provided that Emmett's usual assumption of 16.2 sq. Å. as the area of the nitrogen molecule is adopted. On account of the much higher accuracy in the calorimetry with the sample of area 13.8 m.^{2}g.$^{-1}$, this is the only result which should be compared with that obtained by us by the method of B. E. T.

CHICAGO, ILLINOIS RECEIVED APRIL 28, 1944

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO, AND THE UNIVERSAL OIL PRODUCTS COMPANY, PAPER 112 OF THE LABORATORY OF SURFACE CHEMISTRY]

Surfaces of Solids. XIII. A Vapor Adsorption Method for the Determination of the Area of a Solid without the Assumption of a Molecular Area, and the Areas Occupied by Nitrogen and Other Molecules on the Surface of a Solid

BY WILLIAM D. HARKINS AND GEORGE JURA

I. Introduction

In 1938 Brunauer, Emmett and Teller[1] (BET) developed a kinetic theory of adsorption, which makes it possible to calculate from an adsorption isotherm, in which the pressure is given as a function of the amount of vapor adsorbed, the number (N) of molecules of vapor necessary to complete a monolayer on the surface of a solid. It is obvious that this would make it possible to calculate the area of the surface provided the mean area occupied per molecule in the completed monolayer were known.

In the section which follows, a method is developed by means of which the area of a solid may be obtained without the use of a molecular area. It is obvious that if the number (N) of molecules required to cover the surface of a gram of solid, and (Σ), the area of the solid are both known, then the mean area (σ) per molecule is given by the relation

$$\sigma = \Sigma/N \qquad (1)$$

and

$$\Sigma = N\sigma \qquad (2)$$

In the BET procedure it is necessary to use Eq. 2, and since Eq. 1 involves Σ, the area which is to be determined, it is necessary for them to estimate the molecular area in some other way. This was done[2] by the use of the equation

$$\sigma = (4)\ (0.866)\ (M/4\sqrt{2}\,A\rho)^{2/3}$$

which assumes close packing in the surface. Here ρ represents the density of the solid or of the liquid adsorbate, M is the molecular weight, and A is Avogadro's number. This equation gave the following molecular areas: 16.24 sq. Å. for nitrogen (liquid) at −195.8°, 13.8 sq. Å. (solid) at −252.5°, and 32.1 sq. Å. for butane (liquid) at 0°. These values are important in connection with a later discussion of molecular areas. It is remarkable that when either of the two molecular areas of the nitrogen molecule is used, the values of the areas of solids obtained by their method and by ours, are as closely in agreement as is possible when the areas involved are as divergent as 13.8 and 16.2 sq. Å. per molecule. However, the error in the area (Σ) of a solid produced by the uncertainty in the molecular areas used in their method is small when compared with the error in methods earlier than theirs.

It is customary for Emmett to use the area 16.2 sq. Å., as obtained from the liquid, and in paper XII of this series it is shown that a sample of crystalline anatase (TiO_2) gave an area of 13.9 sq. meters per gram by their method on the basis of this molecular area for nitrogen, while our extremely different absolute method gave 13.8 sq. meters per gram. As tested by the methods developed by us, the BET method is remarkably well adapted to the determination of the area of solids. However, when porous solids of the type of silica alumina gels are under investigation, somewhat lower values for the area of the nitrogen molecule, as given later, give better agreement with the areas of such solids, when these are determined by the new method.

II. Experimental Methods for the Determination of the Adsorption Isotherm

For the determination of the areas of solids in general the most suitable vapor is that of nitrogen, provided either nitrogen or air is available in the liquefied form. Argon may be used if preferred. The apparatus and technique used for the determination of the isotherms of liquids such as water and n-heptane at 25°, which have low values of p_0, the vapor pressure at saturation, are described in an earlier contribution.[3]

A diagram of the apparatus for the determination of the nitrogen isotherms is exhibited in Fig. 1. The part of the apparatus used for the higher pressures is the same in its essential features as that of Emmett and Brunauer.[4] The variations in technique and design are not of a major type, but they contribute markedly to the precision of the results and are, therefore, important. The diagram shows also the attachment and necessary stopcocks for the use of either the low or higher pressure manometer. The changes in design are the addition of (1) a vapor pressure thermometer as described in the following paragraph, of (2) a wide bore, 25-mm. diameter, manometer for low pressure work, and the use of (3) only one U-tube before the sample, thus decreasing the dead space.

---

[1] S. Brunauer, P. H. Emmett and E. Teller, THIS JOURNAL, 60, 309 (1938).

[2] P. H. Emmett and S. Brunauer, *ibid.*, 59, 1553 (1937).

[3] G. Jura and W. D. Harkins, *ibid.*, 66, 1356 (1944).

[4] P. H. Emmett and S. Brunauer, *ibid.*, 56, 35 (1934).

