The effects of catalyst poisons on sorption isotherms
by Seymour J Birstein

A THESIS Submitted to the Graduate Committee in partial fulfillment of the requirements for the degree of Master of Science in Chemistry
Montana State University

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The sorption isotherms of benzene and water on silica gel and the modification of each of these isotherms by the presence of varying amounts of the other vapor as a poison were studied in an effort to differentiate between adsorption and absorption in the sorption process.

From the modification of the curves in the presence of increasing amounts of poison, it was concluded that the sorption of water on silica gel is due to Capillary condensation and the Sorption of benzene on silica gel is due to monolayer adsorption followed by capillary condensation.

The apparatus and the techniques employed in running the isotherms are described. It is believed that these techniques can be extended to the study of systems other than that studied by us.

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I. ABSTRACT

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From the modification of the curves in the presence of increasing amounts of poison, it was concluded that the sorption of water on silica gel is due to capillary condensation and the sorption of benzene on silica gel is due to monolayer adsorption followed by capillary condensation.

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II. INTRODUCTION

Although the phenomenon of sorption was first observed more than 100 years ago, attempts to explain the process quantitatively have been more recent.

The terms "sorption", "adsorption", and "absorption" have been used by various authors often without adequate difinition or discrimination. As used in this discussion "adsorption" will refer only to the holding of molecules of a vapor or gas at a surface. "Absorption" will refer to the taking up of such molecules by other processes as, for example, by capillary condensation. The more general term "sorption" will be used where it is inadvisable or unnecessary to discriminate between the mechanisms by which sorbate molecules are held. Experimental data, in general, provide information only as to the total amount of vapor or gas retained by the sorbent without providing information about the relative contribution of the adsorptive and absorptive processes. In discussing such data it is considered preferable to use the noncommital "sorption" unless there is reason to specify one of these mechanisms.

LITERATURE SURVEY

Empirical Interpretations

One of the first empirical equations for the sorption isotherm was developed by Freundlich (23) on a purely empirical basis. The Freundlich equation, which makes no assumptions about the mechanism of sorption, can be written in the following form:

$$\frac{x}{m} = kc^{\frac{1}{n}} \qquad (1)$$

where $\frac{x}{m}$ is the weight of substance sorbed per gram of sorbent and c is equilibrium concentration of sorbate.

If the equation is written in the following way:

$$\log x/m = \log k + 1/n \ \log c \qquad (2)$$

and log x/m is plotted against log c on rectangular coordinate paper and a straight line can be fitted to the experimental data, then k and 1/n may be evaluated for the system. Since a straight line is obtained only for the first part of the sorption isotherm, the use of the Freundlich equation is limited to sorption at low pressures.

Polanyi (23) formulated a compressed film theory to explain sorption. According to Polanyi, a thick compressed film was formed on the surface of the sorbent. The compressed film theory assumed the existance of long range attractive forces which extended out from the surface of the sorbent and put the adsorbed gas or vapor under pressures which could amount to as much as 37,000 atmospheres near the surface of the solid. The compressed film theory has been largely abandoned because it has been shown that the forces acting between molecules are of very short range and incapable of exerting high pressures over considerable distances.

Theoretical Interpretations

The first satisfactory quantitative expression derived from assumptions concerning the mechanism of adsorption was that of Langmuir(14). Langmuir concluded that when adsorption occurs it is due to the accumulation of molecules in a surface layer. Unless the molecules which strike a solid surface rebound eleastically, there is a higher concentration of molecules on the surface of the sorbent than in the gas. Studies showed that a large proportion of the gas molecules striking a surface do not rebound elastically.

If μ represents the number of gram molecules striking each square centimeter of surface per second, α represents the fraction of molecules which condense upon striking the surface and θ represents the fraction of surface which is bare, the rate of condensation is equal to $\alpha\mu\theta$. The rate of evaporation of molecules from the surface is equal to the product of v_1, the rate at which the molecules would evaporate if the surface were completely covered, and θ_1, the fraction of surface covered.

At equilibrium

$$\alpha\mu\theta = v_1\theta_1 \tag{3}$$

Furthermore

$$\theta + \theta_1 = 1 \tag{4}$$

Therefore

$$\theta_1 = \frac{\alpha\mu}{v_1 + \alpha\mu} \tag{5}$$

The quantity θ_1 is a measure of the amount of gas adsorbed. At low pressures the amount of adsorbed gas is proportional to the pressure. At low temperatures the value of v_1 is small and the adsorption is large and nearly independent of the pressure. At higher temperatures the value of v_1 is large and the amount of adsorption is small and proportional to the pressure.

The tendency of a gas to be adsorbed is determined by v_1, the rate of evaporation from the surface; v_1 depends on the magnitude of the forces acting between the solid and the adsorbed substance.

The forces acting between the surface of the sorbent and the first layer of adsorbed molecules are usually much greater than those acting between two layers of gas molecules. Therefore, the rate of evaporation from a second or higher layer will be so rapid that only a monomolecular layer will be formed if part of the sorbent's surface is still uncovered.

The sorption isotherms obtained when nonpolar substances are sorbed on charcoal are curves which are satisfactorily described by the Langmuir equation. It is generally believed that these curves represent monolayer adsorption.

With other sorbents and sorbates isotherms of a strikingly different appearance are obtained. In the low pressure portion of the curve their appearance is much like that of the Langmuir isotherm. At higher partial pressures of sorbate, where the Langmuir curve is approaching asymptotically a limiting value, some curves swing rather sharply upward forming the well known S-shaped isotherm. It is also observed that when desorption as well as sorption isotherms are run on such systems, there is a typical hysteresis cycle.

It is apparent that Langmuir's hypothesis that adsorption results in the formation of a monolayer cannot satisfactorily explain these phenomena even if it is extended to the consideration of patches of varying activity on different portions of the surface.

Much of the recent work on sorption has been based on one or the other of two likely explanations. Emmett and his coworkers have based their explanation largely on the assumption of multilayer formation.

Others have preferred the explanation that these curves are due to monolayer formation followed by capillary condensation.

Patrick (9,17,18) and coworkers, working on the sorption of vapors on silica gel explained the curves which they found on the basis of solution of the vapors sorbed in the residual water of the gel followed by capillary condensation. The sorption, according to Patrick, depends only on the structure of the pores of the silica gel and there is no chemical inter-action between the sorbent and sorbate.

After a correction is made for the vapor dissolved in the residual water, the relationship between the volume of vapor sorbed and the pressure can be expressed by the following equation:

$$v = K\left(\frac{P\sigma}{P_o}\right)^{1/n} \qquad (6)$$

where v is the volume of vapor in cc. sorbed per gram of gel, P is the equilibrium pressure, P_o is the saturation pressure and σ is the surface tension. K and n are constants.

When working with substances like butane, which is insoluble in water, no correction has to be made for the vapor dissolved in the residual water of the silica gel. The volumes of different vapors sorbed by a sample of silica gel agree closely after corrections have been made for the solubility in residual water.

Cohan(7,8) has advanced a hypothesis to account for the hysteresis which is observed when sorption and desorption isotherms are plotted. He suggests that the sorption process involves condensation occurring along the walls of the interstices in an annular ring, while desorption occurs from a hemispherical meniscus.

Prior workers had calculated pore-sizes using the Kelvin equation relating condensation pressure and capillary radius:

$$\ln \frac{P_r}{P_o} = - \frac{2 \sigma \bar{V} \cos \theta}{r RT} \qquad (7)$$

here P_o is the saturation vapor pressure, P_r is the pressure of the vapor in equilibrium with liquid condensed in capillaries of radius r, σ is the surface tension of the liquid, $\bar{V}$ is the molal volume, and θ is the contact angle. According to Cohan desorption follows the Kelvin equation while sorption is described by the same equation modified by the omission of the numerical factor 2.

Cohan also concluded that no hysteresis would occur in capillaries having a diameter of less than four molecular diameters. From his assumptions regarding hysteresis, Cohan concluded that sorption is due to the formation of a monomolecular layer on the surface of the sorbent followed by capillary condensation.

