

Quantum Mechanics of Physisorption
Part I: Disproof of the BET and other theories

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Title:

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Part I: Disproof of the BET and other theories

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Abstract:

Of all the physical adsorption (physisorption) hypotheses the BET, of a class called “Henry’s Law,” is the only generally accepted one. The BET however it is very flawed, since it 1) yields the wrong answer for surface area, 2) works for only 2 of the 6 “Types” of isotherms, 3) can only be used on about 1/3 of the data for each experiment, 4) even in the BET (1/3) range has a typically a 5% std. dev. for amount adsorbed, 5) predicts a property for adsorption that is false – a definite disproof. Never-the-less, there are strong barriers to any publication that contradicts the “Henry’s Law” concept for physisorption.

Since there is strong, unscientific opposition to above statements, this Part I provides proof of the falsehood of the “Henry’s Law” applied to physisorption as well as the Dubinin based isotherm with multiple experimental indisputable evidence. It also provides other statistical and practical evidence of these hypotheses not providing useful information, although in Part III methods of partial recovery is provided.

However, even though the disproofs are very strong, without the BET how can one analyze the isotherm? This series has the answer. This exposé requires several parts, all of which are necessary for full comprehension. They require knowledge of simple Quantum Mechanical perturbation theory and of the Grand Canonical Partition Function.

It will be psychologically difficult to abandon the familiar ideas, which promise to yield the parameter wanted. The reward will be enlightenment with a better sense of how physisorption works.

Main Text:

Quantum Mechanics of Physisorption

Part I: Disproof of the BET and other theories

Introduction:

This group of papers specifically addresses physical adsorption, and the quantum mechanics associated with the phenomenon. However, it is also obvious that it can be expanded to explain phenomena such as long-range surface forces¹ and perhaps on the short scale range for some biological phenomena.

In the first part of this report, the predictions of the “Henry’s law” isotherm analysis and the Dubinin, et al., analysis are presented. These predictions are then proven false by examining experimental data in a disprovability test. This test says that all theories should be disprovable (Webster definition: able to be proved false or wrong : capable of being disproved) by some means, usually by predicting outcomes of additional experimental trails. If the prediction is incorrect, then the theory is proven false as it current exists. If the prediction is correct, it provides support for a hypothesis, but it cannot prove it is correct. In any case, such a test should be reliable and repeatable by other investigators. A disproved hypothesis then must either be replaced, if possible, or modified. If there is no replacement available, then the old hypothesis might be modified and used as an empirical law, perhaps with restrictions. For example, Newton’s laws are still used today with success for “human scale” predictions, even though they are not always accurate to the appropriate degree. The problem with modifications and restrictions is they can begin to “pile up” until it becomes clear that there are too many exceptions for the law to be useful, or the hypothesis may still yield wrong answers unexpectedly.

These problems in physisorption seem to be solved with the quantum mechanical (QM) approach, but any theoretical success is dependent upon the assumptions made. The assumptions for this use of QM are as follows:

1. the adsorbent surface, although it might have high and low for very local potentials, due to the fluid nature of the adsorbate an overall average, at least on microscale is important. This is normally today referred to as non-local in other treatments.
2. Furthermore, the size of the adsorbate molecule is extremely small compared to aliquots of surface patches. This assumption has been referred to as the “big box” assumption^{2,3}. If this assumption is broken there are probably ways to make a fix.
3. The wave functions can be separated by the principle of separation of variables, with the wave function in the plane of the surface (2D) can be solved separate from the normal to the surface (1D).
4. The adsorbed molecule provides a perturbation on the surface. This has been referred to as the particle in-a-box with a “tooth,” that is, a positive perturbation. Mathematically as each particle is adsorbed it becomes part of the surface energetics, and its potential is small enough that the next adsorbed particle is not localized. In other words. the adsorbate attraction still “sees” the delocalize potential with the previous adsorbed particles as part of the overall in-plane wave potential.

At this point, presenting the perturbation derivation in Part I would be a distraction and divert the purpose of this report. This report also deals only with the reason for looking for some other isotherm representation. Subsequent papers present:

Part II Experimental Problems which lead to false conclusion, a comparison of BET versus QM, and the first modification, heterogeneity.

Part III Using Quantum Mechanics to possibly interpret the output of previous BET analysis.

Part IV Derivation of the QM Perturbation theory-based equations and the Grand Canonical Partition Function (GCPF) to yield the χ -plot, $\Delta\chi$ -plot, the Schichten Equations (replacing the N -layer approach) and the Log-law Plot. This part presents the now 3rd derivation using the Hellmann-Feynman theorem which is simpler than perturbation⁴ or WKB⁵ approximation*. Furthermore, this report will concentrate on the QM hypothesis, but the results from QM is concordant with ESW (Excess Surface Work) by Adolphs^{6,7,8,9}. The primary difference between the two hypotheses is QM concentrates on energy, whereas ESW examines the forces.

Part V Calculation of microporosity – monolayer and other steric restrictions using the schichten equations

Part VI mesoporosity – from energy balance

Part VII calculation of the heat of adsorption correlating to the isotherm and binary isotherms in the low “coverage” range.

Definition of physisorption (physical adsorption):

It is assumed that the reader is familiar with the language associated with physisorption (physical adsorption,) but for clarity, definitions used in this report are given in Appendix 1. Symbols are from the IUPAC¹⁰ convention (some are the alternative IUPAC) in Appendix 2.

It is important to be clear about the definition of physisorption since there seems to be some confusion in the literature. The forces involved in physisorption are what chemist call “intermolecular” forces and not “Chemical bonds.” There are many attempts to distinguish between these two, such as energy release in the formation of the attraction and position of the molecule. The best way, however, is to define the difference by the topology of the electrons in the adsorbate molecule.

