an isotherm for a very much larger molecule, butane, is used, the area calculated from the point B is only of the same order of magnitude.

Again let us consider the derivation of equation (2). The vapor pressure of a liquid condensed in a porous solid is given by equation (1). Now, if the structure of the porous solid is non-uniform, successive increments of liquid condensing will wet different areas, and equation (1) or (2) can be put into the form

$$p/p_0 = e^{-M\sigma\,\mathrm{d}A/RT\,\mathrm{d}W} \qquad (3)$$

where W is the weight of liquid condensed and A is the area wet by this liquid. Equation (3) can be put into the more convenient form

$$\frac{\mathrm{d}A}{\mathrm{d}W} = 2.3\,\frac{RT}{M\sigma}\log\frac{p_0}{p} \qquad (4)$$

It will be noted that equation (3) has a close resemblance to the Thomson equation,[12] $p/p_0 = e^{-2\sigma V/RT}$, becoming identical with it when the structure is assumed to be made up of tubules of uniform diameter.

In view of the fact that very few porous materials can be shown to contain spaces even remotely resembling tubules, it has been astonishing to us to find how universal has been the custom of treating capillary condensation as though it occurred in cylindrical pores. To be sure, some investigators have generalized the concept, but the Thomson equation has always been retained and the language has continued to refer to pore radii.

The emphasis here is upon the fact that in silica aerogel and xerogel, and in many other porous substances, the structure must more closely resemble a felt than tubules, and the concept of cylindrical tubules becomes particularly artificial. However, regardless of the nature of the passages in the porous substance, equation (4) describes the relationship between surface area wet and the vapor pressure of an included liquid without conjuring up some artificial picture of the elements of structure as a mental crutch.

Equation (4) enables one to evaluate the total wet surface within a porous body in which a liquid has been condensed, provided that: (1) the liquid wets the solid perfectly; (2) the surface tension of the liquid in the confined spaces can be evaluated; (3) the quantity of vapor condensed can be distinguished from that which has been adsorbed on the surface or absorbed within the solid structure; and (4) that true equilibrium exists between vapor and liquid during the condensation process.

Taking up these conditions one at a time, there is little doubt that water perfectly wets clean silica. Should there be a characteristic contact angle between liquid and solid, there is the likelihood of a difference between the angles at an advancing and a receding surface, which would mean that true equilibrium might be difficult to attain.

Much speculation has been expended on the probable surface tension of a liquid in very narrow spaces. The most pertinent facts to be borne in mind, however, are that the surface tension is a measure of the energy required to extend the area of the liquid and is consequently but little concerned with the shape of that area as long as the confining spaces are large enough so that the molecules are in a liquid environment; and that the decay of interatomic forces is so rapid that the molecules in the second molecular layer from the surface are already in an approximately normal environment. It is to be expected, therefore, that the measured surface tension of a liquid will be a good first approximation to its tension in a channel whose width is greater than four molecular diameters.

The distinction between liquid condensed and liquid absorbed by the structure will not be dealt with here since there is little evidence of an absorption of water by silica gel, that reported by Harvey[6] being small in magnitude and negligible compared to other errors involved in the evaluation of surface area. The distinction between

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(11) Emmett and Brunauer, THIS JOURNAL, **59**, 1553, 2682 (1937).

(12) Thomson, *Proc. Roy. Soc. Edinburgh*, **1**, 63 (1869); *Phil. Mag.*, (4) **42**, 448 (1871); *Z. physik. Chem.*, **88**, 212 (1914).

adsorbed and condensed liquid cannot be so lightly passed over. If the energy required to remove a molecule from the first layer on the surface is much higher than that required to remove a molecule from condensed liquid in the confined spaces, which is the case with water on silica, there will be substantial adsorption at low pressures. In this case, the first layer may not be complete before capillary condensation sets in, but it will usually have progressed far enough to enable an evaluation of the constants of the Langmuir equation, from which the quantity of liquid in the completed first layer can be approximated. If initial sorption is low and monomolecular sorption does not precede capillary condensation, it is still possible to approximate the volume of the immobilized first layer.

