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# Theory of Adsorption of Gases on Solids

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Studies of the physical and chemical adsorption of gases on solids have been eminently successful in developing the characteristics and extent of solid surfaces. The work of Langmuir, Harkins and collaborators, Brunauer, Emmett and Teller, Polanyi and numerous others,[1] in fact, suggest that it may be possible to deduce most of the important properties of solid surfaces from adsorption data. The most complete and successful theory of physical adsorption to date is the multimolecular adsorption theory of Brunauer, Emmett and Teller (BET),[2] an excellent description of the development and applications of this theory being given by Brunauer.[1] The BET theory has been particularly successful in treating surface area and the pore structure of finely divided solids, and in explaining qualitatively the numerous and in many cases rather complex adsorption isotherms.

**Type II Isotherms.**—Adsorption isotherms have been classified into five types only one of which, the sigmoid or Type II isotherm, will be discussed in this article. For Type II isotherms the BET theory agrees quantitatively with observed isotherms only in the range of relative pressure $p/p_0$ ($p_0$ = saturation pressure) from about 0.05 to 0.35. Below $p/p_0 = 0.05$ discrepancies in the BET theory have been attributed quite logically to surface heterogeneities. Recently McMillan[3] and Walker and Zettlemoyer[4] have shown that the BET theory may be improved in the region $p/p_0 < 0.05$ without affecting the agreement for $0.05 < p/p_0 < 0.35$ by assuming a two component or dual instead of a homogeneous surface.

In the high pressure range ($p/p_0 > 0.35$) the discrepancies in the BET theory for Type II isotherms have been attributed to restricted adsorption by other factors than capillary condensation (ref. 1, p. 154), for capillary condensation is treated in the BET theory separately. The indefiniteness of the type of restrictions involved raises some question regarding the validity of this explanation. The evidence for it as far as Type II isotherms are concerned appears to be the failure of the BET theory (for $n = \infty$) to show quantitative agreement with experimental isotherms for $p/p_0 > 0.35$. It is, however, quite possible that the discrepancy in this region is related to the approximations of the theory rather than to restricted adsorption. BET assumed that the rate of evaporation from the various layers of an adsorbed film may be expressed in terms of the heat of adsorption, and that the heats of adsorption in all layers of the film except the first one are the same as in the liquid state, *i. e.*, $E_2 = E_3 = \ldots = E_i = E_L$. Experimentally we are dealing, even at low relative pressures, with concentrations of adsorbate approximately the same as in the liquid state, if anything a little higher. Evidently the free energy decrease in adsorption is thus greater than that in liquefaction in all adsorbed layers. This will be accounted for therefore either on the basis that the heat liberated in adsorption is greater than the heat given off in liquefaction, the entropy is greater in the adsorbed film than in the liquid, or both factors are contributing to the greater decrease in free energy in adsorption. In other words it is possible that $E_i \leq E_l$ ($E_i$ = total heat given up in adsorption on the $i$th layer) only if the entropy is greater in the adsorbed film than in the corresponding liquid state. This situation has, of course, been recognized in one way or another previously.[1,5,6,7]

In assuming the evaporation–condensation properties in second and higher adsorbed layers to be the same as in the liquid state, BET disregarded the energy of interaction of the adsorbed gases with the underlying adsorbent. They based this on the fact that van der Waals forces are not considered to be appreciable beyond one molecular diameter which is quite true in bulk matter where the van der Waals forces vary as $r^{-7}$. However, the forces of interaction of adsorbate with the surfaces of solids according to modern theory are supposed to follow a quite different dependence upon $r$. Thus, if we assume that the algebraic sum of the repulsive, quadrupole and higher interaction term is negligible, the adsorbate–adsorbent interaction energy for all but homopolar solids should vary as $r^{-3}$. Under the $r^{-3}$ law one obtains appreciable adsorbate–adsorbent interaction even at several molecular diameters from the surface.

At first sight the BET method of handling adsorbate–adsorbate interactions appears approximately correct. That is, $E_1$ will, of course, contain both adsorbate–adsorbent and adsorbate–adsorbate factors, and, under the approximation that the film resembles the liquid state, the average coördination number of a molecule on the outermost layer would be the same in a film as in the liquid state even though the average coördination number of all molecules in the film will be somewhat lower than in the liquid state. The subject of the adsorbate–adsorbate interaction

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[1] S. Brunauer, "The Adsorption of Gases and Vapors," Princeton University Press, Princeton, N. J., 1942.

