The Adsorption of Water Vapor on Silica Surfaces, by Direct Weighing

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Two general methods have been used to measure the adsorption of vapors on solids: the measurement of reduction in pressure caused by adsorption of part of the vapor, and measurement by direct weighing with some type of microbalance.

In the former method fairly low pressures must be used, and the measurement of the dead space is of doubtful accuracy when finely powdered adsorbents are used. A number of attempts have been made to measure adsorption by direct weighing. Probably the most successful of these were made with the quartz fiber spring balance of McBain and Bakr.[1] This is, however, of insufficient sensitivity for measuring the adsorption on silica surfaces. Other attempts to measure this small adsorption by some direct weighing method have been unsatisfactory on account of difficulties mentioned below.

The measurement of adsorption of water vapor on silica requires a balance having a sensitivity of 10^{-7} g. with a capacity of about half a gram of adsorbent. The main difficulties to be overcome are errors due to electrostatic effects, vibrations from the floor, changing zero point, and the adsorption on the balance itself. Much of the preliminary work in the design of the balance used in this research was done by Messrs. Barrett and Cohen. The final design which overcame these difficulties and the measurements described in this paper were made by A. W. Birnie. A modification of the original design used in determinations of heavy water has been described by Barrett.[2]

The apparatus consists of a long-armed, horizontal, hollow glass balance beam supported at the center by a fine tungsten torsion filament. An electrically shielded and grounded basket is hung at one end on another horizontal filament. An increase in the weight of the basket is determined by the movement of a pointer at the other end of the beam, read by a microscope. An iron rider inside one arm of the balance moved by a solenoid and observed through another microscope serves to calibrate the instrument. The balance rests in a water-jacketed, evacuated glass tube fitted at one end with a large ground glass stopper for inserting and removing the basket, and at the other end with

(1) J. W. McBain and A. M. Bakr, THIS JOURNAL, 48, 690 (1926).
(2) H. M. Barrett, C. H. Best and J. H. Ridout, J. Physiol., 93, 367 (1938).

the apparatus necessary for evacuation, admission of water vapor, and measurement of pressure. The inner surface of the tube is coated with a grounded silver mirror in which windows have been cut for viewing the pointer and rider. The balance is shown in Fig. 1.
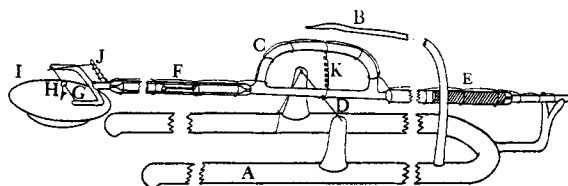

Fig. 1.—The adsorption of water vapor on silica surfaces.

The stand, A, made from 5-mm. soft glass rod, and coated with a silver mirror, touches the balance tube at four points, namely, the three small feet and the glass spring, B, which holds the stand in place. The glass arch, C, prevents the sagging of the beam when the seal is made to the torsion fiber, D, a tungsten wire 0.017 mm. in diameter.

The seal is made by heating the glass with a small torch until it flows readily, removing the flame, and quickly lowering the balance onto the wire. In this manner oxidation of the tungsten wire is reduced to a minimum.

The pointer half of the beam is a thin-walled glass tube which contains firmly sealed at one end a platinum compensating weight, E. The pointer consists of a short length of 0.05 mm. tungsten wire. The other half of the beam is made of a thin-walled glass tube (1.5 mm. in diameter) sealed within another glass tube (about 2 mm. diameter) and enclosing the rider, F, weighing 0.0310 g. The rider is constructed with triangular end-pieces so arranged that it always rests on three points of contact. Between the two concentric tubes is wedged a thin strip of photographic film bearing a mm. scale (not shown in the diagram). The purpose of this scale is to provide reference points from which to measure movements of the rider. This half of the beam terminates in a small glass fork bearing a suspension, G, to the center of which is sealed a small glass bead, H, bearing a hook of fine tungsten wire. The hook is so bent that any displacement of the load on the hook will be parallel to the suspension.

