THE EFFECT OF HEAT-TREATMENT ON THE SORPTION-DESCRIPTION HYSTERESIS
CHARACTERISTICS OF SILICA GEL

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HISTORICAL

A. INTRODUCTION

In 1896, van Bemmelen (6) published the original work on the subject of sorption of water vapor by silica gel. He obtained the sorption-desorption cycle by use of the so-called static technique of allowing gels to come to equilibrium with the moisture in an atmosphere the humidity of which was fixed by the vapor pressure of an aqueous solution of sulfuric acid. The main points of the observations were (1) that the gel had a very high sorptive capacity, (2) that this capacity was markedly lowered after the first dehydration, (3) that the sorption is irreversible over a definite portion of the cycle, and (4) that two regions of reversibility occurred, one at low fractional values of saturation in the vapor state, and another at relatively high partial pressures.

The curious shape of the cycle, together with the lack of evidence indicating hydrate formation (7), led to the proposal of numerous explanations. As early as 1911 Zsigmondy (33), after being unable to resolve the gel structure microscopically, suggested the now widely accepted capillary concept. The amicroscopic structure, he reasoned, must consist of fine pores of capillaries, the large volume of vapor sorbed at high partial pressures, therefore, corresponding to vapor condensed into capillaries in accordance with the well-known lowering of vapor pressure over highly concave liquid-vapor interfaces (18). Zsigmondy pursued his argument by calculating the diameter of pores present in the structure from the observed vapor pressure lowering. He considered the most probable value of pore diameter to be in the order of magnitude of 50 Å.

The phenomenon of irreversibility was also responsible for considerable speculation. Zsigmondy held the view that irreversibility was caused by the presence of sorbed permanent gases, and that the desorption branch of an isotherm should retrace the sorption curve exactly if the effect of fixed gases could be eliminated. Accordingly, improvements were made on the van Bemmelen technique such that the entire system could be outgassed. Zsigmondy, Bachmann, and Stevenson (34), Bachmann (2) and later Bachmann and Maier (3) described vacuum apparatus with which they had determined the water concentration as a function of pressure.

Contrary to Zsigmondy's original view, all the investigators were able to obtain characteristic van Bemmelen hysteresis even after careful exclusion of air and other permanent gases.

In spite of this verification of the van Bemmelen Phenomenon, Patrick (24) showed that by sufficiently rigorous methods reversibility could be obtained. His work was stimulated by results of experiments done by McGavack and Patrick (23) concerning the sorption of sulfur dioxide by silica gel. In this study the workers were able to demonstrate that hysteresis observed in the sulfur dioxide-gel system could be eliminated by evacuation coupled with simultaneous flushing of the surface with sorbate. The hysteresis, they noted, made a dramatic reappearance if the degassed samples were briefly exposed to a small partial pressure of a permanent gas. With these observations in mind, Patrick constructed an apparatus wherein the samples could be strongly evacuated at elevated temperatures (350°). Between the vigorous outgassings, the gel was carried through several sorption cycles in order to assist in purifying the surface. Use of the exhaustive treatment according to Patrick yielded isotherms which were

completely reversible with no indication of the hysteresis loop.

Other reports of reversible sorption in the silica gel-water system are scarce indeed. Within recent years, however, Kistler, Fischer, and Freeman (19) have reported that their results indicate reversibility of the desorption cycle. Although they obtained isothermal pressure concentration diagrams showing considerable hysteresis, they believe that if certain correction factors in connection with their experimental arrangements were applied, the equilibrium values for p-c obtained during desorption would be within experimental error of those observed under conditions of increasing water concentration.

More recently, Taylor (30) determined Isoteres for the water vapor-silica gel system. By a somewhat elaborate experimental procedure he found that the pressure-temperature relationship at a given temperature was independent of the direction along the temperature axis from which the given temperature is approached. This might well be expected in the light of some of the theories of hysteresis to be discussed in the next section.

Aside from the few isolated instances mentioned, there is substantially no report of reversible cycles. On the other hand, Rao offers a striking evidence for the validity of hysteresis (28). In a vacuum apparatus he retraced the cycle of water vapor on silica gel a total of nineteen times and obtained identical hysteresis loops in each cycle except the first. His findings are essentially in agreement with those of earlier investigators who obtained loops. The reproducibility, however, was not characteristic of earlier data which showed hysteresis loops to be subject to large drifts. For example, Lambert and Foster (20), who worked with gels activated in a vacuum at 150° obtained an augmented hysteresis by repetition of the cycle on the same samples. It is of interest to note

briefly that an explanation of the changes has been advanced in which the drift is attributed to a modification of gel volume brought about by changing water content (9).

Another in the list of workers verifying hysteresis is Pidgeon (27), who in trying to account for the result obtained by Patrick found that evacuation of gels at elevated temperatures was without effect in connection with the magnitude of hysteresis, since this phenomenon was observed with gels subjected to very vigorous evacuation at 300° for periods of several hours. The investigations described by Pidgeon will be discussed later in connection with theories of Hysteresis.

B. BRIEF REVIEW OF THEORIES OF HYSTERESIS

The sorption system water-silica gel, as is widely recognized, is one in which capillary condensation must play an important role. In general, there are two schools of thought among supporters of a condensation theory (1) that of Zsigmondy and his followers who rely upon the Kelvin Equation down to submicroscopic dimensions, and (2) that composed of Patrick and his co-workers who substitute an empirical form of the relation. The difference is not fundamental since Patrick's objection to the unmodified equation is merely a reluctance to assume that the molal volume and surface tension of a liquid have the same values in minute pores as those measured in the bulk liquid.