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

[3] S. McMillan, *J. Chem. Phys.*, **15**, 390 (1947).

[4] W. C. Walker and A. C. Zettlemoyer, *J. Phys. Colloid Chem.*, **52**, 47, 58 (1948).

[5] A. B. Cassie, *Trans. Faraday Soc.*, **41**, 450 (1945).

[6] H. Cassel, *J. Phys. Chem.*, **48**, 195 (1944).

[7] T. E. Hill, *J. Chem. Phys.*, **15**, 767 (1947); **14**, 263, 268, 441 (1946).

has been discussed by Cassel[6] and treated quite extensively by Hill.[7] For pragmatic reasons, however, we shall not make use of the work of these authors, but shall attempt to introduce this factor on a more simplified but largely empirical basis. This is justified from the viewpoint that our immediate interest in this study is for fitting and extrapolating adsorption isotherms, and the further consideration that the simplified evaluation of adsorbate–adsorbate interaction discussed here makes it possible to extend the agreement between theory and experiment into the region $p/p_0 > 0.35$ while at the same time giving the same agreement at the BET theory below $p/p_0 = 0.35$. Our results, in fact, indicate that sigmoid isotherms (and presumably this will be true also of type III isotherms) are really equilibrium unrestricted adsorption isotherms over the entire range of $x = p/p_0$. Evidently the theory also may be extended readily to include Type IV and V isotherms by working into this theory the capillary condensation concepts along the lines suggested by the work of BET and of Brunauer, Deming, Deming and Teller.[8]

**Development of Equations.**—We shall make use of the BET arguments and assumptions (reference 1, Chapter VI) leading to the following equations.

$$\begin{aligned} a_1 p s_0 &= b_1 s_1 \exp.\,(-E_1'/RT) \\ a_2 p s_1 &= b_2 s_2 \exp.\,(-E_2'/RT) \\ &\vdots \\ a_i p s_{i-1} &= b_i s_i \exp.\,(-E'/RT) \end{aligned} \qquad (1)$$

$$\begin{aligned} s_1 &= Z_1 s_0 \\ s_2 &= Z_1 Z_2 s_0 \\ &\vdots \\ s_i &= Z_1 Z_2 \cdots Z_i s_0 \end{aligned} \qquad (2)$$

$$Z_i = (a_i/b_i)p \exp.\, E_i'/RT \qquad (3)$$

$$A = \sum_0^\infty s_i = s_0 \sum_0^\infty Z_1 Z_2 \cdots Z_i \qquad (4)$$

$$v = v_0 \sum_1^\infty i s_i = s_0\, v_0 \sum_1^\infty i Z_1 Z_2 \cdots Z_i \qquad (5)$$

$$\frac{v}{v_m} = \frac{v}{A v_0} = \frac{\sum_1^\infty i Z_1 Z_2 \cdots Z_i}{1 + \sum_1^\infty Z_1 Z_2 \cdots Z_i} \qquad (6)$$

Here the same symbols are used as in the BET theory, except for the prime designations on the energy of adsorption. Also we shall assume with BET the relations

$$(a_1/b_1) = a_2/b_2 = \cdots = a_i/b_i = g \qquad (7)$$

Evidence from isosteric and calorimetric heat determinations mentioned below indicates that the heat of adsorption in the $i^{\text{th}}$ layer is usually greater than $E_L$, and that the heat of adsorption may actually describe satisfactorily the evaporation-condensation properties in film. Although the assumption $g = a_1/b_1$ was not included in the formal derivation of the BET equation it was assumed in the BET theory in interpreting $c$ in terms of $E_1 - E_L$. Various authors[6,7,9] including BET have considered that in general $a_1/b_1 \neq a_2/b_2$ which is quite true if $E_i'$'s in the present theory are taken to be the total heat of adsorption on the $i^{\text{th}}$ layer. ($E_i'$ here has the same meaning as BET's $E_i$.) As a matter of fact, one would also expect that all of the $g_i = a_i/b_i$ in equation (7) would be at least slightly different if the $E_i'$'s are to be used in the BET sense. Whatever the variain the $g_i$'s, however, it would be of the nature of an entropy variation from one layer to the next and could thus be included in the exponential form making $E_i'$ a free energy of adsorption. We shall consider that the $c_i$ factors which are introduced largely empirically below will include any variations of this character in the $g_i$'s thus making equations (7) strictly correct even for the first layer.