When capillary condensation takes place in a porous structure of highly irregular channels, such as would exist in a felt or a granular solid, it is a matter of simple mechanics that, in general, true equilibrium cannot be attained. As a concomitant, hysteresis is to be expected. Kraemer,[13] Foster,[14] McBain,[15] Cohan,[16] and Rao[17] have concluded that restricted openings to cavities offer an explanation for hysteresis. The mechanics of the hysteresis phenomenon are such that the curve of true equilibrium lies between the two halves of the loop. Calculations of surface area based on sorption and on desorption, therefore, serve to furnish limits within which the true value must lie.

In the application of equation (4) to the three gels of Fig. 1, we must bear in mind that no desorption data were taken, and that, as a consequence, it is not possible to estimate the maximum error that may arise in the calculation of areas. The influence of the compression of the gel on hysteresis is unknown.

Calculation of Surface Area from Capillary Condensation Data.—The data for Fig. 1 were not taken to low pressures since capillary condensation was the object of the study. In order to extrapolate to the lower limit of capillary condensation and enable an estimate of the total surface area to be made, the data for aerogel I were extended downward by matching with that for water on gel IV, which was a gel made by the same procedure but not from the same batch. It is not considered that a serious error was thus introduced.

Figure 6 is a graph of the completed curve, plotting weight sorbed by 1 g. of aerogel against log p_0/p. The curve is intersected by a vertical broken line where the data from the two gels were matched. It is at once apparent from an inspection of equation (4) that the area under the curve of Fig. 6, when corrected for monomolecular adsorption, will give the total gel area if multiplied by 2.3 $RT/M\sigma$.

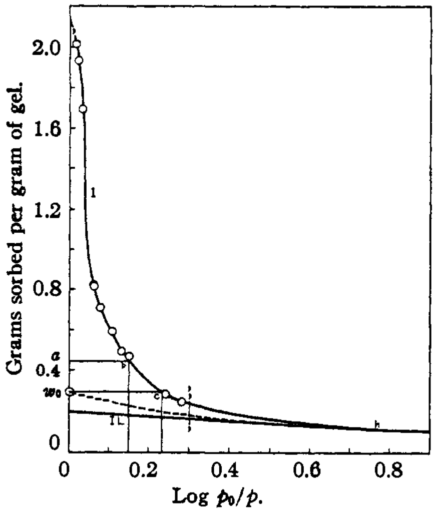

Fig. 6.—The sorption for gel I, Fig. 1, replotted with log p_0/p as the abscissa.

From the low pressure data on gel IV, the constants of the Langmuir equation

$$\frac{W_1}{W_0} = \frac{p}{c + p} \tag{5}$$

were found to be $W_0 = 0.25$ and $C = 25$. W_1 is the weight adsorbed per gram of gel, W_0 is the weight of a monomolecular layer, and p is the vapor pressure. Using this equation curve IL was calculated, which represents the values of W due to monomolecular adsorption if no capillary condensation should occur.

In Langmuir's equation no recognition of the saturation point is made, and the monomolecular layer is not ideally complete short of infinite pressure. As both Langmuir[18] and Frenkel[19] have pointed out, when the saturation pressure is approached, the attractions of adjacent molecules on the surface for new vapor molecules become large enough so that patches of close-packed

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[13] Kraemer, Taylor's "Treatise on Physical Chemistry," D. Van Nostrand Co., New York, N. Y., 1931, p. 1661.

[14] Foster, *Proc. Roy. Soc.* (London), **A148**, 129 (1934).

[15] McBain, THIS JOURNAL, **57**, 699 (1935).

[16] Cohan, *ibid.*, **60**, 433 (1938).

[17] Rao, *J. Phys. Chem.*, **45**, 506 (1941).

[18] Langmuir, *Phys. Rev.*, **6**, 79 (1915).

[19] Frenkel, *Z. Physik*, **26**, 117 (1924).

molecules occur and spread to cover the whole surface. The quantity adsorbed at saturation must then be W_0 or 0.25 plus 0.035, the residual water in the gel on evacuating.

Now in the actual case, capillary condensation continually reduces the free area of the gel as saturation is approached so that the area uncovered by a monomolecular layer approaches zero and the point described by Langmuir and Frenkel at which the surface suddenly becomes completely covered is probably never attained.