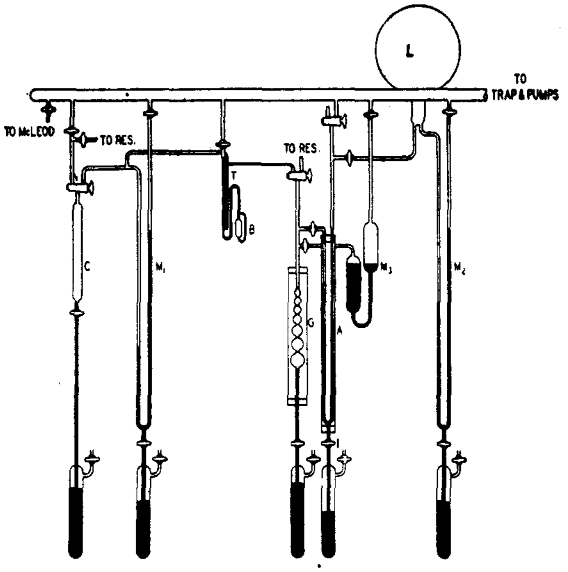

Fig. 1.—Apparatus for the determination of adsorption isotherms at pressures from 10 to 760 mm. Tubes labeled "To Res." lead to flasks, like L, not shown, used for the storage of helium and nitrogen, etc. Butane, heptane, water, etc., are stored as liquids in tubes.

A compression chamber C and the tube leading to the manometer M_1 are filled with the gas whose adsorption isotherm is to be determined. The gas is then compressed by filling C with mercury, thus condensing the vapor into liquid in T, which is immersed in the same bath as the adsorption bulb. The vapor pressure of the liquid is then read on the manometer M_1.

The buret system is composed of the bulbs G and the left-hand side of the mercury cut-off, A. The latter is a tube 60 cm. long with a 5-cc. capacity graduated in 0.01 cc. The graduations were checked by the volume of mercury delivered. The calibration of the bulbs and the other tubing is described in paper XI of this series.[3]

The following procedures are used for the determination of the gas pressure. For low pressures the manometer M_3 is used in conjunction with a travelling microscope. The details for this are given in paper XI.[3] The maximum working pressure for this manometer is between 90 and 100 mm. For higher pressures, the manometer M_2 of an external diameter of 12 mm. is used. The difference in height of the mercury is obtained either with a cathetometer or a meter stick. With the cathetometer no attempt is made to obtain the pressure to better than 0.1 mm. When the meter stick is used, a slide arrangement with projecting arms is used, which gives the pressure with an accuracy of 0.4 mm. The scale on the meter stick was calibrated by that of the cathetometer. The pressure measured by M_2 is that of the gas in the 5-liter bulb, L, whose purpose is to permit ease in the variation of the pressure.

The pressure in the buret system is made equal to the pressure in L by the following procedure. The mercury in the cut-off A is pulled down and the cut-off is evacuated. After this the mercury is allowed to rise. On the left side the meniscus of the mercury is brought exactly to one of the graduation marks. The amount of mercury in the cut-off is maintained constant by closing stopcock 1. As long as the temperature remains constant, the pressures on the right and left hand sides are equal when the mercury is at the chosen graduation mark. When this method is used it is possible to reproduce pressures to 0.05 mm. with a maximum deviation of 0.10 mm.

This method of determining pressures was chosen because, due to small internal diameter of the buret, small variations in diameter have a marked effect on the level due to capillary depression. In the system now in use, the difference in height of the mercury in the two arms with a vacuum on both sides is −2 to about +3 mm. as the mercury is moved up. Thus, if it were assumed that the pressure on both sides is the same when the arms are level, an error of as much as 3 mm. might be made. The per cent. error would of course depend on the absolute value of the pressure. Working with nitrogen at −195.8° at a relative pressure of 0.2, the error in the pressure reading could be as high as 4%. This error would obviously also be reflected in the calculation of the adsorbed volume of gas. The isotherm is obtained by successive additions of vapor.

This apparatus has been used primarily for nitrogen adsorptions at −195.8°. Figure 2 shows two sets of isotherms, of which the upper one is for a sample of TiO_2, with an area of 13.8 $m.^2\ g.^{-1}$ by our absolute method. The excellent agreement between the values for this sample in the three determinations shown is of interest since they were made on three independent experimental units, each with an entirely independent calibration. The concordance in the three sets of measurements indicates high accuracy, as well as precision, in the results. The agreement among the three sets of data is shown by the fact that if 16.20 sq. Å. is used for the area of the nitrogen molecule in conjunction with the BET theory, the area is found to be 13.92 $m.^2\ g.^{-1}$, with an average deviation for the three of only 0.06 $m.^2\ g.^{-1}$. The lower curve shows the results of duplicate

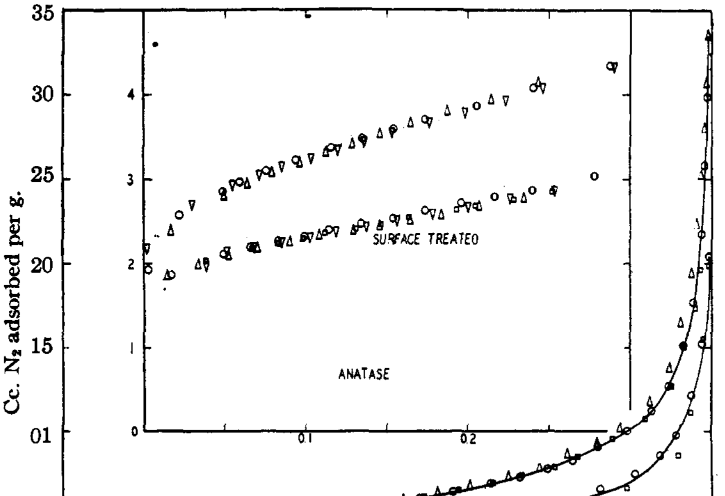

Fig. 2.—Nitrogen isotherms for anatase and surface treated anatase.

