is doubtful whether any significance can be attached to the negative slopes of the latter, because in the range $M = 0$ to 0.725 the variation of $\Delta C_{p_1}{}^{0*}$ is only 0.7 cal. deg.$^{-1}$ mole^{-1}, which is probably less than the experimental error.

The author wishes to thank Professors H. S. Harned, B. B. Owen and S. E. Wood for many helpful discussions.

Summary

Electromotive forces of the cells $H_2 \mid Z^* (m_1)$, $HZCl(m_2)$, $NaCl(M—m_2) \mid AgCl–Ag$ have been determined at five-degree intervals from 5 to 55° and at six constant ionic strengths from 0.1 to 3 molal. From these, the first ionization constants of glycine in salt solutions, $K_1{}^* = [m_H m_Z/m_{HZ}]_{0.M}$, have been computed. The first ionization constants of glycine in water have been obtained by extrapolation of the results in salt solutions.

Equations for computing $-\log K_1{}^*$ as a function of temperature are given. From them, the derived thermodynamic quantities $[\gamma_H\gamma_Z/\gamma_{HZ}]_{0.M}$, $[\gamma_{HZ}\gamma_{OH}/\gamma_Z a_{H_2O}]_{0.M}$, $\Delta F_1{}^{0*}$, $\Delta H_1{}^{0*}$, $\Delta C_{p_1}{}^{0*}$, and $\Delta S_1{}^{0*}$ have been calculated and their variations with salt concentration illustrated by plots and tables.

NEW HAVEN, CONN.

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Surface Area Measurements of Activated Carbons, Silica Gel and other Adsorbents

BY LESLIE G. JOYNER,[1] EDWARD B. WEINBERGER AND C. W. MONTGOMERY

Since the development by Brunauer, Emmett and Teller (BET)[2] of an equation for an adsorption isotherm based on a multilayer theory, considerably increased interest has been shown in the physical adsorption of gases on solids. The BET equation was the first to give good agreement with the experimental data for all types of vapor-on-solid adsorption and made possible the calculation of a reasonably accurate value for the area of the adsorbent.

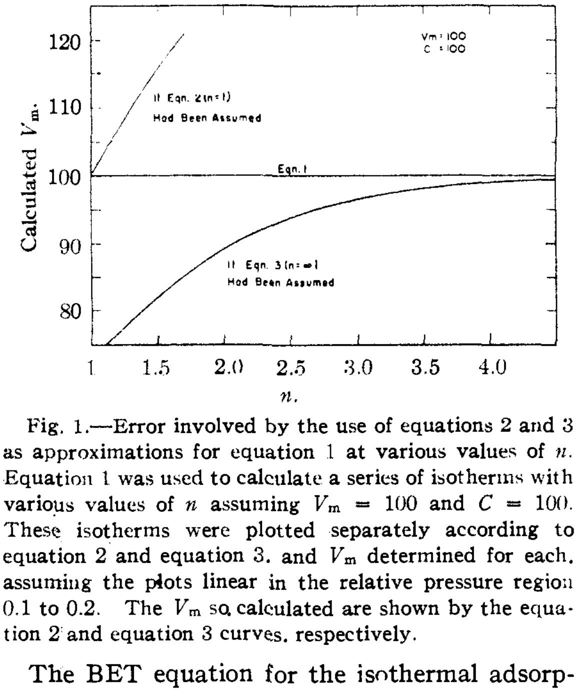

Fig. 1.—Error involved by the use of equations 2 and 3 as approximations for equation 1 at various values of n. Equation 1 was used to calculate a series of isotherms with various values of n assuming $V_m = 100$ and $C = 100$. These isotherms were plotted separately according to equation 2 and equation 3, and V_m determined for each, assuming the plots linear in the relative pressure region 0.1 to 0.2. The V_m so calculated are shown by the equation 2 and equation 3 curves, respectively.

The BET equation for the isothermal adsorption is

$$V = \frac{V_m CX}{(1 - X)}\left(\frac{1 - (n + 1)X^n + nX^{n+1}}{1 + (C - 1)X - CX^{n+1}}\right) \quad (1)$$

where V_m is the volume of gas (S.T.P.) necessary to form a monolayer; C is related to the heat of adsorption of the monolayer (E_l) and the heat of liquefaction (E_L) by the relation $RT \ln C = E_l - E_L$; n is the number of layers to which the gas is limited; X is the relative pressure and V the volume of gas (S. T. P.) adsorbed.

For the purpose of calculating the surface area of solids, equation 1 is commonly used in one of its two limiting forms

$$\frac{X}{V} = \frac{1}{CV_m} + \frac{X}{V_m} \qquad n = 1 \quad (2)$$

or

$$\frac{X}{V(1 - X)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C}X \qquad n = \infty \quad (3)$$

For values of n greater than 3 or 4 and for values of X up to 0.25, equation 3 is a fair approximation to equation 1, providing C is considerably greater than unity. On the other hand, equation 2 can be used only for isotherms which have an n value very close to unity.