In order to eliminate electrostatic charges on the balance, and to ground the basket, the beam was wound with fine platinum wire (0.08 mm. diameter), successive loops being about 8 mm. apart. This wire was connected to the platinum basket and shield, I, through a fine platinum wire fastened to the bar, J, and pressing lightly against the end of the suspension, G. The suspension was electrically connected to the basket by means of a small strip of platinum foil pinched onto the suspension and onto the shaft of the hook sealed into H. The platinum beam windings are connected to the center suspension by a small platinum helical spring, K, hooked to the suspension at the center seal. The center suspension is connected to the silvered

stand through a platinum ribbon pinched on the suspension at the outer seal and wound around the stand. The stand rests on the grounded, silvered surface of the balance tube, thus maintaining the balance stand, beam windings, basket, and shield at zero potential. An additional precaution was taken by placing a roll of fine copper gauze, connected to the ground, in the line admitting vapor to the balance tube. The basket which contains the adsorbent during an experiment consists of a small platinum pan about 20 mm. in diameter and 4 mm. deep, constructed of thin foil, shielded by the circular disk of platinum foil slightly larger than the pan.

The balance tube is lagged with felt, and water from a thermostat, kept at constant temperature to within 0.01°, is pumped through the jacket, from the center to the two ends. The balance tube is supported on a table the legs of which rest on a series of wooden slabs, 5″ × 5″ × 1″, separated by short lengths of pressure tubing. This eliminates practically all vibrations coming from the concrete floor. Vibrations in the water jacket caused by the water pump are removed by passing the water line into the top of a two liter bottle, with an air space at the top. It was necessary to mount the microscopes on a separate table so that the balance table would not be disturbed when a reading was being made.

Determination of Sensitivity.—The balance is loaded with the basket and a fused silica counter weight to take the place of the adsorbent. The balance tube is evacuated to a pressure of about 10 mm. By means of the solenoid the rider is moved along the beam until the balance is swinging freely. When the balance has come to equilibrium, the pointer position is read by means of a microscope with eyepiece scale and the position of the rider relative to a line on the mm. scale is determined by means of a similar microscope. The rider is now moved through a small distance and the positions of the rider and the pointer again observed. From the weight of the rider and the distance of the center suspension from the basket (205 mm.) the change in load corresponding to a given pointer movement may be calculated. Such determinations of sensitivity were made over the whole range of the pointer swing. The results of several determinations of sensitivity in grams per scale division ×10⁷ were: 2.58, 2.81, 2.81, 2.83, 2.82, 2.75, 2.74, 2.85, 2.80, 2.80. One scale division corresponds to a pointer movement of 0.01 mm. A slight displacement of the center suspension from a horizontal position did not alter the sensitivity. The sensitivity could be adjusted readily by bending the basket-end of the beam near where the fork is attached, thereby raising or lowering the center of gravity. Sensitivities as high as 10^{-9} g. per division could be attained, but without better temperature control this increased sensitivity is valueless.

Electrostatic Effects.—In the study of previously constructed balances, which had not been equipped with ground wires, tests were made for the presence of electrostatic effects by introducing a flat electrode under the basket. This electrode was insulated from the balance tube and, by means of suitable connections through wires sealed through the large glass stopper, could be charged to a potential above or below that of the mirror. In one case, for instance, with a charge of +45 volts the basket moved down 78 divisions and with a charge of −45 volts the

movement was up 56 divisions, showing that the balance was electrically unsymmetrical. Contrary to expectation the admission of water vapor was found to enhance the electrical asymmetry. This enhanced effect died down in time but the introduction of radioactive material did not appreciably hasten the decrease in the amount of asymmetry.

