

This amount of oxygen can be recovered in a dibasic acid which is probably a dimer of the original acid. Three-fourths of the absorbed

oxygen in this product is removed by treatment with alkali.

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[CONTRIBUTION FROM KENT CHEMICAL LABORATORY, THE UNIVERSITY OF CHICAGO]

Cross-Sectional Areas of Molecules Adsorbed on Solid Surfaces^{1a}

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The data relating to the cross-sectional areas of molecules in insoluble monolayers adsorbed on water are quite extensive. Adam² has listed limiting area values for 26 different classes of molecules. Recently, an increasing number of adsorption studies for gases and vapors adsorbed on solid surfaces of *known area* have been reported.³ This is principally due to the development of an adsorption theory⁴ which permits the calculation of the specific surface of any solid for which vapor adsorption data are available. Therefore, it should be possible to establish a body of area data for vapor molecules adsorbed on solid surfaces analogous to the data for insoluble molecules adsorbed on liquid surfaces.

As will be explained in the following section, cross-sectional area data for molecules adsorbed on solid surfaces are subject to restriction in that they are based on specific surface data which, in turn, are based on cross-sectional area data. If the experimental results are properly interrelated, however, it is possible to obtain accurate relative values for molecular cross-sectional areas.

Theoretical.—Brunauer, Emmett and Teller⁴ have developed an equation in the form

$$q_m = \frac{q(p_0 - p)(p_0 - p + cp)}{cp p_0} \quad (1)$$

q_m = quantity of vapor adsorbed when a monomolecular layer exists, g. per g. of adsorbent.

q = quantity of vapor adsorbed at any pressure, g. per g. of adsorbent.

p = pressure; p_0 = saturation pressure.

c = $(a_1 b_1 / a_i b_i) \exp. (E_1 - RT.E_i) /$

E = energy of adsorption.

a and b are probability factors in the equations:

ap = number of molecules condensing per unit area;

$b \exp. (E/RT)$ = number of molecules evaporating per unit area.

Subscripts "1" refer to first layer of adsorbed molecules.

Subscripts "i" refer to all other layers (average values).

As pointed out in their paper, the equation may be transposed to give

$$p/q(p_0 - p) = 1/cq_m + p(c - 1)/cq_m p_0 \quad (2)$$

Since p and q can be measured, this straight-line form of the equation can be used to evaluate c and

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(2) Adam, "The Physics and Chemistry of Surfaces," Oxford Press, New York, N. Y., 1941, p. 50.

(3) Brunauer, "The Adsorption of Gases and Vapors. Vol. I. Physical Adsorption," Princeton University Press, Princeton, 1943.

(4) Brunauer, Emmett and Teller, *THIS JOURNAL*, **60**, 309 (1938).

q_m . The specific surface of the adsorbent is given by the equation

$$\Sigma = Nq_m\sigma/M \quad (3)$$

Σ = specific surface, sq. cm. per g. of adsorbent.

N = Avogadro number.

σ = cross-sectional area of a single molecule (in plane of adsorbent surface), sq. cm.

M = molecular weight.

Therefore if σ is known, Σ can be calculated. Emmett⁵ has given a detailed treatment of this method as applied to the low temperature adsorption of nitrogen.

When pressure-area curves are determined for insoluble monolayers spread on water, the area per molecule is obtained from the equation

$$A = MS/WN \quad (4)$$

A = area per molecule, sq. cm.

W = weight of insoluble material spread on surface, g.

S = total area available to monolayer, sq. cm.

In the same manner, the area available to each molecule adsorbed on a solid surface can be calculated from the analogous equation

$$A = M\Sigma/qN \quad (5)$$

With pressure-area data for insoluble monolayers, it is possible to recognize one portion of the curve as corresponding to close-packed chains. The area per molecule in this region is accepted as being equivalent to the actual area of the molecule in a plane parallel to the adsorbing surface, that is, the cross-sectional area (hereafter referred to as "section area"). This section area is found to be approximately equal to that which would be predicted from measurements of molecular dimensions in the normal condensed phases (liquid or solid).

