

321. *The Adsorption Method of Measuring Surface Areas.*

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In order to investigate the accuracy of the adsorption method of measuring surface areas, a group of Brunauer, Emmett, and Teller (B.E.T.)-type multilayer isotherms has been derived, and examined by use of experimental sorption data obtained on montmorillonite and attapulgite. In the isotherms, the volatility of sorbate molecules was assumed to increase the higher the layer in which they were situated. This has the effect of reducing the excessive sorption given at higher relative pressure by the original B.E.T. equation. A number of the isotherms were in good agreement with the experimental data, and the v_m values derived from each of the successful isotherms were in satisfactory agreement. It is suggested that the adsorption method can in this case be a good absolute measure of surface area. If, as is quite often true of the original B.E.T. or Huttig equations, the isotherm fit is not good, values of v_m are less consistent and it is then considered that surface areas as determined by the adsorption method may not be accurate.

THE adsorption method is among the commonest of the means of measuring the surface areas of finely divided solids. Most recent users of the method have employed the B.E.T. procedure (Brunauer, Emmett, and Teller, *J. Amer. Chem. Soc.*, 1938, **60**, 309; Brunauer, "Physical Adsorption of Gases," Oxford Univ. Press, 1944, pp. 155 *et seq.*) and a lesser number the Harkins and Jura (*J. Chem. Phys.*, 1943, **11**, 430; 1944, **12**, 112) or the Huttig (Ross, *J. Phys. Coll. Chem.*, 1949, **53**, 383) procedure. Recently, B.E.T. and Huttig isotherms have been compared in suitability for surface-area determinations (Corrin, *ibid.*, 1951, **55**, 612). Molecular cross-sections in adsorbed films were determined by using a sample of titania of known area, determined by the Harkins and Jura calorimetric method (*J. Amer. Chem. Soc.*, 1944, **66**, 1362). It was then noted that the cross-sections differed to some extent for B.E.T. and Huttig isotherms. Conversely, if equal cross-sections are taken for any molecule (*e.g.*, nitrogen), then B.E.T. and Huttig linear plots may lead to appreciably different surface areas. Similar observations have been made in using porous glass as sorbent (Barrer and Barrie, in preparation).

These results raise the question of the absolute as distinct from the comparative accuracy of surface-area measurements through adsorption. We have approached this problem by developing a series of B.E.T.-type multilayer isotherms all of which have at least as reasonable a physical basis as the standard B.E.T. equation. We have then used these isotherms, together with the standard B.E.T. and Huttig equations, to measure the surface areas of attapulgite and montmorillonite. It appears that it is not enough to determine surface areas always by use of a single type of isotherm; one should employ a group of isotherms to check the areas obtained with each against those obtained with the others. This should give a better idea of the probable absolute accuracy of such determinations.

B.E.T.-type Multilayer Adsorption Isotherms.—A limitation of the B.E.T. isotherm lies in the omission of lateral interactions between sorbate molecules (Hill, *J. Chem. Phys.*, 1946, **14**, 263; 1947, **15**, 767). Similarly, Huttig's isotherm is thermodynamically consistent if the sorbate is considered as a succession of independent layers in a field of potential due to sorbent and to lateral sorbate-sorbate interactions. This time vertical sorbate-sorbate interactions must be omitted (Barrer, *J.*, 1951, 1874). A second limitation of both isotherms as usually employed is that all sorbate molecules in layers other than the first are assumed to have liquid-like evaporation-condensation properties. It is this assumption which we propose to modify for the B.E.T. isotherm by making molecules more and more volatile the higher the layer. This will have the effect of smoothing the otherwise "wavy" surface of the B.E.T. adsorbed film, for it will make it highly improbable that any one molecular column can appreciably exceed any other in length. It will also reduce the total sorption at higher relative pressures, so partially correcting for the excessive sorption predicted by the isotherm at such pressures.

TABLE 1. Special cases of isotherm equation (3).