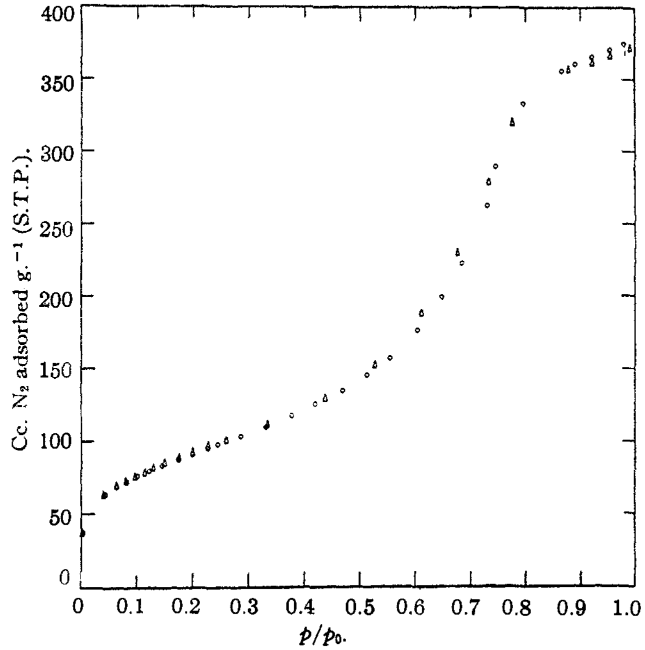

Fig. 3.—Nitrogen isotherms for a silica–alumina gel.

determinations of a sample of anatase, surface treated with aluminum oxide, whose area is 9.6 m.^{2} g.$^{-1}$. This curve represents the *least* precise set of measurements obtained in all of our work. The low precision is due to the low area of the sample. With a lower area the precision would be even lower.

Figure 3 shows the precision obtained with a porous solid. The areas determined from these two isotherms were found to be 320.2 and 320.7 m.^{2} g.$^{-1}$. All of the above determinations were made on entirely different samples.

III. A Relative Method for the Determination of the Area of a Solid

The area of a solid may be calculated very simply from the adsorption isotherm of a vapor, provided that the adsorbed film forms a condensed phase in a part of the isotherm. In the following paper (XIV) of this series the isothermal equation of state for a condensed film is given as

$$\pi = b - a\sigma \qquad (3)$$

This may be transferred by the methods given there into the equation

$$\log (f/f_0) = B - A/v^2 \qquad (4a)$$

More accurately, what is involved is log f/f_0, but the ratio of the pressures is so nearly the same that the equation is usually used in the form

$$\log (p/p_0) \cong B - A/v^2 \qquad (4b)$$

If now, log (p/p_0) is plotted (Fig. 4) against the reciprocal of the square of the amount (volume at S.T.P., mass, moles or molecules) adsorbed, a linear relation is exhibited where the π–σ relation is linear, *i. e.*, where the film is condensed. If the film is not condensed for any value of p/p_0 of the adsorbate employed, it is necessary either to lower the temperature, or else to change to an adsorbate which gives a condensed phase at a suitable temperature.[5]

When the first set of isotherms for nitrogen obtained at −195.8°, was plotted in this way, it was at once noticed that as the area of the solid increases the numerical value of the slope, A also increases. It was then found very quickly that the area (Σ) of the solid is proportional to the square root ($A^{1/2}$) of this slope. Thus the area of the solid is given by the equation

$$\Sigma = kA^{1/2} = ks^{1/2} \qquad (5)$$

where the slope is represented by A or by s.

The way in which the square root of the slope becomes involved is as follows. The value of the constant A in Eq. 4 is

$$A = \frac{10^{16}V^2a\Sigma^2}{2RTN_0}$$

where 10^{16} is the conversion unit from cm.^{2} to Å.,^{2} V is the molar volume of gas, a is the constant in Eq. 3, R the gas constant, T the absolute temperature, and N_0 is Avogadro's number. It has been observed that when the aqueous subphase under an insoluble film is changed, the area at which a phase appears may be altered, *i. e.*, the value of b in Eq. 3 is altered. However, there is no change, or only a very slight change, in the value of a. The assumption is made that this is also true of the films on the surfaces of solids. On this basis Eq. 5 follows. In some of the films studied, two condensed phases are present. When this situation exists, the slope of the phase appearing at the lower pressures should be used for the

---

[5] **Condensed Phases.**—In three-dimensional systems the condensed phases are the liquid and the solid. In early work with a film balance, it was noted that those oil films on water which exhibit the lowest molecular areas give a linear relation between film pressure and molecular area. These films are monolayers and have been designated as (1) liquid condensed, and as (2) solid (condensed). A third condensed phase has been discovered, but it occurs so rarely in films on water that it need not be considered here. No other phase of higher general molecular area exhibits such a linear relation.