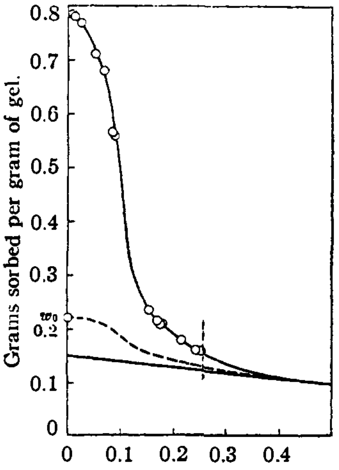

Fig. 7.—The sorption curve for gel II, Fig. 1, replotted with log p_0/p as the abscissa.

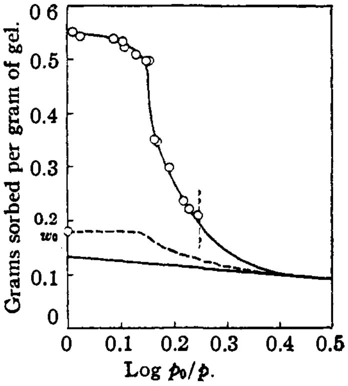

Fig. 8.—The sorption curve for gel III, Fig. 1, replotted with log p_0/p as the abscissa.

The true curve representing the monomolecular adsorption accompanying capillary condensation therefore lies above IL, and is drawn in as the broken line ending at the point W_0. Its position is obtained as follows: Let ΔA represent the area of gel surface not covered by condensed liquid at pressure p. Then from Langmuir's equation

$$A_2 = \Delta A p/(c + p)$$

where A_2 is the portion of ΔA that is covered by a monomolecular layer. Similarly, the portion of ΔA that is still bare at the pressure p is $\Delta A - \Delta A p/(c + p) = \Delta A c/(c + p)$. Therefore the total area A_1 of gel covered by monomolecular layer is

$$A_1 = A_0 - \Delta A \frac{c}{c + p} \tag{6}$$

Now as defined above

$$\Delta A = 2.3 \frac{RT}{M\sigma} \int_p^{p_0} \log \frac{p_0}{p} \, \mathrm{d}W$$

which is $2.3RT/M\sigma$ times the area under curve I on Fig. 7 above the point p. To illustrate, at log $p_0/p = 0.15$, ΔA will be the area under the curve above the line ab multiplied by $2.3RT/M\sigma$. If W_1 is the weight of the monomolecular layer at p, it follows that

$$W_1 = W_0 - \frac{\Delta A}{\alpha} \frac{c}{c + p} \tag{7}$$

where α is the area covered by one gram of adsorbed molecules on the surface.

At the point h where capillary condensation sets in, $\Delta A = A_0$, the total area of the gel, and $\Delta A/\alpha = W_0$. The three curves must, therefore, be tangent to each other at this point.

It is obviously a simple matter to graph in the values of W_1 from log $p_0/p = 0$ to the value at the point c, by assuming a value for α. An estimation of the area chW_0 can now be made and W_1 calculated for the point h. If this does not coincide with the curve for I, a second approximation for α is tried, and again the value of W_1 calculated. Usually not more than three trial values of α need be tried. Since this toe of the curve is a small fraction of the total area, a substantial error in this approximation will not make a serious error in the estimation of A_0.

Figures 7 and 8 are plots of the data for gels II and III with the same coördinates as Fig. 6. The low pressure ends of these curves were matched as well as possible by approximations to the curves for gels IV and V, respectively.

Table III gives the results for the three gels. Also it includes the calculated areas neglecting the correction to the Langmuir equation. The value of $2.3RT/M\sigma = 4.66 \times 10^7$ sq. cm.

TABLE III

AREAS OF GELS I, II AND III

Gel	Density	Corrected area, sq. cm.	Area neglecting correction, sq. cm.	Area above p = 24.2 mm., sq. cm.
I	0.15	4.2×10^6	4.7×10^6	4.2×10^6
II	.44	2.7×10^6	3.1×10^6	2.8×10^6
III	.92	3.3×10^6	3.8×10^6	2.9×10^6

As would be expected, there is some loss in available area for capillary condensation as the gel is compressed from its initial voluminous state. The apparently greater area of the most compressed gel is probably due, at least in part, to errors in extrapolation to low pressures. If, for example, the areas are integrated for pressures greater than 24.2 mm. (log $p_0/p = 0.25$) the results, shown in column five, indicate virtual equality of the two denser gels.