Section area data obtained from pressure-area data for insoluble monolayers are known to vary with the temperature or surface pressure. It would be expected that similar results would be obtained with adsorbed layers on solids, and therefore σ -values used in equation (3) would vary somewhat with temperature, surface pressure, and solid surface.

By use of equation (2), the adsorption corresponding to a complete monolayer can be calculated. The molecular area, A , at this point is equivalent to the actual cross-sectional area occupied by the molecules measured in a plane parallel to the adsorbing surface. Accordingly, when

(5) Emmett, *Advances in Colloid Sci.*, **1**, 1 (1942).

$q = q_m$, $A = \sigma$, and equation (5) is identical with equation (3) at this point. Thus, A is the area available to each molecule, which will be very great at the beginning of adsorption, while σ is the area which is effectively occupied by each molecule. This area will be very similar to that which is determined from considerations of the atomic volumes involved, but will depend on the packing which the molecules adopt.

It should be emphasized that this treatment is based on the monomolecular adsorption as calculated by the equation of Brunauer, Emmett and Teller, and the results are subject to the same limitations as is their theory. Recent publications have questioned the validity of the equation. Kistler, Fischer and Freeman⁶ have objected to the derivation on two counts. They point out that if E_1 is greater than E_i (see equation (1)), as Brunauer, Emmett and Teller assume, molecules in the second layer will distill to fill any bare space in the first layer if that layer is not yet complete. However, one would not expect the energy of adsorption on the bare solid surface to be a constant throughout the process of adsorption. It would seem that E_1 represents an average value, and when the solid surface is almost completely covered, the energy of adsorption on the few bare spaces remaining is so small that condensation in the second or subsequent layers is more probable. Statistically, however, the rate of evaporation over the entire first layer remains equal to $b \exp. (E_1/RT)$. Thus E_1 and E_i , like a and b , are constants of the equation and should be interpreted primarily as such. The second objection of Kistler, Fischer and Freeman is that capillary condensation is neglected in equation (1). Inasmuch as the equation fits experimental data very well for pressures up to $p/p_0 = 0.3$, even for many porous solids, the objection is not serious for the portion of the isotherm which determines q_m . This would be especially true for crystalline non-porous adsorbents such as those used in the present work.

Rowley and Innes⁷ have applied a two-dimensional phase rule to determine that multilayers adsorbed from vapors onto solids must exist as gaseous two-dimensional films. They conclude that the energy of vaporization in layers after the first cannot be a factor in equation (1). Again, this objection does not appear to invalidate the equation in its original form. Although Brunauer, Emmett and Teller have suggested that E_1 is approximately equal to the energy of vaporization of the bulk liquid, this assumption has no effect on the fundamental theory. It is only necessary that E_1 be equal to the energy involved in multilayer formation, whatever the source of the energy. The layers may be gaseous, liquid, or solid without affecting the result. If E_1 is not equal to the energy of vaporization, equation (1) must be modified to a form in which p_0 is replaced

by a new constant. The writer has studied this possibility and found that the value of this constant has relatively little effect on the form of the theoretical isotherm when p/p_0 is less than 0.3; that is, in the range where the equation fits experimental data.

In this connection, it is interesting that the new adsorption isotherm of Jura and Harkins⁸ is based on the assumption that the adsorbed films obey the pressure-area relations developed for condensed monolayers on water surfaces. This would seem to contradict the conclusion of Rowley and Innes to the effect that the films are gaseous rather than condensed. The Gibbs equation for vapor-solid adsorption (see Boyd and Livingston,⁹ equation (15)) is

$$\pi = (RT/M\Sigma) \int_0^p (q/p) dp \quad (6)$$

π = surface pressure of the adsorbed film on the solid surface. If equations (1) and (3) are substituted into this equation

$$\pi = (RT/N\sigma) \ln [(p_0 - p + cp)/(p_0 - p)] \quad (7)$$

This is the relation between π , the surface pressure, and the gas pressure for adsorptions to which the equation of Brunauer, Emmett and Teller applies. It can be shown that pressure-area plots constructed from equations (7) and (5) show a considerable portion which is approximately a straight line. That is, the basic equation of Jura and Harkins

$$\pi = a - bA \quad (8)$$

is in agreement with the equation of Brunauer, Emmett and Teller over a considerable range of pressure. For example, the data of Table I can be fitted to the equation

$$(N\sigma/RT)\pi = 2.58 - 1.65 A/\sigma \quad (9)$$

over the pressure range $p/p_0 = 0.07$ to $p/p_0 = 0.5$. This is very similar to the range of agreement reported for the isotherm of Jura and Harkins.

