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THE DERIVATION OF A SIMPLE, PRACTICAL EQUATION FOR THE ANALYSIS OF THE ENTIRE SURFACE PHYSICAL ADSORPTION ISOTHERM

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SUMMARY

An equation is derived from statistical mechanics to describe the entire physical adsorption isotherm. This equation is derived from a few simple assumptions, which include the indistinguishability, the following of the adsorbed molecules, and a statistical mechanical "big box" to model the surface. The equation has been demonstrated to fit the adsorption isotherms for the materials studied. The derived equation has the quality that allows the direct calculation of surface area without any arbitrary proportionality constant. The only other equation of physical adsorption that has this feature is the Brunaur, Emmett, Teller (BET) equation. However, the presently derived equation also applies over the entire range of physical adsorption, in contrast to the BET equation. Also, for the materials studied, the statistical fit over the BET range was significantly better. Furthermore, the treatment can account for first-layer adsorption on specific sites (such as chemisorption and microporosity) and still yield the surface-area measurement. In this latter case, it will separate out the first-layer isotherm from the contribution of subsequent layers. The equation without the first-layer specific site adsorption is most easily used in the form similar to that discovered by deBoer and Zwikker as

$$\ln[-\ln(P/P_0)] = -\theta + \ln\{-\ln[P(\theta=0)/P_0]\} ,$$

where

P = the adsorbing gas pressure,
P_0 = the liquid vapor pressure of the adsorbing gas, and
θ = the equivalent of one monolayer of adsorbed gas.

With very-high-energy localized sites, the isotherm approaches the Langmuir isotherm at low surface coverages.

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ABSTRACT

An equation is derived from statistical mechanics to describe the entire physical adsorption isotherm. This equation is derived from the following assumptions.

1. The surface may be described as a large potential box, either with or without localized areas of high bonding energy.
2. The molecules adsorbed on the surface are completely mobile and may either skate around, over, or under each other.
3. The bonding energy between a molecule in a high-energy localized site and a molecule in the next layer is equal to the energy of liquefaction.
4. The bonding energy of molecules whenever they are in the first layer is greater than the energy of liquefaction.
5. All other bond energies between adsorbed molecules is equivalent to the energy of liquefaction (including lateral bonding).

6. The adsorbed molecules are indistinguishable from each other.

The equation has been demonstrated to fit the adsorption isotherms for the materials studied. The derived equation has the quality that allows the direct calculation of surface area without any arbitrary proportionality constant. The only other equation of physical adsorption that has this feature is the Brunaur, Emmett, Teller (BET) equation. However, the presently derived equation also applies over the entire range of physical adsorption, in contrast to the BET equation. Also, for the materials studied, the statistical fit over the BET range was significantly better. Furthermore, the treatment can account for first-layer adsorption on specific sites (such as chemisorption and microporosity) and still yield the surface-area measurement. In this latter case, it will separate out the first-layer isotherm from the contribution of subsequent layers. The equation without the first-layer specific site adsorption is most

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1. INTRODUCTION

The primary method used to determine this surface area of finely divided materials has been physical adsorption of inert gases at low temperatures on the material's surface. To the present time, there has been no method for relating the full isotherm (i.e., all of the data of pressure vs the amount of adsorbed gas) of the adsorption to the surface area without some arbitrary assumptions, such as a proportionality constant. The usefulness of the Brunaur, Emmett, Teller (BET)[1] equation is that it has no such proportionality constant; however, the BET equation does not fully describe the isotherm.

A recent article by E. L. Fuller[2] has demonstrated the usefulness of the shielded physisorption equation, originally referred to as the "polarization isotherm" and first applied by deBoer and Zwikker.[3] The arguments against this equation were theoretical; that is, polarization was not sufficient to account for the interactions, and, consequently, the equation has not been generally applied. The empirical fit to the isotherm, however, has been known to be excellent, and Fuller suggested that it was not due to polarization at all but, rather, to the surface being masked as molecules adsorb. For this reason, he has referred to this isotherm equation as the "shielded equation." This equation is applicable from a coverage of essentially zero up to the liquid phase. Thus, it can yield not only the surface area but also the pore structure of solids. In an earlier report,[4] it was demonstrated that the shielded equation is statistically better than any other gas-adsorption equation. This included the BET equation over the range where the BET equation is the most precise. Indeed, if we expand the BET from a two-parameter equation to a four-parameter equation (i.e., two independent absorbing planes), the shielded adsorption equation is still statistically superior. (One of the interesting features of the shielded equation is that, if we make a similar assumption of multiple adsorbing planes, we still have a two-parameter fit in the leastsquares fitting to the untransformed equation. Thus, the shielding equation cannot in a practical sense ever be more than a two-parameter equation.) This report demonstrates the theoretical foundation for this shielded equation and gives, for the first time, a method to unambiguously determine the surface area by using the full physisorption isotherm. No assumptions are made of any proportionality constants to arrive at the surface coverage value. This is a significant advancement over all previous theoretical treatments.