Figure 1 demonstrates the approximate error involved in the use of either equation 2 or 3 rather than the full BET equation for isotherms with n less than 4 and C equal to 100. The curves of Fig. 1 were prepared by assuming an adsorbent with a fixed true value of V_m and C. Isotherms with various values of n were calculated from equation 1 and from them, apparent values for V_m and C were recalculated by equation 2 or 3, assuming a linear plot between $X = 0.1$ and 0.2. From Fig. 1, it is apparent that neither equation 2 or 3 will give V_m within 5% of the true value, if the isotherm has an n in the range 1.15 to 2.7.

In the course of the examination of a great many and variety of isotherms, we have found a number, for which n was less than 4 and greater than 1.

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[2] Brunauer, Emmett and Teller, THIS JOURNAL, 60, 309 (1938).

The present paper comprises a presentation of a number of these isotherms together with a description of an improved method for applying equation 1 to them. A comparison is also included between the surface areas as calculated by the methods of Kistler, Fischer and Freeman,[3] by that of Harvey,[4] and by equation 1.

Experimental

The isotherms were determined on a standard Emmett and Brunauer[5] apparatus. To obtain greater precision, a wide bore manometer was used with a vernier attachment which enabled the pressure to be read to 0.1 mm. For pressures below 5 cm., a micro-cathetometer was used to read the pressures to 0.01 mm. The gases used were prepurified nitrogen and C. P. *n*-butane, both dried over phosphorus pentoxide. Calibration was by helium purified by passing over activated carbon at liquid nitrogen temperatures.

The adsorbents used were two commercial cracking catalysts of the alumina–silica variety, several activated carbons of various types and a commercial silica gel (Davidson Chem. Co., Grade 6956—160). The material was first crushed to 14 to 18-mesh and introduced into the adsorption bulb as 0.1 to 0.6 g. samples. The sample was then baked at 200° for one hour with the mercury diffusion pumps on. More severe degassing conditions were tried but no difference in either the isotherm or the weight could be detected. The dry weight of the sample was determined before the run and again at the end as a check.

Figure 2 indicates the excellent precision obtained. The four determinations shown are for separate samples of the adsorbent and were made by various operators.

In order to fit the isotherms to the linear equations, the linear portion of plots according to equation 2 or 3 was selected visually and the method of least squares was then applied to the points in this linear region. The procedure for fitting the isotherm to equation 1 will be described later.

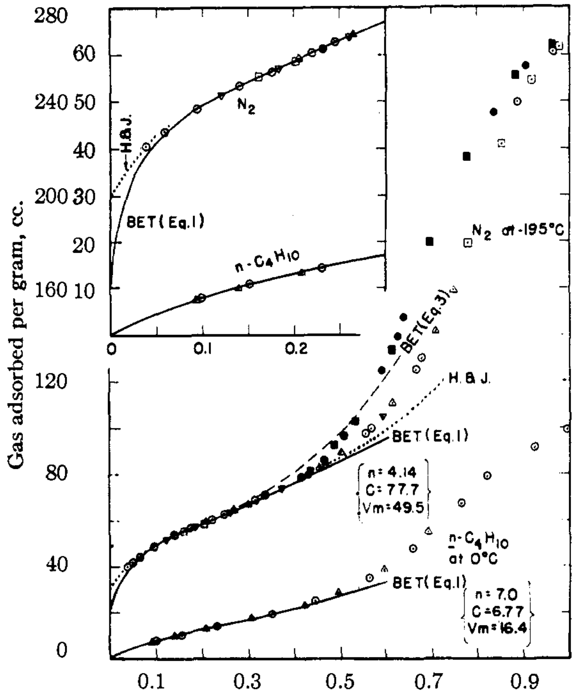

Fig. 2.—Nitrogen and *n*-butane isotherms for Al_2O_3–SiO_2 I: adsorption ⊙, △, ▽, ⊡; desorption ●, ■.