Designation	Values of m in eqn. (2) $m_1 = 1, m_2 = 2, m_3 = 3, \text{ etc.}$	Liquid-like evaporation properties shown by	Isotherm: $v/v_m =$	Characteristic linear plot
A		2nd layer	$\frac{Cx e^x(1+x)}{1+Cx e^x}$	$\frac{1}{Cv_m} + \frac{1}{v_m} x e^x = \frac{x}{v} e^x(1+x)$
B		3rd layer	$\frac{2Cx e^{2x}(1+2x)}{1+2Cx e^{2x}}$	$\frac{1}{Cv_m} + \frac{2}{v_m} x e^{2x} = \frac{2x}{v} e^{2x}(1+2x)$
C		$(i+1)$ th layer	$\frac{iCx e^{ix}(1+ix)}{1+iCx e^{ix}}$	$\frac{1}{Cv_m} + \frac{i}{v_m} x e^{ix} = \frac{ix}{v} e^{ix}(1+ix)$
D	$m_1 = 2, m_2 = 3, m_3 = 4, \text{ etc.}$	2nd layer	$\frac{2Cx e^{2x}}{1+C(e^{2x}-1)}$	$\frac{1}{v_m} e^{2x} = \frac{2x}{v} e^{2x} + \frac{1}{v_m} \cdot \frac{C-1}{C}$
E		i th layer	$\frac{iCx e^{ix}}{1+C(e^{ix}-1)}$	$\frac{1}{v_m} e^{ix} = \frac{ix}{v} e^{ix} + \frac{1}{v_m} \cdot \frac{C-1}{C}$
F	$m_1 = m_2 = 1, m_3 = 2, m_4 = 3, \text{ etc.}$	2nd and 3rd layers	$\frac{Cx\{1+x(2+x)e^x\}}{1+Cx(1+x)e^x}$	$\frac{1}{Cv_m} + \frac{1}{v_m} x(1+x)e^x = \frac{x}{v}(1+x(2+x))e^x$
G		$(i+2)$ th layer	$\frac{iCx\{1+ix(2+ix)e^{ix}\}}{1+iCx(1+ix)e^{ix}}$	$\frac{1}{Cv_m} + \frac{1}{v_m} ix(1+ix)e^{ix} = \frac{ix}{v}\{1+ix(2+ix)\}e^{ix}$
H	$m_1 = 1, m_2 = m_3 = \dots = m$	2nd layer	$\frac{Cx\left(1 + \frac{2mx}{m-x} + \frac{m x^2}{(m-x)^2}\right)}{1 + Cx + \frac{C m x^2}{m-x}}$	$\frac{1}{Cv_m} + \frac{x}{v_m} \left(1 + \frac{mx}{m-x}\right) = \frac{x}{v} \left(1 + \frac{2mx}{m-x} + \frac{m x^2}{(m-x)^2}\right)$
I		3rd and higher layers	$\frac{Cx\left(1 + \frac{2mx}{1-x} + \frac{m x^2}{(1-x)^2}\right)}{1 + Cx + \frac{C m x^2}{1-x}}$	$\frac{1}{Cv_m} + \frac{x}{v_m} \left(1 + \frac{mx}{1-x}\right) = \frac{x}{v} \left(1 + \frac{2mx}{1-x} + \frac{m x^2}{(1-x)^2}\right)$
J		2nd and all higher layers, but only as $x \rightarrow 1$	$\frac{Cx}{\left(1 - \frac{x}{m^{(i)}}\right) \left(1 - \frac{x}{m^{(i)}} + Cx\right)}$	$\frac{1}{Cv_m} + \frac{x m^{(i)}}{v_m(m^{(i)}-x)} = \frac{x m^{2(i)}}{v(m^{(i)}-x)^2}$
K		2nd layer; and then in all higher layers when $x \rightarrow 1$	$Cx \left\{ 1 + \frac{2x}{1 - \frac{x}{m^{(i)}}} + \frac{x^2}{m^{(i)} \left(1 - \frac{x}{m^{(i)}}\right)^2} \right\} \left\{ 1 + Cx + \frac{Cx^2}{1 - \frac{x}{m^{(i)}}} \right\}$	$\frac{1}{Cv_m} + \frac{x}{v_m} \left(1 + \frac{m^{(i)} \cdot x}{m^{(i)}-x}\right) = \frac{x}{v} \left(1 + \frac{2m^{(i)} \cdot x}{m^{(i)}-x} + \frac{m^{(i)} \cdot x^2}{(m^{(i)}-x)^2}\right)$