Thus an oil film on water which adheres to the relation expressed by equation (3) is designated as a condensed film. Obviously, since the relation expressed by Eq. 4 is linear if that given by Eq. 3 is linear, any oil film which exhibits a linear relation between log (p/p_0), or more accurately, by log (f/f_0), is considered as a condensed film. However, it is much better to employ a plot of Eq. 3 in judging which region is condensed, since it exhibits much more curvature than that of Eq. 4 if the film is not condensed.

The criterion used to determine whether or not a film adsorbed on the surface of a solid is *condensed* is exactly the same: *i. e.*, where the π–σ relation is found to be linear, the film is considered as condensed. Every one of the 86 nitrogen isotherms determined over the whole range from $p/p_0 = 0$ to $p/p_0 = 1$ indicates that the condensed phase puts in its appearance while the film is still monomolecular (by the BET theory), and remains condensed after the film becomes polymolecular up to $(p/p_0) = 1$. However this does not mean that only a single condensed phase exists up to such a high vapor pressure. In the case of some other adsorbates (*e. g.*, butane or heptane on anatase), the condensed phase, as thus defined, does not begin until the number of molecules adsorbed is higher than that given for a complete monolayer by the BET theory.

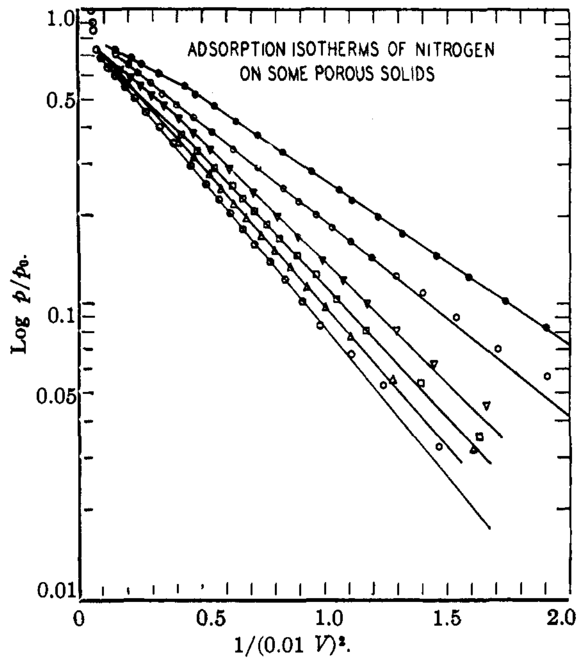

Fig. 4.—Nitrogen isotherms on porous solids of areas, beginning at the top, of 321, 365, 395, 409, 438, and 455 square meters per gram. These areas are 4.06 times the square roots of the linear portion of the isotherm.

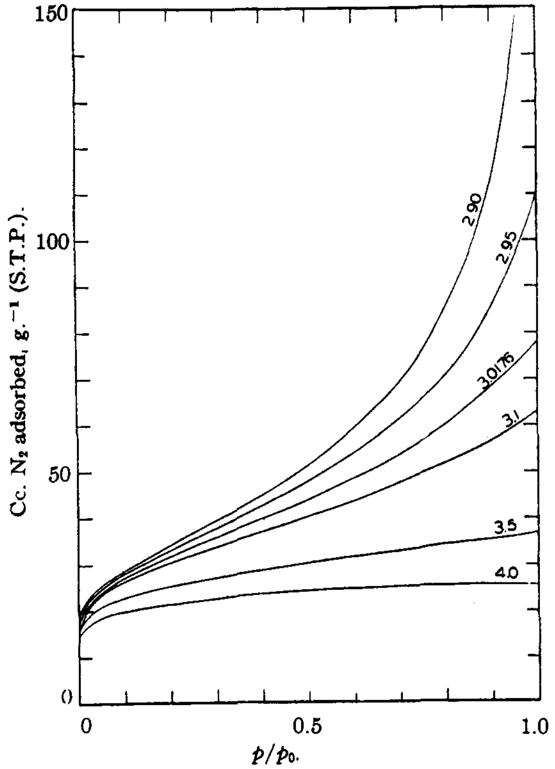

Fig. 5.—Effect of a change in the value of B (Eq. 4b) on the shape of the adsorption isotherm.

calculation of the area, inasmuch as this is the phase in which the monolayer is completely built up and a polymolecular film appears.

If, now, the area (Σ) of a single crystalline solid is determined by our absolute method (Paper XII) the value of k is given by

$$k = \frac{\Sigma}{A^{1/2}} \tag{6}$$

According to the usual convention the values of these quantities are those for one gram of the solid.

If nitrogen at −195.8° is the vapor adsorbed, then $k = 4.06$ and

$$\Sigma = 4.06A^{1/2} \tag{7}$$

gives the area (Σ) in square meters per gram. With other adsorbates or at different temperatures, the constant is different. The values thus far obtained are: water at 25°, $k = 3.83$; nitrogen at −195.8°, $k = 4.06$; n-butane at 0°, $k = 13.6$; n-heptane at 25°, $k = 16.9$.