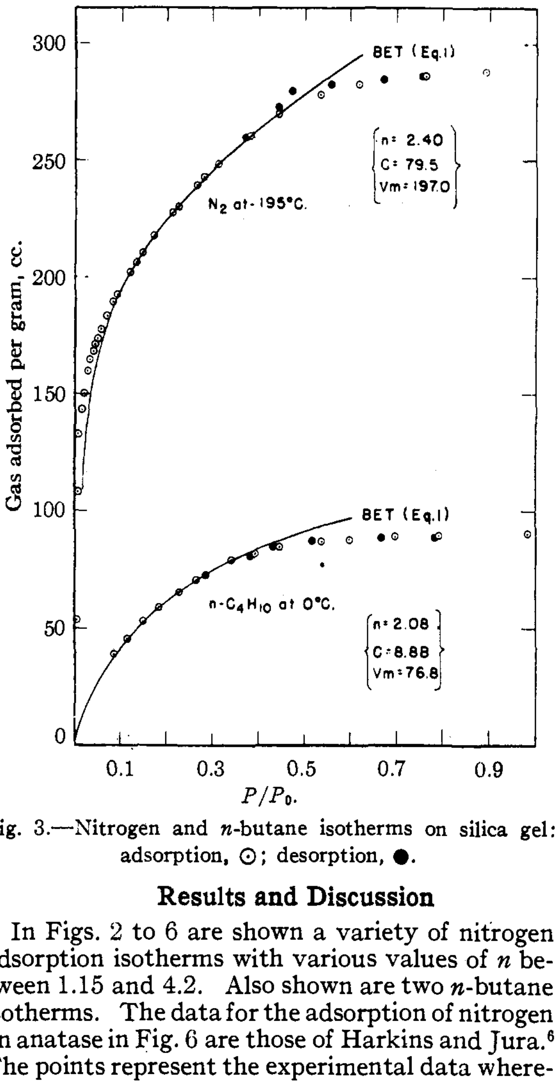

Fig. 3.—Nitrogen and *n*-butane isotherms on silica gel: adsorption, ⊙; desorption, ●.

Results and Discussion

In Figs. 2 to 6 are shown a variety of nitrogen adsorption isotherms with various values of *n* between 1.15 and 4.2. Also shown are two *n*-butane isotherms. The data for the adsorption of nitrogen on anatase in Fig. 6 are those of Harkins and Jura.[6] The points represent the experimental data whereas the solid line is the calculated isotherm using equation 1. The calculated isotherms of equation 2 or 3 are shown as dashed lines. The constants obtained by the various equations are given in Table I. The area of the adsorbent is given in Table III along with the area calculated by other methods.

Deitz and Gleysteen[7] first suggested a method of using equation 1 in which experimental values of V at two relative pressures are substituted into the equation. Upon assuming different values for n, the resulting calculated values for V_m and C are tested by comparing the remaining part of the isotherm with the experimental data. This method proved to be rather cumbersome and it

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

(4) Harvey, *ibid.*, 65, 2343 (1943).

(5) Emmett and Brunauer, *ibid.*, 56, 35 (1934).

(6) Private communication. These data are represented by the circles in Fig. 2. Harkins and Jura, THIS JOURNAL, 66, 1366 (1944).

(7) Deitz and Gleysteen, *J. Research Natl. Bur. Standards*, 29, 191 (1942).

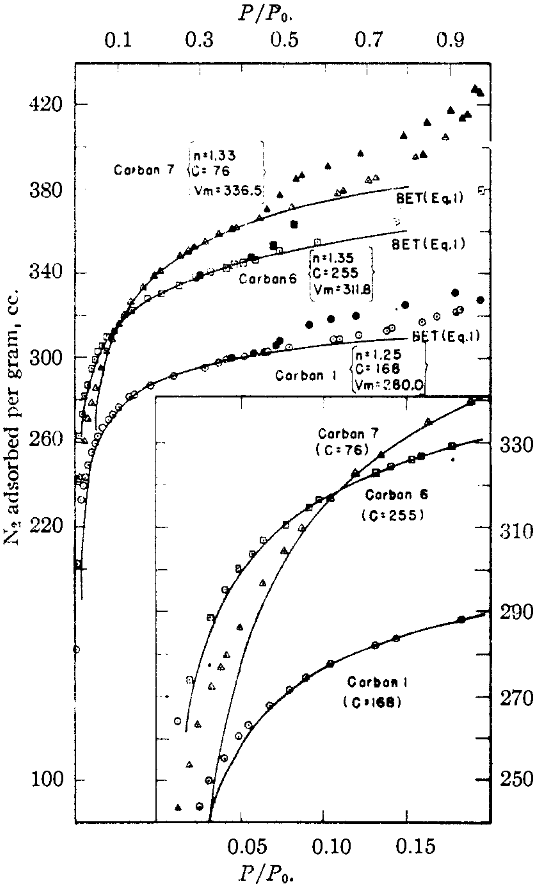

Fig. 4.—Nitrogen isotherms for carbons showing increased divergence of equation 1 from the experimental data at relative pressures less than 0.1 as the head of adsorption (C) decreases: adsorption ○. △, □; desorption, ●, ▲, ■.

was difficult to determine when the best values of the constants had been obtained.

The method presented here is much simpler once the preliminary calculations have been made. It also leads to the best value of V_m and C in accord with equation 1.