Hence, the modified isotherms will not rest upon any worse premises than does the original B.E.T. isotherm, and indeed in the above respect may be physically more realistic. If we consider equilibrium between the $(i - 1)$ th and i th layers, we have

$$a_i x S_{i-1} = b_i S_i \quad \dots \quad (1)$$

where S_i, S_{i-1} denote respectively the fractions of the surface occupied by columns i and $(i - 1)$ molecules long, $x = p/p_0$ is the relative pressure, and a_i and b are the velocity constants for condensation and evaporation respectively. We may introduce the idea of increasing volatility of sorbate as i increases through the set of relations

$$\left. \begin{aligned} b_1/a_1 &= C \\ b_2/m_1 a_2 &= b_3/m_2 a_3 = \dots = b_i/m_{i-1} a_i = \dots = g \end{aligned} \right\} \quad \dots \quad (2)$$

where $m_1, m_2, \dots, m_{i-1}, \dots$ are numbers integral or fractional, and g is a constant. If one endows *second*-layer molecules with the evaporation-condensation property of a liquid, $m_1 g = 1$; if the *third* layer, then $m_2 g = 1$, and so on (cf. Brunauer, *op. cit.*, p. 153). Then the general form of the isotherm can readily be derived (cf. Dole, *J. Chem. Phys.*, 1948, 16, 25) :

$$\frac{v}{v_m} = y \, d \ln \left(1 + \frac{C y}{m_1} + \frac{C y^2}{m_1 m_2} + \dots + \frac{C y^i}{m_1 m_2 \dots m_i} + \dots \right) \quad \dots \quad (3)$$

where $y = x/g$ and v, v_m have their usual B.E.T. significance.

Possible particular cases are then obtained by summation of the series of equation (3), and are summarised, with the underlying assumptions, in Table 1. In the last column of this table are given the linear plots relevant to the different isotherms. One may note that isotherm *A* recalls the original Huttig isotherm in form. Also for small enough values of x all isotherms tend to follow Henry's law, as expected, while for large C and smaller x they approach Langmuir's isotherm. Isotherms *D, E, F,* and *G,* on expansion of the exponentials and omission of terms in x^2 and higher powers, all take the form of Huttig's isotherm.

For the equations *A* to *G,* numerical values of $m_1, m_2,$ etc., are assigned as reasonable possibilities, but from *H* onwards particular values of m are not assigned. Isotherm *I,* which gives more sorption at higher relative pressures than does the B.E.T. equation, need not be considered further. Equation *H* is, however, important and useful, as will be seen later.

In the case of the isotherms *J* and *K* a new idea is introduced. As the film thickens and x approaches unity, all layers should tend to develop liquid-like properties. This is allowed for in a semi-empirical manner by replacing m by $m^{f(x)}$, where $f(x)$ is a function of x such that as $x \rightarrow 1, f(x) \rightarrow 0$ and so $m^{f(x)} \rightarrow 1$. Thus, if we wish to derive the isotherm corresponding to *H,* but with the above modification, we replace part of equation (2) by

$$\frac{b_2}{m_1^{f(x)} a_2} = \frac{b_3}{m_2^{f(x)} a_3} = \dots = \frac{b_i}{m_{i-1}^{f(x)} a_i} = \dots = g \quad \dots \quad (2a)$$