In place of the BET assumption $E_2 = E_3 = \cdots = E_i = E_L$ we shall assume that the energy of adsorption $E_i'$ (which compares with BET's $E_i$,s) may be divided into two parts, (1) that due to interaction between the adsorbate molecules and the adsorbent, designated $E_i$ for the $i^{\text{th}}$ layer, ($E_1$ of the present theory is thus to be compared with BET's $E_1 - E_L$), and (2) that due to interaction between adsorbate molecules themselves, taken as $c_i E_L$ for the $i^{\text{th}}$ layer. Here $c_i$ is a factor accounting for a difference in the average interaction energy between molecules in the $i^{\text{th}}$ molecular layer and the liquid state.

If the BET method were really correct for the adsorbate–adsorbate interaction, the introduction of the $r^{-3}$ law for the adsorbent–adsorbate term would appear to be a step in the wrong direction because it predicts even more adsorption in the region $p/p_0 > 0.35$ than the BET theory which already predicts too much. On the other hand the $r^{-3}$ law must surely apply in physical adsorption. The situation is not improved by introducing repulsive and other attractive terms in the description of the adsorbent–adsorbate interaction, since these terms (involving higher powers of $r$) even if they were important would come in to an appreciable extent only in the first adsorbed layer. The conclusion seems forced therefore that the difficulty comes in the adsorbate–adsorbate interaction. This factor will thus merit considerable fundamental study. The present study, while successful in developing an expression for this factor which, together with the $r^{-3}$ law, leads to agreement with experiment, can hardly be regarded as accomplishing any more toward a fundamental solution than indicating the direction which further study should take.

Approaching the problem empirically the first notion considered was to introduce the adsorbate interaction by comparing the average coördination number of the entire film with that in the liquid

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(8) S. Brauner, L. Deming, W. Deming and E. Teller, THIS JOURNAL, **62**, 1723 (1940).

(9) Davis and DeWitt, *ibid.*, **10**, 1135 (1948).

state rather than just the average coordination number of molecules in the respective surface layers. By simply taking $c_i$ as the ratio of the average coördination number of the whole film to that in the corresponding liquid state, calculated geometrically relative to one empirical constant ($c_1$), we obtained excellent agreement with experiment. Since this accomplished in a simple and satisfactory way the primary objective of this study, it remained only to give an after-the-fact justification from which perhaps one could also obtain the differential net heats of adsorption for comparison with observed isosteric and calorimetric heats. One would expect the constant $c_1$ to be about 0.5 (coördination number in the liquid about 12, in monolayer about 6), but to obtain agreement with observation, values between 0.8 and 0.9 were required in the examples studied. The whole procedure, of course, may be a matter of compensating errors. As far as $c_1$ is concerned the failure to obtain physically significant values could be due to compensations of the neglected adsorbate–adsorbent interactions. For all others, however, if there are compensating errors, which seems unlikely, they must be between the various adsorbate interaction terms in the series. It seems, on the other hand, that at least some of the apparent physical non-reality of $c_1$ may be logically accounted for, *i. e.*, the ratio $c_i$ may depend on the impressed field of the solid surface which may increase the coördination number over that in the liquid state by increasing the density. Also, $c_i$ should be a function of the extent of filling of the layer, and the tendency to cluster which should be greater where the total potential (sum of both interaction terms) is larger. (It is not unlikely as has been previously recognized[6,7] that at least as much of the disagreement between theory and observation in the region $p/p_0 > 0.05$ may be due to the variation of $c_1$ with $\theta$, the fraction of the surface covered, as to heterogeneities in the properties of the surface.)