TABLE I

COMPARISON OF CONSTANTS OBTAINED FROM THE FULL BET EQUATION WITH THOSE FROM THE LIMITED EQUATIONS 2 AND 3

Adsorbent	Full BET equation 1 n	 C	 V_m	Limited BET equation 2 or 3 Eqn.	 C	 V_m
(N_2 at −195°)						
Al_2O_3–SiO_2 I	4.14	77.7	49.5	3	81.8	49.2
Al_2O_3–SiO_2 II	4.05	89.1	63.3	3	112	62.4
Anatase[a]	3.47	68.5	3.313	3	110	3.198
Silica gel	2.40	79.5	197.0	Neither eq. 2 nor 3 is linear		
Carbon 5	1.45	224	179.1	2	78.8	205
Carbon 6	1.35	255	311.8	2	95.3	350
Carbon 7	1.33	76.0	336.5	2	40.1	383
Carbon 2	1.30	144	318.3	2	66.9	356
Carbon 1	1.25	168	280.0	2	86.0	306
Carbon 4	1.15	79.6	426.6	2	57.6	456
(n-C_4H_{10} at 0°)						
Al_2O_3–SiO_2 I	7.0	6.77	16.4			
Silica gel	2.08	8.88	76.8			

[a] Data for this isotherm are from Harkins and Jura (ref. 6).

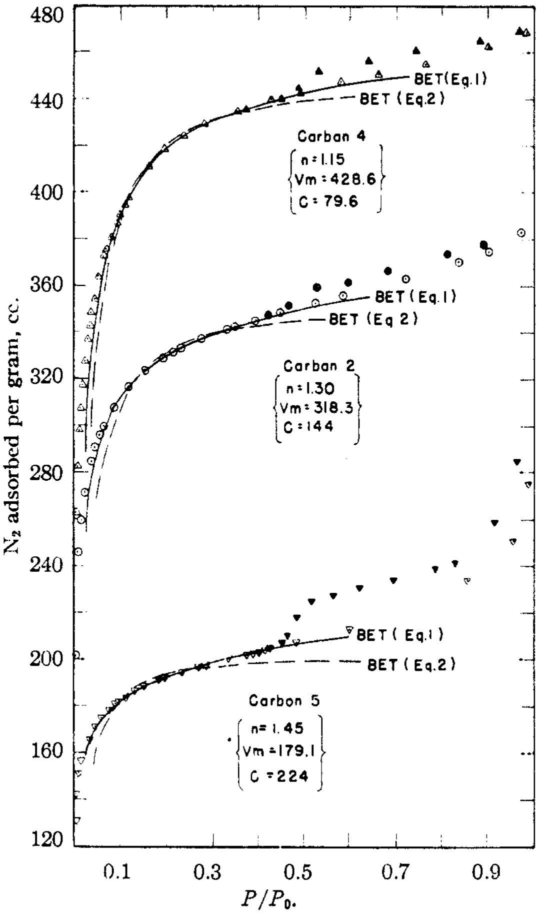

Fig. 5.—Nitrogen isotherms for three carbons with different values of n: adsorption, ▽. ○. △; desorption, ▼, ●, ▲.

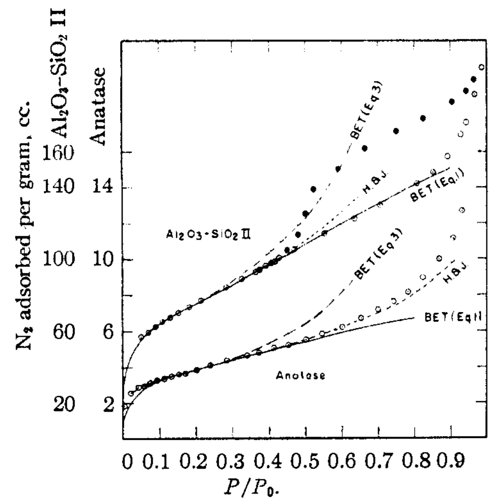

Fig. 6.—Nitrogen isotherms for Al_2O_3–SiO_2 II and anatase: adsorption, ⊙; desorption, ●.

By a simple algebraic transformation equation 1 can be put into the more convenient form

$$V = \frac{V_m C\Phi(n, x)}{1 + C\Theta(n, x)} \qquad (4)$$

where

$$\Phi(n,x) = \frac{X[(1 - X^n) - nX^n(1 - X)]}{(1 - X)^2}$$

and

$$\Theta(n, x) = \frac{X(1 - X^n)}{1 - X}$$

Equation 4 can be rearranged into a linear form

$$\frac{\Phi(n, x)}{V} = \frac{1}{V_m C} + \frac{\Theta(n, x)}{V_m} \qquad (5)$$

The functions $\Phi(n, x)$ and $\Theta(n, x)$ have been calculated for values of X from 0.1 to 0.6 in intervals of 0.05 (in most cases, however, they are only used up to a relative pressure of 0.4) and for values of n from 1 to 9 in intervals of 0.05 near unity but farther apart at the higher values. Space does not warrant the publishing of these tables as they can be easily calculated or obtained from the authors.

Since $\Phi(n, x)$ and $\Theta(n, x)$ are only known for the above values of X, it is necessary to select the corresponding values of V from the isotherm. An approximate value of n is then selected and $\Phi(n, x)/V$ plotted against $\Theta(n, x)$.