and in the usual way derive the isotherm

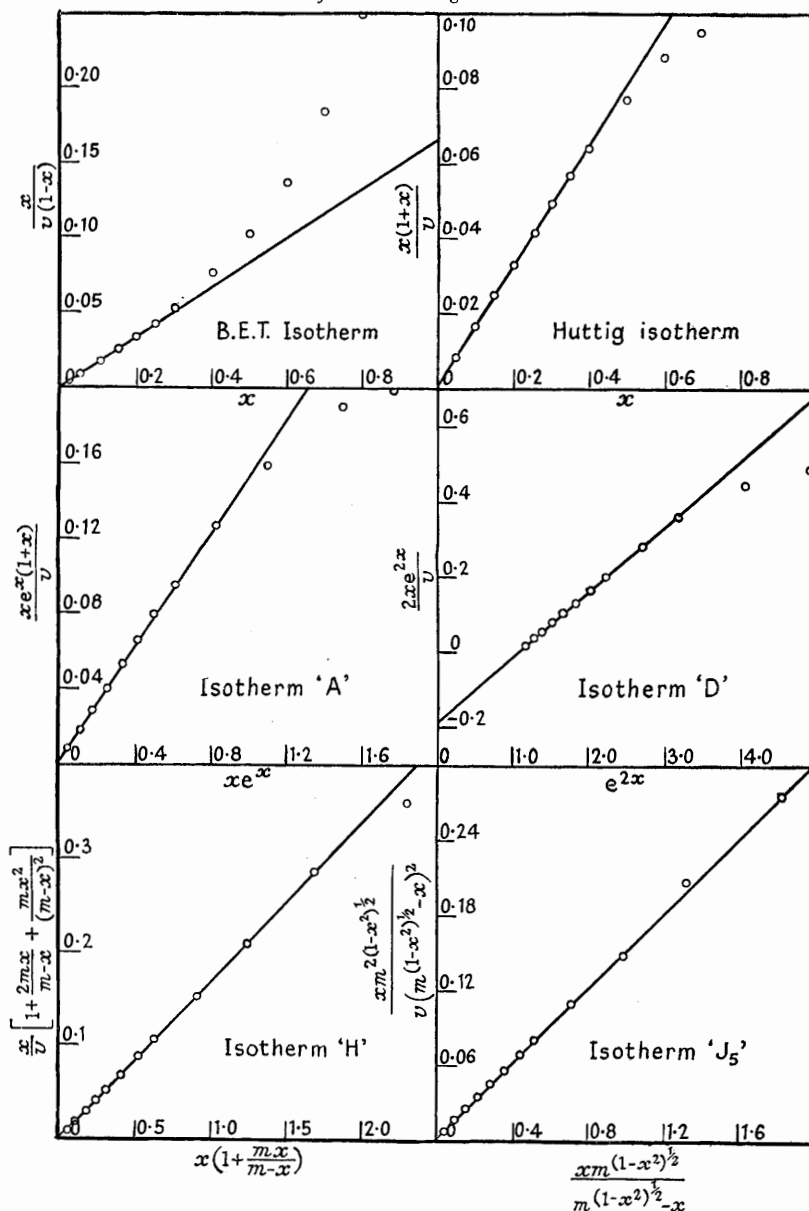
$$\frac{v}{v_m} = \frac{C x \left\{ 1 + \frac{2x}{1 - \frac{x}{m^{f(x)}}} + \frac{x^2}{m^{f(x)} \left(1 - \frac{x}{m^{f(x)}} \right)^2} \right\}}{\left\{ 1 + C x + \frac{C x^2}{\left(1 - \frac{x}{m^{f(x)}} \right)} \right\}} \quad \dots \quad (4)$$

Similarly, corresponding to the original B.E.T. isotherm one obtains

$$\frac{v}{v_m} = \frac{C x}{\left(1 - \frac{x}{m^{f(x)}} \right) \left(1 - \frac{x}{m^{f(x)}} + C x \right)} \quad \dots \quad (5)$$

Suitable empirical functions $f(x)$ which have the requisite properties include: $(1 - x)$, $(1 - x)^{\frac{1}{2}}$, $(1 - x^2)$, $(1 - x^2)^{\frac{1}{2}}$, and so on. Equations J and K of Tables 2 and 3 exemplify these isotherm forms, and Figs. 3 and 4 illustrate their use.

FIG. 1. *Linear plots for comparison of theoretical isotherms. Nitrogen on montmorillonite at 78° K. Values of m are those given in Table 2.*