Fineman, Guest and McIntosh(10), working on the sorption of water on carbon disregarded the monolayer formation, which they concluded was negligible for the particular system under consideration, and applied Cohan's equation to calculate the area of the carbon as the area of a system of capillaries.

Deviations from the Langmuir isotherm have been explained by some investigators on the basis of the formation of multimolecular layers of sorbate on the surface of the sorbent. Brunauer, Emmett and Teller,(4) working with the sorption of carbon monoxide on iron ammonia catalysts, developed their "Point B" method for determining the point on the isotherm corresponding to the formation of a monomolecular layer. They calculated the areas of the catalysts from their measurements, and checked the calculated areas with those obtained from the sorption of nitrogen and argon on the same catalysts. The maximum deviation from the calculated mean areas was less than five per cent.

A quantitative equation was later derived by Brunauer, Emmett and Teller(5) to explain the formation of multimolecular layers. This equation, which is a generalization of the Langmuir equation, makes the following assumptions:

(1) The rate of condensation on the bare surface is equal at equilibrium to the rate of evaporation from the first layer.

(2) At equilibrium the rate of condensation on top of the first layer is equal to the rate of evaporation from the second layer

(3) This argument can be extended to include an infinite number of layers.

(4) The heat of adsorption of the second layer is equal to the heat of adsorption of the third layer and each subsequent layer.

(5) The heat of adsorption of each of these layers is equal to the heat of liquefaction.

The equation obtained was the following:

$$v = \frac{v_m\, cP}{(P_o - P)\,[1 + (C-1)\;P/P_o]} \qquad (8)$$

where v is the total volume of vapor sorbed, v_m is the volume necessary for a complete monomolecular layer, P is the pressure, P_o is the saturation vapor pressure and c is a constant.

In order to evaluate c, the equation is written in the following form:

$$\frac{P}{v(P_o - P)} = \frac{1}{v_m c} + \frac{c-1}{v_m c} \quad \frac{P}{P_o} \qquad (9)$$

and $\frac{P}{v(P_o - P)}$ is plotted against P/P_o. A straight line should be obtained with an intercept equal to $1/v_m c$ and a slope equal to $(c-1)/v_m c$.

It was found that this equation does not agree well with experimental results when P/P_o approaches unity. The original equation is based on the premise that an infinite number of monolayers are formed as the condensation pressure is apporached. The assumption was then made that a finite, rather than infinite, number of layers are formed. When a parameter "n", which represents the number of layers capable of formation, is introduced the equation becomes:

$$v = \frac{v_m c x}{(1-x)} \left[\frac{1-(n+1) \quad x^n \quad n \; x^{n+1}}{1+(c-1) \quad x - c \; x^{n+1}} \right] \qquad (10)$$

where x equals P/P_o

When curves representing various values of this parameter are plotted and compared with experimental data a good fit is obtained to values of P/P_o to the order of 0.5.

The limitations of the finite layer theory, according to Brunauer, Emmett and Teller are the following:

(1) When n equals 1 the equation reduces to the Langmuir equation.

(2) When n equals infinity the equation becomes similar to equation (10).

When Brunauer, Emmett and Teller's equation was applied to S-shaped isotherms and the results obtained for the area of the surface were compared with the results obtained by the "Point B" method, the results seldom differed by more than twelve percent.

When isotherms were run with charcoal as the sorbent, no S-shaped isotherms were obtained. Langmuir type isotherms were obtained and the area of the sorbent could be evaluated by using equation (11) and letting n equal 1.

Cassie(6) has attempted to justify the Brunauer, Emmett and Teller concept by means of a thermodynamic approach. He has explained the presence of liquid layers exerting a pressure less than the saturation pressure of the liquid. These liquid layers can exist, according to Cassie, if their free energy is less than that of the bulk liquid. If the free energy of the liquid layers is less than that of the bulk liquid the assumption that they are identical is contradicted.

Cassie claims to overcome this contradiction. He assumes that the entropy of the molecules in the liquid form is increased by sorption. It is this increase in entropy, corresponding to the decrease in free energy, which permits the liquid layers to exist below the saturation vapor pressure.

The increase in entropy is brought about by the molecules in the liquid state interchanging with molecules sorbed on low energy sites to give an entropy of mixing. It is this entropy of mixing that makes possible the condensation of molecules in the liquid form in the presence of molecules on low energy sites at pressures less than the saturation pressure of the liquid.

Assuming that multimolecular sorption occurs on localized sites, Cassie derives the following equation for the sorption isotherm:

$$A = \frac{BP}{(P_o - P)[\beta + (1 - \beta)\, P/P_o]} \qquad (11)$$

where A equals the number of moles of pure liquid sorbed per unit mass of solid. P equals the pressure, P_o equals the saturation vapor pressure, B equals the number of localized sites per unit mass of solid, and β is a constant. This equation is identical in form with that derived by Brunauer, Emmett and Teller (10) for sorption with the formation of an infinite number of layers.

Another equation for a sorption isotherm was derived by Harkins and Jura(11,12).

Harkins and Jura first developed an absolute method for the determination of the area of a finely divided solid. If a small crystal which is nonporous is suspended in the saturated vapor of a liquid it becomes coated with a sorbed film. If the liquid gives a zero contact angle with the solid the sorbed film thickens until, at equilibrium, its surface energy becomes equal to that of the liquid in bulk.

The system is allowed to come to equilibrium in a sensitive calorimeter and then the crystal is dropped into the liquid. The change in energy which occurs is due to the disappearance of the surface of the sorbed film. If the surface energy per unit area of the liquid is known the surface area of the crystal can be found by dividing the total energy change by the surface energy per unit area.

The equation for the sorption isotherm develped by Harkins and Jura is:

$$\log P/P_o = B - A/v^2 \qquad (12)$$

where P is the pressure of the sorbate, P_o is its saturation vapor pressure, v is the volume of sorbate sorbed and B and A are constants.

If log P/P_o is plotted against $1/v^2$ a straight line is obtained and -A is its slope. The relationship between A and the area of the sorbent is

$$\Sigma = kA^{\frac{1}{2}} \qquad (13)$$

where Σ is the area of the sorbent and k is a constant which depends on the particular vapor.

k may be evaluated for a particular vapor by use of the absolute method. Σ is found for a regular crystal and A is calculated. The value of k is then obtained from equation (13).

The area of a porous solid is obtained by calculating A for the system under consideration and by using this value of A and the value of k for the vapor being sorbed, which was found by the absolute method, to calculate the area of the sorbent, equation (13).

When the area of a solid is obtained by the Harkins and Jura method no assumptions are made about the molecular area of the sorbate. The Brunauer, Emmett and Teller equation (11) can be used to find the point on the sorption isotherm corresponding to the formation of a monolayer. If the number of molecules in a monolayer is calculated from the weight of vapor sorbed, and an area is assigned to each molecule, the area of the sorbent can be found.

Although the Harkins and Jura method makes no assumptions about the area occupied by a sorbate molecule and the Brunauer, Emmett and Teller method assigns a definite area to each sorbate molecule, areas obtained for the same sorbent by both methods are in close agreement.

Livingston (15) has compared the Brunauer, Emmett and Teller isotherm with the Harkins and Jura isotherm. He has shown that the mathematical agreement between the two sorption isotherms is extremely good. The constants in the Brunauer, Emmett and Teller equation can be related to the constants in the Harkins and Jura equation. Between P/P_0 values of 0.07 to 0.50, data which obeys the Brunauer, Emmett and Teller equation also obeys the Harkins and Jura equation with a deviation of about ± 3%, which is the limit of accuracy in the evaluation of the constants in the Gibbs equation for sorption on solid surfaces, the equation upon which the Harkins and Jura isotherm is based.