TABLE I

THEORETICAL PRESSURE-AREA DATA		
Calculated from equations (7), (1) and (5), with $c = 50$.		
p/p_0	$(N\sigma/RT)\pi$	A/σ
0.01	0.176	2.95
.05	.559	1.31
.06	.622	1.23
.075	.704	1.15
.09	.774	1.09
.10	.816	1.06
.125	.910	0.996
.15	.992	.946
.175	1.06	.903
.20	1.13	.865
.30	1.35	.733
.40	1.54	.619
.50	1.71	.510

Accordingly, the new isotherm seems to be closely related to that of Brunauer, Emmett and

(6) Kistler, Fischer and Freeman, *THIS JOURNAL*, **65**, 1909 (1943).

(7) Rowley and Innes, *J. Phys. Chem.*, **46**, 694 (1942).

(8) Jura and Harkins, *J. Chem. Phys.*, **11**, 430 (1943).

(9) Boyd and Livingston, *THIS JOURNAL*, **64**, 2383 (1942).

Teller, although it is perhaps superior at higher pressures. The success of the Jura-Harkins isotherm increases our confidence in the Brunauer-Emmett-Teller theory.

Measurements.—Emmett and Brunauer have described the adsorption apparatus which they have used for measurement with oxygen or nitrogen at or near their boiling points.¹⁰ A facsimile of this apparatus has been used in this work for determining the nitrogen isotherms. Boyd and Livingston⁹ have described an apparatus which is very satisfactory for adsorption studies with vapors which liquefy at room temperature and atmospheric pressure. They use a gravimetric method employing the McBain-Bakr silica spring balance,¹¹ which is especially designed for use with organic vapors which attack stopcock grease. This apparatus was used for determining the adsorption isotherms of water, *n*-propyl alcohol, and *n*-heptane on the same sample of four different crystalline powders: quartz, anatase, barium sulfate and graphite. These adsorption isotherms have been reported previously.⁹ All of the isotherms have been fitted to the Brunauer-Emmett-Teller equation with least square calculations, using the straight line form, equation (2). Thus, for any single sample of powdered solid, it was possible to determine the constants of the Brunauer, Emmett and Teller equation with several different vapors. These are reported in Table II.

TABLE II

THE CONSTANTS OF THE BRUNAUER-EMMETT-TELLER EQUATION

Solid	Adsorption measurements at 24°					
	Water		Propyl alcohol		Heptane	
	q_m	c	q_m	c	q_m	c
Anatase	2.32	82.2	4.09	66.8	2.22	37.6
Quartz	0.85	72.0	1.47	106.8	0.92	29.1
BaSO ₄	0.57	218	0.86	132	0.64	44.1
Graphite					9.36	72.0

The Section Area of Adsorbed Molecules.—

For many molecules there are a number of independent methods for determining the molecular area, so that a most probable value can be developed from the consideration of the several methods. The effective dimensions of a molecule can be calculated from the density of the bulk phase if the nature of the packing is known and the molecules are spherical. The value of σ can be calculated for all combinations of the three simplest three-dimensional packings and the two simplest two-dimensional packings. The equation which is used is

$$\sigma = F(M/N\rho)^{1/3} \quad (10)$$

where ρ = the density of the bulk phase. The values of F , the packing factor, are given in Table III.

For the closest possible packing, $F = 1.091$. This is the factor which Emmett and Brunauer¹⁰

(10) Emmett and Brunauer, *THIS JOURNAL*, **59**, 1553 (1937).
 (11) McBain and Bakr, *ibid.*, **48**, 690 (1926).