For physisorption, the topology of the electrons in the adsorbate molecule does not change for the process of adsorption. This is not the case for “chemisorption” where the attraction is chemical bonds, which are formed with the adsorbate and thus the electron topology changes.

The physical adsorption addressed in this report is for all cases where the temperature is between the freezing point and the critical point of the adsorptive. There may be occasion where the equations can be used for temperatures below the freezing point, but the process below the temperature is usually “epitaxy.” In principle it also applies above the critical temperature.

* A 4th method has also been used to check the assumptions, that is digital calculation. This confirmed several calculations, but the relative scaling is impractical to achieve.

Also, most measurements addressed are in the range where nonideality is not a problem. Corrections for nonideal behavior are not addressed but except possibly for supercritical fluids they can probably be corrected.

The “Henry’s Law” and Dubinin class isotherms:

“Henry’s Law” as applied to physisorption* states that as the pressure of the adsorptive goes to zero when the adsorbate goes to zero and visa-versa.

$$P/n_a = C \text{ as } P \rightarrow 0 \text{ or } n_a \rightarrow 0 \quad \text{Equation 1}$$

Where n_a is the amount adsorbed (usually in mmol) and P is the pressure, usually the relative pressure is used, $X := P/P_{\text{vap}}$. In other words, the isotherm, the graph of amount adsorbed versus relative pressure, is predicted by Equation 1 to pass through $[0,0]$. (The isotherm equation is usually expressed with the relative pressure, X , associated with the abscissa and the amount adsorbed given on the ordinate. In fits it is usually assumed the independent variable is very accurate and precise and the dependent variable contains most of the uncertainty.) The BET (Brunauer, Emmitt and Teller^{11,12}.) equation fulfills the “Henry’s Law” criterion. This is obvious from inspection of the BET equation, Equation 2:

$$\theta := \frac{n_a}{n_m} = \frac{CX}{(1-X)(1+[C-1]X)} \quad \text{Equation 2}$$

where the Greek letter “ θ ” is defined here and is called the “coverage.” “ C ” is the “BET” “constant,” a parameter, assumed to be a chemical equilibrium constant. Clearly, as X goes to 0, so does θ , or n_a , since the denominator is a finite amount.[†] The n_m parameter represents the monolayer amount, that is, the adsorbate amount distributed if all molecules touched the surface to cover it with one layer. The parameter[‡] n_m has a slightly different definition in the QM model. The n_a and n_m are reported normally being divided by the adsorbent mass in grams (thus having the units usually of mmol g^{-1} , but older reports may use the amount of gas removed from the adsorptive in mL g^{-1} .)

The Langmuir isotherm and a variety of other isotherm, some with exponentials and powers, but they all qualify if Equation 2 holds. Freundlich isotherm is sometimes said to have this property. Why are so many isotherms fit to the “Henry’s law?” The history of the question is complex, but summarizing, the chemists were always thinking in terms of chemical bonds and chemical equilibrium, which is consistent with that mathematics. Intermolecular and other physical forces, and the causes of phase boundaries, were just beginning to be appreciated when these hypotheses were being proposed.

* Let’s make something clear: Henry’s law was formulated to describe the behavior of a solute in low concentration in a solution and has a thermodynamic connected law, which is Raoult’s law for the solvent. There is no Raoult’s law for a single adsorbent in physisorption. Furthermore, there is no theoretical reason for it. It was postulated that it existed by the extrapolation from the lowest data point to $[0,0]$ in the isotherm representation. It became attached to physisorption as an analogy. Analogies are good teaching tools but very bad science.

[†] Usually, one can inspect the equation being used to determine if it is a “Henry’s law” isotherm and L’Hôpital’s rule is not needed

[‡] Webster definition: “Parameter: (1a) an arbitrary constant whose value characterizes a member of a system (such as a family of curves.)” Thus, it is a situational constant versus a given (universal) constant. Determination of a constant indicates that constant is a parameter (situational,) but once this constant is determined and used without change it becomes a (universal) constant. The difference is extremely important here. See also: <https://math4teaching.com/variables-constants-parameters/>

Examples in physisorption:

variables: n_a , X , etc., constant: R and conversion factors, parameters: n_m , E_a and some others later.

Another class of physical adsorption hypothesis equations is the Dubinin class. They are summarized by Equation 3 in a simpler form suggested by Rouquerol, Llewellyn and Sing¹³:

$$\frac{n_a}{n_0} = \mathbf{exp} \left\{ - \left(\frac{A}{\beta E} \right)^k \right\} \quad k \geq 2 \quad A = -RT \ln \left(\frac{P}{P_{\text{vap}}} \right) \quad \text{Equation 3}$$

The k can be changed depending on the Type of isotherm, so it is a parameter along with A and n_0 . One could also add a series of $n_{a,1}$, $n_{a,2}$, etc. If $k = 2$, this is the Dubinin-Radushkevich equation and other authors names are associated with differing values and summations. Using this usually involves taking the log of both sides and plotting log value versus log value. This yields an almost linear plot near $X = 1$ which is used in the extrapolation to $X = 1$, to determine the volume of pores. This is a more reliable method of obtaining the Gurvitsch value for the pore volume. Theoretically, the extrapolation of the isotherm itself should give this value, but the external area adds an error. This method, mathematically “compresses” the external area measurement to a smaller portion of the plot, making it easier to ignore.

The equation does extrapolate to $[0,0]$ but is strictly not a Henry’s law isotherm since n_a/P ratio is not constant. This is similar statement may be made about the Freundlich isotherm where this ratio is also rarely constant. However, the extrapolation to $[0,0]$ falls into the category 1) in the following sections.

Methods that Disprove and Justify Replacement of a Theory:

There are three or four methods of disproving theories.