Repetition of these experiments on the grounded balance showed that the effects had been considerably reduced but the action of the balance was still electrically unsymmetrical. This, however, was found to be completely removed when the size of the mirror windows was cut down, which was accomplished by sliding a cylindrical shield of gold-plated copper into the balance tube between the balance and the silvered wall. The shield had small windows, 8 × 20 mm., cut out for viewing the rider. It appears that the previously encountered electrostatic effects were due not so much to the presence of charges on the balance but chiefly to charges resident on the unsilvered windows which were about five times the size of those cut in the shield. Since the introduction of the shield there has been no evidence of electrostatic effects even after the sudden admission of water vapor.

Temperature Effects.—It was found that changing the temperature of the balance as a whole by 1° changed the pointer reading by four divisions, while changing the temperature difference between the two ends of the balance by 1°, by cutting down the outflow of water from one end of the jacket, resulted in a pointer change of 40 divisions. The fact that the latter was very nearly the change calculated from the coefficient of expansion of the balance arm shows that the effect of convection currents is negligible. Since the temperature of the balance as a whole was regulated to within 0.01°, temperature effects are negligible. To eliminate any temperature differences in the tube due to radiation the lighting was cut down to a minimum and the light for illuminating the pointer was filtered through a water cell.

Pointer Shifts Due to Changing Room Temperature.—Changes in room temperature changed the relative height of the microscope table and balance table and also caused slight tilts in the latter. The slight tilting was avoided by keeping the room temperature constant to ≈1° and correction for the remaining slight change in relative height of the tables was made by means of a series of reference points (a grid of platinum wire) fixed inside the balance tube near the plane of the pointer movement.

Blank Effect of Water Vapor on the Balance.—This is a combination of adsorption effects due to slight differences in area and quality of surface, on the two ends of the balance, and buoyancy effects due to differences in volume. At first the blank adsorption was found to be rather large. After washing the balance in turn with water, alcohol, ether, alcohol, water, the blank water vapor effect was reduced to about 3×10^{-6} g. at 25 mm., and was quite reproducible when the evacuation was carried out for the same length of time. The blank water vapor effect on the balance as well as the time–adsorption relationships for the balance are shown in Fig. 2.

In carrying out the time–adsorption experiment on the balance the system was only evacuated to a pressure of 0.02 mm. due to trouble with the vacuum pump. On

admission of water vapor to 10.6 mm. the change in pointer reading was 6 divisions after one-half hour. Since previous experiments on the balance, in which the evacuation had been completed, had shown a change of 10 divisions under these conditions, the readings in the time–adsorption experiments were increased by 4 divisions to make them consistent with the results plotted in the first part of Fig. 2.

Sorption of Water Vapor by Ground Fused Silica. Preparation and Sizing of Adsorbent.— Clear fused silica rods (Vitreosil) were crushed with as little grinding motion as possible in an agate mortar. The ground material was shaken in a set of bronze sieves until each size-fraction was as uniform as possible when viewed under the microscope. It was found that even prolonged shaking was inadequate to eliminate entirely a small amount of very fine particles which clung to the larger particles. These were removed by blowing filtered air through a sample of the powder held between sieves fine enough to retain the main size but which allowed the very fine material to be blown away. In this manner samples of no. 230–no. 270 mesh size were prepared.

Estimation of Surface.—On the assumption that the particles are cubes having the length of one side equal to the average size of the mesh openings for the no. 230 and no. 270 sieves (0.065 mm. and 0.053 mm.), the area per gram of adsorbent is 460 sq. cm. This figure is too small since it does not take into account any irregularities in particle size, shape, or surface roughness. An estimation of surface area taking into account irregularities both in size and shape was made. This estimation was based on the fact that for any solid body having no re-entrant angles, the average projection area of the body when randomly orientated is one-fourth of the actual surface area of the body (see previous paper).