It is gratifying to observe that areas calculated from heat conductivity data (4.1×10^6 sq. cm.) and from capillary sorption for gel I are so close.

It is greatly to be wished that both sorption and desorption data had been taken on the three gels down to low pressures. However, complete sorption data have been taken on one sample of commercial aerogel (Santocel) by Harvey[6] using butane at 0°. He also used water, but observed a decided aging effect that was absent with butane. Figure 9 presents the data for butane on a weight-log p_0/p chart. The original data show failure of the hysteresis loop to close completely due to a leaky stopcock. A correction is applied to the desorption curve presented here to compensate for that error. Even if this correction had not been applied, the error would have been very small.

At 0°, the vapor pressure of the butane was 778 mm. and the surface tension was 14.9 dynes, so that $2.3RT/M\sigma = 6.05 \times 10^7 \text{cm}^2$. From the observations at low pressure, the Langmuir constants are found to be $C = 235$, $W_0 = 0.20$ g. With these data the Langmuir curve was drawn in and the corrected curve for the adsorbed layer obtained as above. The total area of one gram of gel by capillary condensation was then found to be

$$A_0 \text{ (sorption)} = 7.7 \times 10^6 \text{ sq. cm.}$$
$$A_0 \text{ (desorption)} = 7.9 \times 10^6 \text{ sq. cm.}$$

Calculation of the area of an adsorbed butane molecule from $A_0 = 7.8 \times 10^6$ sq. cm. and $W_0 = 0.20$ g. gives Area per molecule = 37 sq. Å. which is a very reasonable value. Emmett and Brunauer[11] have calculated from molecular data that the area is 32 sq. Å.

Knowing the area covered by an adsorbed molecule, the area of the gel can be calculated from W_0, obtained from the Langmuir equation. This area will coincide with A_0 provided that there are no crevices into which only one or two layers of molecules can creep and that adsorption will occur equally as well on top of water molecules that cannot be removed by moderate heat and high vacuum as on free areas. Of course, the limitations of the Langmuir equation must be borne in mind.

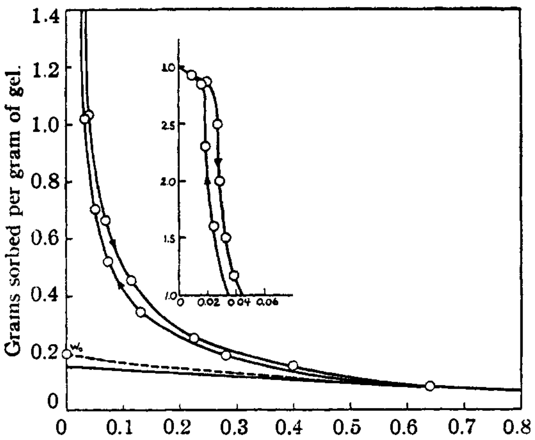

Fig. 9.—Harvey's data for the sorption of butane on silica aerogel.

Area Calculated from Sorption of Carbon Tetrachloride and Benzene.—Replotting Figs. 4 and 5 with log p_0/p as abscissa enables the areas given in Table IV to be determined. The curves for sorption on gel V at both 28.5 and 40.9° fall very close together and yield areas nearly identical. There is a distinct difference in shape, however, and we are at present in doubt as to whether or not this difference is real or due to experimental error and the limited number of measurements. It will be seen from Table IV that the areas calculated from sorption and desorption measurements of carbon tetrachloride and benzene on gel V overlap, and also check closely areas in Table III of a similar gel (III) when water was used.

The width of the hysteresis loop when different vapors are sorbed is a matter of much interest but one to which we have given comparatively little thought. It depends doubtless upon molecular size and shape, as well as surface tension and in some cases the angle of wetting.