- 1) As mentioned about, if a hypothesis predicts something which is incorrect as stated, it is a disproof of the hypothesis even if this happens only once. However, given the weakness of humans, this disproof must be supported by other independent observers. Even so, it may be useful as an approximation to another hypothesis which has been proven more reliable. For example, Newtonian laws are good approximation of General Theory of Relativity for most human scale calculations.
- 2) The tested hypotheses is inferior in explaining the data than an alternative theory, or the alternative is derived upon more fundamental principles. This is not as strong a disproof as 1) but if the alternative predicts more data with the same or fewer parameters and is more reliable, it is hard to justify the inferior hypothesis. (The reverse is also true for the creation of a new hypothesis.)
- 3) The tested hypotheses must not generate an anomaly. An anomaly is referred to as a hypothesis's death sentence.
- 4) ...and in addition: The hypotheses should provide useful parameters. All parameters should have a connection to some physical parameters relatable to reality. Speculation about the meanings of the parameters must be demonstrational. This inconvenience is often overlooked but the resultant theoretical calculation might be excellent. These could serve as an empirical law*. However, the creation of new and unrecognized parameters often happened in physics, later to be understood in the light of experimental reality.

Examination of the Dubinin, et al. and “Henry’s Law” classes of isotherms.

The Dubinin, et al., class.

First the Dubinin, et al., class will be examined. The hypothesis contain three hard to justifiable parameters, especially the variability of the k parameter. Dubinin's primary contribution was the observation of the Dubinin “Thermodynamic Criterion,”[†] which predicts the entropy of adsorption from the liquid phase at the temperature of the adsorbent is nearly zero. This was supported by experiments by Fuller³ as being correct. The hypothesis calculates the pore volume which could be just as accurately to be obtained with the Gurvitsch rule, but not much else. The extrapolation to [0,0] is the same problem as Henry's law presents.

The Freundlich isotherm was mentioned above. It also extrapolates to [0.0].

* What is the difference between a law and a theory? A law fits the observation reliably but does not have an explanation about the phenomenon. Example: Newton's laws. A theory provides not just the fit but also an explanation for the fit. Example 2: Theory of General Relativity provides an explanation. However, both need to be tested in an attempt to disprove.

[†] Extremely criticized by Einstein and Brunauer and therefore dropped.

Theories Based on a “Force Field”:

In recent years there has been a revival of the Polanyi idea of a force field approach. The idea was put forth by Tarazona^{14,15,16}, who referred to it as the “external potential,” and calculations were made for confined geometries for liquids. The approach was referred to as Density Functional Theory DFT (applied to physisorption.) Theoretically the problem is that one can bring back the old arguments that Brunauer used. What is this “external potential” that has a decay constant of one monolayer thickness regardless of the amount adsorbed. None of the intermolecular attractions contain this field, but never-the-less it has been used*.

It has been used mostly unsuccessfully so there have been several variations of it. The problem was to obtain high enough energy, one needed to use localized attractions (chemical bonds,) which in turn created adsorption curves that were stepped as if the adsorbate were a solid and not delocalized. Freeing up the localization, of course, caused other problems. The main problem remains, where does the exponential decay force come from? Strangely, some investigators have unjustifiably used the publication by Churaev, Stark and Adolphs⁸, which assumed the validity of the disjoining pressure but not an external potential, to justify the exponential decay. This is an ironic reference that eventually led to the ESW derivation. (The disjoining pressure can be justified by the QM derivation. See reference 2 for the relationship between the QM $\Delta^{\mu}E$ and the ESW $H_{(disjoining)}$.)

DFT and its variants (designated XXDFT in this publication) however, create a very pleasing spectral analysis for porosity, but it is being disputed today in the literature¹⁷. Even so, the final analysis relates back to measuring the surface area using the BET, which we are here in the process of disproving. Perhaps, the use of the QM analysis for the surface area would work better with DFT, but there is an alternative already in place for porosity measurement using the QM approach.

* ...and sanctioned by IUPAC.

Experimental evidence in disproof of “Henry’s Law” hypotheses.

The most important and widely used isotherm hypotheses are the Langmuir¹⁸ and the BET¹¹. The Langmuir “theory” is used mostly for chemisorption since it has very little relationship to the physisorption isotherm past the inflection point at $X = 0.3678\dots$ (the “Fuller magic point.”) The BET also has problems fitting the isotherms. Never-the-less, in general many other theories have fits that are probabilistic and for any one experiment are not convincing. However, for physisorption this is not the case. Most modern isotherms are good at $\leq 1\%$ of the full data range* (FDR) between repeated experiments.

To disprove this “Henry’s law” concept and thus the Langmuir and BET, two examples will be presented and references to others given. The first example is a very important publication for reasons other than “Henry’s law” disproof. This disproof is not even mentioned in the paper.†

Example 1) Data by Silvestre-Alberto, Silvestre-Alberto, Llewellyn and Rodríguez-Reinoso:

The data of N₂ adsorbed on porous carbon by Silvestre-Albero, Silvestre-Albero, Llewellyn, and Rodríguez-Reinoso¹⁹ (SSLR) evidences a finite on-set (from hereout referred to as a “threshold”) pressure at $\sim 2 \times 10^{-7}$ bar (**ln** being -15.4445 or **log** being -6.707.). The adsorbent was microporous activated carbon (LMA233.) In **Figure 1** is a graph of data for the SSLR paper. (This starts with the monolayer restricted QM-log-law and measures the external monolayer equivalence with a χ -plot, one of the standard QM plots. This point will be explained later.)

They also observed a threshold pressure for the adsorption of N₂ adsorbed on ordered mesoporous silica SBA-15 at $\sim 2 \times 10^{-6}$ bar and on activated carbon DD52 at $\sim 6.5 \times 10^{-6}$ bar.

Although the purpose of this paper was to warn researchers how to handle “dead space” gas outgassing, as a side issue it clearly shows the threshold pressure in the high vacuum range.

