

Title:

**Part III: Quantum Mechanics and Physisorption:
Interpreting the BET with Quantum Mechanics**

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Abstract:

The Brunauer-Emmitt-Teller¹ (BET) theory has long been known to be deficient and difficult theoretically to deal with. In part I of this paper, one each of theoretical and practical problems are reviewed. The details of these selected problems is presented in Parts I and II. These *should* suffice to eliminate the BET and its derivatives as the standard characterization theory. However, other data in the literature will be cited as supporting evidence.

Given these problems, the question then becomes, “What should one do with BET results for which there is insufficient data to recalculate?” In part IV it is proposed that quantum mechanics (QM) perturbation theory, be used to reassign the two BET parameters A , “surface area,” and C , the BET constant, by converted to the values of n_m , the monolayer equivalence, and E_a , the preexponential for the internal energy, $\mathbf{E}(n_{\text{ads}}) = E_a \exp(-n_{\text{ads}})$, in the QM representation. There is no 1:1 mathematical expression between the BET and QM parameters, but the paired parameters over a wide range are monotonic to each other, therefore tables may be written to convert. The reason to do this is to provide the correct monolayer equivalence not only for application but correctly analyze the isotherm for other features, such as porosity, that depend upon the value of A .

The correspondence is dependent upon the calculation method and the range selected for the BET calculation; therefore, three tables are created to do the conversion. The first two methods use the tradition BET transform and a linear regression to fit a straight line. The third uses a non-linear, least-squares routine. These tables assume:

- Table 1: The selected BET range is from 0.01 to 0.35 for P/P_{vap} and the traditional BET transform is used with a linear regression.
- Table 2: The selected BET range is from 0.01 to $\max [n_{\text{ads}}(1-P/P_{\text{vap}}.)]$, the “Rouquerol criterion.” This is analyzed also with a linear regression using the BET transform.
- Table 3: The selected range is the same as the 2nd choice, but a non-linear least squares routine is used to fit the data to the BET equation directly without a transform.

In case other conventions were used, the equations to make the conversion are presented. There is a preliminary discussion about the equations used in the analysis and the reasons that the BET should not be a preferred method to report data due to loss of detail.

If other data ranges are used, especially the limit $X > 0.01$, the calculation needs to be custom calculated. This is a potential problem since there doesn't seem to be any convention about the about the low pressure limit.

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Introduction:

The Brunauer-Emmitt-Teller¹ (BET) theory has long been known to be deficient and difficult theoretically to deal with. In parts I and II some problems inherent to the BET are presented. There are many problems that have been listed for the BET by many authors, but the problems presented in this series have not been thoroughly presented. The most important being a solid disproof of the “Henry’s law” requirement and the very poor fit to the data, even when 2/3 of the data is ignored. This latter point was known for many years and documented by Prof. Arthur Adamson².

Given the above, the question is “Why was the BET ‘theory’ the one that gained favor?” The answer is, as Adamson recalls is, “...partly from tradition and familiarity, and partly because v_m enters in it so explicitly, the BET is in fact almost exclusively used.” There is some extreme questions about the word “explicitly” since the model mimics the Langmuir model and the concept of “sites” and “solid Ar” is invoked^{3*}, either explicitly or implied. However, the psychological need to obtain a value for the surface area, a classical mechanical concept, excludes the quantum mechanical uncertainty for the location of the adsorbate molecule.

In this paper, Part III, only two theoretical problems and a few practical problems will be reviewed. This should suffice to be a convincing argument that the BET and its derivatives need to be replaced as the standard method of surface measurement. Why this is important is that the area parameter, A , is used in other surface and porosity calculations and an error factor from 1/3 to 3 in A is usually present, depending on the data range selected. If this is correct, then there is a lot of publications for which the answers for surface area are invalid. Unfortunately, it is normal that the experimental data is no longer retrievable. The question is, “Can something be done to retrieve the essence of these publications or are they lost forever?”

To answer this, one first needs to answer a very fundamental question of “What is physical adsorption or physisorption?” This may seem to be a trivial question, but it is not. This question has been treated, in part, too cavalierly and presumptuously. The definition should follow standard thermodynamic treatments such as the Gibbs’ phase rule. What are the phases and components? How does one know this? In summary, the answer is that the physical adsorbed material is part of the liquid phase in the expanded Gibbs’ rule⁴ that considers the adsorbate amount, n_a , and surface energy, E , as well as P , T , S , V and μ . With proper definitions of components and phases it becomes obvious that the start of the liquid-gas phase boundary is at low pressures and not at high pressures, which Brunauer was forced to postulate⁵.

* “We shall assume, to start with, that the separation of the argon atoms in the adsorbed state is about the same as in the solid state.

Given the thermodynamic background, the next point is, “Can the BET stand up to the test required of a theory?” The test is: “Does the theory predict some things that according to it *must* be true *always*?” If a prediction proves false, even once, unless there has been some error in the test, the theory is *unqualified proven false as is*. In principle, only one negative result is needed, but given the fallibility of human endeavor, to make the disproof believable it is best to obtain multiple instances from different sources. However, to be clear about this, if all predictions prove true, this does *not prove* a theory. but it does provide confidence in it.