TABLE IV

AREA PER GRAM OF GEL V FROM DATA ON CAPILLARY CONDENSATION OF CARBON TETRACHLORIDE AND BENZENE

	Carbon tetrachloride, sq. cm.	Benzene, sq. cm.
Sorption, 40.9°	3.6×10^6	2.9×10^6
Sorption, 28.6°		2.7×10^6
Desorption, 40.9°	4.7×10^6	4.5×10^6
Average at 40.9°	4.1×10^6	3.7×10^6

Sorption by Strictly Anhydrous Silica Gel and Aerogel.—The data for carbon tetrachloride and benzene on gels IV and V do not differ in any striking way from many previous results obtained with gels containing residual water. It would appear, therefore, that the sorption characteristics of these gels are not much influenced by the residual water. In fact, since there is good assurance that gels IV and V have close to the same surface area per gram and that the surface characteristics of both gels are similar, most of the observed sorption by gel V is due to capillary condensation and is necessarily independent of the surface chemistry after the first layer of molecules is laid down.

Other Sorption Methods for the Determination of Surface Area.—Reference has already been made to the work of Emmett and Brunauer. Since their methods of surface area calculation, based upon an impressive volume of work, have gained great popularity and in a large measure seem to be successful, we feel that it is desirable to call attention to the fact that the method using the point (B in their terminology) at which the sorption curve ceases to be concave to the pressure axis relies upon a single point on a curve as a mark of the completion of the first monolayer. Areas estimated from it can be in large error, as for example when butane is used, due to the fact that the point B depends upon the slope and curvature of the adsorption curve for the first monolayer of molecules adsorbed, and upon the slope and position of the curve for capillary condensation. The monomolecular adsorption curve in turn depends for its steepness upon the energy with which the molecules are held to the surface, while the character of the capillary condensation curve depends upon surface tension of the liquid and the configurations and juxtapositions of the elements of structure of the solid, all of which are variables with little or no connection with the area covered by a monolayer or the area of a molecule.

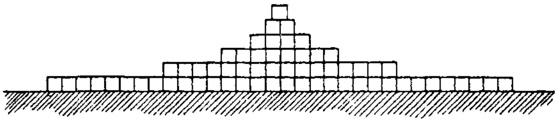

Fig. 10.—The type of sorption postulated by Brunauer, Emmett and Teller. This figure is for a ratio of $p/p_0 = 0.5$.

If the monomolecular adsorption occurs readily at low pressures approaching completion before capillary condensation sets in, the point B may well give a rough value for a completed monolayer. This condition seems to have prevailed with most of the vapors and solids studied by Emmett and Brunauer.

Their second method[20] relies upon an equation described as "a generalization of Langmuir's theory to multimolecular adsorption." This equation is undoubtedly useful for curve fitting at low partial pressures and has been helpful in making comparisons of surface areas. It, however, contains two fundamental errors in its derivation and therefore is not theoretically satisfactory.

The first of these errors is the multimolecular assumption. Letting S_1, S_2, S_3, . . ., S_i represent the areas of the surface covered by 1, 2, 3, . ., i layers of molecules, the tacit assumption contained in the final equation is that

$$\frac{S_2}{S_1} = \frac{S_3}{S_2} = \cdots \frac{S_i}{S_{i-1}} = \frac{p}{p_0}$$

where p is the vapor pressure and p_0 is the saturation pressure. This very artificial assumption is illustrated in Fig. 10. Now if the energy with which molecules in the first layer are held to the surface is greater than that with which second layer molecules are held to the first layer, the vapor pressure of the second layer will be greater than the first, and if any bare surface exists the second layer will distill to it. Thus at equilibrium under the above conditions no second layer can form until the first is complete, as was pointed out by both Langmuir and Frenkel. There seems to be no experimental justification for pyramiding the molecules in this way.

There is also a fundamental incompatibility between the point B in the earlier work and the quantity adsorbed in the first monolayer as calculated from the equation. Point B was assumed to be the point on an isotherm at which the first monolayer is complete. In the data in reference 9, the point B is found to occur at ratios of p/p_0 varying between 0.025 and 0.33. When $p/p_0 = 0.1$, the total amount sorbed, as calculated from the above assumption of multimolecular adsorption, will be 11% more than that contained in the first layer, while at $p/p_0 = 0.33$, the total becomes 62% greater than in the first layer.