TABLE III
PACKING FACTORS¹²

Type of three-dimensional lattice	Packing Factor	
	Square Two-dimensional packing, 4 nearest neighbors	Hexagonal Two-dimensional packing, 6 nearest neighbors
Simple cubic, 6 nearest neighbors	1.000	0.866
Body-centered cubic, 8 nearest neighbors	1.190	1.023
Face-centered cubic, 12 nearest neighbors	1.260	1.091

have used in their calculations. For nitrogen, this leads to cross-sectional areas of 16.2 and 13.8 Å. per molecule, based on liquid density at -196° and solid density at -252°, respectively. In their early publications, Emmett and Brunauer used both areas, but Emmett and DeWitt¹³ used the liquid value exclusively. Ruhemann¹⁴ reports that β -nitrogen (the form which is stable above 35° K.) crystallizes in the form of spheres with closest possible packing. This indicates that 1.091 is the correct packing factor and the section area at -196° is between 13.8 and 16.2 sq. Å.

The water molecule is not spherical, but the volume of hydrogen is so small in comparison with oxygen that the molecule must be almost a sphere. Ice crystals exhibit low symmetry, indicating that packing is somewhat looser than for any of the types referred to in Table III. It is very difficult to predict the area of the water molecule by use of equation (10), but if F is taken to be 1.091, the section area can be calculated to be 11.1 sq. Å., based on the solid density at 0°, or 10.6 sq. Å., based on the liquid density at 24°.

From X-ray crystallographic measurements, Müller¹⁵ has concluded that the distance of nearest approach between normal hydrocarbon molecules is 4.75 Å. and the length of the molecules is 1.29 Å. per carbon. Accordingly, the *n*-heptane molecule may be treated as a cylinder 4.8 Å. in diameter and 9.1 Å. long. Stewart¹⁶ has studied the X-ray diffraction pattern of liquid hydrocarbons at room temperature and reported 4.63 Å. as the distance of nearest approach. With either of these values, the area occupied by a *n*-heptane molecule with the long axis perpendicular to the solid surface would be approximately 20 sq. Å. If the molecule were oriented with the long axis parallel to the solid surface, the area would be 42.3 sq. Å. for the closest possible packing. This value would be greater for a less ordered arrangement.

From X-ray studies of the long-chain alcohols, Bernal¹⁷ has concluded that their molecular di-

(12) This table was developed with the assistance of Prof. W. H. Zachariasen.

(13) Emmett and DeWitt, *Ind. Eng. Chem., Anal. Ed.*, **13**, 28 (1941).

(14) Ruhemann, *Z. Physik*, **76**, 368 (1932).

(15) Müller, *Trans. Faraday Soc.*, **29**, 990 (1933).

(16) Stewart, *Phys. Rev.*, **31**, 174 (1928).

(17) Bernal, *Z. Krist.*, **83**, 153 (1932).

mensions are similar to those for hydrocarbons, except that the molecular length is increased by 1.0 Å. by the hydroxyl group. His data indicate that the *n*-propyl alcohol molecule is 4.9 Å. long and 4.8 Å. in diameter. Stewart and Morrow¹⁸ found liquid *n*-propyl alcohol molecules to give a diffraction pattern corresponding to 4.3 Å. for the distance of closest approach and 5.1 Å. for the molecular length (4.8 Å. from a smooth curve). If the propyl alcohol molecule is considered to be a sphere 4.8 Å. in diameter, the section area will be 23.0 sq. Å. per molecule if square packing is assumed, and 19.9 sq. Å. per molecule for close packing. Film balance measurements can be used to determine the cross-sectional area of alcohol molecules oriented with the hydroxyl to the water surface. The extrapolation to zero pressure of the pressure-area curve for liquid films is considered to give the area of the alcohol group. The best available data are those of Copeland, Harkins and Boyd¹⁹ for eicosyl alcohol at 24°, which give 22.4 sq. Å. molecule. It is not certain that this zero pressure value has much relation to the area of a propyl alcohol molecule which is on a solid surface under a surface pressure⁹ of 60 dynes per cm.

Results.—On the basis of the considerations developed in the preceding paragraphs, values of σ have been chosen which will give satisfactory agreement among all the adsorption data. It was concluded that the section areas are in the ratio

$$\text{N}_2:\text{H}_2\text{O}:\text{PROH}:\text{Heptane} = 15.4:10.6:20.0:55.0$$

The data supporting this conclusion are presented in Table IV. The high section area obtained for heptane indicates that the molecules are oriented with the long axis parallel to the solid surface, or at least that the molecules are spaced so that there is room for such a flat orientation.