The average projection of the particles was obtained by taking photomicrographs of the particles on a microscope slide. The photomicrographs were projected on a screen giving a magnification of about 440 diameters. The outlines of about 300 particles were traced on the screen and the areas of the outlines measured with a planimeter. The average projection area per particle was calculated and found to be 6.13×10^{-5} sq. cm.

In order to ensure that there was random orientation of the particles on the slide, determinations were made with the particles suspended in several different ways. In one experiment a microscope slide was painted with a sus-
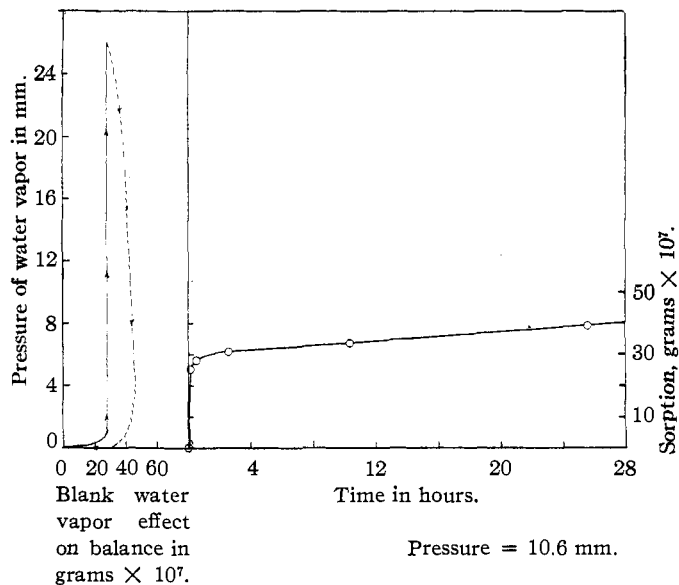

Fig. 2.—Time–sorption effect on balance at $T = 30.1°$.

pension of the particles in hot agar solution, the slide being rotated about two axes at right angles until the gel had set. In another experiment the powder was lightly sprinkled onto a slide bearing a thin coating of stiff grease. In a third method successive layers of particles were picked off a pile of powder by carefully lowering greased cover glasses until they just touched the top of the pile. When the top of the pile had a small flat area the particles picked up were photographed. The average particle area determined by these methods agreed within 5%. The average area per particle was 24.5×10^{-5} sq. cm.

The number of particles per gram of powder was determined by weighing an evenly scattered layer of the powder on a thinly greased cover glass, and counting the particles in sample strips with a microscope. The average number of particles per gram was 2.275×10^{6}, agreement between different determinations was within 3%. The specific surface of no. 230–no. 270 silica was found to be 558 sq. cm. per gram. This value is slightly inaccurate insofar as it is based on the assumption that there are no re-entrant angles on the particles. Microscopic examination showed that this was not rigorously true, but certainly sharp re-entrant angles were not common. A further objection is that this method does not take into account slight roughness in the surface. However, the determination serves very well to characterize the adsorbent used, and is a decided improvement over the usual estimates based on

the assumption that the particles are cubes. Experiments are being carried out on the adsorption of methylene blue by silica with a view to learning something about the roughness of broken silica surfaces.

Adsorption Measurements; Experimental Procedure.—In all experiments the temperature of the balance tube was kept at 30.1°.

A sample of silica powder, weighed to within 0.5 mg. of the weight of the silica counter weight was placed in the basket and the latter hooked onto the balance. The apparatus was evacuated to about 0.003 mm. and kept at this pressure for about twenty hours. After adjusting the rider until the balance was swinging freely, the apparatus was cut off from the pump and the position of the pointer observed. Water vapor was next admitted from a side-tube connected to the balance tube through a stopcock. After ten minutes the pointer position and pressure were again read. It was found that equilibrium between adsorbed water and the water vapor was rapidly established, no further change in pointer reading taking place other than a very slow change which is mentioned below. Similar readings were made at pressures increasing in steps of about 5 mm. every ten minutes until a pressure of about 25 mm. had been reached. The pressure was then decreased in a similar manner. At the conclusion of such an experiment the apparatus was evacuated for about twenty-four hours before the next experiment was carried out.

