



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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Abstract:

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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TABLE OF CONTENTS

	Page
I. ABSTRACTS	3
II. INTRODUCTION	4
Literature Survey	4
Objectives	18
III. EXPERIMENTAL	20
Materials	20
Apparatus	21
Assembly and Testing of the Apparatus	28
Calibration of Apparatus	28
Procedure	30
IV. THE DATA AND DISCUSSION	33
The Data	33
Discussion	40
V. SUMMARY	44
VI. ACKNOWLEDGEMENTS	46
VII. LITERATURE CITED	47

I. ABSTRACT

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.

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 definition 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 noncommittal "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:

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

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:

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

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 existence 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 elastically, 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

$$\alpha \mu \theta = v_1 \theta_1 \quad (3)$$

Furthermore

$$\theta + \theta_1 = 1 \quad (4)$$

Therefore

$$\theta_1 = \frac{\alpha \mu}{v_1 + \alpha \mu} \quad (5)$$

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:

$$v = K \left(\frac{P - \sigma}{P_0} \right)^{1/n} \quad (6)$$

where v is the volume of vapor in cc. sorbed per gram of gel, P is the equilibrium pressure, P_0 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:

$$\ln \frac{P_r}{P_0} = - \frac{2\sigma \bar{V} \cos \theta}{RT} \quad (7)$$

here P_0 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:

$$v = \frac{v_m cP}{(P_0 - P) [1 + (C-1) P/P_0]} \quad (8)$$

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_0 is the saturation

vapor pressure and c is a constant.

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

$$\frac{P}{v(P_0 - P)} = \frac{1}{v_{mc}} + \frac{c-1}{v_{mc}} \frac{P}{P_0} \quad (9)$$

and $\frac{P}{v(P_0 - P)}$ is plotted against P/P_0 . A straight line should be obtained with an intercept equal to $1/v_{mc}$ and a slope equal to $(c-1)/v_{mc}$.

It was found that this equation does not agree well with experimental results when P/P_0 approaches unity. The original equation is based on the premise that an infinite number of monolayers are formed as the condensation pressure is approached. 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:

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

where x equals P/P_0

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_0 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:

$$A = \frac{BP}{(P_0 - P)^B + (1 - B) P/P_0} \quad (11)$$

where A equals the number of moles of pure liquid sorbed per unit mass of solid, P equals the pressure, P₀ equals the saturation vapor pressure, B equals the number of localized sites per unit mass of solid, and B 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 developed by Harkins and Jura is:

$$\log P/P_0 = B + A/v^2 \quad (12)$$

where P is the pressure of the sorbate, P_0 is its saturation vapor pressure, v is the volume of sorbate sorbed and B and A are constants.

If $\log P/P_0$ 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

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

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 $\pm 3\%$, 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.

Pickett⁽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 completely 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:

$$v_s - v = \pi \int_R^{\infty} (R-T)^2 L(r) dr \quad (14)$$

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 micropore 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, Fischer 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.