It is interesting that this derivation is a simplification in mathematical representation compared with other theories, such as the virial representation, and yet it is less restrictive. This is not philosophically inconsistent; after all, it fulfills a definition of scientific advance—Ocham's Razor. Today's cutting edge of this statement is a favorable Student t-test or F-test from statistical analysis. That criterion has already been met in the previous publications and is out of the scope of the present discussion.

Two derivations are presented, corresponding to two important surface conditions. These derivations are for

1. the no-register case in which the molecules are free to travel in the plane of the surface and
2. the in-register (or epitaxy) case in which the adsorbing molecules' motions are restricted in the plane of the surface.

These two cases are compared to determine under what conditions each applies. The no-register case, considered first, is the case for most of the physisorption work done with inert gas molecules. This case applies to the isotherms performed near the gas-liquefaction temperature at 1 atm. It is widely used for practical surface area measurements.

2. GAS ADSORPTION ONTO A SURFACE WITH FREE PLANAR TRANSLATION

The first case, the physisorption into a surface condition resembling the liquid state, is characterized by the complete mobility of the molecules in the plane of the surface. There is a two-part attractive surface potential for molecules normal to the surface:

1. the attraction between the molecule and the surface experienced at positions where there are no intervening adsorbed molecules and
2. the attraction between the adsorbed molecules.

Each molecule is traversing the surface freely enough to experience an average attractive potential consisting of both of these potentials. The potentials of the free surface are not strong enough to localize the position of the adsorbed molecules; thus, the entire surface is experienced by each adsorbed molecule. Molecules also do not interfere with each other's motion on the surface. If two molecules attempt to occupy the same space, then they simply stack, at least momentarily. A consequence of this quality is that there is only one statistical "big box" into which the adsorbing molecules are placed, which determines the construction of the ensemble. This condition exists even though, at any one instance, the molecules will have defined positions. In quantum mechanical terms, the following is implied: the energy state of each adsorbed molecule is higher than the tops of the potential wells associated with specific positions but low enough to favor staying in the vicinity of the surface. The molecules are, therefore, reacting to an average observed potential energy.

With these considerations, the grand canonical ensemble can be created. Because there is only one box, there is only one configuration seen by the individual molecule. The average potential is dependent on how many molecules are adsorbed. To obtain the average energy, first consider extra energy for the surface-adsorbate attraction. This energy is here defined as the energy in excess of the adsorbate-adsorbate attraction. The adsorbate-adsorbate attraction is the energy assumed to exist between all of the adsorbed molecules with one exception. This exception, which will be discussed later, is for the interaction between molecules adsorbed in the high-energy localized sites and second-layer molecules. For the mth molecule adsorbed, the potential it will observe with assumed absolute randomness (with the exception of maximizing the ensemble, which comes later) is given by

$$\langle \text{Extra Energy for the mth molecule} \rangle = (E-\epsilon)\ (1 - a/A)^{m-1} \quad , \qquad (1)$$

where

a = The area of an adsorbed molecule,
A = the total area,
m = the number of molecules adsorbed,
E = the attractive surface-adsorbate potential ($E<0$), and
ϵ = the attractive adsorbate-adsorbate potential.

For a more thorough discussion of the reasoning behind Eq. (1), see Appendix A. The term $(1 - a/A)^{m-1}$ is the fraction of the surface that has not been covered after $m - 1$ molecules have adsorbed, if randomness is assumed. The total energy for n molecules adsorbed is

$$\langle \text{Total Excess Energy} \rangle \sum_{m=0}^{n} (E - \epsilon)\ (1 - a/A)^{m-1} \quad . \qquad (2)$$

Because $n\text{-}1 \simeq n = \theta A/a$ and $A >>> a$, then from the definition of the value of e,

$$(1 - a/A)^{n-1} = (1 - \theta/n)^{n-1} \simeq e^{-\theta} \quad . \qquad (3)$$

[Although Eq. (3) is from the definition of the value of e, it may not be obvious to some readers. A quick way to see that Eq. (3) is correct and how quickly it converges is to put in some numbers for a, A, and n. For areas of more than ~20 molecular areas, the error in Eq. (3) is not experimentally distinguishable. See the discussion on multiple small surface areas and pores further on.] Furthermore, because there are many molecules adsorbing, the summation may be replaced with an integral. The total excess energy is then given by

$$\langle \text{Total Excess Energy} \rangle = \int (E - \epsilon) e^{-\theta} dn \quad . \qquad (4)$$