Aside from this slight difference, however, workers are willing to agree that capillary condensation in some form is responsible for the large sorption observed at high partial pressures. Therefore, because of the wide acceptance of the view of condensation, there are three classical theories stemming from the capillary concept, devised

to explain the cause of irreversibility in sorption-desorption isotherms:

- (1) The Constricted Pore Theory
- (2) The Open Pore Theory
- (3) The Incomplete Wetting Theory

1. The Constricted Pore Theory

The hypothesis proposes the existence of amicroscopic pores which are so shaped as to have exposed ends of smaller radius than that of the underlying structure. Vapor condensing in a pore at some fraction of saturation has a pressure given by the Kelvin Equation (one form of which is shown below) corresponding to $r = r_1$, the radius of the large underlying capillary. However, after the pore has been filled at saturation, the vapor pressure due to the condensed liquid is determined by the same relation with $r = r_2$, the radius of the smaller constricted neck. The ratios of the pressures for each case can be seen from the exponential relation to be a very sensitive function of the amount of constriction, i.e. a very small constrictive effect could give rise to an appreciable hysteresis.

In order to see the form of the relation, we may examine an expression of the Kelvin Equation

$$P = p_0 e^{-2\gamma V/rRT}$$

where p_0 is the normal vapor pressure of liquid at the absolute temperature T , p is the vapor pressure of liquid filling a pore of radius r , γ the surface tension, V the molal volume of the liquid, and R the gas constant in consistent units.

2. The Open Pore Theory

If an open pore is placed in an atmosphere of vapor, and if the diameter of the pore is several times greater than that of the vapor molecules, condensation may not occur in the pore even at pressures considerably over theoretical values calculated from the Kelvin expression. The fact that no concave interface is present accounts for the behavior. By the same token, then, no condensation can occur until a sufficient number of multisorbed layers have formed to bridge the pore and give rise to an interface. Once the interface is formed, the Kelvin relation determines the vapor pressure so that further condensation takes place in accordance with the logarithmic function.

After the cycle is carried through saturation, desorption takes place from a structure all the pores of which contain liquid. The vapor pressure, then, is determined by the size of pores being evacuated. Since this pressure will be lower than the pressure corresponding to a multilayer at the same overall water concentration, hysteresis results. This explanation would lead to the conclusion that the desorption branch of the isotherm is the true equilibrium, whereas the previous theory indicates that desorption is a metastable equilibrium and that the sorption branch of a p - c curve represents true condensation.

3. The Incomplete Wetting Theory

Since an important factor in the vapor pressure of a liquid is the curvature of its surface, it must be expected that if the liquid wetted the wall of a containing pore with difficulty, it would present a smaller radius of concave curvature when evaporating than when condensing. Such a change in curvature would cause a lower vapor pressure to exist over an emptying capillary than over one being filled, the condition ob-

served in hysteresis.

Barkas (5) has proposed a more general explanation relating to the inelasticity of gels. He shows that gels may undergo a semipermanent distortion under shear stresses which would tend to decrease the work done by the gels under desorption conditions to a value less than that done on the gels during the preceeding swelling. Barkas, while admitting that the effect is not universally applicable, states that in view of the plasticity of gels it seems "inescapable, thermodynamically" that the work difference be a potential source of hysteresis.

C. DISCUSSION OF THEORIES

It would seem advantageous to the understanding of the limitations of the various explanations made of why or why not hysteresis occurs, to cite several experimental facts and discuss the theories with respect both to agreements and inconsistencies. Unfortunately, as yet there have been proposed no concepts which fit experimental cases without special modification to account for the unexpected phenomena observed in individual examples.

Patrick's view, earlier held by Zsigmondy, that sorption is a spurious phenomenon due to the effect of sorbed permanent gases, suggests certain inconsistencies since it is not clear why the presence of non-condensable gas should cause an irreversibility over only a part of the sorption-desorption cycle, as is apparently the case regardless of whether the cycle is carried out in air or in a vacuum. On the other hand there have been explanations, which seem very reasonable, to account for the fact that Patrick (24) obtained p-c curves showing no evidence of a hysteresis loop. Pidgeon (27) accounts for the apparent reversibility by pointing out that Patrick tested an extremely large quantity of gel

(1200 ml.), in an apparatus only slightly larger, following the cycle by admitting and withdrawing water vapor intermittently. According to Pidgeon the effect of this procedure is a simultaneous tracing of both sorption and desorption, regardless of whether the overall concentration is increasing or decreasing. The reasoning embodied in this criticism seems logical since, under the experimental conditions described, the vapor pressure must necessarily execute excursions over wide ranges during the transfer of large quantities of sorbate. For example, as sorption progresses, vapor must be added in increasingly large amounts; consequently, as the gel takes up vapor from a high humidity atmosphere, the resulting decrease in pressure allows the most accessible pores, which come to equilibrium rapidly to take up vapor at a relatively high pressure. As equilibrium with the entire gel is being attained, however, these pores are subjected to conditions approximating those of desorption. Thus a situation wherein a large quantity of gel takes up water from a relatively small total vapor volume could easily give rise to a heterogeneous "equilibrium" in which the apparent ascending and descending curves differ by less than experimental error. Pidgeon, who had used a continuous pressure control method in connection with McBain-Bakr silica spring balances (thereby obtaining a large hysteresis effect) was able to produce a slight diminution in the magnitude of hysteresis by modifying his apparatus so that vapor was added intermittently. As further evidence to support his view he was able to eliminate hysteresis almost entirely by the presence of a large amount of gel in the dead space of his apparatus during sorption-desorption cycles followed by intermittent addition or subtraction of sorbate from the system.

Though Pidgeon's explanation seems plausible, in addition Brunauer (12) points out that even the shape of Patrick's isotherms differs^s from the usual S-shaped curves, rather tending to follow the Langmuir-type relation, i.e. one for which a plot of p/c versus p is a straight line. Brunauer considers that this may suggest a difference of pore structure which alone would account for the disappearance of hysteresis. If this suggestion is valid, there then arises the question regarding the cause of the pore structure change. This is another point investigated by Pidgeon concerning the treatment described by Patrick for evacuating the gel surface. In the course of the degassing, the gel was repeatedly heated to a moderately elevated temperature while being strongly evacuated. This procedure was at once believed to have modified the gel structure, but as mentioned before, the findings of Pidgeon indicate that the effect of heat treatment is essentially independent of any pressure lowering of the surrounding atmosphere. On this point he is in agreement with the workers who have investigated the effect of evacuation at elevated temperature (9, 15, 4) so that any modification of Patrick's gel must be assumed to be due to causes other than the conditions originally described.