The second error resides in the total neglect of capillary condensation. That capillary condensation can and does occur in porous solids at suitable vapor pressures is a fact that can no more be questioned than the fact that liquids that wet the

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(20) Brunauer, Emmett and Teller, This Journal, 60, 309 (1938).

walls will rise in a narrow tube. Yet Brunauer and co-workers[21] have gone to some length to discredit capillary condensation as an explanation of the higher portions of the isotherms. It may be needless to add that the formidable equation developed in this reference is based upon the same two errors.

It should be mentioned, however, that Emmett in his latest publication on the subject[22] has admitted the fact of capillary condensation although without clarification of its relationship to the equation developed.

The intention of these remarks is to emphasize the fact that the relation between sorption and surface area has not yet been adequately treated theoretically. It is hoped that others will take up the matter where it now stands and put it into more acceptable shape.

Summary

Sorption data on silica aerogel and silica xerogel are presented. It is shown that the area under the sorption curve, when plotted with log p_0/p as the abscissa, is a direct measure of the total surface area of the gel.

Capillary condensation is shown to influence greatly the course of all the curves studied, and in the case of non-aqueous liquids on silica gel may account for nearly all of the sorption measured.

Thorough removal of residual water from the surface of silica gel did not succeed in transforming the sorption curve to another type, as has been reported.

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[21] Brunauer, Deming, Deming and Teller, THIS JOURNAL, **62**, 1723 (1940).

[22] Emmett, "Advances in Colloid Science," Interscience Publishers, New York, N. Y., 1942, p. 1.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Kinetics of the Decomposition of Trinitrobenzoic Acid in Dioxane–Water Mixtures[1]

BY DAN TRIVICH[2] AND FRANK H. VERHOEK

In a previous paper[3] it was shown that the decomposition of 2,4,6-trinitrobenzoic acid in ethyl alcohol solution had as the rate-determining step the decomposition of the trinitrobenzoate ion. The decomposition proceeds at a faster rate in alcohol than in water, even though, as a result of the lower dielectric constant, the dissociation of the acid, and hence the concentration of the trinitrobenzoate ion, is smaller in the former solvent. Studies of the reaction in other solvents[4] have shown that the rate is dependent upon the solvent to a marked degree.

In order to secure further information concerning the effect of changes in solvent on this reaction, a study has been made of the decomposition of trinitrobenzoic acid in solvent mixtures of water and dioxane. The use of these two liquids permits a continuous variation in the composition of the solvent in a system for which the dielectric constant for each solvent mixture is known.[5]

The over-all reaction is a decarboxylation of trinitrobenzoic acid to form carbon dioxide and trinitrobenzene.

The rate of reaction was determined by keeping individual reaction flasks containing measured samples of solution at known temperatures, removing the flasks from the constant temperature baths after measured time intervals, and titrating with alkali the trinitrobenzoic acid remaining undecomposed.

Each solution was prepared by diluting a stock solution of trinitrobenzoic acid in pure dioxane with the proper amounts of water and dioxane to give the desired composition of solvent. Ten-ml. samples of the resulting solution were pipetted and placed in individual reaction vessels, which were covered and immersed in the thermostat. Samples were removed from the bath after given intervals of time and the reaction stopped by chilling the sample in ice water. Nitrogen was then passed through the solution for ten minutes to remove the carbon dioxide, and the solution was titrated with 0.01 *N* sodium hydroxide using brom thymol blue or phenol red as the indicator. In the experiments at the higher percentages of dioxane, sufficient water was added to the sample before analysis that the final composition did not exceed about 30% dioxane. The initial concentrations were so chosen that the first sample removed from the thermostat was approximately 0.01 *N* in trinitrobenzoic acid.

The dioxane was purified by a method similar to that of Hess and Frahm[6] except that the recrystallizations were

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[1] From a dissertation submitted by Dan Trivich to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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[3] Verhoek, THIS JOURNAL, **61**, 186 (1939).

[4] Moelwyn-Hughes and Hinshelwood, *Proc. Roy. Soc.* (London), **A131**, 186 (1931).

[5] Åkerlöf and Short, THIS JOURNAL, **58**, 1241 (1936).

[6] Hess and Frahm, *Ber.*, **71B**, 2629 (1938).