Brunauer, Deming, Deming and Teller(3) have extended the Brunauer, Emmett and Teller equation to cover isotherms which the Brunauer, Emmett and Teller equation does not cover. The extension covers:

(1) The cases where the heat of sorption of the first layer is smaller than the heat of liquefaction, and

(2) the cases where the capillaries of the sorbent are completely filled and the heat of sorption in the last layer is greater than the heat of liquefaction.

Anderson (1) has extended the range of the Brunauer, Emmett and Teller equation to relative pressures as high as 0.70. He has derived an equation similar to the Brunauer, Emmett and Teller equation with one exception. He has assumed that the heat of sorption of the second to ninth layers is less than the heat of liquefaction.

A further modification of the Brunauer, Emmett and Teller equation by Anderson assumes that, for porous substances, the area of the surface layer available to molecules in each subsequent layer decreases. When this concept is applied instead of the concept of the formation of a finite number of layers with equal areas, the range of the Brunauer, Emmett and Teller equation can be extended to relative pressures of 0.98.

Picket(20) has assumed that the probability of escape of molecules from the nth sorbed layer decreases as more of the surface becomes covered with n layers. The Brunauer, Emmett and Teller equation assumes that the rate of evaporation from the nth sorbed layer is independent of the number of layers on any adjacent element of surface.

By making this assumption, Pickett shows that the pores of the sorbent are completed filled at the saturation vapor pressure. Pickett's equation is in good agreement with experimental data for the entire range of relative vapor pressures if the assumption is made that the size distribution of the larger capillaries is exponential.

Schull (21) has applied a combined multilayer and capillary condensation theory introduced by Wheeler to determine pore size distributions from sorption data. Wheeler's theory can be summarized by the following equation:

$$v_s - v = \pi \int_{R}^{\infty} (R-T)^2 \; L(r) \, dr \qquad (14)$$

where v_s is the volume of gas sorbed at saturation vapor pressure, v is the volume of gas sorbed at pressure P, R is the corrected Kelvin radius, T is the multilayer thickness at P, and L(r)dr is the total length of pores with radii between r and r dr.

Pore size distributions were obtained by plotting $v_s - v$ of the experimental isotherm against the Kelvin radius R. The pore size distribution was assumed to be Gaussian and a series of standard isotherms were plotted for various mean pore sizes. The experimental isotherm was compared with the standard isotherms and the pore size distribution obtained.

The mean pore diameters of a series of silica and silica-alumina gels were calculated by Schull, Elkin and Ross (22) from the Wheeler equation and from the specific micorpore volumes of the gels. The results obtained were in good agreement and, according to the authors, the Wheeler equation seems to be valid at least for the materials studied.

Kistler, Fischer and Freeman (13) have studied the sorption of vapors on silica gel. Three samples of silica gel were made simultaneously, left in contact with water for the same length of time, and then dried differently. The variation in the gels, according to the authors, was due to the differences in compression of the structure on drying. When sorption isotherms were run on the three gel samples different amounts of vapors were sorbed.

Kistler, Fishher and Freeman explain the sorption on the basis of capillary condensation. The differences in the isotherms are said to be due to different pore size distributions.

The authors criticize the Brunauer, Emmett and Teller concept of multilayer formation and point out that, if sorption occurs in layers, the first layer is held on the surface of the sorbent more strongly than the second layer is held to the first layer. If this is the case, they say, the vapor pressure of the second layer will be greater than the vapor pressure of the first layer and if any portion of the surface of the sorbent is bare the second layer will distill over into the first layer.

Kistler, Fischer and Freeman have developed an equation for the monomolecular sorption accompanying capillary condensation.

Anderson and Hall(2) have compared Anderson's equation with the Kistler, Fischer and Freeman equation. It is interesting to note that while one assumes multilayer formation only and the other assumes monolayer formation and capillary condensation, the area of silica gel samples calculated by both equations were in excellent agreement.

OBJECTIVES

This work was undertaken to contribute to the body of fundamental knowledge from which a satisfactory theory of the mechanism of sorption may eventually be devised. Among the requirements for the development of this theory is a method which will permit the evaluation of the roles of adsorption and absorption in the sorption process.

In pursuit of a method which would differentiate between adsorption and absorption it was planned to investigate the successive sorption of two vapors on the same surface. The system chosen for investigation was silica gel-water-benzene. This system was selected because it was desired that one of the liquids be polar and one nonpolar, and that one be more strongly sorbed than the other. Information was available from the literature to show that this system would fulfill our requirements.

It was believed that modification of the sorption isotherm of each vapor by varying amounts of the other would permit estimation of the contribution of adsorption and absorption to at least one of these isotherms.

EXPERIMENTAL

MATERIALS

Silica Gel

The silica gel used in these experiments was prepared by slightly modifying a procedure used by Kistler, Fisher and Freeman(13).

A solution of water glass was diluted to a specific gravity of 1.18. Specific gravity measurements were made with a Westphal balance. An equal volume of 4 N acetic acid was added and the solution was filtered rapidly. The filtrate was collected in a paraffined crystallizing dish and allowed to gel. The gel was thoroughly washed with distilled water and allowed to dry to one-third its original weight. After drying the silica gel was oxidized for five hours with nitric acid vapor and then washed with 95% ethyl alcohol. The silica gel was then placed in a vacum furnace and dried overnight at 150° and a pressure of about 10 millimeters. The silica gel was then broken into small pieces, weighed, and used.

Benzene

The benzene used in the sorption studies was prepared by Mr. Robert Crowe by carefully redistilling a sample of Bakers C. P. thiophene free benzene under anhydrous conditions.

Water

The water used in all the sorption studies was conductivity water which was prepared by redistilling regular distilled water from an alkaline solution of potassium permanganate.

Mercury

C. P. redistilled mercury was used in all parts of the Pearson gauge.

APPARATUS

High Vacuum System

The high vacuum system (Figure 1) consisted of the following components:

(1) Fore-pump

The fore-pump was a Cenco-Hyvac pump filled with Cenco Hyvac oil.

(2) Mercury Diffusion Pump

(3) Heater

A 550 watt heater was used to heat the mercury in the mercury diffusion pump.

(4) Capillary Leak

(5) Mercury Seal

(6) McLeod Gauge

(7) Dry Ice Trap

The dry ice trap had a standard taper connection on the bottom to facilitate the removal of condensed vapors.

Sorption System

The sorption system (Figure 2) consisted of the following components:

(1) Reservoirs

Two reservoirs were made by sealing the bottoms of 19/38 standard taper pyrex joints and connecting the tops to the rest of the