The effect produced by a change in the value of the constant B upon the form of the adsorption isotherm is exhibited in Fig. 5. For a porous aluminum trioxide of area 118 sq. meters per gram, the following equation holds:[6]

$$\log_{10}p = (842.7/v^2) + 3.0176$$

In the figure, the value of B covers a range of values from 2.9 to 4.0. If B is 2.9 the isotherm is of the general (sigmoid) form we have obtained for non-porous and, except for the highest pressures, porous solids, and at the highest pressures the film is highly polymolecular. By merely changing B to 4, the curve takes on a form which exhibits some of the characteristics of the Langmuir isotherm, although the $B = 4$ curve gives a better fit to the experimental data in the one case studied. At the highest pressures the film is now not much thicker than a monolayer. It is evident that a still further increase in B would flatten the curve still more. One difference between this and the Langmuir curve is that the latter gives too low volumes adsorbed at the lower pressures while the new curve gives too high values.

The remarkable feature is that although they appear to exhibit considerable variation in shape, all of the isotherms represent *exactly the same area*

Table I

Comparison of Areas Obtained by the New Theory and That of Brunauer, Emmett and Teller as the Value of B of the New Theory is Varied (Σ in m.²g.⁻¹)

For $B = 3.1$, the Brunauer, Emmett and Teller equation no longer fits above 0.2 for p/p_0. and for $B = 3.5$, gives too short a linear region to be used. For $B \gtreqqless 3.02$ the BET isotherm is valid over the region in which BET consider their simple equation to be valid.

B	v_m	16.2 sq. Å. BET	New
2.90	28.41	124	118
2.95	27.56	120	118
3.0176	25.88	113	118
3.1	25.04	109	118

---

(6) In this equation, as is customary, the values of the constants include a last figure which is not significant.

by the new theory. The two lowest isotherms have a shape which the BET theory does not fit. The points on the four upper curves were considered as representing experimental data, and the areas were calculated by the BET theory. Moderately good agreement with the area (118 m.^{2} g.$^{-1}$) is exhibited as shown in Table I.

IV. Comparison of Values for the Areas of Solids Obtained by the New Theory and by That of Brunauer, Emmett and Teller

In Table II, A and B give a comparison of the areas of solids calculated from the new theory and by that of Brunauer, Emmett and Teller. For the area of the nitrogen molecule the value of 16.2 sq. Å. usually employed by Emmett and Brunauer[2] was used. When this area is adopted for calculations by the BET theory, *the area of any one of the six non-porous crystalline solids is almost exactly the same when calculated either by their method or by ours. This is extremely remarkable when the very great differences between the two theories, one kinetic and the other thermodynamic, are taken into consideration.*

Any disagreement between the two methods with the other vapors is due to a considerable extent to the values used for the molecular areas. The area of 32 sq. Å. for n-butane is that given by them; the 10.5 sq. Å. for water was calculated by the use of their equation, and that of 45 sq. Å. for n-heptane was calculated from crystallographic data.

If the area per nitrogen molecule is taken as the 16.2 sq. Å. which is so successful with the crystalline solids, then molecular areas which give better general agreement are: water, 12.2, n-heptane, 62, and n-butane, 54 sq. Å., although for this type of solid the data for butane are too few to make this particular value of any real significance.

TABLE II

AREAS OF SOLIDS BY THE NEW METHOD AND BY THAT OF BRUNAUER, EMMETT AND TELLER (AREAS IN SQUARE METERS PER GRAM)

A. Crystalline Solids

		BET Method				New Method			
	Absolute method	N_2 16.2	H_2O 10.5	n-Butane 32	n-Heptane 45	N_2	H_2O	n-Butane	n-Heptane
TiO_2 I	13.8	13.9	9.8	7.8	9.8	13.8[a]	13.8[a]	13.8[a]	13.8[a]
TiO_2–Al_2O_3	8.9	9.6	8.9			9.6	11.8		
$ZrSiO_4$		2.8	2.5			2.9	2.7		
TiO_2 II		8.7	8.3		6.1	8.7	8.4		8.7
$BaSO_4$		2.4	2.0	1.5	1.7	2.4	2.3	2.2	2.3
SiO_2		3.2	3.0		2.5	3.2	3.3		3.3

B. Porous Solids from Adsorption of Nitrogen[b]

$SiO_2 + Al_2O_3$		Other compositions	
BET (σ_{N_2} = 15.4 sq. Å.)	New	BET	New
633	602	208	203
415	415	178	185
475	505	132	132
373	370	105	106
254	257	80	82
129	131	37	35

For a comparison for 86 solids see Fig. 6

[a] The value of 13.8 is that determined by our absolute method (Paper XII). This value is used in the determination of the value of k (Eq. 5) of our relative method.

[b] For the BET calculation for porous solids the area of N_2 is assumed to be 15.4 Å.[2]

Data were obtained for the adsorption of butane and nitrogen on seven porous solids. Now, if 16.2 sq. Å. is considered correct for the area of the nitrogen molecule, then the area per butane molecule must vary from 37 to 52 sq. Å. when the BET theory is used for both sets of calculations, *i. e.*, with butane and with nitrogen. This demonstrates the fact that their assumption of a constant molecular area for an adsorbate, in its completed monolayer, is not justified.

Evidence for the validity of our method for the determination of molecular areas is given by Table IIA. This shows that when the area of one solid (as TiO_2 I) is fixed by our absolute method, the values for the others exhibit excellent agreement when any one of the three or four vapors is used. Water on anatase coated with aluminum trioxide is the only exception (see note, Table III).