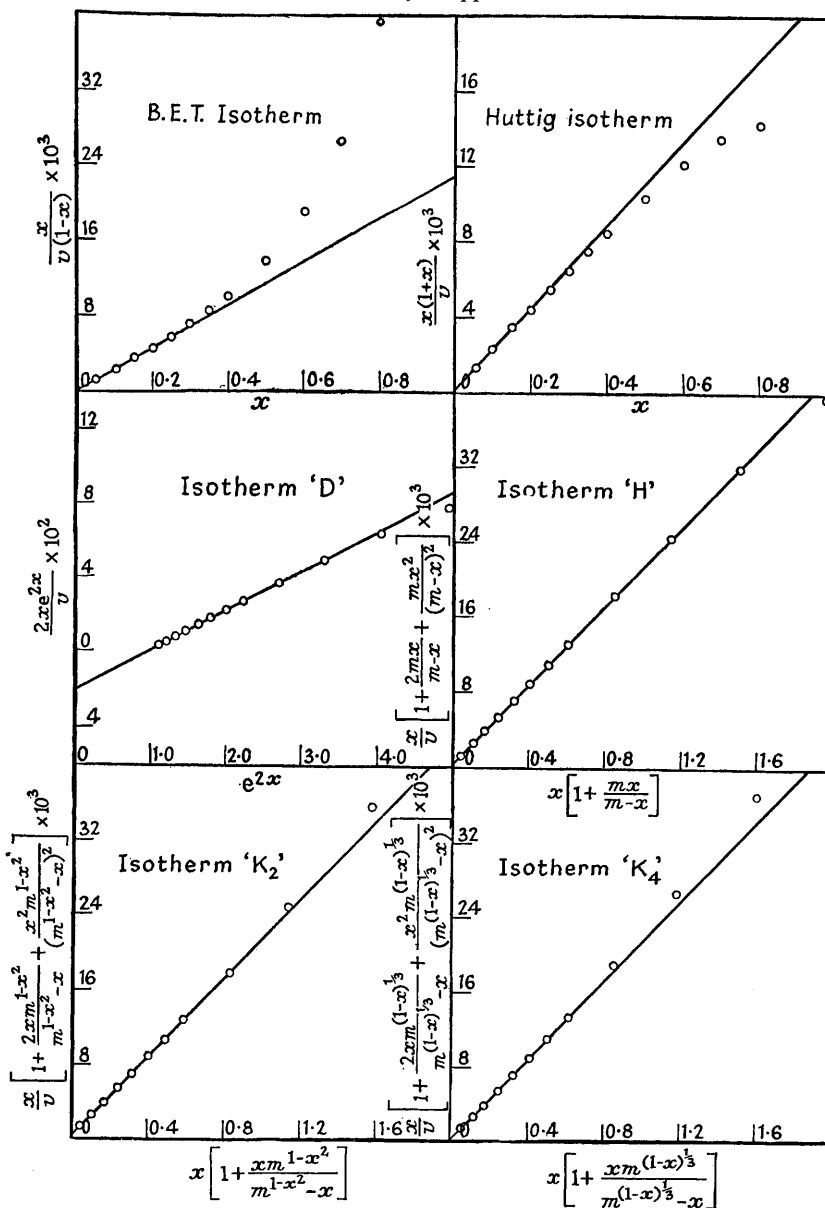


Applicability of the Isotherms: Surface Areas.—Sorption isotherms, which were of Type II in Brunauer's classification (*op. cit.*, p. 150), were measured for nitrogen at -195° on montmorillonite and attapulgite, and also for ammonia at -63.5° (the melting temperature of chloroform) on attapulgite. Isotherms on attapulgite showed little hysteresis; those on montmorillonite led at higher relative pressures to closed hysteresis loops. Where

hysteresis was obtained the equations of Table 1 were used to describe only the ascending part of the experimental isotherm.

Most of the theoretical isotherms, when applied to the experimental data after

FIG. 2. Linear plots for comparison of theoretical isotherms. Nitrogen on attapulgite at 78° K. Relevant values of m appear in Table 3.



rearrangement to the linear equations of column 5, Table 1, were found to give straight-line graphs over a considerable range in relative pressure. Examples of this behaviour are given in Figs. 1 and 2 which, for comparison, also show original B.E.T. and Huttig linear plots. The slopes of the linear part of such graphs in all cases give v_m , the amount of sorbate required to complete a monolayer of adsorbed gas. The intercepts, with v_m ,

give the appropriate values of $C = \exp(-\Delta A_0/RT)$, where $\Delta A_0 \approx \Delta G_0$ is the standard free energy of transfer from liquid sorbate to a Langmuir monolayer film (Barrer and Riley, *Trans. Faraday Soc.*, 1950, **46**, 853).