In giving theoretical significance to the $c_i$'s calculated in the manner described above, taking into account the experimental evidence that differential net heats of adsorption are apparently positive in all layers, it is considered that, in films where the number of layers $i$ is small, molecules may evaporate from any of the $i$ layers followed by a rearrangement of the molecules in the film so that the net result is as though the evaporating molecule had come from the surface layer. If the rearrangement process is slow relative to evaporation, all of the potential energy may not be involved in the evaporation–condensation equilibrium; that involved in the rearrangement process being developed after evaporation of the molecule with the creation of the defect causing rearrangement. It is considered that this is possible from the fact that the difference in average adsorbate interaction between an $(i - 1)$ and $i$ layer film (*e. g.*, $(c_3 - c_2)E_L$) may be quite a bit greater than the adsorbent–adsorbate potential energy for these layers. While this explanation may seem rather unsound the experimental evidence seems to necessitate something of this sort. To consider that the average coördination number in the surface layer of an $i$ layer film ($i = 2$) is less than in the surface of the bulk liquid would explain the adsorption curve but would not explain the fact that observed differential net heats of adsorption are positive.

Following the above considerations the $c_i$'s may be expressed in terms of $c_1$ by the equation

$$c_i = (c_1 + i - 1)/i \qquad (8)$$

If, in the theory of van der Waals adsorbate–adsorbent interaction, only the $r^{-3}$ term is considered important, the contribution to the potential energy from this factor will be $E_i = A_0/r_i^3$, where $A_0$ is a constant and $r_i$ the distance of the $i^{\text{th}}$ layer from the solid surface. It will be assumed that the density of adsorbed material is constant throughout the film. While it will not be necessary for the present purposes, one could correct this approximation in more refined studies by the Polanyi theory[1] by employing the equation

$$\epsilon_i = RT \log_e p_0/p_i \qquad (9)$$

$\epsilon_i$ being the adsorption potential on the $i^{\text{th}}$ layer. In the present work the error introduced by the assumption of constant density will be largely compensated in $c_1$. Under the assumption of constant density $r_i = ir_1$, and the heat of interaction of the adsorbed gases with the field of surface will be given by the equation

$$E_i = A_0/r_i^3 = E_1/i^3 \qquad (10)$$

Hence the total heat of adsorption in the $i^{\text{th}}$ layer of the film should be

$$E_i' = E_1/i^3 + E_L(c_1 + i - 1)/i \qquad (11)$$

Equation (6) may now be written

$$\frac{v}{v_m} = \frac{\sum\limits_{i=1}^{\infty} i\,(gp)^i \exp.\,(E_1' + E_2' + \cdots + E')/RT}{1 + \sum\limits_{i=1}^{\infty} (gp)^i \exp.\,(E_1' + E_2' + \cdots + E_i')/RT} =$$

$$\frac{\sum\limits_{1}^{\infty} i\,(gp \exp.\,E_L/RT)^i \exp.\,(E_1' + E_2' + \cdots + E' - E_L)/RT}{+ \sum\limits_{1}^{\infty} (gp \exp.\,E_L/RT)^i \exp.\,(E_1' + E_2' + \cdots E_i' - iE_L)/RT} \qquad (12)$$

Substituting equation (11) in (12) gives

$$\frac{v}{v_m} = \frac{\sum\limits_{1}^{\infty} ix^i \exp.\,[E_1(1 + 1/8 + \cdots + 1/i^3) + E_L(c_1 + c_2 + \cdots + c_i - i)]/RT}{1 + \sum\limits_{1}^{\infty} x^i \exp\,[E_1(1 + 1/8 + \cdots + 1/i^3) + E_L(c_1 + c_2 + \cdots + c_i - i)]/RT} \qquad (13)$$

where $x = gp$ exp. $E_L/RT$. For practical purposes the series $1 + 1/8 + \cdots + i/i^3$ and $(c_1 - 1) + (c_2 - 1) + \cdots + (c_i - 1)$ may be considered to become constant after a finite number ($q$) of terms. Actually the latter series is divergent but this will not affect the present arguments since the major series converges strongly enough for values of $x$ which do not approach too closely to 1.0. With this approximation equation (13) becomes

$$\frac{v}{v_m} = \frac{\sum_{1}^{q} i\,x^i \text{ exp. } [E_1(1 + 1/8 + \cdots + 1/i^3) + E_L(c_1 + c_2 + \cdots + c_i - i)]/RT + k \sum_{q+1}^{\infty} ix^i}{1 + \sum_{1}^{q} x^i \text{ exp. } [E_1(1 + 1/8 + \cdots + 1/i^3) + E_L(c_1 + c_2 + \cdots + c_i - i)]/RT + k \sum_{q+1}^{\infty} x^i} \quad (14)$$

where

$$k = \text{exp. } [E_1(1 + 1/8 + \cdots + 1/q)^3 + E_L(c_1 + c_2 + \cdots + c_q - q)]/RT \quad (15)$$

Equation (14) is useful in deciding how many terms are needed in evaluating $v/v_m$ at any particular $x$.