On the other side of the question, it is seen that the classical theories meet with some success in accounting for the van Bemmelen Phenomenon. The Constricted Pore Theory, for example, is in good agreement with the experiments of Rao (28) who determined the course of the pressure-concentration curve by changing from sorption to desorption, and vice versa, at points below and intermediate to the region of irreversibility. He found that if desorption is tried from a point of

the main sorption branch, the p-c curve cuts directly across the loop and follows the main desorption branch down to zero pressure. If, on the other hand, from a point on the main desorption branch, sorption is tried, a separate curve is traced, parallel to the main sorption curve becoming coincident with it at saturation. In a number of such experiments he was able to prove that the only way a point on the main sorption branch, other than the saturation point, could be reached was by sorption initiating from a point in the region of reversibility below the tail-end of the hysteresis loop.

These phenomena can readily be accounted for on the basis of the Constricted Pore Theory as well as the Open Pore Theory. In terms of the former, a point on the desorption branch represents a condition in which a number of pores are completely filled, a number completely empty and none partially filled. As desorption proceeds, more pores empty completely, in accordance with the basic concept of the mechanism. If sorption is tried starting from a point on the desorption branch, the emptied pores begin filling. The resulting total sorption corresponding to any pressure is the sum of the liquid held in the full capillaries plus that in those partially filled. As long as sorption was begun when any of the constricted pores held liquid, the equilibrium sorption curve should lie above that for a previously dried gel. As desorption is tried from the sorption curve, the partially filled pores empty first; then, when only full pores remain, the condition corresponds to a point on the main desorption branch.

The Open Pore concept is equally convenient for explaining the behavior. By this view, as sorption proceeds, the pores form menisci and

fill when a multilayer thick enough to bridge their diameters has been adsorbed. They then fill completely the connecting pores which have sufficiently small diameters. If desorption is tried from a point on the sorption branch, representing a certain number of filled pores, the pores empty in accordance with the pressure relation given by the Kelvin equation, the expression which is a representation of the desorption branch. As sorption is initiated from points on the desorption curve, which represent a number of emptying pores, the concentration corresponding to any pressure depends on the sum of the amounts of liquid held in the partially filled capillaries in accordance with the Kelvin relationship, plus the amount held in any emptied pores refilled by normal sorption processes in addition to multilayers adsorbed by walls of capillaries containing no liquid. This represents a concentration higher than that observed on the main sorption branch.

The Theory of Incomplete Wetting does not so neatly account for the separate parallel sorption branches since nothing in the hypothesis would suggest that the main sorption curve could not be reached irrespective of the previous direction of vapor transfer. That this is so is easily seen by considering that by this concept the vapor pressure is influenced only by the direction of motion of the meniscus with respect to the containing wall.

Another example which might be given as further material to test the theories is the interesting fact reported by Bonnell (10) concerning the effect of the presence of certain salts on hysteresis. Bonnell found that gels precipitated from sodium silicate solution with either hydrochloric, sulfuric, or acetic acids all showed van Bemmelen hysteresis after removal of the residual sodium salts by dialysis. If, however, this purification is omitted, the sorption-desorption cycle apparently

becomes reversible.

Usual forms of the Constricted Pore Theory fail to indicate any sort of reasonable explanation of the data. If the explanation is to be found by considering this concept, it is necessary to assume either that the salt decreases the diameter associated with the non-constricted portions of pores, leaving the constrictions unaffected, or that the mildly hygroscopic nature of the salts sufficiently decreases the initial condensation pressure to cause condensation and evaporation to take place at more nearly the same pressure. Neither of the assumptions seems even plausible.

The Open Pore Theory fares slightly better in accounting for the phenomenon. It can reasonably be assumed that the presence of salt in the pores hastens the adsorption of vapor, and thus the formation of a meniscus. Since there is a decreased delay in the formation of a meniscus there results a diminished lag of the sorption curve, and because the process can be considered analagous to condensing and evaporating vapor from a salt solution, the vapor pressure could be expected to be independent of the direction of the process.

The Incomplete Wetting Theory also offers a somewhat more plausible explanation. Since according to this hypothesis hysteresis is caused by the difference in radius of concave curvature of the meniscus as it moves along the surface of the capillary in different directions, any agent rendering the surface more hydrophillic would tend to reduce the magnitude of the difference. An adsorbed layer of a soluble salt might easily serve as such an agent and thereby should tend to lessen hysteresis.

D. EFFECT OF METHODS OF PREPARATION

In general, silicic acid gels are prepared by the action of some acid substance on a solution of Na_2SiO_3 . Differences in concentrations of the reagents seem to have the effect of altering the magnitude but not the character of the sorption isotherms reported by the various investigators.

Other particulars of the preparation, however, apparently have a more marked effect. As has already been mentioned Bonnell (10) precipitated gels with hydrochloric, sulfuric, and acetic acids and obtained hysteresis in the isotherms only when he used dialyzed gels.

Weiser, Milligan, and Holmes (32) were able to diminish hysteresis greatly by preparing gels at the boiling point. The effect seems to have been the result of aging at the boiling point of the colloidal silica present in sodium silicate, since a diminution of the hysteresis in silica gels prepared from boiling solutions of sodium metasilicate was not obtained unless the metasilicate was boiled for a sufficiently long period to produce colloidal silica by hydrolysis. It might be of interest to note that the effect is faintly reminiscent of the results obtained by Berl and Urban (3) who were able to eliminate hysteresis from the isotherms of silica gels by boiling with HCl and then igniting to drive off the acid. At first sight the similarity between the two cases may not be apparent, but in the light of the recent experiments of Hurd and Merz (17) who studied the dialysis of sodium silicate, freshly formed silica sol, and silica hydrogel, it appears that the mechanism of altering the structures responsible for hysteresis might be quite similar. According to these workers the precipitated gel apparently contains what

is taken to be a sort of equilibrium amount of sol particles, small enough to dialyze through collodion membranes. The sol-particle concentration appears to be associated with a process closely analogous to chemical equilibrium since the slow dialysis will proceed so long as fresh water is provided to remove the inflowing particles. If, then, the aging process really effects a change in the structure of the colloidal particle, the structure of the whole gel might easily be modified by boiling merely with water for a short time. To the knowledge of the author, no such experiments of boiling in the absence of electrolytes have been carried out.