The q_m values from the nitrogen isotherms were used for calculating the specific surface of the finely-divided solids, according to the method out-

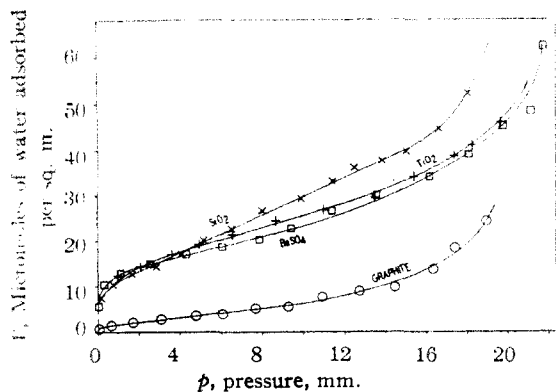


Fig. 1.—The adsorption of water by various solids (saturation pressure = 22.4 mm., temperature 24°).

(18) Stewart and Morrow, *Phys. Rev.*, **30**, 232 (1927).

(19) Copeland, Harkins, and Boyd, *J. Chem. Phys.*, **10**, 357 (1942).

TABLE IV
COMPARISON OF SPECIFIC SURFACE AND SECTION AREA VALUES

Vapor	Value of σ used, Å. ² per molecule	Specific surface, sq. m./g., corresponding to each value of σ			
		TiO ₂	SiO ₂	BaSO ₄	Graphite
Nitrogen	16.2	8.70	3.20	2.39	27.6
	15.4	8.27	3.05	2.27	26.2
Water	10.6	8.28	3.03	2.03	
Propyl alcohol	20.0	8.25	2.99	1.74	
Heptane	20.0	2.68	0.70	0.49	7.1
	43.6	5.85	2.42	1.70	24.7
	55.0	7.39	3.08	2.14	31.2

lined by Emmett.⁵ Equation (3) was used, with 15.4 sq. Å. taken as the section area of the nitrogen molecule, instead of 16.2 which Emmett prefers. This value of 15.4 coincides with the most frequent and also the average value reported by Jura and Harkins²⁰ on the basis of 60 isotherms. This value was obtained by reference to a sample of anatase the area of which had been measured by a calorimetric technique which was independent of cross-sectional area data for the adsorbed molecules.²¹ This new technique offers an interesting method of checking section area values.

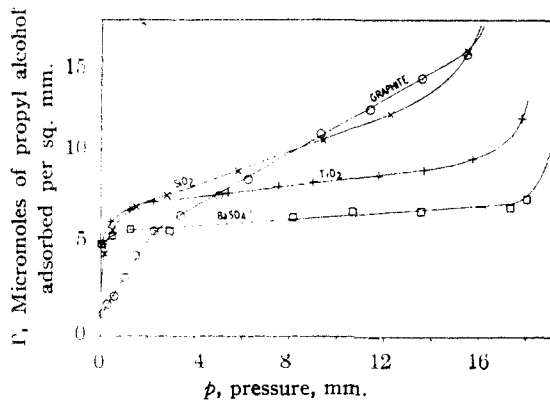


Fig. 2.—The adsorption of *n*-propyl alcohol by various solids (saturation pressure = 19.3 mm., temperature 24°).

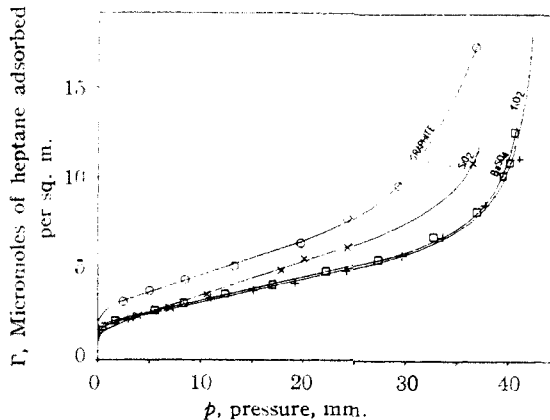


Fig. 3.—The adsorption of *n*-heptane by various solids (saturation pressure = 44.6 mm., temperature 24°).