If the value of n selected is too low, the points will fall on a curve concave to the $\Theta(n, x)$ axis and if it is too high, the points will be convex. A second value of n is then selected and the process repeated until the n which gives the best straight line is found. The constants V_m and C may then be calculated from the slope and intercept of this straight line. Figure 7 shows such a plot (for carbon 2).

Since the curvature of equation 5 is not very sensitive to n, we have found it advantageous to determine the best straight line through the points by the method of least squares. This also eliminates the error involved in estimating the intercept and consequently results in a more accurate value of the constant C. The volume adsorbed is then calculated by equation 4 and compared with the original isotherm. When n was desired to greater precision, it was sometimes found difficult to select the better of two apparently straight lines on the equation 5 plot. In this case, the constants obtained from both lines were used to calculate separate isotherms and the constants of the isotherm which gave the lowest mean deviation from the experimental isotherm were used.

For all the isotherms of this paper, mean deviations of less than 0.1 cc. (the approximate experimental error) were obtained between relative pressures of 0.1 and 0.4, and in some cases over an even greater range. It is interesting that the deviation generally begins just below the hysteresis point but this is probably coincidental since anatase, which should have no hysteresis loop, also deviates at a similar relative pressure.

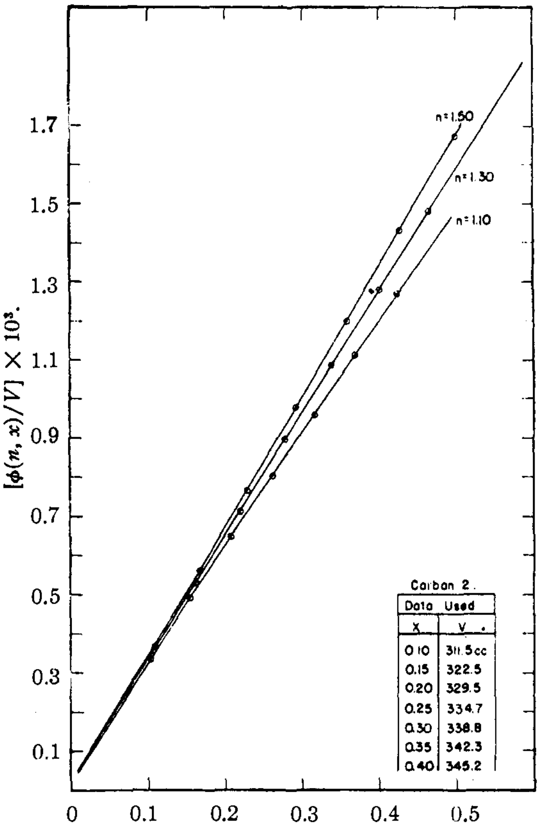

Fig. 7.—Isotherms of carbon 2 plotted according to equation 5, showing the effect of a high and a low value of n.

Above a relative pressure of about 0.4, the experimental isotherm is higher than that calculated from equation 1, if the best values for n, C and V_m are used, for all substances thus far studied, except silica gel and the alumina silica II. For this last adsorbent, equation 1 fits the isotherm to a relative pressure of almost 0.8. This indicates that the multimolecular theory has ignored some factor which contributes to the adsorption at higher pressures. The isotherm for silica gel is rather unusual in that apparently only very small pores exist in the gel. Ninety per cent. of the total adsorption is accounted for by multimolecular adsorption, according to equation 1, before the lack of larger pores cuts off further adsorption. For this type of isotherm, a correction to equation 1 along the lines of Brunauer, Deming, Deming and Teller[8] should probably be made.

Below a relative pressure of about 0.1, the BET isotherm again deviates below the experimental curve. This is because the value of C, as determined from the higher points, is an average value over the less active portion of the surface. So far, no isotherm has been examined for which the curve of equation 1 does not drop below the ex-

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(8) Brunauer, Deming, Deming and Teller, THIS JOURNAL, **62**, 1723 (1940).

perimental points at relative pressures below 0.1. In Table II, the deviations, below a relative pressure of 0.1, of the BET equation from the experimental isotherm, are given for a series of adsorbents having similar values of *n* but various values of *C*. The higher the value of *C*, *i. e.*, the higher the average heat of adsorption, the smaller is the deviation. This is probably due to the percentage difference between the average heat of adsorption and that of the more active portion being less, the higher the average heat.