As was mentioned before, Taylor (30) determined a series of isotherms for the water-silica gel system, and reported a complete reversibility for the pressure-temperature relation. This would really have been predicted on the basis of all the theories mentioned in the last section. However, in a description of the experimental procedure, Taylor speaks of "flushing the surface of the evacuated samples with water vapor at elevated temperature", a procedure which may conceivably have altered the gel by a process similar to that discussed above.

The effect of the temperature of "activation" on the water-silica gel isotherms does not appear to have been adequately studied. van Bemmelen (6) in his original work made reference to the fact that a silica gel heated to red heat still gave the characteristic p-c relations. Berl and Urban (8), working with gels heated to 300° and 1000° for a period of 10 minutes also obtained the characteristic irreversibility. Patrick, Frazer, and Rush (25) studied the effect of two hour periods of heating air-dried gels at temperatures up to

1100° on the sorption of carbon tetrachloride vapor. No data were reported for desorption in this system. The results of the observations indicated that there was practically no difference between isotherms for samples activated below 900°; above this temperature the total sorption fell off rapidly to a very low figure at 1000°.

van Bemmelen, Berl and Urban as well as Patrick, Frazer, and Rush made use of a dynamic technique, employing a current of air.

Since it is believed that a systematic study of the sorption-desorption isotherms of water vapor on silica gel activated throughout a range of temperatures might be helpful not only in indicating something concerning the nature of the process of activation but also in shedding some light on the phenomenon of hysteresis, it is the object of the study described in the following sections to determine the isotherms for the gels so prepared.

E. DETERMINATION OF SPECIFIC SURFACE

The question of surface area may seem to have little connection with a discussion of hysteresis effects, but the somewhat nebulous nature of the gel structure would make the estimation of surface area of considerable importance in any sort of postulation concerning factors influencing gel behavior.

In general, surface area is derived by algebraic manipulation of some form of analytic expression of the sorption isotherm. Numerous such expressions relating pressure to sorbate concentration have been devised; some fit observed data in only very special cases, whereas other relations are sufficiently general to agree with essentially all

observed values, the generality, however, being a serious limitation on their usefulness.

During the past several years two important expressions of the sorption isotherm have been proposed (1) the so-called kinetic postulation of Brunauer, Emmett, and Teller (14) and (2) the "thermodynamic" expression derived by Harkins and Jura(16) from a combination of the linear relation of the surface pressure and surface area with the Gibbs isotherm for solid surfaces. Strikingly enough the isotherms show amazingly close agreement with each other as well as with experimental values, although apparently the form is quite different, Livingston (21) has pointed out in this connection, however, that he has been able at least in one case to show that the fundamental equation of the Harkins-Jura theory can be arrived at by a combination of the Brunauer Emmett-Teller equation with the Gibbs isotherm.

The Brunauer-Emmett-Teller (BET) isotherm leads to the evaluation of the surface area from the calculated value of adsorption corresponding to a complete monolayer. This value of single layer adsorption, called point "B" by the authors can be combined with values of molecular area to give the total surface. An analytical procedure advanced by Emmett for the location of "B" consists of plotting $p/(v)(p_0-p)$ versus p_0/p and determining the slope and intercept of the straight line function (14). From the relationship derived by BET,

$$\frac{p}{v(p_0-p)} = \frac{1}{V_m C} + \frac{C-1(p)}{V_m C p_0}$$

it is possible to evaluate V_m or "B". In order to calculate the area occupied by a molecule, these investigators assumed that the spacing of molecules of sorbate in the condensed film has the same value as the

spacing in a hexagonally close packed structure of the solidified or liquified vapor. The expression of the area occupied by a molecule becomes

$$\text{Area/Molecule} = 4(0.866) \left[\frac{M}{4(2)^{1/2} N \rho} \right]^{2/3}$$

where M is the molecular weight, N is Avogadro's Number, ρ is the density in the solid or liquid phase. A combination of the calculated molecular area with the value determined for "B" is then sufficient to give an estimate of the total surface area.

The method of Harkins and Jura stems from a combination of the observed relation

$$\pi = b - a\sigma$$

where π is the surface pressure, a and b are constants, and σ is the area occupied by a molecule, with the thermodynamically derived Gibbs adsorption isotherm for solid surfaces

$$d\pi = (RT/V\Sigma) (V/p) dp,$$

in which R is the gas constant, T the absolute temperature, V the molal volume, Σ the total surface area, the p the equilibrium pressure, to give the relation

$$\ln p = B + A/v^2$$

where A and B are constants and v the amount adsorbed. The dependence of A on the surface area can be seen to be a second power function from the correspondence

$$A = a\Sigma^2 v^2 / 2N_0 RT$$

where N_0 is Avogadro's Number. The surface area is proportional to the square root of A as

$$\Sigma = k A^{1/2}$$

in which k is a constant dependent only on the adsorbate and temperature and is determined by absolute methods from a consideration of heats of wetting of crystalline surfaces. The value of k given by Harkins and Jura for water vapor at 25° is 3.83, which when corrected for the temperature difference yields $k = 3.75$ at 12.00° . A can easily be determined by plotting $\log p/p_0$ against $1/v^2$, v representing volume of vapor measured at standard conditions.

EXPERIMENTAL

A. PREPARATION OF SAMPLES

In order to investigate the effect of the heat-treatment temperature on the water-silica gel sorption-desorption isotherm, it was necessary to study samples of gel identical in every other respect. To this end, great care was taken in the various steps of preparation to ensure that in so far as possible the only variable in the procedure was the temperature to which the gel was heated.

As starting material, a sample of moist silica gel was chosen which was allowed to come to equilibrium with moisture in the atmosphere. After several days the air-dried material was translucent and faintly opalescent, and although apparently dry presented an unctuous surface to the touch and yielded a slightly moist white powder when crushed.