A second energy term results from the interaction of each molecule with all the other molecules on the surface, or ϵ, where ϵ is the adsorbate-adsorbate attractive energy. (Keep in mind that each of the molecules is seeing an average potential and is very mobile on the surface.) The third energy term is that of the translational energy in two dimensions. Each translation for each molecule is 0.5 kT, so the total translational energy is nkT. Ultimately, this translational difference will be seen as irrelevant. This energy term is indeed present; however, it is also present on the surface of the liquid state, against which the derived isotherm will ultimately be referenced. Although not likely, one could propose other energy additions due to molecular energy level during adsorption. States that have been suggested are the spin states and spin-spin interactions, but others could be added. (As will be seen from the derivation below, this proposal is ultimately irrelevant.) All of these additions may be expressed as a function f(T) for each molecule for a total of nf(T) of extra energy. As with the translational energy, these levels should also be present on the surface of the referenced liquid. Notice that, although the grand canonical ensemble is constructed as if the molecules were coming from the gas phase, ultimately the derivation refers back to the liquid state.

The grand canonical ensemble can thus be written as

$$\Xi = \sum_n \lambda Z^n + e^{-[\int (E-\epsilon) e^{-\theta} dn \, + \, \epsilon n \, + \, nkT \, + \, nf(T)]/kT} \quad , \qquad (5)$$

where

λ = the activity of the adsorbate, and
Z = the canonical partition function for the adsorbate on the surface.

A comment is in order at this point for those who are not familiar with the grand canonical ensemble. This ensemble is used when the concern is energy transport by addition or subtraction of particles. The origin of the energy terms is irrelevant, provided a proper accounting is made of the terms. In the original manuscript the term f(T) was not included since all the terms of this nature were the same in the referenced liquid state as in the adsorbed state. The same is true for the terms associated with ϵ, and any argument as to the orientation of the various molecules with respect to each other is totally irrelevant. Equation (5), as written, is correct and conservative and is the grand canonical ensemble as presented in standard textbooks.

Continuing the derivation, the steps are now according to the usual rote method, that is, using the maximum term and differentiating with respect to n

$$\frac{\partial \ln(\text{max term } \Xi)}{\partial n} = \ln(\lambda Z) - [(E-\epsilon)e^{-\theta} + \epsilon + kT + f(T)]/kT \quad . \tag{6}$$

To simplify further, one uses $\ln(\lambda Z) = \ln(P)$, and finds the maximum of the grand canonical partition function by setting

$$\frac{\partial \ln(\text{max term } \Xi)}{\partial n} = 0 \quad . \tag{7}$$

Therefore

$$\ln(P) = [(E - \epsilon)e^{-\theta} + \epsilon + f(T)]/kT + 1 \quad . \tag{8}$$

As $\theta \rightarrow \infty$, the gas pressure becomes the vapor pressure of the liquid P_0. Thus,

$$\ln(P_0) = \epsilon/kT + 1 + f(T)/kT \quad , \tag{9}$$

as expected.

Equation (9), in the form before the addition of f(T), was criticized for not being the form of the equation for the vapor pressure of a liquid as a function of temperature. This is certainly incorrect, since one can rearrange Eq. (9) by selecting the standard state to give the vapor pressure in the form of a linear Van Hoff plot. Granted, there are heat capacity effects which distort this plot somewhat, but this is truly a trivial correction. Equation (9) does indeed correspond to normal liquid behavior.

As $\theta \rightarrow 0$, notice that the vapor pressure does not drop to zero. This is totally appropriate for this type of phase behavior, that is,

$$\ln[P(\theta = 0)/P_0] = (E - \epsilon)/kT \quad . \tag{10}$$

Note that this equation, indeed, expresses one feature of the observed adsorption behavior that is normally ignored, that is, there is a threshold value for the first molecule to be **physically** (note the emphasis) adsorbed. This threshold is usually in the high vacuum range, if not the ultra-high vacuum range, and not normally observed directly in physisorption measurements. It is, however, commonly observed in ultra-high vacuum work and is observable from an extrapolation of physical adsorption work, as Fuller demonstrated. What is more interesting is the argument that Henry's Law is not followed. The answer to this argument is first, there is no physical law that says Henry's Law must be followed in this instance, and second, it does follow the law within the normally accepted limits of it application.