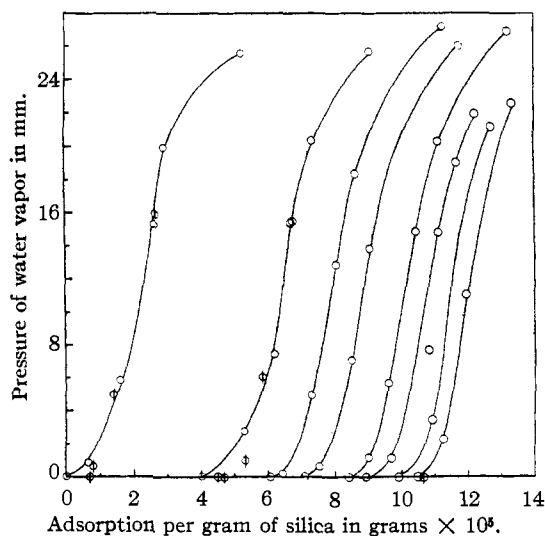**Acid-Washed Silica.**—The adsorption of water vapor at 30.1° on a sample of no. 230–no. 270 mesh

silica powder was measured at pressures ranging from less than 0.1 mm. up to 26 mm. Since it was later shown that the powder contained traces of metallic impurities (less than 0.01% copper by a rough colorimetric estimate) scoured from the sieves, these experiments on unwashed silica are not reported. The powder was warmed on the water-bath with concentrated nitric acid for fifteen minutes, then carefully washed with distilled water. The adsorption of water vapor on this sample is shown in Fig. 3. The results are corrected for blank water vapor effect and expressed in grams of water vapor adsorbed per gram of powder. In all cases the desorption curves retraced the adsorption curves except at low pressures. Examples of the desorption points ⊕ are shown on the first two and the last curves. Each curve shows therefore the rapid reversible adsorption. The reversible adsorption on the washed powder was about 35% less than on the unwashed powder. The distance between successive curves indicates a slow non-reversible sorption which takes place chiefly during the twenty-four hours at pressures below 0.01 mm. Thus each experiment was started with increasing quantities of non-reversibly sorbed water in the silica. The time between the first and second experiments was forty-eight hours; between the others, twenty-four hours. It will be noted that the isothermals for each experiment are of the same shape. This is better indicated in Fig. 4, in which the results of a number of experiments are plotted with the starting point of all the curves taken as zero adsorption. Fair agreement is obtained between different experiments. The
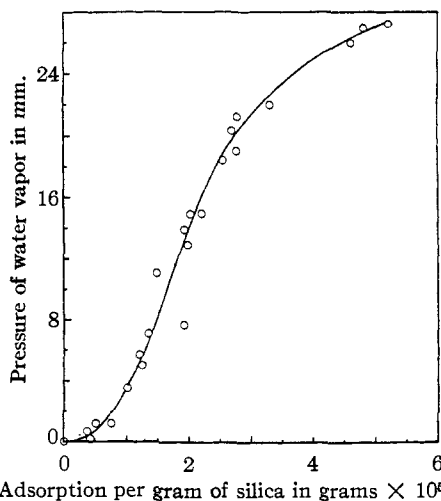

Fig. 3.—Adsorption on acid washed silica at $T = 30.2°$.

Fig. 4.—Adsorption on acid-washed silica at $T = 30.2°$.

nature of the increase in weight between successive experiments is discussed below under time–sorption experiments.