HIGH VACUUM SYSTEM

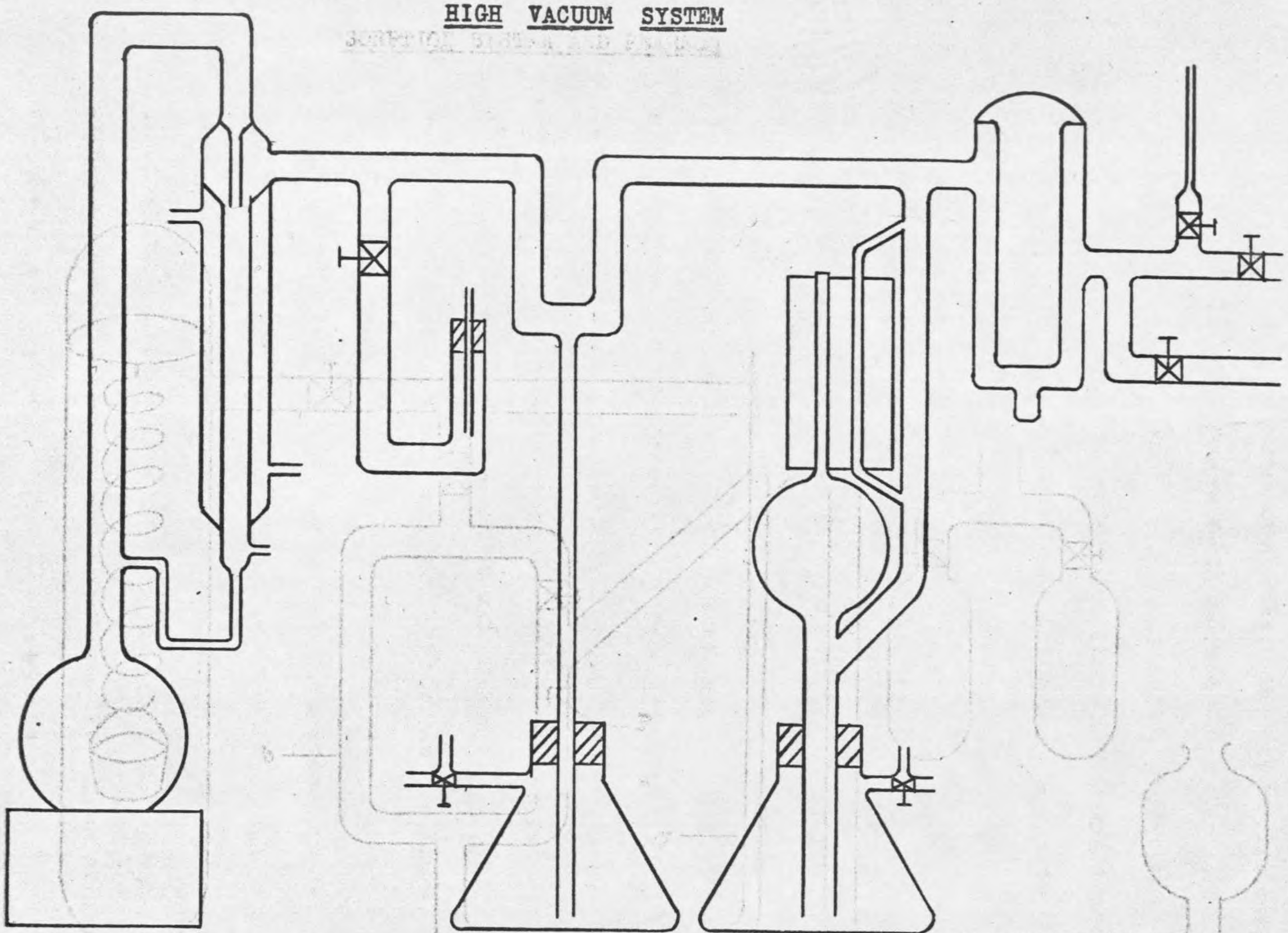

Figure 1

SORPTION SYSTEM AND PEARSON GAUGE

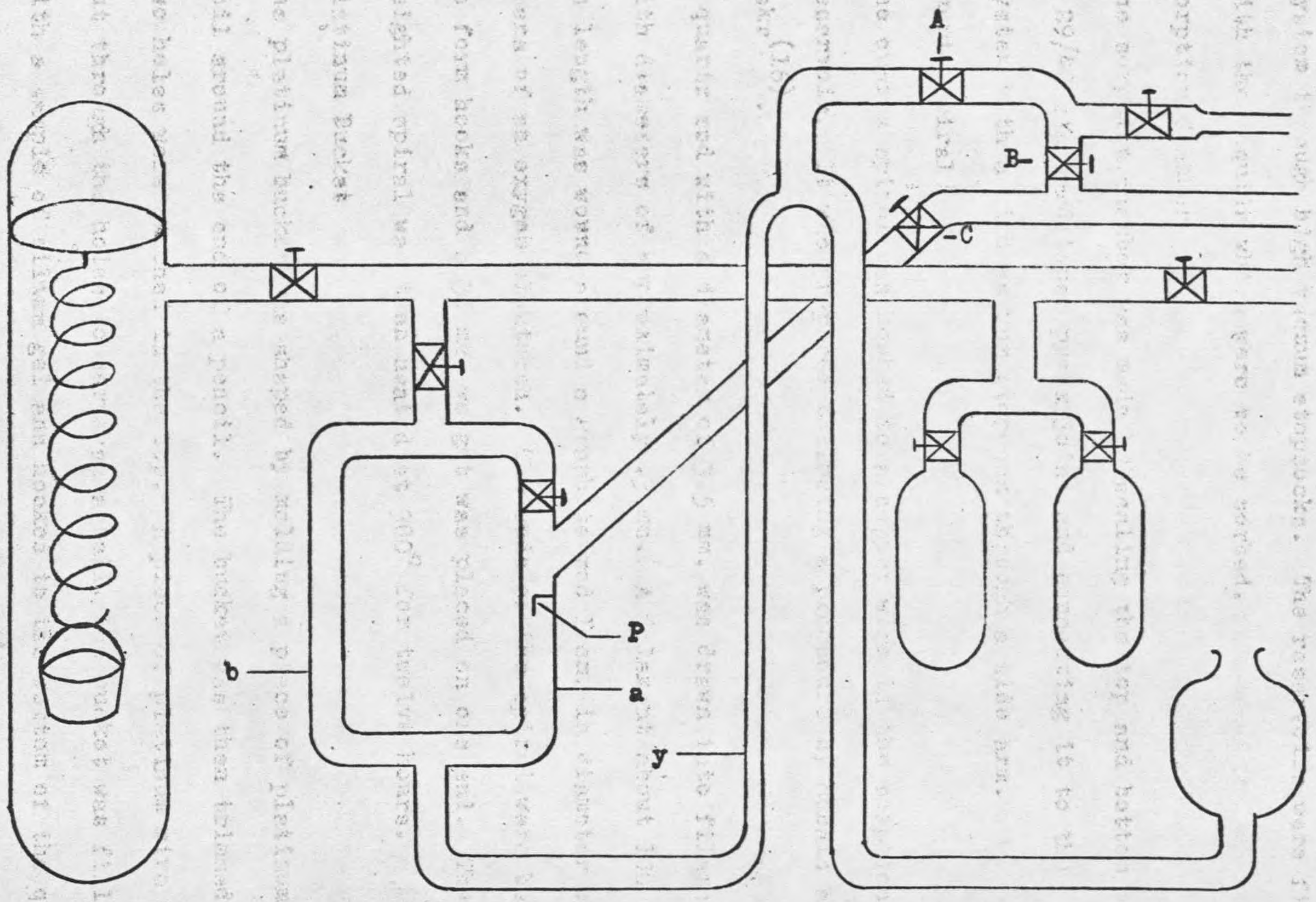

Figure 2

system through high vacuum stopcocks. The reservoirs were filled with the liquids which were to be sorbed.

(2) Sorption Chamber

The sorption chamber was made by sealing the top and bottom of a 29/42 standard taper pyrex joint and connecting it to the system with a high vacuum stopcock through a side arm.

(3) Quartz Spiral

The quartz spiral was hooked to a copper wire in the sorption reservoir. It was prepared following a procedure by McBain and Bakr(16).

A quartz rod with a diameter of 3.5 mm. was drawn into filaments with diameters of approximately .3 mm. A filament about 100 cm. in length was wound around a graphite rod 1 cm. in diameter by means of an oxygen blowtorch. The ends of the spiral were bent to form hooks and a 30 mg. weight was placed on one end. The weighted spiral was then heated at 300° for twelve hours.

(4) Platinum Bucket

The platinum bucket was shaped by molding a piece of platinum foil around the end of a pencil. The bucket was then trimmed and two holes were punched in the top. A piece of platinum wire was put through the holes to serve as a bail, the bucket was filled with a sample of silica gel and hooked to the bottom of the quartz spiral.

Measuring Instruments

The measuring instruments were those used to determine the pressure at which sorption took place and the weight of material sorbed. They consisted of the following:

(1) Pearson Gauge(19).

The Pearson Gauge (Figure 2) was essentially an U-tube monometer (a, b) with the addition of a capillary leg (y) and a platinum point (p) in one of the arms (a). This point permitted precise adjustment of the mercury level in that arm. Arm (a) was kept at a reference pressure and arm (b) was open to the rest of the system.