From the above equations the final equation is

$$\ln(P/P_0) = e^{-\theta}\ln[P(\theta = 0)/P_0] \quad . \tag{11}$$

Notice that the function f(T) is indeed irrelevant when the isotherm is expressed in the practical form of Eq. (11). When this equation was applied to the isotherms and tested statistically, the untransformed form was used. This was true for the fit to the BET equation as well. For a quicker and easier method of determining θ, the following transformed equation may be more useful:

$$\ln[-\ln(P/P_0)] = -\theta + \ln\{-\ln[P(\theta = 0)/P_0]\} \quad . \tag{12}$$

The value of θ or the amount per surface area is directly obtainable from this equation through a linear fit of the adsorption data, or

$$\text{surface area} = \frac{\text{Area}}{\text{molecule}} \times \frac{-d(\text{amount})}{d\{\ln[-\ln(P/P_0)]\}} \times \text{conversion factor} \quad ,$$

where the conversion factor is the number of molecules per unit amount appropriate to the measurement.

3. INSENSITIVITY TO SURFACE POTENTIAL HETEROGENEITY

It is easy to demonstrate that the no-register case is not affected by differing potentials on the surface. Assuming a mixture of surface patches (due to different planes, inhomogeneous chemical composition, or whatever) labeled 1,2...n with the following:

$E_1, E_2, \ldots E_n$ = attractive potentials peculiar to each patch,
$X_1, X_2, \ldots X_n$ = amount adsorbed on each patch, and
$\sigma_1, \sigma_2, \ldots \sigma_n$ = surface area of each patch,

results in

$$\theta_m = X_m/\sigma_m \quad . \tag{13}$$

Each patch is independent; therefore,

$$\begin{array}{rcl} \ln[-\ln(P/P_0)] & = & -\theta_1 + \ln(-E_1/kT) \\ \ln[-\ln(P/P_0)] & = & -\theta_2 + \ln(-E_2/kT) \\ \cdot & = & \cdot \\ \cdot & = & \cdot \\ \cdot & = & \cdot \\ \ln[-\ln(P/P_0)] & = & -\theta_n + \ln(-E_n/kT) \quad . \end{array} \tag{14}$$

Multiplying each by its respective σ's and adding

$$A\ln[-\ln(P/P_0)] = \sum_m X_m + \sum_m \sigma_m \ln(-E_m/kT) \quad , \tag{15}$$

where

$$A = \sum_m \sigma_m \quad . \tag{16}$$

Letting <E> be the geometrical average energy which is weighted by the area, or

$$\langle E \rangle = \prod_m E_m \ (\sigma_m/A) \quad , \tag{17}$$

then

$$\ln[-\ln(P/P_0)] = -\theta + \ln(-\langle E \rangle/kT) \quad , \tag{18}$$

where

$$\theta = (\sum_m X_m)/A \quad , \tag{19}$$

or the overall surface coverage. Thus, the isotherm equation is not sensitive to patches of high and low energy and yields an overall coverage and a geometric average surface energy. This result is important for the discussion in the next section, where there are high-energy sites on the surface that can immobilize some to the first-layer molecules.

What is stated above is that the equation is invariant with a heterogeneous surface, which does not imply that the surface area or the adsorption energy cannot change with some physicochemical treatment. One of the practical implications of the above discussion is that the no-register isotherm is **always** a two-parameter fit and can never be expanded to more. The BET equation, however, can be expanded to high parameter fits by assuming heterogeneity (i.e., the actual form of the equation changes). This is also true of many of the other isotherms such as the virial equations.

4. GAS ADSORPTION ONTO A SURFACE WITH EPITAXY

Inclusion of the in-register or epitaxy assumes there are discrete positions of the surface. These positions can effectively immobilize the adsorbed molecules. Two likely sources for the high-energy immobilizing sites are

1. imperfections on the surface, such as impurities and micropores, and

2. regular, periodic high-energy adsorption sites that possibly cannot all be filled due to steric interferences between the adsorbing molecules.

The assumption made in this section amounts to saying that the energy of the adsorbate molecules is less than the top of these particular potential wells on the surface, and the residence time at each well is large compared to the time of its translation on the surface. This condition will be assumed for the first layer of adsorbed molecules. Beyond the first layer, the assumptions of the previous derivation will be used with one exception—the excess energy or extra surface potential is decreased proportionally by the coverage in the first layer; thus, the extra energy term for the mth molecule in layers other than the first is now

$$\langle \text{Extra Energy} \rangle = [(E - \epsilon)(1 - \alpha) + \epsilon](1 - a/A)^{m-1} \quad , \qquad (20)$$

where

α = ia/A and is the first-layer surface coverage, and
i = the total number of first-layer adsorbate molecules.

The distribution for the first layer is the familiar one:

$$\text{First-Layer Combinations} = \frac{N!}{i!\ (N - i)!} \quad , \qquad (21)$$

where

N = the number of the high-energy localized surface sites.