Experimentally, $v$ goes to infinity, or at least becomes very large, as $p$ approaches $p_0$. This condition must be accounted for in the term $k \sum_{q+1}^{\infty} ix^i$ of equation (14) since all other terms of the numerator (or from equation (5) by making similar substitutions) will remain finite as $p \rightarrow p_0$. However, this series diverges for $x \geq 1$ and converges for $x < 1$. Hence, $g$ exp. $E_L/RT = 1/p_0$, and $x = p/p_0$, which is the result found by BET. The divergence of the minor series $c_1 + c_2 + \cdots + c_i - i$ will not, as far as practical considerations are concerned, affect this argument, although technically one sees that the divergence of this series really prevents the major series from going to infinity at $x = 1$. However, this is exactly the condition that is needed to ensure that equation (21) below will give finite values of $\gamma_s - \gamma_{(sf)}$ for $x = 1$. Equation (14) thus contains three unknown constants: $v_m$, $E_1$ and $c_1$. The first one may be evaluated by the BET method of plotting $x/v(1 - x)$ against $x$ for $0.05 < x < 0.35$. One obtains a straight line, the slope ($S_0$) of which is $(c - 1)/v_mc$ and the intercept ($I_0$), $1/cv_m$ (where $c = (\text{exp. } (E_1 - E_L)/RT)\cdot a_1b_2/a_2b_1$ according to the BET notation). Hence $v_m = 1/(S_0 + I_0)$. In many cases $I_0$ is so near zero that a slight error in drawing the curve may amount to a large percentage error in $I_0$. This is reflected in a large percentage error in $c$ and it is then not justifiable to evaluate $c$ by solving simultaneously the equations $I_0 = 1/v_mc$ and $S_0 = (c - 1)/cv_m$. In any event the BET method should be quite accurate for $v_m$.

As a matter of interest and to show the consistency of employing the BET method of evaluating $v_m$, equation (14) may be developed in terms of $x/v(1 - x)$ *vs.* $x$ which BET have shown to be linear in the range of roughly $0.05 < x < 0.35$. Defining

$$d_i = \text{exp. } [E_1(1 + 1/8 + \cdots + 1/i^3) + E_L(c_1 + c_2 \cdots + c_i - i)]/RT \quad (16)$$

equation (14) becomes

$$v/v_m = \sum_{1}^{\infty} ix^i d_i/(1 + \sum_{1}^{\infty} x^i\, d_i) \quad (14a)$$

Then

$$\frac{x}{v(1 - x)} = \frac{1}{v_m(1 - x) \sum_{1}^{\infty} ix^{i-1}\, d_i} + \frac{\sum_{1}^{\infty} d_i\, x^{i-1}}{v_m(1 - x) \sum_{1}^{\infty} ix^{i-1}\, d_i} x =$$

$$\frac{1}{v_m\,[d_1 + (2d_2 - d_1)x + (3d_3 - 2d_2)x^2 \cdots]} + \frac{d_1 + d_2x + d_3x^2 + \cdots}{v_m[(d_1 + (2d_2 - d_1)x + (3d_3 - 2d_2)x^2 + \cdots]}x \quad (14b)$$

Thus, $x/v(1 - x)$ will vary approximately linearly with $x$ for small values of $x$ providing the terms $id_i - (i - 1)d_{(i-1)}$ are not greatly different from $d_1$ which will be true in most cases for small values of $i$. Terms corresponding to large values of $i$ will drop out in the range $0.05 < x < 0.35$. Of course, if all the $d_i$'s were equal, equations (14a and b) would reduce to the BET equation