The graph by the SSLR paper shows the isotherm as a log-law. This law is predicted from the QM/ESW hypothesis or adsorption that is physically restricted to one monolayer. (To be explained in parts II and IV.) Notice that the data points do not end at $(n_a, P/P_{\text{vap}}) = (0,0)$, but end at $(0, \sim 2 \times 10^{-7}$ bar), $(0, 2 \times 10^{-6}$ bar) and $(0, 6.5 \times 10^{-6}$ bar.)

Thus, these isotherms disprove the “Henry’s Law” prediction and invalidate not just the BET but all “theories” that extrapolate to [0,0].

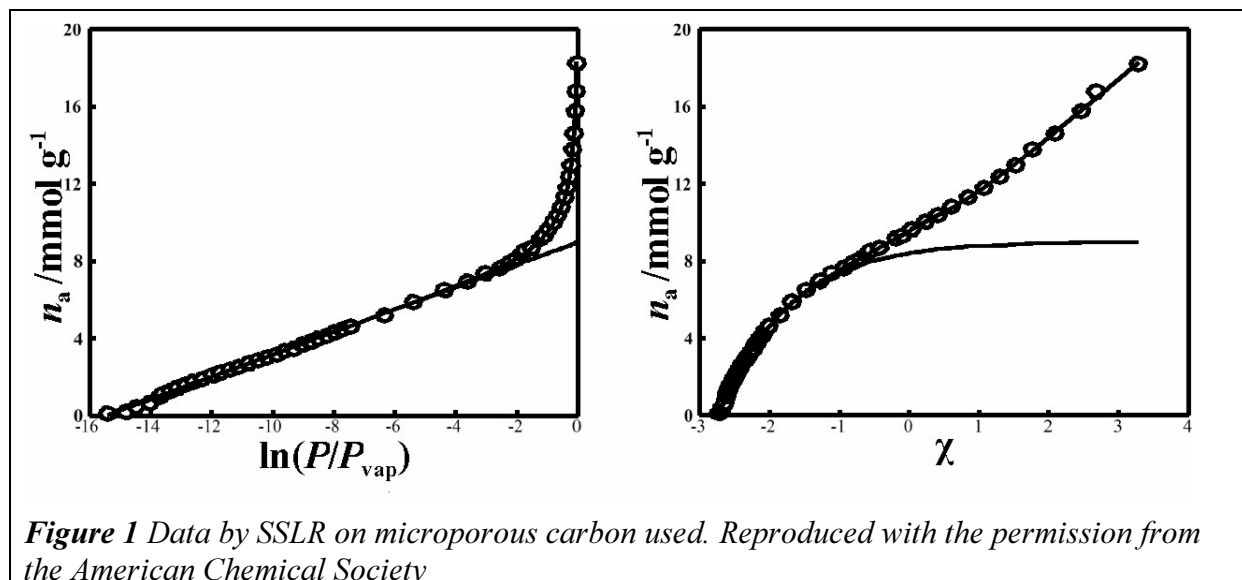
The original purpose of this publication was to illustrate the presence and effect of residual dead space gas, He, which is not shown here. However, the isotherm without the dead space gas problem‡ is shown and clearly indicates the threshold pressure. The fit shown here is the sum of the linear log-law plus the “multi-layer” χ -plot for the higher energy external adsorption, which are two of the possible QM fits described in this and following reports.

More detailed analysis of this data is presented later, especially how the fit shown as solid lines was determined.

* For the simple QM fits the acceptable FDR has been selected as $\leq 1\%$ FRD. An absolute value for the precision is not meaningful since the error is proportional to the amount that can be potentially adsorbed which is dependent on numerous physical quantities of the sample.

† If they had known and pointed it out the paper would probably not have been accepted for publication.

‡ The dead space problem is not shown here, but it increases the value of the threshold pressure. The paper concentrates on this artifact and is important reading.



Example 2) The Nguyen and Du Data.

The threshold pressure can be seen from the data by Nguyen and Do²⁰, of argon adsorbed on microporous carbon. This is shown in the left graph of **Figure 2** or directly in their figure number four. A full analysis of this data is presented in Table 1 to illustrate what information one can obtain.

In both frames, there is a gray line which passes through the lower pressure data points. This is the fit for a monolayer restricted portion. In the right frame ($\Delta\chi$ -plot) the black line extrapolate to the ordinate, yields the micropore volume. Both types of plots will be explained later. The important point is that that the isotherm line passed to a position to the abscissa that is not [0,0]. If it had, the energy of adsorption would be infinite, which is quite troubling. (By definition, the $\Delta\chi$ plot, the fit does pass through [0,0].) The small vertical line in the left frame is approximately where the external area departs from the monolayer masking.

This is a clear example of the Dubinin “Thermodynamic Criterion” is very problematic for conventional analysis. Notice that the straight line in the left frame implies $\Delta_1^a E = -RT \ln(X)$ so $\Delta_1^a S \approx 0$ (to within experimental error) which is Dubinin’s criterion.

These subtleties will be explained later, but for now the fact of the threshold pressure contradicts the predicted “Henry’s law” behavior a sound disproof.

What additional meaningful parameters can one extract from this isotherm? Table 1 is provided that illustrates the information that is obtainable for this sample. From the data one can obtain the total monolayer coverage for the pores and external area, n_m , the volume of the pores, n_{pore} , the parameter E_a , the energy of the first adsorbate molecule (from χ_c a threshold parameter,) and the external monolayer equivalence, $n_{m,\text{ext}}$. (For now, you need not worry about the meaning of the parameters. These meanings should become clear with further readings.)