The distribution for subsequent layers is assumed to be the same as the no-register case (i.e., the "big box"). Using the following definitions:

j = the total number of molecules in layers subsequent to the first layer, and
β = the coverage due to all layers except the first one so that $\theta = \alpha + \beta$,

then the grand partition function is

$$\Xi = \sum_i \sum_j \frac{N!}{i! \quad (N-i)!} + \lambda Z^{i+j}$$

$$+ e^{-\{E_i + \int[(E - \epsilon)(1 - \alpha) + \epsilon]e^{\beta}dj + jkT + jf(T)\}/kT} \quad . \qquad (22)$$

Differentiating the log(max term Ξ) with respect to i, setting it to zero, and noting that the value of Ea/A is very small (from the differentiation of E[1 - α) result in

$$\ln(P) = \ln[\alpha/(1 - \alpha)] + E/kT \quad , \qquad (23)$$

which is the Langmuir isotherm in the first layer.

Differentiating with respect to j and setting it to zero gives

$$\ln(P) = \{[(E - \epsilon)(1 - \alpha) + \epsilon]e^{-\beta} + \epsilon + f(T)\}/kT + 1 \quad . \qquad (24)$$

Again as $\theta \to \infty$ the pressure becomes P_0. However, as $\theta \to 0$ at some pressure, the coverage in the subsequent layers goes to zero. This is similar to the condition before; however, the total coverage does not drop to zero. Overall,

$$\therefore \text{ if } \theta \to 0, \text{ then } P \to 0 \quad . \qquad (25)$$

Taking the log of the equation above yields a function similar to that used for the no-register case.

$$\ln[-\ln(P/P_0)] = \ln\{-[(E - \epsilon)(1 - \alpha) + \epsilon]/kT\} - \beta \quad . \qquad (26)$$

As the pressure increases, $\alpha \to 1$ and the equation approaches the line

$$\ln[-\ln(P/P_0)] = \ln(-\epsilon/kT) - \beta \quad . \qquad (27)$$

To ensure that most of the first-layer effects are not present in the slope, we use an offset in the subsequent layer coverages of at least $\beta > 1$, so that $P/P_0 >$ **0.51**. Above this value, it would be safe to take the slope as before to determine the surface area.

Note that the pressure criterion of $P/P_0 > 0.51$ is not quite high enough to encounter macroporous problems upon adsorption (but maybe not desorption). This illustrates one of the strengths of this method of analysis. The answer for the surface area is obtained in a pressure range that is not affected by surface inhomogeneities, micropores, registry considerations, or macropores. Mesopores will also not affect the isotherm analysis greatly, since they will not alter the general shape of the curve but, rather, will produce steps. This condition can be seen by examining the original approximation made to arrive at the exponential term $e^{-\theta}$. Assume, for example, a large number of mesopores of a cross-sectional area of exactly ten molecules. Now, instead of a "big box" or individual sites, we have a box of intermediate size. The breakdown of the approximation that leads to the exponent term, $e^{-\theta}$, will yield a step at each of the coverages of 0.1, 0.19, 0.27, 0.34, 0.41, 0.47, 0.52, etc. The more gas that is adsorbed, the closer the steps become, until they fade into the experimental error.

In this section, the most rigorous condition was assumed for the in-register, first layer (call it the perfect epitaxy)—for a full first layer, each high-energy site was filled and there is perfect coverage (no gaps in close-packed fashion). It would be very unusual for such a condition to exist even for perfectly regular, close-packed planes, since either some steric hindrances or undersizing are likely. The coefficient in the excess energy term is more like

$$[(1 - \alpha f)\ (E - \epsilon) + \epsilon] \quad , \qquad (28)$$

where $f < 1$. Working through each case is not necessary due to the additivity principle described in the previous section. The result is the same as if we were to add two weighted isotherms. This is done in the log(-log) form of the equation (as done previously). One of these isotherms is the perfect epitaxy case weighted by an area of f, and the other is the no-register case weighted by an area of 1 - f.

This additivity makes the analysis of the low-pressure deviations from the no-register case simple. Subtraction of the extrapolated curve from the experimental curve yields the first-layer isotherm only. This capability could prove to be an extremely useful tool for analysis of the surface state of materials.

5. COMPARISONS OF THE ISOTHERMS

A few isotherms are generated here to illustrate the use of the analysis. Figure 1 shows four generated isotherms for which E/kT is 1.0, 3.0, 5.0, and 10.0. Analysis of the 3.0, 5.0, and 10.0 curves by the BET method yielded a surface coverage of 1.05, 0.84, and 0.60, respectively (along with the BET constants of 4.8, 13, and 35). The BET analysis of the 1.0 curve is uncertain but yields a surface coverage of between 1.0 and 2.5. To generate curves for the epitaxy case, a value of ϵ/kT needs to be selected. For argon this value is about 8.9, for nitrogen it is about 8.6. Using the argon value, the isotherms of Fig. 2 were generated with E/kT values of 1.0, 2.0, 4.0, and 8.0. Figure 3 shows the same data plotted in the log(-log) form. The approach to the slope of 1.0 and the approach to an intercept on the log(-log) axis of 3.2 with higher coverages are evident.