$$\frac{x}{v(1 - x)} = \frac{1}{v_mc} + \frac{c - 1}{v_mc}x$$

The constants $E_1$ and $c_1$ may be evaluated from two points on the adsorption isotherm. It is convenient to select the point $v/v_m = 1$ for one of them and some other point preferably somewhere in the range $0.05 < x < 0.35$ for the other because the major series of equation (14a) converges rapidly for small values of $x$. Also, it is more convincing to show that (14a) gives agreement with experimental isotherms at $x > 0.35$ for constants evaluated at or below $x = 0.35$. For $v/v_m = 1$, $x = x_1$ and

$$1 = d_2x_1^2 + 2d_3x_1^3 + 3d_4x_1^4 + \cdots \quad (17)$$

At $v/v_m = t$, $x = x_2$, and

$$t = \frac{d_1x_2 + 2d_2x_2^2 + 3d_3x_2^3 + \cdots}{1 + d_1x_2 + d_2x_2^2 + d_3x_2^3 + \cdots} \quad (18)$$

The coefficients $d_i$ may be divided into two parts

$$d_i = \alpha_i\beta_i \quad (19)$$

where

$$\alpha_i = \exp.\, E_1(1 + 1/8 + \cdots 1/i^3)/RT \quad (19a)$$

and

$$\beta_i = \exp.\, E_L(c_1 + c_2 + \cdots + c_i - i)/RT \quad (19b)$$

The constants may be obtained from these relations by first assuming a value for $c_1$ and calculating all the $\beta_i$'s corresponding to the assumed $c_1$ from equations (8) and (19b). Substituting the $\beta_i$'s in (17) we obtain

$$1 = \alpha_2(\beta_2 x_1^2) + \alpha_3(\beta_3 x_1^3) + \alpha_4(\beta_4 x_4) + \cdots \quad (17a)$$

from which the $\alpha_i$'s may be evaluated. The assumed $c_1$ may then be checked by calculations from (18) and using the value of $x_2$ corresponding to $t$ taken from the isotherm. If the assumed $c_1$ were correct, the calculated $t$ (from 18) would agree with the experimental $t$ at $x_2$. If not, a new value of $c_1$ may be chosen and the process of successive approximations repeated until the calculated value of $t$ agrees with the experimental one.

## Discussion

Equation (14) was tested on several adsorption isotherms obtained by Emmett and Brunauer[10] and by Palmer and Clark.[11] In these cases constants of equation (14) are given in Table I. It is of interest that the isotherms of nitrogen and argon at both −195.8° and −183° are reproduced quite accurately for $p/p_0 > 0.05$ by equation (14) with the constants given in Table I. This indicates that the temperature coefficient of adsorption also is given satisfactorily by equation (14). However, one must expect that in general it may not be possible to calculate an isotherm by equation (14) and constants evaluated at another temperature because $v_m$, $E_1$ and $c_1$ will frequently vary with temperature.

TABLE I

CONSTANTS OF EQUATION (14). (CONSTANTS EVALUATED AT $x$ = 0.1 AND $x$ = 0.35)

| | $v_m$, cc. | $c_1$ | $E_1$, cal./mole | $E_1 - E_L$ (BET) |
|---|---|---|---|---|
| $N_2$ on Catalyst 954[10] (−195.8 and −183.0°) | 135 | .862 | 898 | 894 |
| $NH_3$ on Catalyst 931[10] (−36°) | 34 | .80 | 3250 | ... |
| A on $Al_2O_3$–Fe Catalyst[10] (−195.8 and −183°) | 126 | .884 | 852 | 700 |
| Methyl acetate on vitreous[11] silica[12] (24°) | 1.12 | .952 | 2410 | ... |

It should be mentioned that Anderson[12] was able to extend to about $x$ = 0.7 the agreement of the BET theory with experimental Type II isotherms by simply introducing in place of $x$ (equation 20a) the quantity $kx$, $k$ being an empirical constant. This leads also to a three constant equation, which, as illustrated by the present work, is always a definite advantage for the naive purpose of fitting isotherms. A much more crucial test of the theory will come when one attempts to fit curves in which experimental data are available at values of $x$ approaching closely to 1.0.