The mercury level in arm (a) was maintained at the tip of reference point (p). An increase in pressure in arm (b) caused its mercury level to fall, and a volume of mercury equal to that displaced in arm (b) rose in the capillary (y).

The ratio of the heights in arm (a) and capillary (y) for the same volume of mercury was inversely proportional to the square of the radii of (b) and (y). Because the radius of (b) was greater than the radius of (y), a decrease in the height of the mercury column in (b), caused a greater rise of the mercury column in (y).

(2) Cathetometer

The cathetometer used to measure the elongation of the quartz spiral could be read to 5 microns and estimated to 0.5 microns. The readings were reproducible to one micron, and since the accuracy of the measurements was limited by the accuracy of the Pearson gauge, it was assumed that the accuracy of the cathetometer was adequate.

(3) Thermostat

An air thermostat was used in the running of all isotherms. It consisted of the following parts:

(a) Cabinet

The inside dimensions of the cabinet were 12 x 12 x 18 inches. The inner box was separated from the outer by a layer of rock wool insulation. The inside was coated with a layer of aluminum paint to reduce the loss of heat. Holes were drilled through the back of the box to admit glass tubing connections. All measurements were made through a glass window in the front of the cabinet.

(4) Thermoregulator

A bimetallic thermoregulator was used.

(5) Circuit

A vacuum tube circuit (Figure 3) developed in this laboratory was employed.

(6) Heater

The heater used was a 25 watt heater which was shielded to prevent direct heating of the sorption apparatus by radiation.

(7) Fan

A fan, the motor of which was mounted on the outside of the thermostat and the blade within the cabinet of the thermostat,

THERMOSTAT CIRCUIT

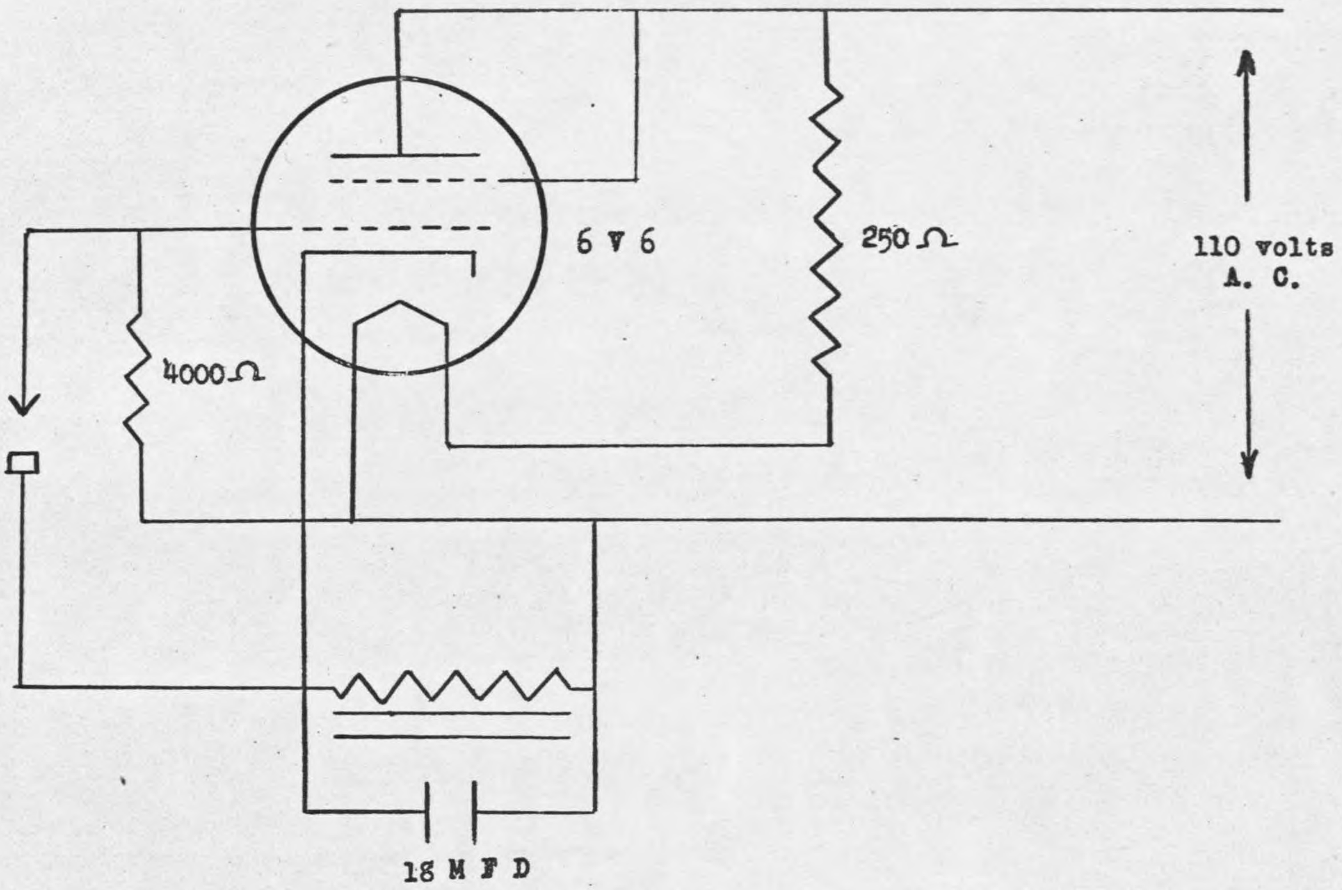

Figure 3

was used to circulate the air.

ASSEMBLY AND TESTING OF THE APPARATUS

The Pearson Gauge and sorption system were blown in this laboratory from pyrex glass. After the system was blown, it was cleaned with dichromate cleaning solution, rinsed with water and acetone, and then dried by passing a current of dry air through it.

The system was then evacuated by means of the Cenco pump and tested for pinholes with a spark coil leak chaser. When the pinholes were sealed, the system was placed in the thermostat and connected to the high vacuum system. The system was then filled with mercury, sealed and evacuated. The high vacuum system, dead ended, attained pressures of less than .01 micron. The entire apparatus was thoroughly evacuated and attained pressures of less than .01 micron. The Pearson gauge and sorption system were then cut off from the high vacuum system and allowed to stand evacuated. When the total leakage into the system was brought down to less than .7 microns per hour, the system was assumed to be tight enough for running sorption isotherms.

CALIBRATION OF APPARATUS

Pearson Gauge

The system was evacuated. Air was then let into the capillary of the Pearson Gauge through a leak, and the mercury brought up to its reference level in the reference arm. The reference arm was sealed off from the other arm (the pressure arm) by closing a high vacuum stopcock. The cathetometer was then focused on the top of the mercury column in the pressure arm. The height of the cathetometer and the height of the mercury column in the cathetometer were both recorded.

Water vapor was let into the system from the water reservoir. The height of the mercury level in the referance arm was brought back to the reference point by partially evacuating the capillary. Fine adjustments were made with the leveling bulb. The decrease in the height of the mercury column was read with the cathetometer. This was equal to the pressure in that arm. The corresponding increase in the height of the mercury column in the capillary was read by means of a millimeter scale. The increase in the height of the mercury in the capillary per millimeter of pressure was then calculated.

The above procedure was repeated at various pressures and the results averaged. The good agreement among the results at the different pressures indicated that the tubing in arm (b) was uniform.

Quartz Balance

The quartz spiral was suspended on a taut copper wire and the platinum bucket was suspended on the bottom of the spiral. The cathetometer was focussed on the bucket and the height of the cathetometer was recorded. A 10 milligram weight was added to the bucket and the elongation of the spiral was measured by refocussing the cathetometer on the same point on the bucket and recording the new height. The difference between the two readings was equal to the elongation of the spiral due to an increase in weight of 10 milligrams. The weight necessary to cause an elongation of one micron was calculated.

The procedure was repeated and the results were averaged.