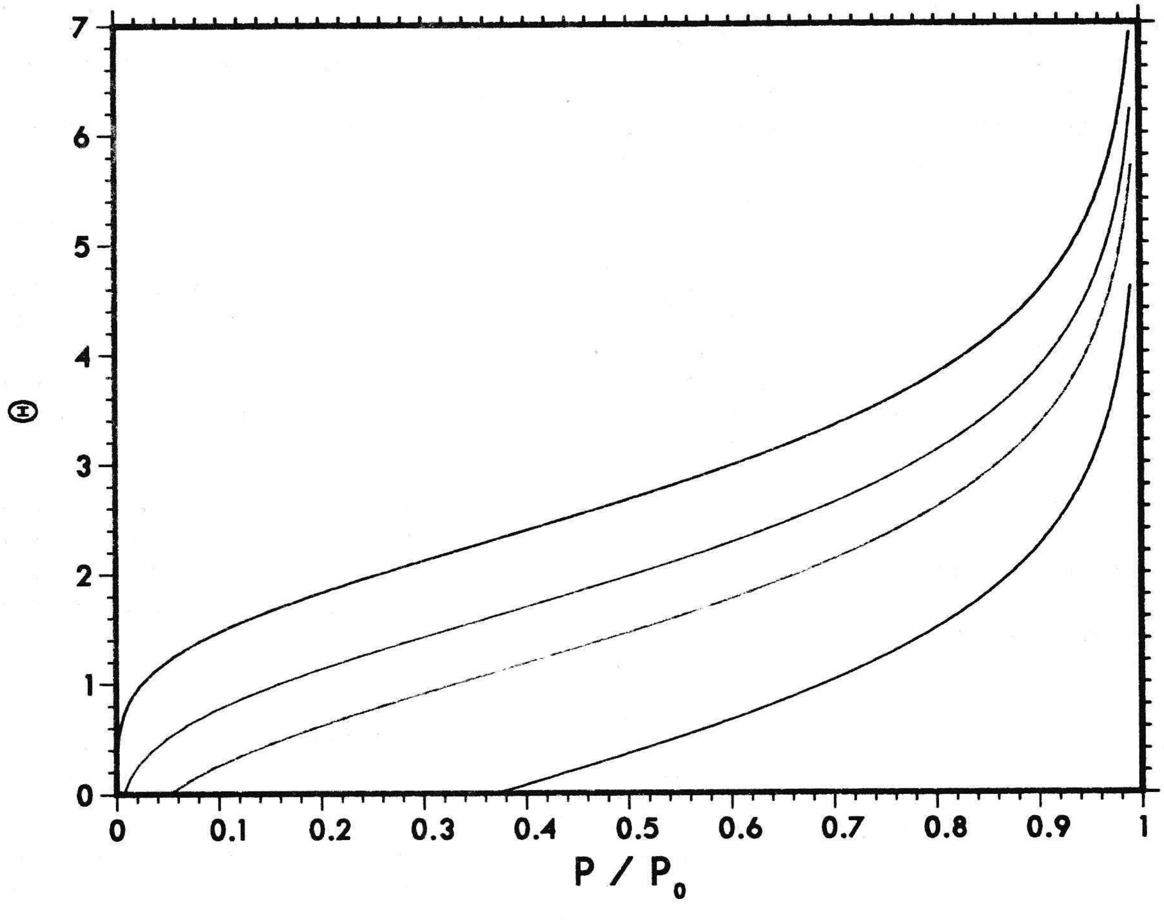

Fig. 1. Isotherms generated using the no-register shielded equation. Values of E/kT used (from bottom to top) are 1.0, 3.0, 5.0, and 10.0.