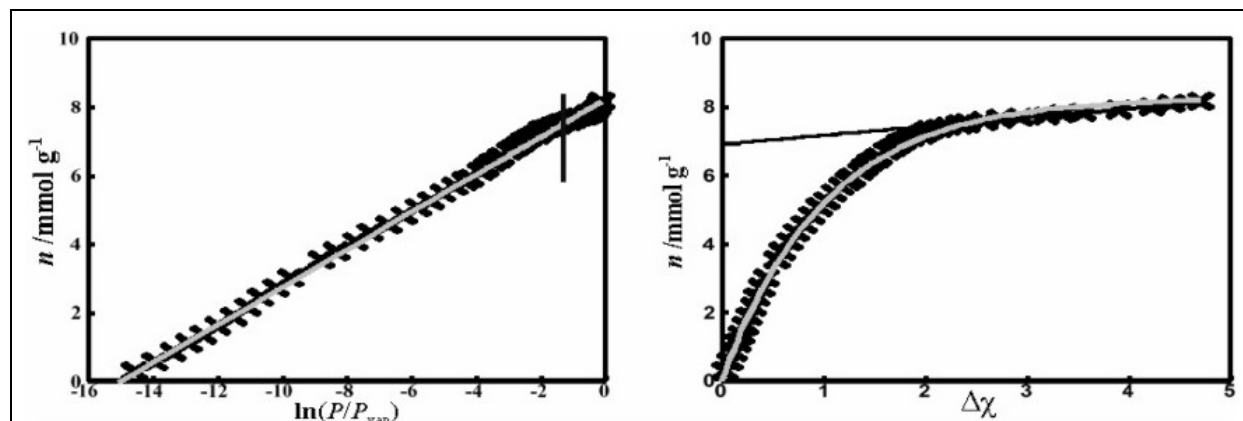


Figure 2 Data by Nguyen and Do of nitrogen adsorbed on microporous carbon. The grey line in the log-law fit (1st layer) the black line in the $\Delta\chi$ plot is the external area line. The vertical line in the log-law plot is approximately where the external line fits. Reproduced with the permission from Elsevier, publisher of “Carbon.”

Table 1 Data analysis of data by Nguyen and Do

Physical quantity	value	absolute precision*	units	relative precision ‡	Interpretation
$n_m =$	8.251	0.020	mmol g ⁻¹	0.24% FDR	monolayer equivalence
$\chi_s^\ddagger =$	-2.7118	0.0027			Threshold X transformed to χ_s
$n_{pore} =$	6.91	0.028	mmol g ⁻¹	0.34% FDR	Amount that fill the pores
$n_{m, ext} =$	0.263	0.007	mmol g ⁻¹	0.094%FDR	Amount outside pores
$E_a^\ddagger =$	-9.763	0.026	kJ mol ⁻¹		Starting adsorption energy
$P_\zeta/P_{vap}^\ddagger =$	2.89×10^{-7}	0.12×10^{-7}			Threshold relative pressure

‡ The precision in these quantities is not as important since they are the independent variable.
* As $\pm 1\sigma$

By the self-imposed of criteria of $\sigma < 1\%$ of full data range (FDR) used for QM fits in n_a , these values of 0.24% are relatively precise. This criterion is used on the dependent variable since the independent variable is controlled by the investigator and is assumed to be as precise as the instruments can read. All these values were obtained using the QM hypotheses and none could be obtained by the BET.

Although some additional information can be extracted from these plots, the important point is that they obviously intersect the abscissa making $P > 0$ (at $\sim 2.9 \times 10^{-7}$ bar) at some low but finite value, that is $P > 0$ at $n_a = 0^+$. This is the concept of “threshold pressure” and is given the symbol P_ζ . This concept is critical for the QM hypotheses and critical in disproving all the “Henry’s Law” isotherms, which is why it has been so controversial and an excuse to reject the QM hypotheses.

Discussion for part I

There is more to be said about this and additional disproofs after the derivations with a knowledge of the QM hypotheses. There are several more examples given in reference **Error! Bookmark not defined.** Comparisons between the most common isotherm representations are in Appendix 3. It is notable that the QM appears in at least the number of extractable parameters. This is obviously not a complete list since there is well over a hundred proposed isotherm models, most of which add parameters unjustified by reality.

Although some additional information can be extracted from the plots so far presented, the important point is that they obviously intersect the abscissae making $P > 0$ at some low but finite value, that is $P > 0$ at $n_a = 0^+$. This is the concept of “threshold pressure” and is given the symbol P_c . This concept is critical for the modern hypotheses and critical in disproving all the “Henry’s Law” isotherms, which is why it has been so controversial and an excuse to reject the quantum mechanical hypotheses.

Conclusion about the invalidity of the BET and similar formulations

The BET equation and equations that yield the “Henry’s law” as applied to physical adsorption are proved false not just inaccurate. One might ask, “How did we get into these problems?” This is addressed in Appendixes 4 and 5 along with mathematical problems in Appendix 6.) Other problems, especially with BET, will be noted in follow-on papers but the disproof is, for the moment, enough to justify looking at more modern theoretical treatments.

You will learn in subsequent papers that the QM/ESW formulation yields much more information and can be expanded from the simple base equations and make obvious modification for more complex isotherms. The basic plots that are used yield the energies, the monolayer equivalence before and after the mesopore interruption, the mesopore volume, the parameters of micropores, the heterogeneity and other information becomes available. But first there is the fit to the “simple” isotherm as a starting basis for almost all the calculations. This is the purpose for part II. Part III will “translate” the parameters of the BET equation into realistic parameters provided by the BET, and part IV will go into the Hellmann-Feynman Theorem to derive the QM based equations.

The application of this theoretical derivation is to be presented in part II. The equations needed are provided but the derivations are not. Only the results of the QM derivation is needed to make comparisons to the other proposed isotherms and to make conversions from the BET parameters to realistic physical variables. The latter will be covered in part III. By part IV there are probably enough questions to justify presenting the derivation. It has been presented in reference **Error! Bookmark not defined.** However, in part IV there is slightly less detail and has been made a little easier and more intuitive by using the Hellmann-Feynman theorem. This theorem looks at the relationship involving energy by extremely small increments.