Thermostat

The following method was used to set the thermostat. A thermometer graduated in fifths of degrees was hung in the thermostat. The temperature was brought up to 30.0 degrees and the thermoregulator was used to turn off the heater.

The temperature was read to a tenth of a degree and usually remained constant at 30.0 ±.1 degree.

It was found necessary to adjust the thermostat before the start of each isotherm.

PROCEDURE

The following procedure was used in the running of a sorption isotherm in these experiments.

The entire system was evacuated for at least five hours before a run was begun. The thermostat was adjusted to 30.0 degrees and the pressure of the system was checked with the McLeod Gauge to determine whether any leaks had developed.

The Pearson Gauge and sorption system were then turned off from the high vacuum system by closing the appropriate high vacuum stopcocks (A, B, C). Air was admitted to the capillary arm through a leak until the level of the mercury in the reference arm just touched the tip of the piece of platinum wire sealed into the arm; fine adjustments were made with the leveling bulb. The reference arm was sealed off from the pressure arm through a high vacuum stopcock. The cathetometer was then focussed on the bucket of the quartz balance and its height recorded.

A portion of the vapor being sorbed was then admitted into the system from its reservoir by turning the stopcock until the vapor slowly leaked in. Care was taken not to open the stopcock enough for the vapor to surge into the system.

Because earlier observations showed that it took the system at least twenty minutes to come to equilibrium after vapor was added, the system was given twenty minutes to come to equilibrium and then the weight of vapor sorbed and the pressure were measured.

The weight of vapor sorbed was obtained by measuring the elongation of the quartz spiral. The reference point on the platinum bucket was approached always from the same direction in order to eliminate the errors which would be caused by the backlash in the cathetometer screw. A series of cathetometer readings were always taken and averaged. The pressure was measured by partially evacuating the capillary arm until the level of the mercury in the reference arm was again at the reference point. Fine adjustments were made with the leveling bulb. The pressure in the system was measured by the change of the height of the mercury in the capillary.

Because of the limited capacity of the Pearson Gauge it was necessary to change the reference pressure during the runs in order to complete the isotherms. At such times the reference arm was opened to the pressure arm and the pressure in the gauge equalized. The reference arm was then again sealed off from the pressure arm and the level of its mercury column brought to the reference point. This procedure provided a new base from which the height of the mercury in the capillary could be measured. The total pressure was taken as the sum of all increments including those prior to the establishment of the new base.

Measurements were continued until a pressure close to the equilibrium vapor pressure was reached.

When a poison was used the poison was first sorbed and its weight and pressure measured. The regular sorption isotherm was then run and the weight and pressure of the vapor sorbed were obtained by subtracting the weight and pressure of the poison from the total weight and pressure in the system after each reading.

THE DATA AND DISCUSSION

THE DATA

The sorption of benzene and water on silica gel at 30° were studied. The modification of the isotherms of each substance by the presence of varying amounts of the other vapor was investigated. The modifying vapor was considered the poison in each case.

The results of the sorption of benzene on silica gel are given in Table I and the results of the sorption of water on silica gel in Table II.

The amount of vapor sorbed is expressed as the weight per unit weight of silica gel (x/m). The pressure is expressed as the fraction of the saturation vapor pressure (P/P_o).

The following formula was used to calculate x/m:

$$\frac{\text{cathetometer reading} \times 22.8}{2 \times 60.3} = x/m$$

The cathetometer reading was divided by two to calculate the elongation of the spiral in millimeters. This value was multiplied by 22.8, the sensitivity of the spiral in milligrams per millimeter, to obtain the weight of material sorbed. x/m was computed by dividing the weight of material sorbed by 60.3, the weight of the sorbent in milligrams.

The formula used to obtain P/P_o for benzene was:

$$\frac{\text{capillary displacement}}{15.9 \times 118.2} = P/P_o$$

The capillary displacement was divided by 15.9 to obtain the pressure in the system. The pressure was divided by 118.2, the saturation vapor pressure of benzene in millimeters at 30°.

TABLE I.

SORPTION OF BENZENE ON SILICA GEL

Ia		Ib		II		III		IVa		IVb	
$(x/m)_o^* = 0$		$(x/m)_o = 0$		$(x/m)_o = 0.0212$		$(x/m)_o = 0.0234$		$(x/m)_o = 0.1267$		$(x/m)_o = 0.1270$	
x/m	P/P_o	x/m	P/P_o	x/m	P/P_o	x/m	P/P_o	x/m	P/P_o	x/m	P/P_o
0.0185	0.019	0.0684	0.045	0.0378	0.028	0.0526	0.037	0.0450	0.029	0.0401	0.029
0.0397	0.034	0.1017	0.079	0.0522	0.044	0.0824	0.060	0.0873	0.060	0.0737	0.054
0.0654	0.058	0.1259	0.158	0.0749	0.056	0.0949	0.091	0.0885	0.125	0.0881	0.112
0.0998	0.071	0.1622	0.237	0.1013	0.096	0.1055	0.124	0.0885	0.193	0.0881	0.190
0.1210	0.134	0.1845	0.328	0.1066	0.112	0.1093	0.169	0.0885	0.266	0.0881	0.263
0.1494	0.204	0.1883	0.406	0.1100	0.154	0.1131	0.221	0.0885	0.347	0.0881	0.355
0.1747	0.272	0.1883	0.503	0.1123	0.180	0.1195	0.250	0.0885	0.427	0.0881	0.448
0.1882	0.344	0.1883	0.595	0.1350	0.274	0.1331	0.288	0.0885	0.510	0.0881	0.546
0.1898	0.418	0.1883	0.684	0.1429	0.348	0.1365	0.329	0.0885	0.590		
0.1898	0.495			0.1429	0.424	0.1365	0.372				
0.1898	0.571					0.1365	0.460				
0.1898	0.652					0.1365	0.551				
0.1898	0.723										
0.1898	0.801										
0.1898	0.868										
0.1898	0.941										
0.1898	0.993										

*$(x/m)_o$ equals the amount of water sorbed.

TABLE II

SORPTION OF WATER ON SILICA GEL

V-a		V-b		VI-a		VI-b		VII-a		VII-b		VIII-a		VIII-b	
$(x/m)_0$* = 0		$(x/m)_0$ = 0		$(x/m)_0$ = 0.0953		$(x/m)_0$ = 0.946		$(x/m)_0$ = 0.1233		$(x/m)_0$ = 0.1240		$(x/m)_0$ = 0.1884		$(x/m)_0$ = 0.1882	
x/m	P/P_0	x/m	P/P_0	x/m	P/P_0	x/m	P/P_0	x/m	P/P_0	x/m	P/P_0	x/m	P/P_0	x/m	P/P_0
0.0011	0.031	0.0045	0.226	0.0015	0.059	0.0030	0.192	0.0019	0.220	0.0023	0.226	0	0.292	0	0.283
0.0088	0.109	0.0136	0.293	0.0061	0.251	0.0083	0.252	0.0185	0.320	0.0121	0.303	0	0.590	0	0.643
0.0049	0.222	0.0424	0.360	0.0098	0.279	0.0227	0.312	0.0427	0.404	0.0556	0.447	0	0.888	0	0.996
0.0098	0.260	0.0609	0.418	0.0302	0.326	0.0458	0.366	0.0741	0.550	0.0767	0.574				
0.0222	0.315	0.1066	0.569	0.0904	0.522	0.0715	0.445	0.0786	0.691	0.0802	0.682				
0.0381	0.345	0.1233	0.617	0.1278	0.637	0.0915	0.524	0.0824	0.832	0.0809	0.752				
0.0595	0.432	0.1282	0.675	0.1320	0.761	0.1115	0.598			0.0809	0.800				
0.0680	0.440	0.1319	0.728			0.1252	0.664								
0.0734	0.455	0.1323	0.761			0.1301	0.725								
0.0744	0.462					0.1316	0.756								
0.0764	0.472					0.1316	0.791								
0.0800	0.483														
0.0849	0.503														
0.0898	0.525														
0.1259	0.626														
0.1301	0.718														
0.2810	1.001														

*$(x/m)_0$ equals the amount of benzene sorbed.