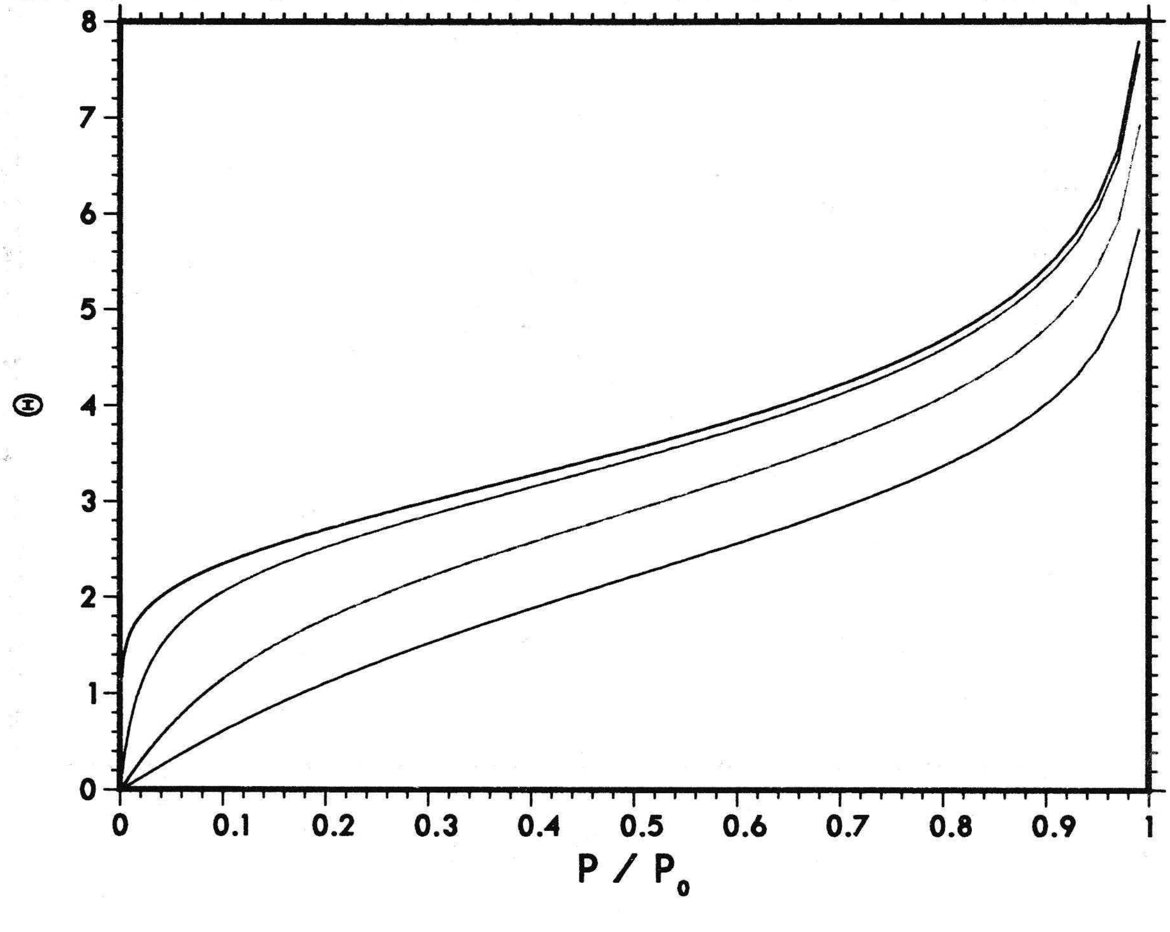

Fig. 2. Isotherm generated using the in-register shielded equation. Argon ($\epsilon/kT = 7.5$) is the assumed adsorbate, and the values of E/kt are (from bottom to top) 1.0, 2.0, 4.0, and 8.0.