(20) Jura and Harkins, *ibid.*, **11**, 431 (1943).

(21) Harkins and Jura, *ibid.*, **11**, 430 (1943).

The specific surface of the solids (in sq. m. per g.) determined by this method were TiO_2 , 8.27; SiO_2 , 3.05; BaSO_4 , 2.27; graphite, 26.2.

The adsorption isotherms presented in a previous publication⁹ have been recalculated and transposed into a form which emphasizes the agreement between the various sets of data. These isotherms have been plotted in Figs. 1, 2 and 3. The ordinate for these plots is Γ , the molar adsorption per unit area, obtained from the equation

$$\Gamma = q/M\Sigma \quad (11)$$

The Σ -value which was obtained from the nitrogen isotherms was used in every case. It will be seen that for quartz, anatase and barium sulfate, the break in the isotherms which corresponds to a complete monolayer⁴ occurs at very nearly the same value of Γ .²² For any vapor, the adsorbed molecules in the monolayer occupy the same area on each of these three solid surfaces. The isotherms for adsorption on graphite are not in agreement with the others. This may be due in part to impurities in the graphite sample (Dixon 0708) or to the extreme difficulty of outgassing graphite surfaces.²³

The isotherm for heptane on graphite appears to be normal except for the higher Γ -value at the break of the curve. This suggests that heptane has a closer packing on the graphite surface than on quartz or the other solids. For heptane molecules on graphite, the section area is found to be 44 sq. Å., as compared to 55 sq. Å. for heptane on other surfaces (see Table IV). This value is very near the minimum area for the flat orientation (42.3). It is interesting that the section area value for heptane adsorbed on solids corresponds to an orientation with the long axis parallel to the solid surface. X-Ray studies of aliphatic molecules have consistently indicated an orientation with the long axis normal to the solid surface.²⁴

Conclusions.—The modified McBain-Bakr adsorption technique which was described by Boyd and Livingston⁹ has been used to determine isotherms for organic molecules and water. The technique can be used to study the cross-sectional

area of organic molecules which are too volatile to be used in film balance work with insoluble monolayers on water.

It has been mentioned that a comparison between specific surface values obtained when different vapors were used with the same solid would make it possible to assemble a complete set of data regarding the section area of adsorbed molecules. All values would be relative; however, X-ray, density, and film balance measurements could be used to calculate area values for each molecule which should be interrelated with the relative values from adsorption data. There would be a degree of uncertainty because some molecules would pack more closely on one surface than on another. This seems to be the case for heptane on graphite, in the present study. Such differences could be recognized easily, as could differences in orientation. The final result of a series of such adsorption measurements would be a table presenting the area of molecules adsorbed as monolayers on solids, and would be analogous to the tabulated data which now exist for substances which form insoluble films on water.²

Acknowledgment.—The writer appreciates the interest and encouragement of Dr. G. E. Boyd, who was senior author of an earlier publication⁹ based on the same experimental data used in the present work.

Summary

For four different finely-divided solids, adsorption isotherms have been measured both by the Brunauer-Emmett low temperature nitrogen adsorption technique and by the McBain-Bakr method, using vapors from substances which boil well above room temperature. By comparison of the various isotherms, the cross-sectional area values for the adsorbed molecules (in Å.² per molecule) have been found to be H_2O , 10.6; PrOH , 20.0; heptane, 55.0, if nitrogen is taken to be 15.4. These areas are in every case in good agreement with the molecular areas of the molecules as determined from density, X-ray, or film balance measurements. The modified McBain-Bakr technique offers a method for measuring the section areas of adsorbed organic molecules of all types. It can also be used for determining the surface area of finely-divided solids from adsorption measurements at room temperature, using the vapors from ordinary volatile liquids.

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(22) Propyl alcohol on barium sulfate seems to be an exception.

(23) The outgassing procedure which was used was as follows: The adsorption chamber was evacuated to 250 mm., heated to 500–650° for two hours, then while still at this temperature evacuated with a mercury diffusion pump for twelve hours and finally with a charcoal trap at liquid air temperatures until a vacuum of 1μ had been indicated for one hour.

(24) Finch, *J. Chem. Soc.*, 1137 (1938).