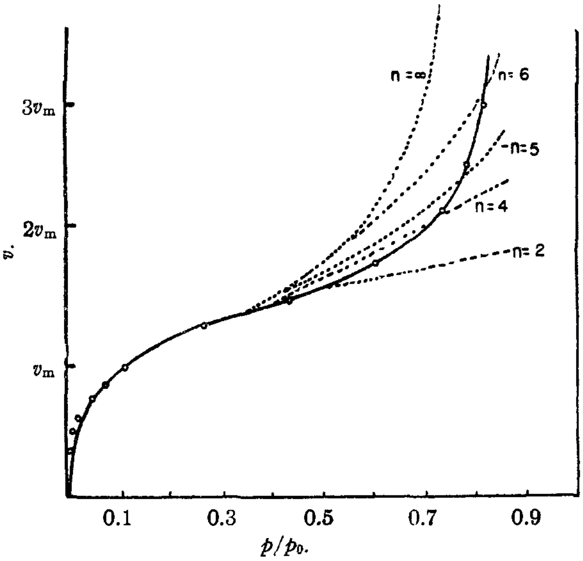

Fig. 1.—Comparison of present theory with BET theory and experiment: O, experimental; —, present theory; ----, BET theory.

Figure 1 compares equation (14a) with the two following equations of the BET theory

$$\frac{v}{v_m} = \frac{cx}{(1 - x)(1 - x + cx)} \quad (20a)$$

$$\frac{v}{v_m} = \frac{cx}{1 - x}\,\frac{1 - (n + 1)x^n + nx^{n+1}}{1 + x(c - 1) - cx^{n+1}} \quad (20b)$$

where (a) is for unrestricted adsorption and (b) is supposed to apply to Type II and III isotherms in which adsorption is restricted to $n$ layers. It appears that Type II curves do not, in general, have the supposed restrictions to account for which equation (20b) was designed, although, one might expect changes in the effective surface area with $x$ in some sigmoid curves which may cause deviations from an unrestricted adsorption isotherm.

An immediate interest in adsorption isotherms is to provide information on the surface pressures of films on solids. As shown by Bangham,[13] one may obtain significant information along these lines by applying the Gibbs adsorption theory from which is obtained the relation

$$\gamma_s - \gamma_{(sf)} = \frac{RT}{V_m \Sigma}\int_0^p \frac{v}{p}\,dp \quad (21)$$

where $\gamma_s$ is the surface tension of the solid, $\gamma_{sf}$ is $\gamma_l + \gamma_{ls}$, $\gamma_l$ is the surface tension of the exposed layer of the film and $\gamma_{ls}$ is the interfacial tension

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(10) P. H. Emmett and S. Brunauer, THIS JOURNAL, **59**, 1553 (1937).

(11) W. G. Palmer and R. E. D. Clark, *Proc. Roy. Soc.* (*London*), **A149**, 360 (1935).

(12) Anderson, THIS JOURNAL, **68**, 686 (1946).

(13) D. H. Bangham and R. I. Razouk, *Proc. Roy. Soc.* (*London*), **A166**, 572 (1938); *Trans. Faraday Soc.*, **33**, 805, 1463 (1947).

between the adsorbed film and the solid. $V_m$ and $\Sigma$ are the molecular volume of the gas, and the total surface area of the solid, respectively. As $\gamma_1 = \gamma_0$ for $p = p_0$ ($\gamma_0$ is the surface tension of the pure liquid) it becomes important to be able to carry out the integration of equation (21) over the entire range of $x$ from zero to one. The present theory evidently accomplishes this over the range of $x$ from 0.05 to 1.0 from adsorption data obtained in the range $0.05 < x < 0.35$. Presumably this problem could be completed by application of McMillan's method in the range $0 < x < 0.05$. Unfortunately, the constants of the McMillan equation must be evaluated from measurements obtained also for $0 < x < 0.05$, which are not always available. Moreover, there are reasons to expect that surface heterogeneities are not the entire explanation of the discrepancy in this region. Jura and Harkins[14] made use of an equation by Armbruster and Austin[15] for this extrapolation from $x = 0.05$ to $x = 0$. In carrying out the extrapolation above $x = 0.35$ for use in equation (21), there is no apparent reason why, in evaluating the constants of equation (14a) one should not employ data taken from all types of physical adsorption isotherms providing the data are taken from the part of the curves representing unrestricted adsorption. Even Types IV and V isotherms usually show unrestricted adsorption for small values of $x$.