V. The Areas Occupied by Molecules in Completed Monolayers Adsorbed on the Surfaces of Solids

If the area (Σ) of a solid is determined by our theory, and the number of molecules (N) in a completed monolayer by the BET theory then, as shown earlier, the area per molecule is given by

$$\sigma_m = \Sigma/N \qquad (1)$$

Inasmuch as the same data are used for the determination of both Σ and N, it is evident that any error in the mean molecular area (σ_m) is due to an error in Σ as determined by the new theory, or in N as determined by the BET theory, or by errors in both Σ and N, provided that accurate experimental data are used.

By the use of Eq. 1 the mean area of the nitrogen molecule in the completed monolayer has been calculated for each of 86 solids, some of which are non-porous and crystalline, though most of them are porous.

The remarkable fact which emerges is that the lowest molecular area found has a value of 13.6 sq. Å. (Emmett and Brunauer's area for solid N_2 = 13.8 sq. Å.), whereas the highest area is 16.8 sq. Å. (E and B area for liquid nitrogen = 16.2 sq. Å.).

The number (N) of non-porous and porous solids which exhibit any fixed value of the area (σ_m) for the molecule of nitrogen is represented in Fig. 6 as a function of the molecular area. Since there is some error in the value of σ_m, all solids for which the calculated values lie within 0.2 sq. Å. are used in plotting a single value of N. Thus 13 (15%) of the 86 solids exhibit the value of 15.15 to 15.35 sq. Å. and 36 (42%) give the area of the nitrogen molecule as between 14.95 and 15.55 sq. Å., with a mean value of 15.25, which may be said to be the preferred area of the nitrogen molecule.

However, every one of the six non-porous crystalline solids gave nitrogen areas which lie in the region of a secondary peak whose maximum is 16.05 sq. Å. This peak includes molecular areas for nitrogen on 18 porous, in addition to the 6 crystalline, solids. The areas for the latter average 16.25 sq. Å., which is practically identical with that assumed by Brunauer and Emmett, as calculated from the density of liquid nitrogen. It should be kept in mind that what is involved here is not the whole duplex film of nitrogen formed at saturation, which approximates a liquid state but only the first complete monolayer.

A second minor peak has a maximum at 14.05 sq. Å., but three solids associated with this peak give values of 13.85 and two of 13.65. It may be noted that Emmett and Brunauer, from the density of solid nitrogen, have calculated the value 13.8 which is close to that for the peak.

The interesting feature of the distribution in the values of the mean area of the nitrogen molecule, as calculated by Eq. 1, is the appearance of the three maxima in the distribution curve. Of the molecular areas, 83% are within 0.3 sq. Å. of the areas at the maxima 14.05, 15.25 and 16.05.

The number of different solids and the variety of surfaces investigated are not, as yet, sufficient to establish these peaks with certainty. However, the indications are very marked that the mean areas of the nitrogen molecule vary greatly as the nature of the surface changes.

Unfortunately, we cannot publish all of the detailed evidence which has been obtained in the experimental work. A typical example of a known change of surface is the following: a silica–alumina gel gave a molecular area for nitrogen of 14.1 sq. Å. The surface was then coated with a carbonaceous deposit by exposing the solid to hydrocarbon vapors for a short time at an elevated temperature. The deposit reduced the area of the solid, but increased the area determined for the nitrogen molecule to 16.2 sq. Å. After the deposit was removed, the area of the solid returned to its original, and the area of the molecule was found to return to 14.2 sq. Å., its initial value within the limits of error.

Five such instances have been investigated. The values with the carbon deposit on the surface were found to be within the narrow range of from 16.0 to 16.3 sq. Å., regardless of the initial value exhibited by the solid without the deposit.

In one series of solids composed of two components, silica and aluminum oxide, the ratio of the two was varied at concentrations of aluminum oxide of 6% or less. The area of the nitrogen molecule was found to be almost constant at 15.2 sq. Å., *but at 8% or more this shifted to 14.0 sq. Å.*

A second two component porous solid, of very different composition, gave a shift in the opposite direction. This exhibited an area of the nitrogen molecule of 15.2 sq. Å. for all samples in which the content of the second component was 2, 4 and 6% by weight, but with 10 to 12%, shifted to 16.2 sq. Å.

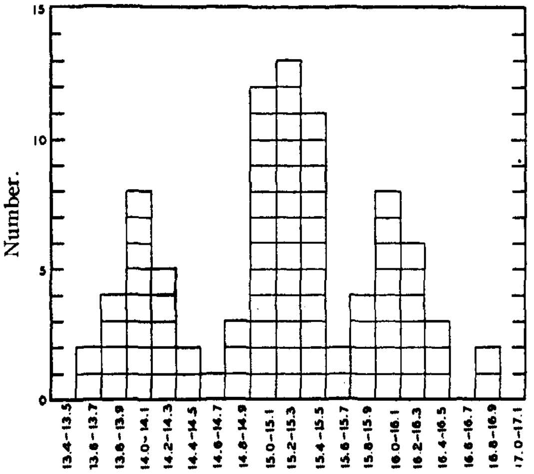

Fig. 6.—Molecular areas of nitrogen on 86 solids as calculated from the equations of Brunauer, Emmett and Teller, and of our new theory. All of the six non-porous crystalline solids investigated give nitrogen areas very close to 16.05 sq. Å., so these lie in the third frequency peak of highest area.