Prior to the present experiments, one attempt had already been made to study the effect of heat-treatment temperature by isothermal examination of twelve samples of gel, six at a time. The slightly irregular results of these isotherms indicated that an unknown variable had been introduced into the experiment by activating the gels in two sets, i. e. activating each set just before introducing it into the apparatus. For this reason it was thought advantageous to treat both sets at the same time; consequently, the powdered gel was divided into twelve samples, each being placed in a marked porcelain crucible and then introduced into an electric furnace preheated to the desired temperature $\pm 10^\circ$. The samples were heated at their designated temperatures for periods of two hours, all twelve being placed in the furnace in as rapid succession as possible.

Since it was believed that a marked change in humidity occurring during the week between the beginnings of two successive runs in the previously described experiment possibly had in some way produced a variation in the properties of the heated gels, it seemed advisable to take steps to eliminate the effect of differing degrees of saturation during the necessary exposure of the heated gel to air before initial evacuation, by allowing the gels to equilibrate in air saturated with water vapor. The saturation was accomplished by placing the samples in marked weighing tubes in a desiccator through which was circulated a current of water-saturated air. The tubes were covered and removed twice weekly for weighing until the change in weight between three successive weighings was less than 1% of the original gel weight, a process requiring about six weeks. The wet material was then removed and allowed once more to come to equilibrium with the atmosphere prior to being placed in the apparatus.

The temperatures to which the gels were heated are 30°, 200°, 300°, 400°, 450°, 500°, 600°, 650°, 725°, 790°, 880° and 930°C.

B. APPARATUS

The isothermal sorption-desorption studies of the gels were carried out by means of a slightly modified form of the apparatus built by Milligan and Simpson; a description of the apparatus is given by Simpson (29) in a recent paper from this laboratory. Substantially, the modifications were those enumerated by Bushey(11) in his description of the arrangement used for determining isotherms at 10-15°C. Both discussions are excellent and provide a very concise picture of the apparatus as well as giving some detail regarding the various special

features devised to expedite the experimental procedure and increase the accuracy.

Essentially the apparatus consists of a means of suspending six samples and six McBain-Bakr fused-silica spring balances in a manifold of glass tubes, the lower ends of which are submerged in a constant temperature water bath controlled to within 0.001°C . by a sensitive mercury-toluene thermo-regulator in conjunction with an amplifying circuit and thyatron-operated heater. The extension of the springs is determined by the use of a traveling measuring-microscope scaled to 0.001 mm. , the measurement being sufficiently accurate to detect weight differences of 0.003 mg. , in accordance with a spring sensitivity of approximately 0.3 mm./mg. A Distillation Products two-stage oil-diffusion pump backed by a Cenco Hyvac rotary oil pump serves to reduce the pressure to 10^{-6} to 10^{-7} cm (indicated by an electronic ionization gauge) during the initial and final outgas periods; in addition the high vacuum provides a reference of "zero" pressure against which the sorbate pressure in the manifold is indicated as a differential on an oil manometer maintained at constant temperature and read with a cathetometer to 0.01 cm. This determination provides a measurement of the value of sorbate-pressure accurate to better than 0.01 mm. of mercury. The pressure of condensible vapors in the system is maintained extremely low by the use both of suitable absorbents and a liquid nitrogen trap connected in series with the diffusion pump. Quantities of sorbate from a pure source are added and withdrawn intermittently in small amounts, allowing sufficient time between successive operations to permit the establishment of constant conditions.

The apparatus volume is approximately seven liters, the large volume having been purposely introduced in order to eliminate Pidgeon's objections

to the use of intermittent addition and withdrawal of sorbate for following sorption-desorption cycles in a small apparatus. It is believed that the almost negligible total sample volume of 1.8 ml. together with the small pressure increments or decrements employed is sufficient precaution to maintain the objectionable phenomena below measurable limits.

C. PROCEDURE

A similar situation obtains in connection with a description of the apparatus. A detailed discussion of the general procedure necessary in obtaining values of the amount of sorbate taken up as a function of the sorbate-pressure has already been given (11), so that a brief review will suffice here.

After the gels had been heated, saturated, and returned to equilibrium with the atmosphere, six were selected over the entire temperature range (30°, 200°, 400°, 600°, 790°, and 930°C.) in order to make both runs as nearly alike as possible. The remaining six gels were left exposed to the air.

Six aluminum buckets prepared from aluminum foil, treated with concentrated nitric acid, washed and dried, were placed empty on the silica springs and the deflections recorded. The buckets were then filled with gels, a sample of each being transferred simultaneously to an ignited, weighed porcelain crucible. Each filled bucket was replaced on its respective spring, the corresponding deflection noted, and the sample-containing crucible re-weighed with the least possible lapse of time between each operation. The crucible was subsequently ignited to constant

weight in order to provide an analysis of the original water content. When all six buckets had been replaced on their silica balances, and the deflections noted, the samples were ready for evacuation of the apparatus.

During the initial evacuation period a number of precautions were found necessary. In order to provide a degassed source of water vapor, a tube containing $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, which connects to the sorption manifold through a grease-seal stopcock, was surrounded by a bath of liquid nitrogen and the stopcock opened. The Hyvac pump was put in operation and by means of a second stopcock, the pressure in the manifold decreased slowly enough to prevent "bumping", an effect which had appeared especially noticeable in previous experiments. After the fore-pressure had attained a sufficiently low value, the diffusion pump heater was energized. Several hours pumping sufficed to bring the pressure within range of the ionization gauge with which the course of evacuation was then followed. The gels were outgassed at the low pressure until, upon being closed off from the vacuum system for an hour, the manifold developed no pressure which could be detected on the oil manometer, and no change in spring deflection was observed during a similar period under outgas conditions; the evacuation required about twelve hours pumping at the lowest pressure attainable.

When it was considered that the degassing operation had proceeded sufficiently far, the manifold was closed off from the vacuum system and the deflections corresponding to "zero" pressure were read. The liquid nitrogen bath was removed from the $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ tube and the air-free crystals warmed electrically to decompose the hydrate and expel

the vapor. After a quantity of water had distilled into the manifold, the heater was turned off and the intervening stopcock closed.