Even though an understanding of the quantum nature of adsorption provides a better understanding and eliminates some of the concept problems* that a quantum model normally creates, it is not necessary to be familiar with QM to use the derived equations. Never-the-less, it would always be useful to receive criticism from experts in applied QM.

* for example, the adsorbate molecule have identical energies and probably entangled. The layers are talked about as having an \bar{a} areal density.

Appendix 1 definitions

Surroundings: The Thermodynamic surroundings of a system is everything outside the system boundaries. However, most of the surroundings are not relevant for the experiment but it is important that all interacting matter and exchanges are considered.

System: A thermodynamic system is a defined space with boundaries corresponding to the limits of the material being investigated. The boundaries of the system correspond to what the observations are. For example: The system for physisorption measurement by the gravimetric equipment is the adsorbent plus adsorbate, since both are being measured together. The system for a volumetric system is a little more complicated, but it is assumed that the adsorbate does not increase the sample volume very little, so the system is at constant volume.

Isotherm: Literally “at constant temperature.” In the case of the normal “physical adsorption isotherm” it is a plot of n_a as the dependent variable as the ordinant and X as the independent variable as the abscissa. The Fuller-Polanyi energy physical isotherm is n_a as the dependent variable and the energy ($\Delta_l^a E$ “system internal energy”) as the independent variable

Coverage: Classical – the molar amount of adsorbate molecules to cover the adsorbent surface.

Coverage: QM – the areal density of either the entire adsorbate or that of in a layer compared to the 100% dense in physical contact with the adsorbent surface.

A Monolayer equivalence = QM: the areal density of the molecules in contact with the adsorbent at infinite coverage.

Adsorbate = the molecules that are attached to the surface in equilibrium with the gas phase of the component the adsorptive.

Adsorptive = the same component as the adsorbate but in the gas phase

Adsorbent = the solid component and phase upon which the adsorbate resides.

Schicht = a word designating the steps away from the adsorbent an admolecule is starting with in-contact as schicht 1. E.g. one may say the areal density of the molecules in the 3rd Schicht is 75%. Definition explained in later parts.

Appendix 2 - Symbols:

The words and symbols will be used throughout the series, so copy and save them.

English:

A = area parameter

A = Dubinin pre-logarithm parameter – $A \ln(X)^k$

b = the intercept (ordinate) for a line

C = BET C Parameter called “BET Constant”

E_a = Preexponential parameter for the exponential internal energy function

E = System internal energy – normal units: J or kJ

$E()$ = System internal energy function.

k = Dubinin class of equation to $A \ln(X)^k$

m = the slope for a line

n_a = amount adsorbate – normal units: mmol g⁻¹ usually but check what is being used.

n_a = The amount of adsorbate as a function - units: mmol g⁻¹

$n_{a,i}$ = The amount of adsorbate as a function before mesopore onset - units: mmol g⁻¹

$n_{a,f}$ = The amount of adsorbate as a function after mesopore onset units: mmol g⁻¹

n_m = monolayer equivalence normal units same as n_a

$n_{m, ext}$ = external monolayer equivalence normal units same as n_a

n_{pore} = amount of adsorbate in the mesopores units same as n_a

n_0 = Dubinin Class: preexponential constant n_0

P = pressure of adsorptive – normal units: bar

P_{vap} = The vapor pressure of the adsorptive at the temperature of the adsorbent.

P_ζ = The threshold pressure (ζ = lower case termination sigma)

S = system entropy

T = system temperature

V = system volume

V_p = pore volume

$X = P/P_{vap}$

y = the ordinate value in the BET transformed graph

$R(n_a, X)$ = Rouquerol criterion function

Embellishments

$\bar{\quad}$ (overline or bar) = the symbol modification indicating “per mole.”* Ex: \bar{E} molar energy

Greek:

$\Delta_l^a \bar{E}_T()$ = The change of the system internal energy going from the adsorptive liquid phase to the adsorbate phase at constant T . normal units J mol⁻¹ or kJ mol⁻¹. Sometimes embellishments are left off.

$\Delta_l^a \mathbf{E}(-n_a)$ = change system internal energy function $\Delta_l^a \mathbf{E} = E_a \mathbf{exp}(-n_a)$

$\Delta\chi(P_\zeta/P_{vap}) = \chi(P/P_{vap}) - \chi_\zeta(P_\zeta/P_{vap})$ – since the arguments are always P/P_{vap} and P_ζ/P_{vap} they are allowed to be left off.

θ = the “coverage” for classical and “monolayer equivalence” for QM.

θ_n = the areal density of the adsorbate in the n^{th} schicht.

μ = system Gibbs’ Free Energy

$\chi(P/P_{vap})$ = the function $-\ln(-\ln(P/P_{vap}))$

$\chi_\zeta(P_\zeta/P_{vap})$ = the function $-\ln(-\ln(P_\zeta/P_{vap}))$

* The IUPAC alternative convention for molar (enplethic) is used since there is a conflict with sub “m” meaning here “monolayer equivalence.

σ = standard deviation of the dependent variable (σ_{fit} if there is a conflict.)

σ_p = standard deviation of the pore volume

Embellishments

$\bar{\quad}$ (overline) = a molar quantity.

ζ = the threshold quantity

Abbreviations:

BETSI = SI standard for using BET endorsed by IUPAC

DFT = Density Functional Theory

ESW = Excess Surface Work

FDR = of Full Data Range

HV = high vacuum

BET = Brunauer, Emmitt and Teller

IUPAC = International Union of Pure and Applied Chemistry

KJO = Krug, Jaroniec and Olivier

NASA = National Aeronautics and Space Administration.

ND

NLDFT = Non-Local DFT

QM = quantum mechanics

QSDFT = Quenched Solid DFT

SSLR =

UHV = ultrahigh vacuum

XXDFT = DFT with fill in XX with the type

QM symbol list

\hbar = the reduced Planck's constant

Ψ = (time dependent) wave function(s)

ψ = time independent wave function(s)

ψ^* = the complex complement of ψ .