TABLE II

DEVIATION OF THE CALCULATED FULL BET ISOTHERM FROM THE EXPERIMENTAL ISOTHERM FOR ISOTHERMS WITH SIMILAR VALUES OF *n* BUT DIFFERENT HEATS OF ADSORPTION

Adsorbent	*n*	*C*	*V* Expt.—*V* BET for indicated values of *X*			
			X = 0.025	0.050	0.075	0.100
Carbon 6	1.350	255	7.4	1.2	0.5	0
Carbon 1	1.255	168	12.5	12.5	1.1	0
Carbon 2	1.305	144	23.7	23.7	1.4	0
Carbon 7	1.330	76	35.2	35.2	2.4	0

The isotherms for activated carbons having values of *n* less than 1.5 illustrate (Fig. 5) one of the great advantages of using this method in the calculation of V_m and C. Figure 8 shows the linear plot obtained when these isotherms are treated by the Langmuir equation (equation 2). The excellent straight line obtained might lead one to believe that the values of V_m and C so obtained would agree with those obtained by equation 1. When these constants are used in equation 2 to calculate the isotherm as in Fig. 5 (dashed line), the agreement with the experimental curve is seen to be much poorer than when the isotherm is treated by the method of this paper (solid lines in Figure 5). What is worse, the value of V_m, calculated by equation 2, differs as much as fifteen per cent. from the value calculated from equation 1 (see Table I).

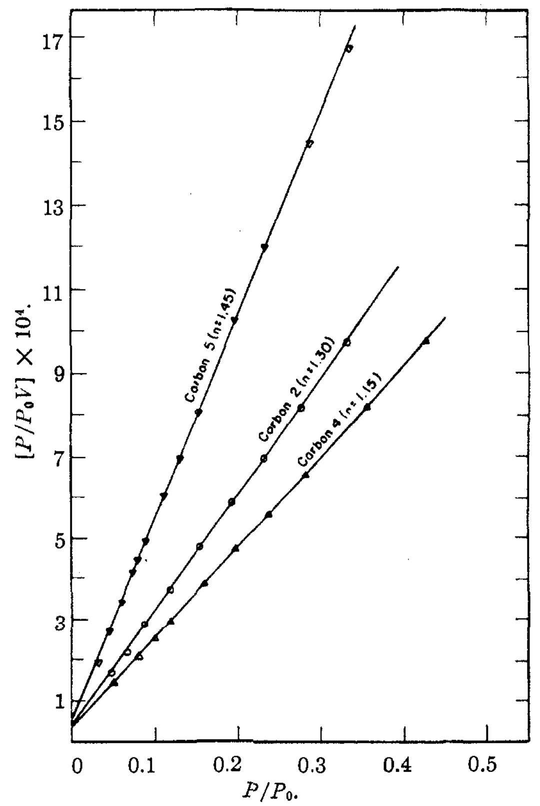

Fig. 8.—Nitrogen isotherms on carbons with different values of *n* plotted according to equation 2.

One of the inherent objections to the use of the BET method for the determination of the area of a porous material is the necessary assumption of a molecular area for the adsorbate in order to convert V_m to the area. Harkins and Jura[9] have recently presented an alternative method for the determination of the area of a solid adsorbent. Their method is based on the isotherm

$$\log p/p_0 = B - A/V^2 \qquad (6)$$

and the area (Σ) of the solid is given by

$$\Sigma = kA^{1/2} \qquad (7)$$

Harkins and Jura determined *k* for various vapors on anatase by obtaining Σ independently from the heat of immersion in water of the nearly saturated crystals and *A* from the adsorption isotherm. Assuming that *k* is independent of the nature or porosity of the adsorbent, equations 6 and 7 can be used to calculate the area directly from the adsorption isotherm.

By the use of both their method and the BET equation, Harkins and Jura[9] found that the mean area (σ) of the adsorbed N_2 molecule varied between 13.6 and 16.9 sq. Å., with peaks at 14.05, 15.25, and 16.05 sq. Å. for a great many adsorbents. Presumably, they used equation 3 rather than equation 1. For all isotherms with a sufficiently large value of *n*, this would not alter the results appreciably. However, for any isotherms with an *n* less than 3, the use of equation 1, instead of the linear equation, may result in a sufficiently different V_m to shift σ from one of the peaks observed by Harkins and Jura to another.

When the isotherms from Figs. 2 to 6 were plotted according to equation 8, quite satisfactory results were obtained for those with a value of *n* greater than 3. In Fig. 2 and 6, the Harkins and Jura isotherms are shown as dotted lines and the area determined by their method is given in Table III. Equation 6 follows the experimental data to lower relative pressures than the BET equation but both equations are about equivalent at higher pressures providing equation 1 is used for the comparison.

Figure 9 shows a plot according to equation 6, for some typical isotherms with values of *n* less than 3. Also shown in Fig. 9 are the lines corresponding to the BET area assuming the Harkins

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[9] Harkins and Jura, THIS JOURNAL, **66**, 1366 (1944).