The sorbate pressure in the manifold was recorded at short intervals until no further change could be detected in either the manometer differential or spring extensions. After the lapse of sufficient time to prove the existence of stable conditions, the spring deflections and sorbate pressure were recorded. More vapor was then added to the system and the process repeated to obtain a second point on the sorption curve. Further repetition of the process traced the sorption branch.

After equilibrium at saturation, desorption was accomplished intermittently by allowing water vapor to bleed off slowly into the vacuum system where it was absorbed and condensed. The terminal point on the desorption curve was finally attained by several hours outgassing under high vacuum conditions.

A slight simplification has been made in the method of calculation described by Bushey, the use of which makes possible the elimination of two weighings as well as any consideration of the spring sensitivity calibration. The procedure is founded on the observed fact that the spring extension is linear with the applied load within measurable accuracy over the range involved. If, then, the deflection is measured twice, once with the bucket empty and again containing the added sample, the deflection corresponding to the sample weight at atmospheric conditions is proportional to the difference between the two values. If the analysis for water content is known, the deflection corresponding to a dry sample would then be proportional to the deflection due to the

wet sample multiplied by one minus the weight fraction of water present plus the deflection due to the empty bucket. A value $\frac{x}{m}$ (mass of sorbate/mass of dry sorbent) can be calculated for any observed deflection since x is proportional to that deflection minus the dry deflection and m is proportional to the deflection due to the dry weight of sample.

Mathematically,

If D_E is the deflection with the bucket empty

D_F is the deflection with the bucket containing gel under atmospheric conditions

y is the weight fraction of water in the gel under atmospheric conditions

D is any observed deflection, then

$$\frac{x}{m} = \frac{D - [(D_F - D_E)(1 - y) + D_E]}{(D_F - D_E)(1 - y)}$$

Example:

The observed spring deflection with bucket A empty was 7.143 mm. and with this bucket containing gel heated to 300° was 31.371 mm. Some of the same gel was placed in an ignited crucible weighing 8.5956 g. resulting in a combined weight of 9.3128 g. before ignition, this weight being reduced to 9.140 by a number of hours heating to 1025°C. The observed deflection of the spring at 8.05 mm. water vapor pressure was 38.976 mm.

$$\frac{x}{m} = \frac{38.976 - [(31.371 - 7.143) \frac{(1 - \frac{9.3128 - 9.140}{9.3128 - 8.5956})}{(31.371 - 7.143)} + 7.143]}{(31.371 - 7.143) \frac{(1 - \frac{9.3128 - 9.140}{9.3128 - 8.5956})}{9.3128 - 8.5956}} = 0.57455$$

The results of calculations made in this way were shown to agree with good precision with those based on the more involved use of weighings

and sensitivity values.

D. ISOTHERMAL PRESSURE-CONCENTRATION RELATIONSHIPS

The values of grams of sorbed vapor per gram of dry silica gel are given below in both graphical (Figures 1-12) and tabular form (Tables I and II, Appendix i and ii). It will be seen that there is manifested a marked hysteresis throughout the entire set of samples, the phenomenon becoming even more pronounced as the "activation" temperature is raised until temperatures are reached at which the sorptive capacity becomes almost negligible.

Another point of interest is the regularity with which the total sorptive capacity and specific surface area decrease with increasing temperature, and for this reason the isotherms provide basis for consideration of application of the theories of Brunauer, Emmett, and Teller and of Harkins and Jura. Since each theory leads to an estimation to the total available active surface area, it will be interesting to compare the values derived both by consideration of analytical determinations of the pressure and composition corresponding to a complete monolayer, and by calculations involving assumptions regarding the condensation of vapor on surfaces in the form of compressible films.

By the use of procedures described in section I-E, the specific areas have been calculated by both methods for eleven of the gels, and corresponding values show remarkably close agreement. The plot of surface area per gram versus temperature of heat treatment (Figure 13)

exhibits this striking parallelism.

A more critical comparison of the gels may be secured by an application of the Kelvin equation. If instead of plotting x/m versus p , the quantity sorbed is expressed as volume V , and graphed as a function of the uncorrected radius, R (i.e. the radius calculated neglecting the thickness of adsorbed layers), corresponding to pores in which condensation is assumed to take place by virtue of vapor pressure lowering in small capillaries, an isotherm similar to the original is obtained since in effect we are now plotting x/m versus $\log p/p_0$. If now the function dV/dR is plotted against R , a curve is traced in which the value of dV/dR for the desorption branch should be an indication of the frequency of occurrence of a pore of radius R , if we are to accept both the Kelvin Equation and the popular belief that desorption is essentially evaporation of capillary condensed vapor. The ascending branch would have the same meaning viewed under the hypotheses of the Constricted Pore Theory, the function dV/dR then corresponding to the frequency of occurrence of constrictions of radius R .

Graphs of V/m versus R , and dV/dR versus R are given for eleven of the gels in Figures 14-24. Values of dV/dR calculated from the desorption branch all show a pronounced maximum at values of pore radius between 28 and 30 Å, whereas corresponding plots (not shown in the figures), determined from the sorption branch show very little more than a smooth distribution over the entire radius range, with a peak occurring in the curve from only one sample, the gel not exposed to elevated temperatures.

X-ray diffraction examination reveals that the entire series of

gels is amorphous, a fact which is especially interesting in view of the almost complete destruction of sorptive capacity effected by treatment at the higher temperatures. This observation is in agreement with previous knowledge that 10 to 15 hours treatment at temperatures over 1000° are necessary to produce sufficient regularity in the silica structure to manifest even broad bands in the diffraction pattern.

One other fact, which might be of interest to those postulating a swelling theory, was observed in a previous experiment for determining water vapor isotherms on a set of activated silica gels. This has to do with the tendency of the samples to "bump", i.e. to decrepitate violently as the external pressure is reduced. The effect becomes especially noticeable in samples activated at the intermediate temperature ranges, 600° to 725°, and is most violent at pressures on the desorption cycle ranging from 4 to 5 centimeters of mercury. The effect might be regarded as an indication that the gel structure becomes increasingly inelastic as the "activation" temperature increases, possibly becoming sufficiently rigid at higher temperatures to withstand the internal pressure.