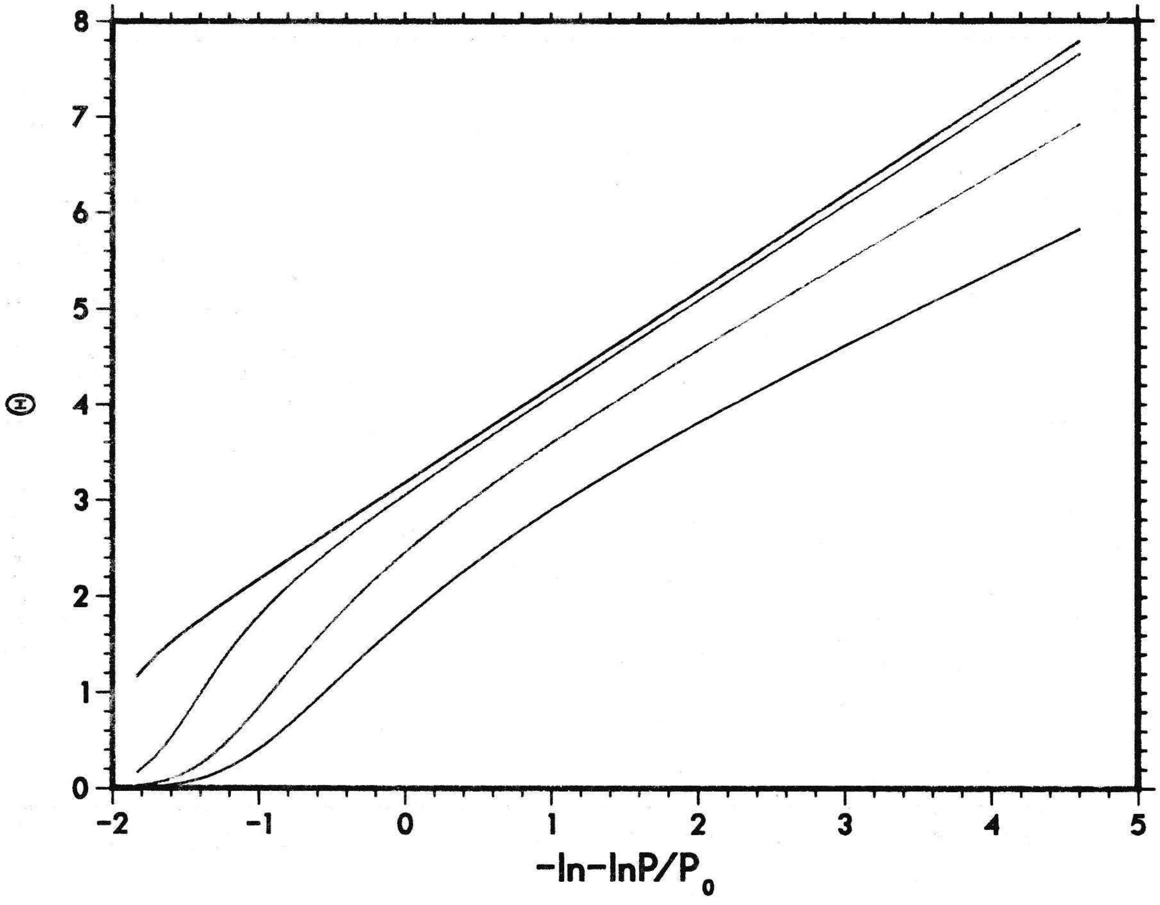

Fig. 3. Isotherms of Fig. 2 replotted to the log(-log) vs *θ* form of the shielded equation.

6. CONCLUSION

The shielded equation is obviously a very powerful description of the sorption isotherm. It is now possible to obtain from this equation an unambiguous number for the surface area. Other information is also available from this isotherm treatment that, with more thorough data collection using computerized instruments, will be useful for characterizing the surface. For the macroporosity information, this characterization has already been demonstrated in refs. 2 and 3, using the shielded equation.

7. ACKNOWLEDGMENT

I thank Dr. E. L. Fuller for his many discussions and inspiration. His work has effectively established the shielded equation as the equation of choice.

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APPENDIX A

Appendix A

THE EXTRA ENERGY OF THE mth ADSORBED MOLECULE

For ease of discussion, consider a surface which has just enough room for 10 molecules. Define the energy of adsorption referenced against the liquid state. Thus the energy of adsorption for the very first molecule is

$$E - \epsilon \text{ for the molecule \#1} \quad , \tag{A1}$$

because we are assuming that the molecule has to leave the liquid state and must take up the energy ϵ to do so (Endothermic). It then releases the energy E (Exothermic) when it adsorbs on the surface in question. Notice that (though not relevant) both are less than 0 by the normal thermodynamic convention. The total amount of surface now left completely bare is 90% of the original surface.

When molecule 2 adsorbs, only 90% of the surface is available for direct adsorption and 10% for adsorption on the first layer. Adsorption onto the first layer releases an energy of ϵ instead of E. Thus, on an average, the energy for the second molecule is

$$0.9(E - \epsilon) + 0.1(\epsilon - \epsilon) \text{ or} \tag{A2}$$

$$0.9(E - \epsilon) \text{ for the molecule \#2} \quad . \tag{A3}$$

It could be argued at this point that the first molecule jumps on top of the second molecule and that only molecule #2 is now on the surface. However, since the molecules are indistinguishable, molecule #1 takes up the role of molecule #2, and the total energy remains the same. Thus, in the classical framework it is irrelevant whether molecule #2 skates under or over molecule #1 when they meet. The total amount of surface now left bare, on an average, is 90% of 90% of the original or 81%. When molecule #3 adsorbs, only 81% of the surface is available for direct adsorption. By an argument similar to that put forth for molecule #2, on an average, the energy for the third molecule is

$$0.81(E - \epsilon) \text{ for the molecule \#3} \quad . \tag{A4}$$

Notice that for each molecule added this is a progression of

$$(1 - 0.1)^{m-1}(E - \epsilon) \text{ for the mth molecule} \quad . \tag{A5}$$

Also notice that the energy term never drops to zero. The 10th molecule does not complete the coverage of the entire surface but rather leaves $(1 - 0.1)^9$ or 0.387 of the surface open.

If we use the value a for the surface area that one molecule can cover and A as the total surface area, then the relationship

$$\langle \text{Total Energy mth molecule} \rangle = (1 - a/A)^{m-1}(E - \epsilon) \qquad \text{(A6)}$$

should be apparent.

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