To calculate P/P_o values for the water isotherms the same procedure was employed but 31.8, the saturation vapor pressure in millimeters of water at 30°, was substituted for 118.2.

A typical data sheet is given in Table III. For all other isotherms only the x/m and P/P_o values are listed (Tables I and II).

The sorption isotherms of benzene on silica gel are shown in Figure 4. The sorption isotherms of water on silica gel in Figure 5.

<u>Sorption of Benzene on Silica Gel</u>

The isotherm obtained for the sorption of benzene on unpoisoned silica gel (Ia) was a typical S-shaped isotherm. When water was first sorbed on the silica gel to an x/m value of 0.0212, an S-shaped isotherm (II) was obtained with a smaller rise in the upper portion of the curve and less benzene sorbed on the silica gel. When still more water (x/m = 0.1267) was sorbed on the silica gel, a Langmuir isotherm (IV) resulted. The curve did not rise again to give an S-shaped isotherm.

When check determinations of the isotherms were run the original curves were essentially duplicated. In each case the curve representing sorption in the presence of varying amounts of water vapor duplicated the previous determination. Therefore we have not drawn separate curves but have simply included all points for both initial and subsequent determinations in the data from which the curves were plotted.

In one case only (curve III) the amount of water was not precisely that sorbed in the original run. The near coincidence of these two curves (II and III) has been taken as verification of the original data.

TABLE III

SORPTION OF WATER ON SILICA GEL VI b

Cath. Reading	x/m	Cap. Displacement	P/P_o
0.016	0.003	97.1	0.192
0.044	0.008	127.3	0.252
0.120	0.023	157.9	0.312
0.242	0.046	185.2	0.366
0.378	0.072	225.1	0.445
0.484	0.092	264.8	0.524
0.590	0.112	302.1	0.598
0.662	0.125	335.8	0.664
0.688	0.130	366.7	0.725
0.696	0.132	382.4	0.756
0.696	0.132	399.8	0.791