For the isotherms H , J , and K the correct value of m has also to be found. To do this, one uses the experimental isotherms to construct the linear graphs for the chosen theoretical isotherm. This is done for several values of m , until the value of m is found which gives the longest linear plot. This value is then the correct one. The corresponding longest straight lines are shown for several cases in Figs. 1 and 2.

One thus sees how the linear plots may serve to give v_m , m , and C . The values of the appropriate constants are collected in Tables 2 and 3 for the various isotherms. It should

TABLE 2. *Nitrogen on montmorillonite.*

Isotherm designation	Values of constants *					
	Sorbent outgassed at 523° K :			Sorbent outgassed at 323° K :		
	v_m	m	C	v_m	m	C
B.E.T.	5.73	—	500	4.38	—	761
Huttig	5.98	—	310	4.77	—	131
<i>A</i>	6.25	—	80	5.05	—	49
<i>B</i>	4.98	—	—ve	3.84	—	153
<i>D</i>	6.00	—	100	4.62	—	26
<i>F</i>	7.69	—	30	6.02	—	30
<i>H</i>	5.79	1.4	600	4.61	1.5	100
$J_1, f(x) = 1 - x$	7.27	5.0	68	5.89	5.0	42
$J_2, f(x) = 1 - x^2$	7.44	3.0	122	6.25	3.0	24
$J_3, f(x) = (1 - x)^{\frac{1}{2}}$	7.22	2.3	38	6.00	3.0	21
$J_4, f(x) = (1 - x)^{\frac{1}{3}}$	6.84	1.8	45	5.00	1.8	96
$J_5, f(x) = (1 - x^2)^{\frac{1}{2}}$	6.68	1.7	77	5.26	1.6	50

* All constants were determined from linear plots.

be noted that the determination of v_m and m is independent of that of C . This is satisfactory because with both montmorillonite and attapulgite the C values are variable over a wide range. The intercepts from which C is derived are often small and the C values therefore uncertain. For larger values of C the form of the isotherm for bigger relative pressures does not depend very significantly upon C . In some instances (Table 3) C was