The X-ray analysis of this solid shows a certain structure at all of the lower percentages but indicates that at 12% a partial change to a second crystal form has occurred. Since X-rays are not sensitive to a small percentage change of structure, it is probable that the shift in the area of the nitrogen molecule was caused by this change in structure and detected the change at a lower concentration than the X-rays.

As a summary of these results it may be said that for the 86 porous and non-porous solids, the molecular areas occupied by nitrogen in its complete first monolayer at −195.8°, as calculated by us, extend from a value obtained from the density of solid nitrogen as a minimum to one obtained from the density of liquid nitrogen as a maximum.

Is it possible that in purely physical adsorption the surface lattice of the solid may increase the nitrogen area to higher values than any of those listed? Unfortunately, we cannot answer this question at the present time. However, the data available indicate that the structure of the solid has an effect on the area occupied by the adsorbed molecule.

Because of the great number of practical uses and almost universal interest in charcoal, one nitrogen isotherm was determined. The new method gave an area of 1350 m.^{2} g.$^{-1}$, the Langmuir theory, 1360 m.^{2} g.$^{-1}$, and the BET theory, 1050 m.^{2} g.$^{-1}$. Whether this agreement with the Langmuir theory is general or merely fortuitous will depend on the results of future work, which will be undertaken as soon as time permits. This work will be based on the more general treatment of the subject in paper XIV of this series.

For charcoal and some inorganic gels, the high adsorption per unit weight is due to the extremely high area, which is, however, possible only if the pores have very small diameters. It is the small size of the pores which limits the adsorbed material to a thickness of one molecule or slightly more. The theory of Langmuir assumes the films to be monomolecular and has thus been the one most generally applicable to the study of these isotherms. Yet this theory is not always in accord with the experimental isotherm. A fundamental question also exists, in the case of charcoal, as to what is meant by the area of the surface. For plane surfaces, non-porous materials, and materials with large pores, the term area has a definite concept. However, the extreme subdivision of charcoal leads to an ambiguity of the meaning of an area of definite size.

VI. Choice of a Method for the Calculation of the Area of a Solid from an Adsorption Isotherm

Although the best general experimental procedure for the determination of the area of a solid is to obtain the pressures and volumes or weights of the vapors adsorbed at constant temperature, it should be realized that no single equation of state is capable of transforming these data into a correct area for a solid in every case.

In calculations by our new method the basic equation is

$$\log p = B' - A/v^2 \text{ or } \log p/p_0 = B - A/v^2$$

so either $\log p$ or $\log p/p_0$ is plotted on the y axis and $1/v^2$ or $1/m^2$ on the x axis. If the linear region is not sufficiently extensive, the method should not be used.

If the equation of Brunauer, Emmett and Teller, which is

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{c-1}{v_m c}\frac{p}{p_0}$$

is to be applied, then $p/v(p_0 - p)$ is plotted against p/p_0. The intercept, if the plot gives a straight line, is $1/v_m c$ and the slope is $(c - 1)/v_m c$. As in the case of the new method, this equation should not be used if the plot is not linear over a sufficient length.

Fortunately, at least with almost every one of the very large number of solids whose isotherms have been determined by us, both methods are valid.

As pointed out earlier, the new method is not applicable unless a condensed film is formed. Thus it cannot be used if only expanded and intermediate phases are present in the adsorbed film, which situation, however, can be remedied by lowering the temperature. Nitrogen films practically always exhibit an extensive condensed phase at the temperatures employed, and are, therefore, particularly adapted to our type of calculation.

The equation of Brunauer, Emmett and Teller is commonly valid for the highest pressure region of the intermediate phase and the lowest region of the condensed phase. Thus, though very rarely their method of calculation may be valid, when ours is not. However, the total valid range of our equation is usually much greater than that of theirs, so in some cases, though rarely, our method may be applicable, when theirs is not.

The advantage of our method is that the area of a solid may be obtained without any knowledge of the area occupied by the adsorbed molecules. The greatest ordinary error in their method is that made in the estimation of this molecular area. Presumably their error from this single cause is ±10% if 15.4 sq. Å. is used as the area for the nitrogen molecule, but with their usual value of 16.2 sq. Å., is not far from +0.0 to +21%. Although these specific values are based upon the assumption that our new method is valid, variations of about this magnitude are to be expected on the basis of theories of the structure of solids.

Since the calculations are not difficult by either method, perhaps the best practice is to use both methods of calculation. That by our new method is much the simpler of the two, and avoids the troublesome estimation of the molecular area.

An advantage sometimes attributed to the BET method is that it gives the value of $E_1 - E_L$. According to their theory this is the energy required to remove one mole of adsorbed vapor from the first monolayer adjacent to the solid, minus the energy for a layer so distant that no effect of the solid is perceptible (molar internal heat of vaporization of the liquid).

However, it has been shown in an earlier paper[7] that the energy values obtained in this way are very much too low. This, however, does not interfere with the calculation of the area.

Thus, by the use of the theory of Brunauer, Emmett and Teller, good values are obtained for the areas of solids, but the energy values are incorrect.