The decreased adsorption resulting from washing the silica with acid may have been due to removal of metals or to a change in the surface of the silica, or to both. Adsorption measurements were made on a powder from which the finest particles were gently blown out. The material was held between no. 270–no. 325 sieves and air gently passed through it. This treatment prevented contamination with metals but of course did not properly size the powder. The adsorption of water vapor on this powder before and after treatment with nitric acid was measured. The results showed that the acid treatment reduced the adsorption by approximately the same amount (about 42%) as had the treatment of a sieved sample known to contain traces of metal. The reduction brought about by washing the silica with acid is therefore chiefly due to a change in the surface. Since two lots of no. 230–no. 270 mesh powder, cleaned with acid, gave the same adsorption, it was thought best to use acid-treated powder for all the measurements.

Acid-Washed and Heated Silica.—The sample of silica used in the experiments reported in Figs. 3 and 4 was heated in a porcelain crucible to dull red heat for ten minutes. Immediately after cooling the sample was placed on the balance and the apparatus evacuated. The first adsorption

experiment after heating is plotted in Fig. 5 (curve 1) along with the adsorption isothermal for unheated silica (curve 2). The results of successive experiments are shown in the remaining curves of Fig. 5 in which the time of evacuation between each experiment was twenty-four hours.

Heating the silica reduced the reversible adsorption of water vapor by about 30% at 16 mm. but made little difference in the slow permanent sorption. There is some indication that the permanent sorption is here even more persistent than that on the unheated silica since in the last experiment (the eighth, Fig. 3) on the unheated silica the starting point for that experiment was very nearly regained on evacuation while after ten experiments on the heated silica the starting point was not regained.

Time–Sorption Experiments.—The last two curves but one in Fig. 5 are for experiments in which the water vapor was quickly admitted to a pressure of about 10 mm. and pointer readings were taken at intervals over a period of about twenty-four hours. The detailed results of these experiments are shown in Fig. 6, corrected for water vapor effect on the balance and for the small time sorption on the balance. The curve for the second experiment shows that the rate of sorption is rapid at first but after about twenty-five minutes falls off to a nearly constant rate of 2.2×10^{-7} g. per gram of silica (4×10^{-10} g. per sq. cm.) per hour. A slight falling off in this rate was observed after twenty-four hours but was not encountered in other experiments. It may be pointed out that this behavior is what would be expected if the process were a diffusion of water into the body of the silica. The rate of slow increase was practically constant in the two experiments as may be seen from the figure.
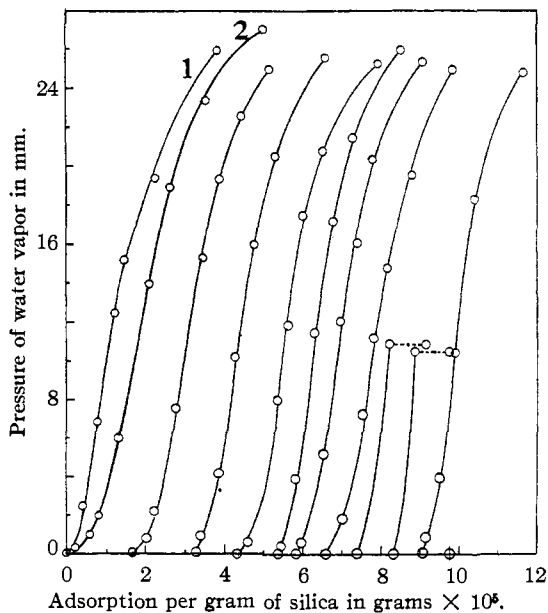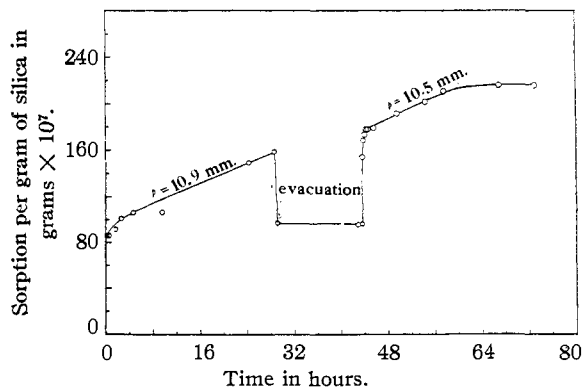

Fig. 5.—Adsorption on heated silica at $T = 30.1°$.