TABLE 3. *Nitrogen and ammonia on attapulgite.*

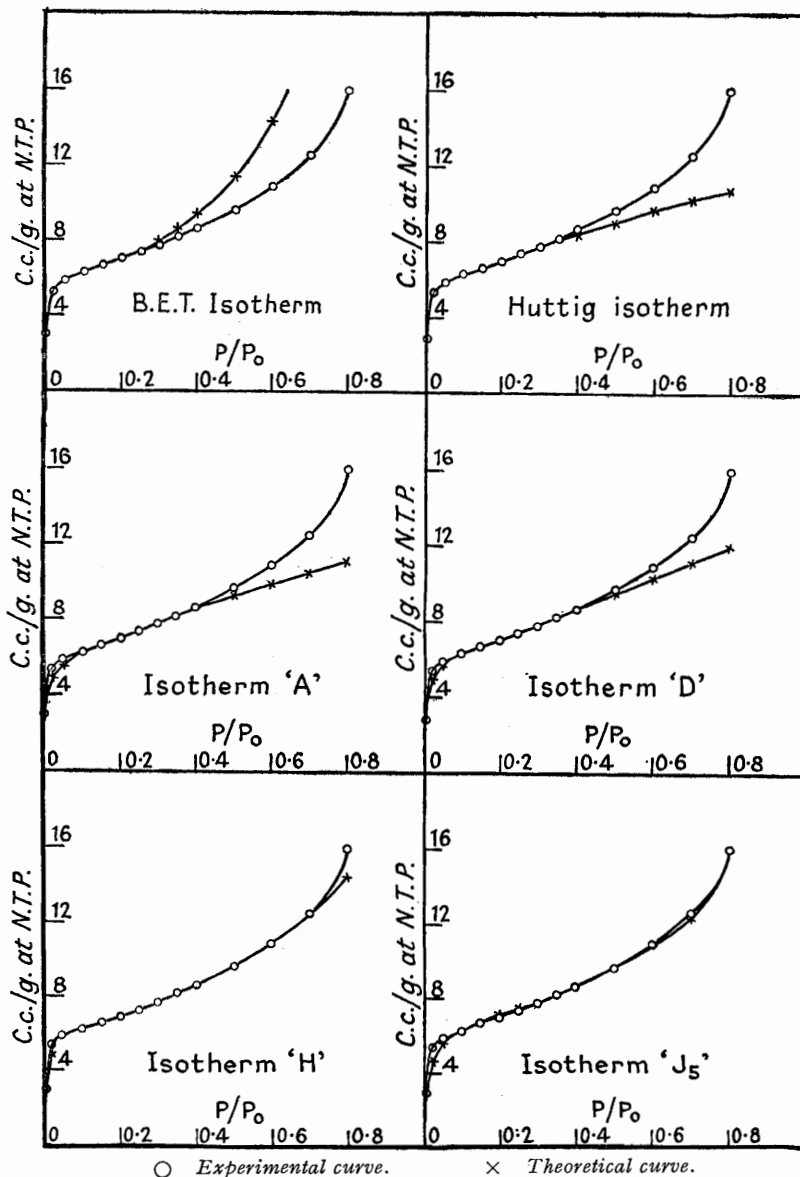
Isotherm designation	Values of constants * for :							
	Nitrogen on sorbent outgassed at room temp.				Ammonia on sorbent outgassed at 625° K			
	v_m	m	C		v_m	m	C	
			by substn.	from linear plot			by substn.	from linear plot
B.E.T.	43.81	—	—	∞	33.5	—	—	28.7
Huttig	47.19	—	—	170	33.22	—	—	43.0
<i>A</i>	46.66	—	200	—	32.64	—	41.5	—
<i>B</i>	40.62	—	2000	—	29.08	—	17.0	—
<i>D</i>	46.05	—	120	—	37.21	—	9.23	—
<i>F</i>	56.07	—	51	—	36.11	—	—	3.46
<i>H</i>	46.31	1.8	207	—	35.98	1.24	21.0	—
$K_1, f(x) = 1 - x$	47.34	3.0	145	—	39.47	2.2	15.5	—
$K_2, f(x) = 1 - x^2$	47.81	2.5	127	—	39.42	1.6	15.0	—
$K_3, f(x) = (1 - x)^{\frac{1}{2}}$	46.78	2.1	175	—	40.42	1.8	13.1	—
$K_4, f(x) = (1 - x)^{\frac{1}{3}}$	46.62	1.9	185	—	—	—	—	—

* v_m and m were in all cases determined from linear plots.

determined (after finding v_m and m from the linear plot) by employing a point on the experimental isotherm to fix this final constant. One is bound to conclude that the variability of C as between the isotherms should make one interpret it with caution; C is nevertheless more consistent when only the better-fitting isotherms are considered (see below).

The constant of greatest importance is v_m . For montmorillonite over the complete group of isotherms of Table 2 and with the mineral activated by outgassing at 523°K and 323°K the extreme ratios in the values of v_m for nitrogen at 78°K are 1 : 1.54 and 1 : 1.57 respectively. With the mineral outgassed at 323°K the best theoretical isotherms among

FIG. 3. Sorption of nitrogen on montmorillonite outgassed at 523°K . Sorption temp. 78°K . See Table 2 for relevant values of m .