\hat{H} = the Hamiltonian

E = the energy from the bottom of the well

$\langle |$ and $| \rangle$ = bra and ket

\mathbf{U} = the unit step function

A = the aliquot limiting area

a = the admolecules cross sectional area.

β = an energy defined with the GCPF

ε = the energy of vaporization of the adsorptive at the temperature of the adsorbent = $\Delta^a \mathbf{E}$

E_1 = the base energy of the well after the first molecule has been adsorbed

E_n = the base energy of the well after the n^{th} molecule has been adsorbed

N = the total number of admolecules

$$\theta = aN/A$$

$\mathbf{E}(N)$ = the energy as a function of total number of molecules.

$$\theta_{\text{MT}} = 1 - \theta_1$$

Appendix 3 Table of Comparisons Between Major Hypothesis for Physisorption

Characteristic	BET	XXDFT	Langmuir	Dubinin etc.	QM/ESW
Range of fit On nonporous*	0.01 to 0.35 [†]	Does not work	0.01 to 0.35	0.1 to 0.95	0 to 0.98
Yields a n_m value	Yes [†]	"	Yes	No	Yes
Typical % σ for stated range	1% - 5% in the transform [‡]	"	Very poor	Very poor	< 1% FDR [§]
Typical % σ FDR with T correction	Extremely high	"	Impossible	unknown	<1 % FDR
Porosity Modification	No	Uses K tables	No	Yes	Yes
External amount n_{ext}	No	No	No	No	Yes
Mesopore volume**	No	Yes**	No	Yes**	Yes
Mesop. distribution	No	Yes	No	No	Yes
Micropore amount	No	No	No	No	Yes
Layer measurements	"N" claimed calculation ^{††}	No?	No	No	Yes
Predicts Henry Law	Yes	Yes	Yes	No	No
Threshold pressure	No	No	No	No	Yes
Approximates n_m	3× high in BET range	No	0.3 × too low in HV	No	Yes – n_m measured
Calculates Δ^aH correctly	No	No	No	No	Yes

* If the calculation of physisorption does not work for the simple case of homogeneous, nonporous adsorbent, it should be considered invalid for any physisorbed case.

† BET predicts a n_m that is different in the high vacuum range than it is in the BET range by a factor of 9.

‡ The precision is usually reported for the transform, but the transform has P in the numerator which creates an artificially better fit.

§ FDR = of Full Data Range. >1 % FDR is also criterion for calculation rejection.

** Pore volume can be approximated using the Gurvitsch rule provided there is insignificant external surface area. Otherwise, one has an unknown high error using this rule.

†† The "N" layer calculation for BET has not proved successful in the literature.

Appendix 4 History: why was the problem of “Henry’s law” ignored?

So long as one used chemical reaction equilibrium and not consider the mathematics of phase changes and Gibbs’ phase rule modification, one will end up with “Henry’s Law” as an extrapolation. Why was this simple point missed considering the numerous arguments against the BET presented early on. A little bit of history is in order.

It was not for the lack of high vacuum systems. Several authors reported problems with the BET in the HV range. Large departures from the BET were noted by Hobson^{21,22} and others where the BET surface area underestimates the surface area by a factor of about 1/3. The argument of surface roughness, used to dismiss the overestimate by a factor of 3 could not possibly be use in these experiments

Regarding the threshold pressure, if observed, it could be dismissed as instrument error and a shift in the zero of the ordinate variables could account for this. Langmuir’s original paper demonstrates this approach along with poor fitting techniques. (For example, effectively two points yields a straight line.) Furthermore, it was rarely reported if seen, but also dismissing all measurements below $X = 0.01$ assures it is not seen. There are more examples of isotherms that violate “Henry’s law.” in reference 4. Some adsorbents, for example Teflon, has a threshold pressure well within the pressure range of low-vacuum, older instruments, and others show the phenomenon when the adsorbent is properly cleaned, for example diamond for which the threshold pressure became a marker for cleanliness and alumina.

Given the above statements, the theoretical proposals of the early 20th century and similar proposals to this day are all invalid. This leaves the question of how to determine the surface area. In the 1960’s attempts in the Oak Ridge laboratory did tomography with TEM and SEM to accomplish this. These trials conflicted with the BET analysis, since the answers were too low in the “BET range,” and they were therefore abandoned by DOE and the Oak Ridge Analytical Division. This should have been a wake-up call and only one researcher believed the result. That researcher was Dr. Loren Fuller, who continued to pursue the line that Polanyi had started.

When an argument seemed reasonable for invalidity of the BET, the question comes up, “How does one relate the empirical model to the surface area?” Various uses of chemical kinetics and thermodynamic equilibrium were used with a variety of parameters and unjustified claims that some parameter or parameters were the surface area. Some methods presented anomaly, and others did not work for a variety of cases. For example, there were cases where chemically identical powders of differing for sizes would have essentially no correlation (inverse) between size and BET surface area*.

So, until about 1985, it seems that there is no method of analyzing the physical adsorption isotherm. There was also absolutely no way to arrive at the thermodynamics connecting the pressure isotherm to the isothermal calorimetry. This latter point was also a great indication that something was wrong[†].

* When I observed this and realize that I was not the only one puzzled by this is when I search out an expert in physical adsorption. I contacted Dr. Fuller since he also worked in Oak Ridge, and what he found out, is that the BET did not really yield a realistic answer. This probably ended his friendly relationship with Emmett.

† Most investigator that tried simply attributed the nonfits to an entropy terms and basically let it stand there.

So, if the BET and all other explanations for the isotherm are invalid, how should one attach physical quantities to an isotherm. The shape of the isotherm would indicate that there should be at least two parameters in the answer, possibly more, but the fewer that work the better.