The question arises as to whether the new theory or that of BET gives the more consistent results. Does our assumption of a constant value of k for each adsorbate give any better concordance in the areas obtained, than the assumption of a constant for the molecular area of the adsorbate?

Data which give evidence (in addition to that presented in Section D) related to the answer to this question are represented by Table III. The area of TiO_2 I is that determined by our absolute method (13.8 m.^{2} g.$^{-1}$) which is much more accurate than either the new relative or the BET method. The molecular areas (σ_m) are those which must be assumed for the BET calculations

---

[7] W. D. Harkins and E. Boyd, THIS JOURNAL, 64, 1195 (1942).

to give the correct area for this solid. The areas obtained by the assumption of a constant k are seen to be much more consistent than those obtained from a constant molecular area in the BET procedure. Similar work needs to be done with porous solids, but for them the molecular size of the material of the adsorbed vapor should be kept small and moderately constant, since otherwise the curvature of the pores may have an appreciable effect.

TABLE III

AREAS OF SOLIDS CALCULATED BY THE NEW METHOD AND BY THAT OF BRUNAUER, EMMETT AND TELLER

(Areas in Square Meters Per Gram)

The data used for both sets of calculations are the same.

A. Crystalline Solids

	New Method				BET Method			
	N_2	H_2O	n-Butane	n-Heptane	N_2 σ = 16.1	H_2O 14.8	n-Butane 56.6	n-Heptane 64.0
TiO_2I (Standard)	13.8	13.8	13.8	13.8	13.8	13.8	13.8	13.8
TiO_2 II	8.7	8.4		8.7	8.6	11.7		8.7
SiO_2 (Quartz)	3.2	3.3		3.3	3.2	4.2		3.6
$BaSO_4$	2.4	2.3	2.2	2.3	2.4	2.8	2.7	2.4
$ZrSiO_4$	2.9	2.7			2.8	3.5		
TiO_2 + Al_2O_3[a]	9.6	11.8			9.5	12.5		

[a] This solid consists of anatase coated with a very slight deposit of Al_2O_3. The adsorption of water was *excessively* slow (requiring seven days to obtain 22 points up to p = 23 mm. at 25°) which suggests the possibility of some other process than that of physical adsorption. The isotherm was by far the poorest of those obtained. With this solid either method gives abnormally high areas with water.

Summary

1. An extremely simple method has been developed for the calculation of the surface area of a solid from the adsorption isotherm. This consists in plotting log p (or better log p/p_0) against the reciprocal of the square of the volume adsorbed ($1/v^2$). In general a straight line, which represents a condensed film, is obtained over a considerable range of the plot. The area (Σ) of the solid is given by the equation $\Sigma = ks^{1/2}$, where s is the slope of the straight line and k is a constant for a given adsorbed vapor at a given temperature. The value of k, as determined by our absolute method is: nitrogen at −195.8°, 4.06; water at 25°, 3.83; n-butane at 0°, 13.6, and n-heptane at 25°, 16.9.

2. The closeness in the agreement between values obtained by this new method and those calculated by the theory of Brunauer, Emmett and Teller by the use of Emmett and Brunauer's favorite area for the nitrogen molecule, is almost unbelievable. This statement must be restricted to the six non-porous crystalline solids for which we determined nitrogen adsorption isotherms at −195.8°. The following list gives the areas of the six solids in sq. m.^{2} g.$^{-1}$, the first value being that by our new method, and the second that calculated from the same data by use of the BET theory: anatase (TiO_2)I, 13.8 and 13.9; TiO_2 + Al_2O_3, 9.6 and 9.6; $ZrSiO_4$, 2.9 and 2.8; TiO_2 II, 8.7 and 8.7; $BaSO_4$, 2.4 and 2.4; and silica, 3.2 and 3.2.

3. Our new method gives directly the area (Σ) of the solid, without the assumption of a molecular area for the adsorbate; that of Brunauer, Emmett and Teller does not give the area of the solid, but does give the number (N) of molecules in the completed first monolayer. A combination of the two methods gives results of great interest, since $\sigma = \Sigma/N$, gives the area (σ) per molecule. The results obtained by the application of this equation show that a diagram which plots the number of solids on which nitrogen occupies a given area against this area, exhibits three peaks, at 14.05, 15.25 and 16.05 sq. Å. The smallest area is close to that for solid and the last to that for liquid nitrogen, as calculated by Emmett and Brunauer.

4. Neither the new method nor that of Brunauer, Emmett and Teller, gives the area of a solid unless the equation of the isotherm gives a sufficiently long linear region. With the new method the linear region occurs only where the adsorbed film is condensed, while the BET equation gives a linear region at vapor pressures slightly below, but only at the lower pressures at which a condensed film exists. With nitrogen as the adsorbate the region in p/p_0 of existence of a linear relation is in general much more extensive for the new, than for the BET method. The criterion used to determine the existence of a condensed film is that the equation $\pi = b - a\sigma$, or $\log (p/p_0) = B - A/v^2$, represents the data. If a condensed film is not formed the temperature may be lowered until this two-dimensional phase appears.

5. The apparatus used for the determination of an adsorption isotherm is described.

CHICAGO, ILLINOIS RECEIVED MARCH 13, 1944