DISCUSSION

As has already been mentioned in a cursory examination of data given in the preceding section, several striking facts are at once apparent: (1) the surface area and total sorptive capacity, which are both initially high, are diminished in a regular fashion by heat treatment, (2) the percentage reduction of surface area is considerably greater than the corresponding diminution in internal volume, and (3) whatever the mechanism of hysteresis, it is evident that the effect is not decreased but rather augmented by heat treatment.

A comparison of the observed decrease in total sorption with results obtained in the previously mentioned work done by Patrick, Frazier and Rush (25), in connection with the effect of heat treatment on the sorption of carbon tetrachloride vapor by silica gel, reveals that while sorption obtained with the aqueous sorbate begins decreasing at a moderately low temperature, the carbon tetrachloride sorption maintains an almost constant value until the temperature is raised above 900°. It is seen, too, that the liquid volume of the sorbed organic vapor is always much less than the corresponding value obtained with water. Such behavior differences could be explained by assuming that part of the structure responsible for sorption is large enough to accommodate water molecules, but too small to be penetrated by those of the larger CCl_4 . If we assume then, as Patrick, Frazier, and Rush do, that the finer structures are more easily affected by heat, a modification of the small pores would not affect the CCl_4 sorption until the effect had progressed sufficiently far to destroy the structure which accommodates large molecules; from similar reasoning, it would be expected that the supposedly finer water-sorbing pores would be attacked at lower temperatures.

Now let us examine the results in connection with hysteresis. A discussion of the observed phenomena in view of the classical theories might aid in revealing what additional requirements of hypothesis result from the experimental facts. The Constricted Pore Theory, for example, must be able to show how hysteresis can be exhibited by gels activated at temperatures high enough to destroy most of the sorptive capacity. If truly such constricted pores exist, the effect of heat must be a selective destruction of those with the smaller bodies. This can be seen from the v/m versus R curves which show that the radius corresponding to a maximum slope, i.e. maximum frequency of occurrence, has essentially the same value for all of the gels and is thus independent of the temperature, but that the radius corresponding to a maximum slope in the sorption branch slowly rises with increasing temperature of heat treatment. The fact that the main sorption curve of the heated gels lies displaced on the pressure axis by an increasingly large value indicates that sorptive activity is the result of large capillaries into which condensation is taking place. In the process of desorption, however, the pores apparently empty at a common pressure independent of the temperature. Since it is difficult to see how a constricted capillary can be rendered inaccessible by any other expedient than that of closing it, this would imply that the large part of the pore be more vulnerable than the constriction; yet at the same time, as we have already considered, the smaller the pore seemingly the more vulnerable the capillary is to closure. These two requirements seem to be almost contradictory.

A consideration of the Open Pore Theory in the light of present findings is little more profitable. This hypothesis postulates that

meniscus formation in an open capillary is delayed until the sorbed layer becomes sufficiently thick to bridge the diameter; this may not occur until the relative pressure has greatly exceeded the vapor pressure of a hypothetical column of liquid in the capillary. Once the meniscus is formed, however, the desorption will take place at a lower pressure corresponding to the vapor pressure over the curved meniscus. It was shown in the preceeding paragraph that the relative pressure at which the greatest amount of sorption takes place is greater the higher the heating temperature; from the hypothesis of the Open Pore Theory this would indicate that the capillaries possessing the characteristic of being most easily bridged by a layer of molecules were rendered inaccessible. There are two possibilities here. Either the pores having surfaces which would sorb many layers at low relative pressures are destroyed at high temperatures, or the smaller pores were either destroyed or enlarged. Since the total sorption was greatly reduced, it is not likely that any substantial number of pores were enlarged. During the desorption portion of the cycle, the vapor pressure of the sorbed liquid was very close to that obtained with unheated gel. This fact would indicate that the diameter of the pores was not essentially different in the two samples. This eliminates the proposed possibility of destruction of smaller pores. The remaining possibility appears to be somewhat more substantial since it assumed only a deactivation of active sorbing centers on capillary walls, centers which were necessary for the building up of a sufficiently thick multilayer to form a meniscus. The explanation, on the other hand does not account for the decrease in total sorption volume without further hypothesis concerning the effect of heating.

In passing, it would seem important to mention in connection with the views discussed above, that it can not readily be assumed that any type of capillary which is easily destructible and not involved in hysteresis phenomena is responsible for the decrease in total capacity, since well over 70% of sorbed vapor is taken up irreversibly.

The notion set forth by the Incomplete Wetting Theory embodies the assumption of capillaries, the surfaces of which have a contact angle with water greater than zero. The vapor pressure of the liquid depends on the radius of curvature of the meniscus, and therefore is dependent on the direction of motion of the liquid vapor surface with respect to the capillary wall. The theory can account reasonably well for the observed fact that increases in the activation temperature should be followed by a raised condensation pressure provided the assumption is made that heating tends to increase the hydrophobic nature of the capillary walls. Thus a higher pressure is required to condense vapor into the vapor-liquid meniscus in a heated sample, since this interface is advancing on a more difficult wet surface, and is therefore less convex than that present under corresponding conditions in the unheated gel. After saturation, when all the pores are filled, the receding meniscus assumes the radius of the pore, which is taken to be unaltered, and exerts the vapor pressure characteristic of this curvature. This accounts for the unchanged desorption pressure and the enhanced hysteresis, but does not indicate by what process the greater part of the total capacity may be rendered inactive.

The remarks above indicate that none of the theories discussed adequately account for the observed phenomena. Better agreement could

be achieved by modification of the concepts to account for (1) the process seemingly analogous to sintering by which the surface is decreased, (2) the relatively larger decrease in surface area than in total sorption volume, and (3) the apparent enhancement of hysteresis arising from an increased condensation pressure but almost unchanged evaporation pressure.

SUMMARY

1. For the purpose of studying sorption-desorption hysteresis and related phenomena, a set of twelve silica gels was prepared. These gels, all as nearly alike as possible were subjected to a heat treatment at various temperatures throughout a range from 30° to 930°C.

2. Isothermal sorption-desorption studies of the system water-silica gel at 12.00° were carried out on the samples described in (1) by means of a vacuum apparatus constructed by Milligan and Simpson. The resulting isotherms not only confirm previously observed hysteresis, but show that the effect is enhanced by moderate heat treatment, and that it persists even after the greater part of the sorptive capacity is thermally destroyed.