“How can you say, ‘at least two parameters,’ when the isotherm has first a negative curvature and then an inflection point thus requiring at least three parameters.?” This is not true, and giving credit, where credit is due, Brunauer, Emmitt and Teller found a way for one constant to do double duty and the derivation for such a curve shape could be justified by chemical equilibrium (actually, they used kinetic expressions) yielding an energy term and the monolayer equivalence. From the monolayer equivalence a conversion to surface area from the liquid density and assumptions about loose close packing in a liquid were made. These assumptions lead to the present-day IUPAC conversion convention.

There was, however, another two-parameter model. This model was by Polanyi²³ and London^{24,25,26,27,28*}, which Adamson^{29†} characterized as the best empirical representation of the isotherm but lacked a reasonable explanation. Deboer and Zwiiker^{30,31,32} and Bradley³³ (See Appendix 7) proposed a similar mechanism with a similar result. Polanyi’s explanation[‡] was that the forces holding the adsorbate to the surface were strong physical forces not chemical bonds. As the adsorbate molecules build up, the influence of the surface-adsorbate forces decreased, and the adsorbate-adsorbate forces began to be more present. Brunauer¹² criticized it on the grounds that the polarization forces could not be passed through the first layer or in a chain through second, third, etc., and were entirely too weak. In other words, Brunauer assumed that each layer had to be completed before the next layer could be deposited. It is interesting that Brunauer did not apply this reasoning to his own theory nor allowed interaction with the adsorbent surface regardless of its source. If he had assumed the fluidity of the adsorbate reactions[§] he might have arrived at the classical analogy that Fuller^{34,35,36,37,38,39,40,41} used to explain the quantum picture in classical terms.

So, the explanation waited to be discovered in the mid-1980s with the combination of Fuller’s insight and the use of QM by someone who was familiar with QM^{**}.

* By breaking away from chemical reaction thermodynamic Polanyi and London were the first to suggest that physical forces were the key.

† Adamson referred to the Polarization Theory as “fundamentally correct. It accounts for the empirical fact that systems at the same value of $RT \ln(P/P^0)$ [“o” means “_{vap}”] are in essentially corresponding states.” He also stated, “There is thus little to choose between the various models, but partly because of tradition and familiarity and partly because v_m [here “_m” for monolayer] enters in it so explicitly, the BET equation is in fact almost exclusively used.” This latter reason no longer applies due to QM.

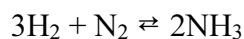
‡ He used the term “polarization,” but other physical force should also work.

§ It’s hard to figure out what Brunauer thought the model was regarding fluidity. When Fuller asked where the phase transition was to the liquid state, he responded that it had to be near the P_{vap} . On the other hand, his model allowed pillars of adsorbate even one molecule around in epitaxy formation in a non-collapsible arrangement, thus simulating the solid phase.

** Note I am saying “familiar with” not “an expert in.”

Appendix 5 inconsistencies with chemical equilibrium:

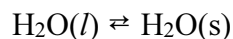
In chemical equilibrium, that is the use of equilibrium constants, there are two cases where the use of equilibrium constants. The first is if new components are being created. (See Denbigh⁴² for thermochemical definitions) For example, in the reaction:



An equilibrium is established, and an equilibrium constant, K , is used to indicate the concentrations:

$$K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

There are three components present in this reaction. If either H_2 or N_2 are totally missing, then NH_3 is absent. This is referred to as a chemical reaction, wherein the electronic structure of the molecules is changed as the reaction proceeds. But, what about a one component equilibrium? Here is a simple example:



Where l and s stand for liquid and solid. The liquid can exist without the present of ice. These are called phases, and they are both together one component. If one warms up $\text{H}_2\text{O}(s)$ above the freezing point the component remains as $\text{H}_2\text{O}(l)$. There is no change in the electronic topology in the reaction. This is called a phase change.

So, in general a chemical reaction equilibrium the reaction stops only when one of the components is missing, and stays missing, whereas a phase equilibrium can disappear with changes in temperature. A phase equilibrium can have a threshold value, a chemical reaction equilibrium it stops when some component becomes, and stays, zero.

Brunauer's derivation assumes that equilibrium is a chemical reaction equilibrium but there must be a phase transition to obtain water liquid on the adsorbent with high enough pressure. This would mean that the phase transition would have to be at $P = P_{\text{vap}}$, which eliminates the threshold at low pressures as predicted by Brunauer. The problem is that one does not observe a phase change near P_{vap} except in pores and one does observe a phase change at low pressure. Furthermore, if it were a chemical reaction, there would have to be reaction sites, as there are for chemisorption, and the first "layer" would be dependent upon the adsorbent and not the adsorbate, as assumed by BET and other isotherms, Implicitly, these "Henry's Law" isotherms assumed the adsorbate determines the measurement for surface area (by IUPAC convention) which is a contradiction.

Appendix 6 How come does the BET transform yield a straight line below approximately the inflection point:

The BET transform is for the ordinate, and in the BET “range” appears nearly linear. The transform is:

$$y = \frac{X}{n_a(1-X)} \quad 0.05 \leq X \leq \mathbf{\max}(n_a(1-X)) \approx 0.39 \quad \text{Equation 4}$$

As n_a increases $(1-X)$ decreases, but never, given the definition of the BET range, approaches 0. Thus, the trend is mostly governed by the numerator, X , whereas the denominator remains nearly constant.

The transform itself is not a proper mathematical operation. It mixes the dependent variable with the independent variable, a very questionable practice. Furthermore, the standard deviation of the transformed plot is meaningless, although it is routinely used to report the goodness of fit which is also meaningless and deceptive.

Appendix 7 Bradley's data

Bardley³³ reported the adsorption of argon on Aluminum Sulfate and Anhydrous Copper Sulfate. The data fit what is call herein as the χ -plot very well Figure X below shows a composite of the

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All the data and materials are available in the open literature and are referenced herein.

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