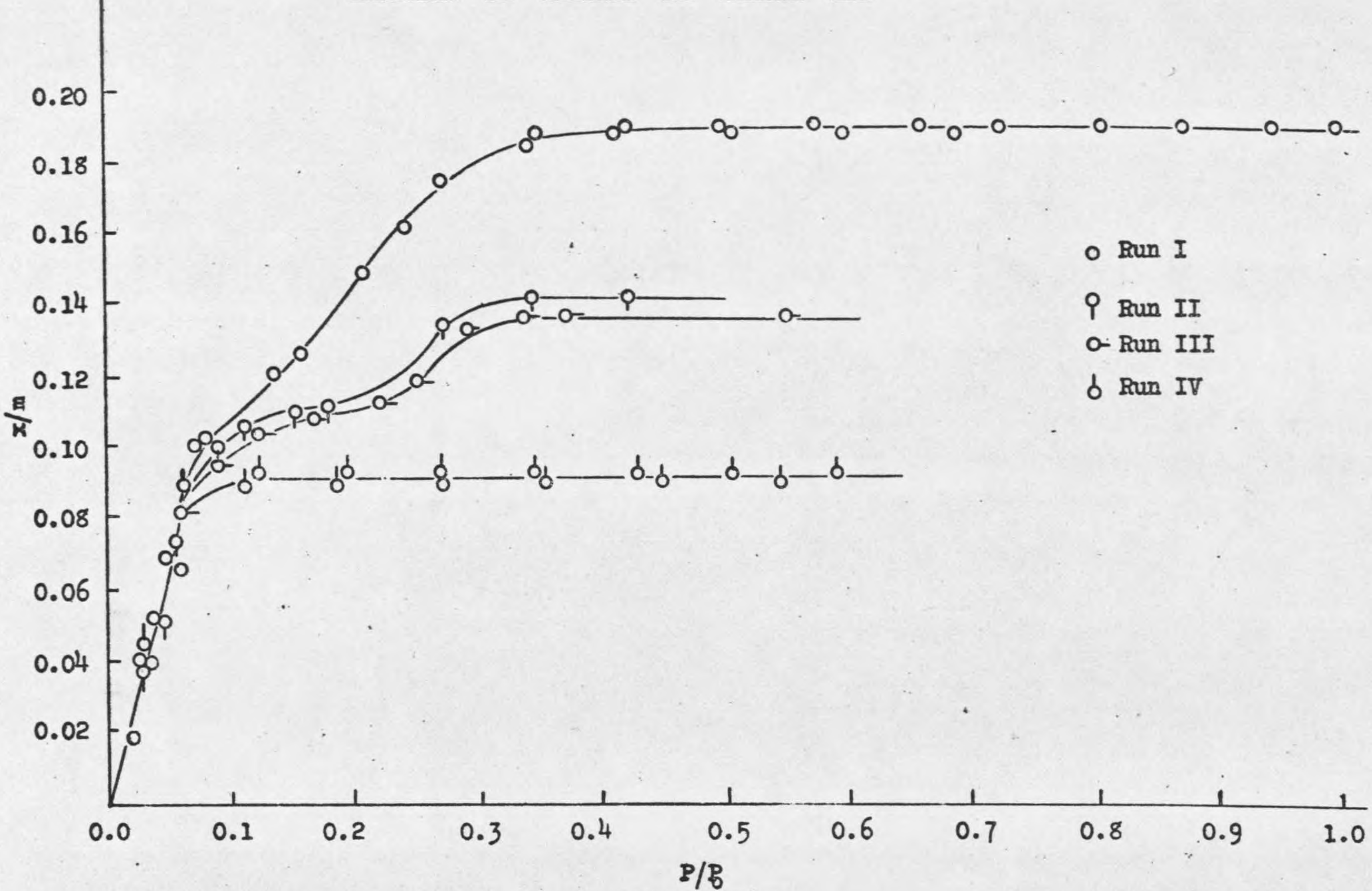
SORPTION OF BENZENE ON SILICA GEL

Figure 4

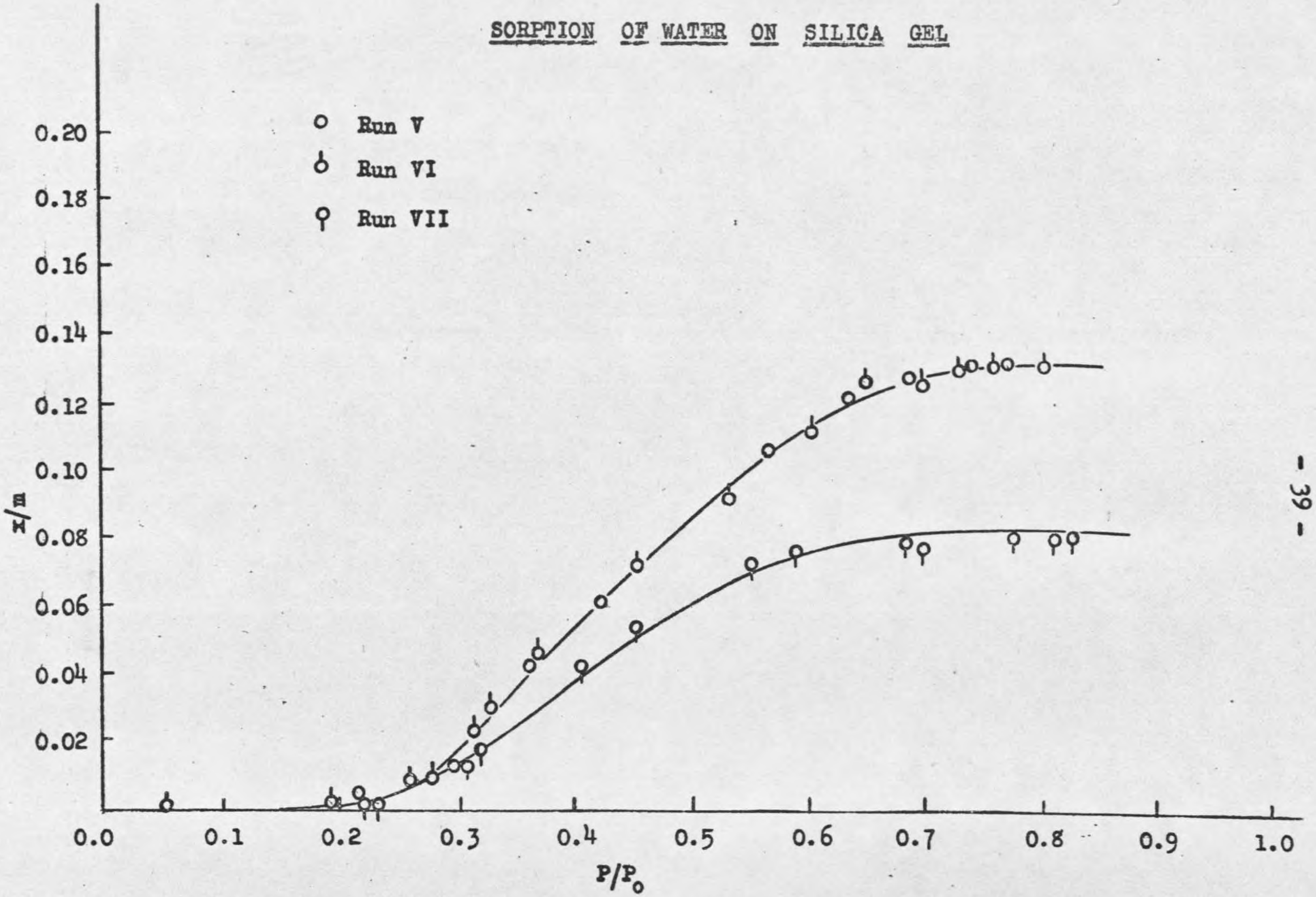
SORPTION OF WATER ON SILICA GEL

Figure 5

Soprtion of Water on Silica Gel

When water was sorbed on unpoisoned silica gel (V a) no sorption occurred until a P/P_o of 0.14 was reached. Sorption started slowly, rose sharply at P/P_o - 0.30 and then leveled off gradually. With benzen poison on the silica gel (x/m = 0.0953) the curve obtained (VI-a) coincided with curve V-a. A still greater amount of benzene (x/m = 0.1233) decreased the total amount of water sorbed VII-a. When benzene was sorbed on silica gel until its saturation vapor pressure was approached (x/m = 0.1884), no water was sorbed (VIII-a).

The water sorption curves were verified in the same manner as the benzene curves. All data from the initial and second run were used in plotting each curve.

The points from run V-a, which was our first determination, have not been included in the plotted data. There were so many points for the sorption of water on unpoisoned silica gel that the inclusion of all would have led to confusion.

DISCUSSION

The following principal conclusions with respect to the system investigated were drawn from the experimental data:

1. When water is sorbed on silica gel no measurable adsorption occurs; the taking up of water vapor is due primarily to capillary condensation.
2. In the benzene isotherm the sorption process is one of monolayer adsorption followed by capillary condensation.

It is generally assumed that the Langmuir equation is valid for the formation of the first adsorbed layer. This equation requires a steep slope of the adsorption isotherm at low P/P_0 values. We observed no sorption at low pressures in running the water isotherms. This has led us to conclude that no first adsorbed layer was formed. Since no first layer was formed, there could be no second or subsequent layers. In view of this evidence we have concluded that the sorption of water on silica gel is due to capillary condensation. Our curves are similar in shape to the curves obtained by Fineman, Guest and McIntosh(10) for the sorption of water on charcoal. Fineman, Guest and McIntosh concluded that the sorption of water in that case is due primarily to capillary condensation.

When water was used as a poison in running the benzene isotherms, the water occupied only the pores of the silica gel, not the surface. Sorption of benzene in the S-shaped portion of the curve decreased when water partially filled the capillaries. When the capillaries were completely filled with water there was no S-shaped portion of the curve, only a Langmuir isotherm was obtained. Since the S-shaped portion of the benzene isotherm can be eliminated by filling the pores of the silica gel with water, and since this does not affect the initial portion of the isotherm, which is explained by monolayer adsorption, and follows the Langmuir equation, we have concluded that in the sorption of benzene on silica gel, where a typical S-shaped isotherm is obtained, the mechanism involved is one of monolayer adsorption followed by capillary condensation.

When benzene was sorbed on the silica gel to an x/m of approximately 0.0950, a value on the initial portion of the benzene isotherm, and a water isotherm was run on the poisoned silica gel, the curve obtained coincided with the curve for water on unpoisoned silica gel. When benzene was sorbed to an x/m of approximately 0.1235, a value on the S-shaped portion of the curve, less sorption of water occurred than had occurred on the unpoisoned silica gel. When the silica gel contained benzene sorbed to an x/m of approximately 0.1880 (as much as it could hold), there was no sorption of water. These results indicate that the intitial sorption of benzene on silica gel is independent of capillary condensation. When some of the capillaries of the silica gel were filled with benzene, less sorption of water occurred. When the capillaries were completely filled with silica gel, no sorption of water (capillary condensation) occurred. This data seems to verify our conclusion that the S-shaped portion of the benzene isotherm is due to capillary condensation.

When benzene was sorbed on unpoisoned silica gel the S-shaped portion appeared to begin at an x/m value of approximately 0.111. The Langmuir isotherm obtained on poisoned silica gel leveled off at an x/m of approximately 0.088. The apparent differences in the amounts of benzene sorbed in the initial portions of the isotherm may best be explained if we consider the walls of the capillaries of the silica gel as being covered by a monolayer of benzene when the sorption is run on unpoisoned silica gel. When the capillaries are first filled with water their walls are unavailable for the formation of a monolayer of sorbed benzene. The difference in the amount of benzene sorbed in the initial portions of curves I and IV can then be considered a measure of the areas occupied by the walls of the capillaries.

GENERAL CONCLUSIONS

1. A useful technique has been developed which can be extended to investigate the roles of adsorption and absorption in the sorption process of systems other than those studied by us.
2. Although it would seem that the conclusions reached regarding the sorption of benzene and water on one particular sample of silica gel can be extended to silica gel in general, no such extension of the conclusions will be made until the experiments are repeated on a sufficient number of silica gels to permit a statistical study of the results.

SUMMARY

1. The sorption isotherms of benzene and water on silica gel and the modification of each of these isotherms by the presence of varying amounts of the other vapor as a poison were studied in an attempt to differentiate between adsorption and absorption in the sorption process.
2. It was found that a McBain-Bakr sorption balance and Pearson Gauge are satisfactory for accurate weight and pressure measurements in the running of the isotherms.
3. The benzene on silica gel isotherm was found to be a typical S-shaped curve.
4. It was found that for the water on silica gel isotherms no sorption occurred at low pressures; sorption began gradually, rose sharply and then leveled off gradually.
5. From the shape of the water on silica gel isotherm it was concluded that the sorption of water on silica gel is due primarily to capillary condensation.
6. The S-shaped portion of the benzene isotherm leveled off as increasing amounts of poison were added and a Langmuir isotherm was finally obtained.
7. From (6) it was concluded that the process of sorption for benzene on silica gel is one of monolayer adsorption followed by capillary condensation.
8. When benzene was used as a poison in running the water isotherms it was

found that the curves obtained were similar to that of water on unpoisoned silica gel until the amounts of benzene sorbed fell on the S-shaped portion of the benzene isotherm; then sorption of water gradually decreased and finally ceased as increasing amounts of benzene were used.

9. It was considered that the pheonomena described in (8) provided confirmation of the conclusion reached (7) ascribing the sorption of benzene on silica gel to monolayer adsorption followed by capillary condensation.

10. A technique has been developed which should prove useful in investigations of the relative contributions of adsorption and absorption to sorption isotherms.

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