Fig. 6.—Time–sorption experiment at $T = 30.1°$.

Other experiments not shown in Fig. 6 gave approximately the same rate of slow sorption.

Rapid Sorption and Desorption.—The results of experiments on both unheated and heated silica indicate that the sorption of water vapor is chiefly made up of an almost reversible adsorption accompanied by a more permanent sorption. Most of the latter is too slow to affect the results of an adsorption–desorption experiment. However, the time–sorption experiments indicate that after the first rapid adsorption an appreciable further sorption occurs in the first half hour. Accordingly three experiments were carried out in which the first was made after tw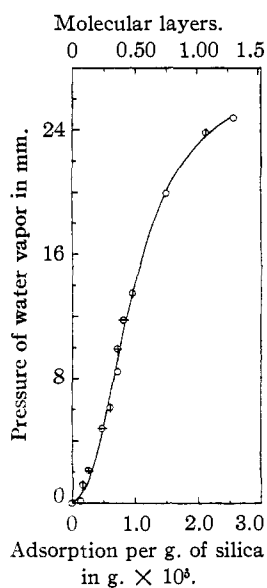enty-four hours of evacuation and the second and third were made in immediate succession and therefore without completely evacuating the system between them. The second and third experiments are shown in Fig. 7. The first showed slight hysteresis on desorption down to 0.01 mm., as well as slightly greater adsorption at the lower pressures than experiments 2 and 3. The second and third experiments were made from initial pressures of about 0.01 mm. of water vapor. It will be noted that the points for adsorption and desorption in these two experiments lie on the same curve. Thus, in order to avoid apparent hysteresis in adsorption and desorption experiments it is necessary either to perform the experiment extremely rapidly, which is impracticable, at least with our apparatus, or to precede the experiment by a similar experiment without a long intervening period at

Molecular layers.

Fig. 7.—O, Adsorption, expt. 2; ⊖, desorption, expt. 2; ⊕, adsorption, expt. 3; ⊕, desorption, expt. 3; all at 30.2°.

low pressure. The results shown in Fig. 7 are probably the most accurate measurements of the reversible adsorption between 0.01 mm. and 25 mm. water vapor, since time–sorption effects are reduced to a minimum. Assuming that each water molecule covers 8.4×10^{-16} sq. cm. the thickness of the adsorbed film in molecular layers was calculated using 558 sq. cm. as the area of 1 g. of 230–270 silica. At a pressure of 1 mm. the adsorption corresponds to 0.1 molecular layer, and at 23.2, to 1.0 molecular layer.

This research was done under the direction of Dr. F. B. Kenrick.

Summary

1. A microbalance of sufficient sensitivity for determining the adsorption of water vapor on silica surfaces has been designed. The usual difficulties due to electrostatic effects and shifting zero points have been overcome.

2. The adsorption of water vapor at 30° on powdered fused silica, 230–270 mesh, has been determined between 0.01 mm. and 26 mm. pressure. It consists of a rapid, reversible adsorption and a slow, non-reversible sorption, the limit of which could not be reached even after two weeks. Treating the silica with acid reduced the reversible adsorption by about 35%. Heating the acid treated powder to dull red heat reduced the reversible adsorption by an additional 30%.

3. A new method for estimating the approximate area of powders has been employed. From this estimate the reversible adsorption of water vapor at 30° on broken surfaces of fused silica has been determined as 0.1 molecular layers at 1 mm., up to a monomolecular layer at 23.2 mm.

4. A measurement of rate of permanent sorption showed that the rate fell off rapidly during the first twenty-five minutes and then became almost constant at 4×10^{-10} g. per sq. cm. per hour, as if the process were a diffusion of water into the silica.