Thus the present theory should have at least a pragmatic value in fitting Types II and III adsorption isotherms and in extrapolating them, in the high pressure range, and in showing how Types IV and V isotherms would go if it were not for restricted adsorption. More than this, however, it should have value in carrying out (evidently more accurately) all of the studies for which the BET theory has proved so valuable. A particular advantage may be realized in obtaining the heat of adsorption in terms of its separate components. In the examples so far studied the $i^{\text{th}}$ layer net heats of adsorption appear to be approximately in line with isosteric and calorimetric determinations. That is, they follow the same type of exponential decay to $E_L$ as observed. They are, for example, roughly consistent as far as decay with increasing $i$ is concerned, with the differential net heats of adsorption found by Harkins and Jura[16] and by Beebe, Biscoe, Smith and Wendell.[17] To illustrate this we note that the net heat of adsorption on the first layer according to the present theory will be $E_1 + (c_1 - 1)E_L$, but on all layers above the first it will be simply $E_i$. In other words, when a second layer forms on top of the first one the average coördination number of the adsorbed molecules is increased by the ratio $c_2/c_1$, but only half of the molecules in a two molecular layer film are subject to the evaporation-condensation conditions expressed by the equations (1). Hence in calculating the heat of adsorption to be attributed to the second layer we must add $(c_2 - c_1)E_L$ to $E_2 + (c_2 - 1)E_L$ giving, upon subtracting $E_L$, simply $E_2$ for the second layer net heat of adsorption, and $E_i$ for the net heat of adsorption on the $i^{\text{th}}$ layer. Table II gives the $i^{\text{th}}$ layer net heats of adsorption calculated from the data in Table I.

As discussed earlier in this report, we shall not expect the agreement between the calculated $i^{\text{th}}$ layer net heats of adsorption to agree perfectly with those measured calorimetrically because of the very approximate nature of the coördination ratio factors. In fact, since we have used factors calculated for completely filled and liquid like layers, the present method should really over-rate the adsorbate interaction term. This error will, however, be largely compensated in the adsorbate–adsorbent terms $E^i$ by underrating them. Hence, it is to be expected that the calculated $i^{\text{th}}$ layer net heats of adsorption will be somewhat low.

TABLE II

$i^{\text{th}}$ NET HEATS OF ADSORPTION (CAL./MOLE) ON SUCCESSIVE LAYERS OF VARIOUS MULTIMOLECULAR FILMS

| | $E_1 + (c_1 - 1)E_L$ | $E_2$ | $E_3$ | $E_4$ | $E_5$ |
|---|---|---|---|---|---|
| $N_2$ on catalyst 945 (−195.8° and −183°) | 700 | 110 | 30 | 13 | 7 |
| $NH_3$ on catalyst 931 (−36°) | 2130 | 405 | 120 | 50 | 26 |
| A on $Al_2O_3$–Fe catalyst (−195.8° and −183°) | 675 | 105 | 30 | 12 | 6 |
| Methyl acetate on vitreous silica (25°) | 2000 | 300 | 90 | 38 | 18 |

## Summary

A theory modeled after the Brunauer–Emmett–Teller theory, is developed for the unrestricted physical adsorption of gases on solids. In this theory an attempt is made to describe more accurately the adsorption forces by introducing terms expressing (1) the interaction forces of adsorbed molecules with the adsorbent and (2) the adsorbate interaction forces, the latter being introduced, however, largely on empirical considerations. The equations derived in this manner are found to agree with the sigmoid isotherms over the entire range of relative pressure $x$ above 0.05, certain obvious modifications being required to provide agreement for $x < 0.05$. Heats of adsorption derived from the theory appear consistent with isosteric and calorimetric heats of adsorption. The theory is found useful, among other things, in extrapolating adsorption isotherms in the high relative pressure range for the purpose of providing information on surface pressures of films on solids.

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[14] G. Jura and W. D. Harkins, THIS JOURNAL, **66**, 1356 (1944); also, "Colloid Chemistry," Vol. VI, Alexander, Chap. 1.

[15] M. H. A. Armbruster and J. B. Austin, THIS JOURNAL, **66**, 159 (1944).

[16] W. D. Harkins and G. Jura, *ibid.*, **66**, 919 (1944).

[17] R. Beebe, J. Biscoe, W. Smith and C. Wendell, *ibid.*, **69**, 95 (1947).