3. The procedure advanced by Brunauer, Emmett, and Teller for estimating surface area ~~from sorption isotherms has been employed in calculating the specific area~~ from sorption isotherms has been employed in calculating the specific area of the various samples. The area has been found to decrease in a regular way with increasing heat-treatment temperature.

4. The new surface-area method of Harkins and Jura was also used to calculate the specific areas, and a graphical comparison of areas calculated by this and the method mentioned in (3) indicates a striking agreement between the two.

5. By the assumption that the Kelvin Equation can be extended to capillaries of amicroscopic dimensions, structure and pore distribution curves have been calculated for eleven of the heated gels. These data

indicate that capillary size is substantially independent of the heat-treatment temperature.

6. A brief review of theories of sorption-desorption hysteresis has been made, and in order to clarify the meaning of the hypothesis, consideration has been made of their relation to phenomena reported in the literature.

7. Application of the various classical theories to explain the observed phenomena arising from heat-treatment shows that all the hypotheses must be modified to account for the facts. A satisfactory hypothesis must explain the following effects: (1) the decrease of surface area with increase in heat-treatment temperature, (2) the relatively larger decrease in surface area than in total volume adsorbed, and (3) the enhancement of hysteresis observed in gels subjected to moderately elevated temperatures

TABLE I

Pressure Mm. Hg.	x/m Gel 30°	x/m Gel 200°	x/m Gel 400°	x/m Gel 600°	x/m Gel 790°	x/m Gel 930°
0.00	0.05445	0.05241	0.04969	0.03933	0.02537	0.00594
0.72	0.08976	0.08915	0.08136	0.06376	0.03899	0.00666
1.76	0.11321	0.11301	0.10331	0.08346	0.04967	0.00673
3.59	0.14789	0.15000	0.13612	0.11384	0.06692	0.00802
4.89	0.18409	0.18850	0.16945	0.14643	0.08252	0.00945
5.60	0.21039	0.21671	0.19501	0.21660	0.09953	0.00914
6.41	0.25969	0.26868	0.24134	0.21763	0.12773	0.00935
7.23	0.36368	0.39178	0.33280	0.30475	0.18862	0.01501
8.41	0.69877	0.70467	0.58110	0.51426	0.35654	0.02694
8.73	0.81085	0.80637	0.70852	0.62789	0.44709	0.03395
10.53	0.89138	0.91022	0.83500	0.77323	0.53588	0.05318
10.38	0.86053	0.88180	0.82043	0.75120	0.52198	0.03552
9.15	0.82647	0.81994	0.79478	0.72775	0.50649	0.03038
7.97	0.76430	0.77058	0.76051	0.70546	0.49297	0.02149
7.33	0.61764	0.66053	0.67193	0.63938	0.43436	0.01267
7.11	0.40436	0.45041	0.56720	0.50960	0.31707	0.01158
6.78	0.29901	0.33012	0.33176	0.34777	0.19488	0.01029
6.01	0.23352	0.24466	0.23104	0.21540	0.12130	0.00970
4.43	0.17041	0.17433	0.15961	0.13305	0.07720	0.00929
2.84	0.13923	0.13885	0.12865	0.10250	0.06162	0.01174
1.83	0.12055	0.11877	0.11045	0.08543	0.05218	0.01155
1.135	0.10678	0.10357	0.09652	0.07236	0.04183	0.01048
0.00	0.05762	0.05402	0.05116	0.03974	0.02542	0.00781

TABLE II

Pressure Mm Hg.	x/m Gel 300°	x/m Gel 450°	x/m Gel 500°	x/m Gel 650°	x/m Gel 724°	x/m Gel 880°
0.00	0.05030	0.04253	0.04517	0.03676	0.03177	0.01434
1.38	0.10402	0.08717	0.08685	0.07171	0.05800	0.02189
3.06	0.13360	0.11420	0.11582	0.09485	0.07787	0.02394
4.29	0.16071	0.13879	0.14093	0.11972	0.09606	0.02697
5.56	0.20369	0.17891	0.18033	0.15791	0.12891	0.03074
6.34	0.25221	0.22404	0.22624	0.20111	0.16756	0.03528
7.175	0.34906	0.31011	0.30804	0.28314	0.24165	0.04637
7.66	0.45877	0.40235	0.39492	0.36959	0.32063	0.06111
8.05	0.57455	0.51300	0.50983	0.47801	0.41797	0.07733
8.85	0.79399	0.74981	0.74392	0.68133	0.59891	0.15732
9.43	0.81269	0.77203	0.76966	0.69726	0.61221	0.20291
10.53	0.87646	0.82027	0.80722	0.73038	0.64147	0.2207
8.99	0.80833	0.76584	0.76509	0.69362	0.60854	0.20060
8.16	0.79008	0.75089	0.75191	0.68511	0.60229	0.18985
7.48	0.69852	0.68251	0.68923	0.63390	0.53521	0.13600
7.23	0.53935	0.55678	0.58275	0.53880	0.44134	0.05638
7.00	0.38567	0.38377	0.42452	0.42070	0.32581	0.04279
6.67	0.30029	0.27726	0.29930	0.29655	0.22923	0.03748
4.23	0.16175	0.13951	0.14322	0.11999	0.09886	0.02759
3.26	0.13945	0.11675	0.12289	0.10057	0.07915	0.02793
1.86	0.11357	0.09761	0.09263	0.08374	0.06214	0.02364
1.28	0.10137	0.08729	0.08483	0.07068	0.05541	0.02135
0.795	0.08978	0.07521	0.07513	0.06216	0.04895	0.01916
0.00	0.05109	0.04282	0.04538	0.03717	0.03168	0.01335

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Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

500°

Figure 6.

Figure 7.

Figure 8.

Figure 9.

Figure 10.

Figure 11.

Figure 12.

Figure 13.

Figure 14.

Figure 15.

Figure 16.

Figure 17.

Figure 18.

Figure 19.

Figure 20.

Figure 21.

Figure 22.

790°

Figure 23.

Figure 24.