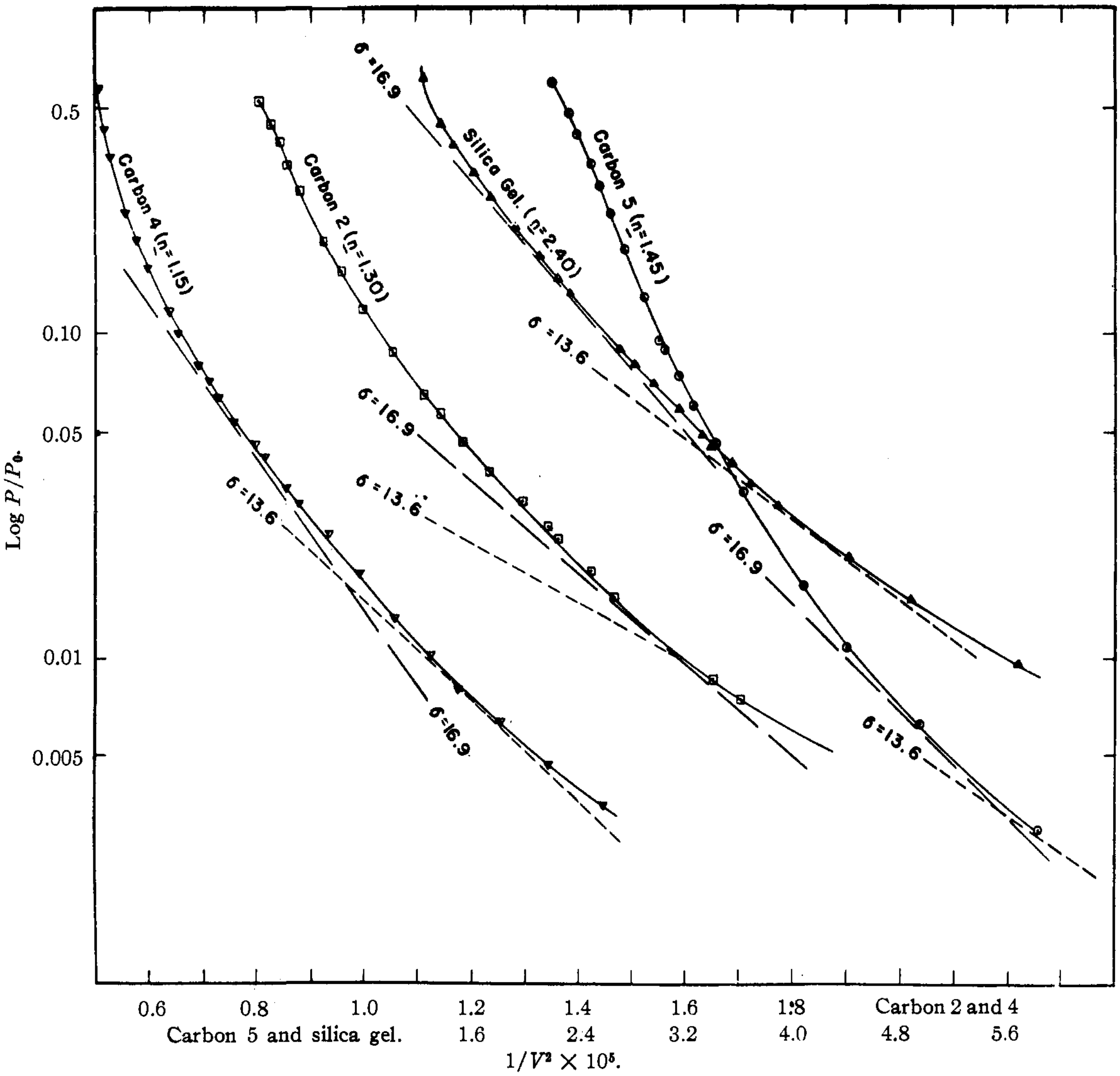

Fig. 9.—Harkins and Jura plot of nitrogen isotherms with values of n less than 3, showing the slope that would be required for the extreme values of the molecular area of nitrogen obtained by Harkins and Jura.

and Jura extreme values of 13.6 and 16.9 sq. Å. for the molecular area of the nitrogen molecule. The points for each isotherm form a smooth curve with no apparent linear portion. If a linear portion exists it should, according to Harkins and Jura, lie somewhere in the region between the points of tangency of the two extreme molecular area lines. For all the isotherms with n less than 3 that we have examined, this region is well below a relative pressure of 0.1 (except the silica gel where it is below 0.15). Such a linear portion appears to exist in the case of the silica gel (n = 2.4) between relative pressures of 0.04 and 0.07, although the precision is hardly great enough to be certain that it is real. For the isotherms with n less than 2, any linear portion that may be present, exists over a much shorter range and at a much lower pressure.

Comparing the Harkins and Jura and the BET methods for determining the area of the porous solids used in the present work, it appears that they give comparable results providing the adsorption isotherm has an n greater than about 3. However, for isotherms with n less than 3, the BET method using equation 1, continues to yield reasonable values for the area and the calculated isotherms are in good agreement with the experimental data over a considerable pressure range, whereas the Harkins and Jura method does not appear to yield a linear plot.