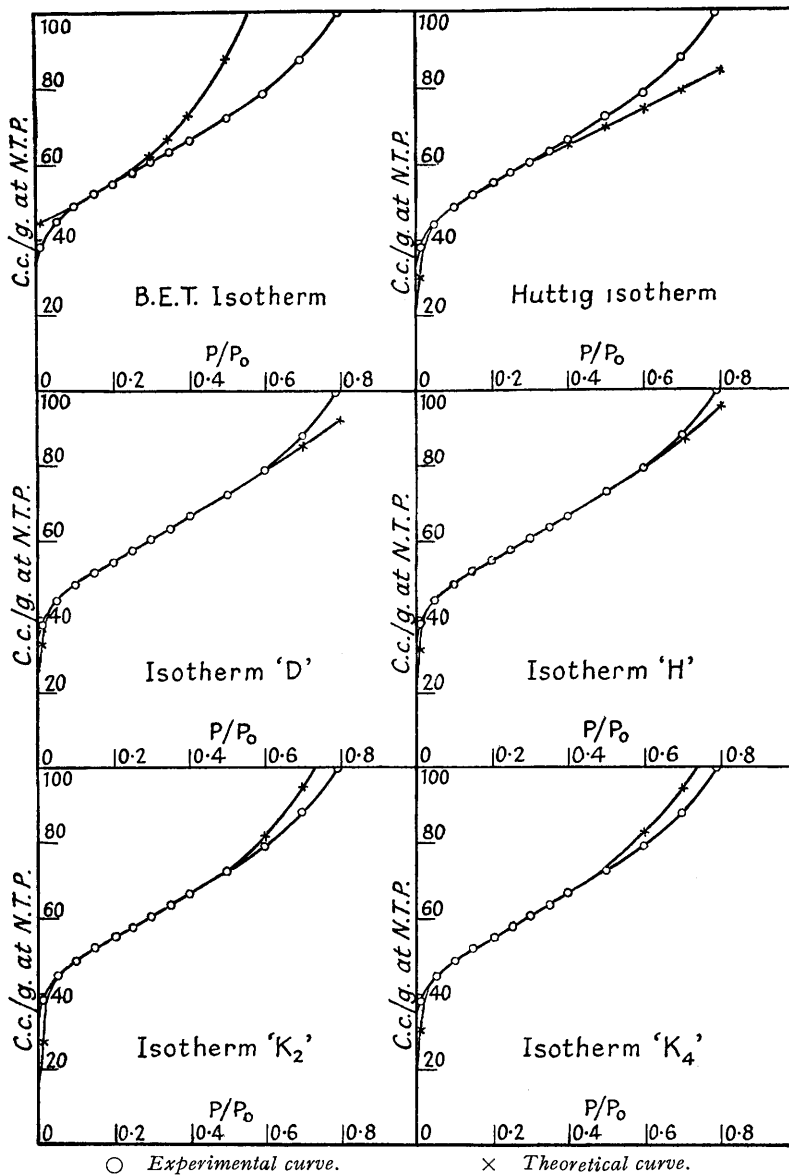


those used are H , J_4 , and J_5 , for which the extreme ratio in v_m is 1 : 1.14. Including the, in this case, less satisfactory B.E.T. and Huttig isotherms the above ratio is 1 : 1.20. When the mineral was outgassed at 523°K the best theoretical isotherms are A , D , H , and J_5 (cf. Fig. 3), giving the extreme range in v_m of 1 : 1.15.

For sorption of nitrogen (at 78°K) on attapulgite outgassed at room temperature, and for ammonia (at 209.5°K) on this mineral outgassed at 625°K , the isotherms employed and

the relevant constants are shown in Table 3. The extreme ratios in v_m are 1 : 1.39 for ammonia, and 1 : 1.38 for nitrogen. The best isotherms for ammonia are H , K_1 , K_2 , and K_3 , for which the ratio in v_m drops to 1 : 1.12. The best isotherms for nitrogen (cf. Fig. 4) are D , H , K_2 , and K_4 , for which the extreme ratio in v_m drops to 1 : 1.04. One may

FIG. 4. Sorption of nitrogen on attapulgitc outgassed at room temperature for 14 days. Sorption temp. 78° K. See Table 3 for relevant values of m .



therefore conclude that if, as would normally be the case, one considers only isotherms which are best able to represent the data, satisfactory agreement is found between values of v_m derived from these isotherms. The absolute value of the surface area so found may then be an accurate one.

On the other hand, many authors have used theoretical isotherms (e.g., B.E.T. and Huttig equations) to derive surface areas from sorption data which these isotherms do

not fit well. In such cases the data in Tables 2 and 3 show that v_m values may differ substantially from corresponding values obtained by using better-fitting theoretical isotherms. The use of poorly-fitting theoretical isotherms could be a misuse of the adsorption method, leading to surface areas of low accuracy. However, a theoretical isotherm which fits poorly the experimental data for one sorbent may represent satisfactorily sorption data obtained with a second sorbent, perhaps because of different pore geometry. Examples of such behaviour were found among isotherms *A*, *B*, *D*, and *F*.

Isotherm *H* was uniformly successful in all our data (cf. Figs. 3 and 4). Also certain of the isotherm forms *K* and *J* were very successful. These are three-constant equations, so one cannot attach particular theoretical significance to their success.

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