Within the past two years, Kistler, Fisher and Freeman[3] and Harvey[4] have each proposed a method for estimating the surface area of porous solids. Both methods assume the adsorption to be due entirely to capillary condensation superimposed upon a Langmuir monolayer.

Harvey assumes capillary condensation to be present in the region where the isotherm is convex

TABLE III

COMPARISON OF THE VALUES FOR THE AREAS OF POROUS SUBSTANCES AS OBTAINED BY VARIOUS METHODS OF CALCULATION FROM THE NITROGEN ADSORPTION ISOTHERMS

		Area, sq. m./gr.						
		BET			Kistler		Harvey	
Adsorbent	n	eq. 1	eq. 2 or 3	H and J	Ads.	Des.	Ads.	Des.
Al_2O_3–SiO_2 I	4.14	217	215	204	307	373	263	384
Al_2O_3–SiO_2 II	4.05	277	273	266	236	310	120	292
Anatase	2.47	14.5	14.0	13.8	16.9	...	25	...
Silica gel	2.40	866	....[a]	...[c]	428	434	...[b]	...[b]
Carbon 5	1.45	784	898	...[c]	64.1	97.4	71	156
Carbon 6	1.35	1366	1532	...[c]	47.1	...	71	...
Carbon 7	1.33	1474	1678	...[c]	44.2	74.6	97	167
Carbon 2	1.30	1394	1559	...[c]	36.6	50.4	75	108
Carbon 1	1.25	1226	1339	...[c]	31.6	53.0	43	89
Carbon 4	1.15	1877	1996	...[e]	20.4	34.7	52	76

[a] Neither equation 2 nor equation 3 gives a straight line for the silica gel used. [b] Harvey's method is not applicable to this silica gel since no portion of the isotherm is convex to the pressure axis. [c] No linear region was obtained on the log X *vs.* V^{-2} plot.

to the pressure axis. Such a region is present in all the isotherms presented here with the exception of the silica gel. The area calculated for the various adsorbents by both the Harvey and the Kistler method are given in Table III and compared with the BET and the Harkins and Jura area.

Kistler, *et al.*, were cognizant of the fact that their method was not applicable to materials with pores too small to be capable of capillary condensation. This might partially account for the very low Kistler area compared to the BET area for those substances which have the smallest pores. However, even for the silica aerogels cited by Kistler, the area calculated by him from the saturated Langmuir monolayer is considerably greater than that calculated from capillary condensation by his method.

The few instances of materials with high values of n, where the Kistler area is greater than the BET area, suggest that a correction for multilayer adsorption, rather than for just the simple Langmuir type adsorption is necessary.

In equation 1, the constant n is defined as the number of layers to which the adsorbed gas is limited. It is often assumed that it is the pore diameter of the adsorbent that does the limiting. Although the pore size is undoubtedly a factor in the determination of n, other properties of the adsorbent must also be involved. The value of n for n-butane on silica gel is, as would be expected from its larger molecular size, smaller than for nitrogen on the same substance; however, for alumina–silica I, the reverse is true. Although only two butane isotherms are shown here, similar ones have been determined for all the other adsorbents and in every case, except the silica gel, the n was greater for butane than for nitrogen. This would suggest that the adsorbate is also a factor in the determination of n.

A possible explanation of the larger n values for butane may lie in the fact that n may be considered as the average number of layers over all size pores. The smaller nitrogen molecule may form single layers in many pores too small to admit butane and hence the average number of layers for nitrogen would be decreased, due to the inclusion of these single layers.

It is also of interest that the isotherm for nitrogen on anatase has an n of 3.47 rather than infinity which might be expected, since the anatase has been shown to be completely free of pores. It should prove to be extremely interesting if a relationship between n and various properties of the adsorbent and adsorbate could be developed.

The authors wish to acknowledge their indebtedness to Dr. Paul H. Emmett for his valuable criticism and helpful advice in the preparation of this paper.

Summary

1. A method of applying the full BET equation, including the parameter n to all adsorption isotherms, is developed.

2. The adsorption and desorption isotherms for N_2 at −195° for two aluminum silicates, six activated carbons and a silica gel have been determined. These isotherms have values of n ranging between 1.15 and 4.2. The isotherms for n-butane at 0° for one of the aluminum silicates and the silica gel have also been determined.

3. When the isotherm has a value of n greater than about 3, both the BET infinity equation and the Harkins and Jura equation appear to be applicable. For isotherms with n less than 3, only the full BET equation yields results which fit the experimental data to a reasonable extent.

4. The parameter n of the BET equation appears to be related not only to the pore size but also to other properties of the adsorbent. The nature of the adsorbate also has an influence on the value of this parameter.

5. The areas of the various adsorbents as determined by the BET, the Harkins and Jura, the Harvey and the Kistler methods, are compared.

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