Another way of discrediting a theory is its poor performance in statistical trials or pointing out the weakness of the application, which is a problem that became obvious with the BET early on. This is especially true if there are alternative theoretical developments that are available for which the statistics are much better. The statistical test available should not be stretched to their limits in this method and it is easy to introduce bias. In other words, if a test, such as the *F*-test, barely yields a decisional answer, it should not be taken too seriously. The test should be clearly overwhelming, not just a close statistical test, without using arguments that are illogical. For example, using a raking test as proof*. Other than standard deviation of the data fit, it is even more important to minimize fitting parameters, and these parameters should have physical meaning that fit in with known physical behavior. BET was the only reasonable choice by these criteria that fit in the known knowledge of the 1930s, at least for chemists. It claimed to yield the surface area and an equilibrium constant, familiar quantities in chemistry. However, in the early years, negative *C* values were reported, which does not have a good explanation.† The appearance of $C < 0$ in many analyses should have been a strong hint the something was wrong.

Both types of the mentioned disproof methods are presented for the BET. The question then is back to the first question, “What to do with old BET results?” The answer is to model the adsorption using Quantum Mechanics and compare the surface adsorption values with the BET values. Since the QM treatment has two output parameters, the monolayer equivalent, n_m , and the initial heat of adsorption, E_a , and the BET also has two, BET n_m or A and the BET “ C ” constant, one should be able to make a correlation provide the equations are monotonic to each other. This latter is fortunately correct over a wide range of values, so it is likely that one can make the conversion in almost all cases.

After some preliminary information this publication consists of four sections:

Section 1 review the BET indicating the important features to examine

Section 2 An alternate hypothesis - Quantum Mechanics applied to Physisorption

Section 3 Weak spot: BET “Henry’s Law” and an alternative hypothesis.

Section 4 Reconciling the BET parameters with the Quantum Mechanics parameters

This publication, Part III, is limited in scope to addressing only the simplest cases of adsorption. It only mentions microporosity to present examples of threshold pressure and does not address mesoporosity at all. The simple case of homogeneous adsorption without the added features of heterogeneity, microporosity or mesoporosity would be preferred, but such clear examples are difficult to find.

* Investigators should not leave reasoning and logic of physics behind a let statistics dictate decisions. For example, correlation is not the same as cause.

† A third disqualifier is if the theory predicts an anomaly. In the normal transform method of the BET analysis, the BET does yield an anomaly. Getting around this creates other mathematical problems. This is not presented here to avoid a long, complicated and perhaps endless mathematical argument.

None of the equations will be derived here. The BET equation is well known and needs no explanation. This is not the case for quantum mechanics and follow-on statistical thermodynamics. The reader will either accept the derived equations as is or look up the derivations in the references given. These advanced subjects have been covered over the last half century in the literature, but an almost complete explanation (up to year 2000) is covered in the textbook written for this purpose.⁶ There are multiple publications dealing with the QM implications^{7,8,9,10,11,12,13,14,15,16,17,18,19,20} as well as a related companion subject Excess Surface Work (ESW^{21,22,23,24,25}.) ESW and QM were developed at about the same time independently by groups that had no information exchange. The two hypotheses end up with the same equation and conclusion, thus they will be often designated by QM/ESW. Another place to obtain information is the lesson plan created for University of Tennessee's surface science group*.

Of necessity, the effect of heterogeneity needs some explaining, since it is nearly impossible to find totally homogeneous samples for illustration.

Section 1 Review - the BET theory.

The BET theory has the following form in *Equation 1*:

$$\frac{n_a}{n_m} = \frac{CX}{(1-X)(1-X+CX)} \quad \text{where} \quad X := \frac{P}{P_{\text{vap}}}$$

Equation 1 the BET equation

The symbolism is as follows:

- n_a = moles of adsorbate
- n_m = the maximum moles of adsorbate that can be in direct contact with the adsorbent surface
- P = the adsorptive pressure
- P_{vap} = the vapor pressure of the adsorptive at the temperature of the adsorbent.
- C = The "BET C" constant

The symbol θ is often used for the ratio n_{ads}/n_m and is called the "coverage."

The BET equation is usually rewritten to yield a linear equation for plotting with the abscissa being the relative pressure, $X = P/P_{\text{vap}}$, and the ordinate, y , a mixture of the dependent and independent variables as given in *Equation 2*:

$$y = \frac{X}{n_a(1-X)}$$

Equation 2 The transform of the ordinate for the BET-plot

* Unfortunately, Professor Larese die before we could put the course on. It is available up to the point of Prof. Larese' passing, which is as far as I went on the internet. Available at https://www.genchem.net/Lessons_in_Chi_hypothesis.pdf or follow link "Chi" from <https://www.genchem.net/> . It is also available on ResearchGate.com.

This graphing method is a widely used way to finally arrive at the output parameters n_a and C . It is assumed that this transformation yields a straight line, and a linear regression can be used to then use to obtain the slope, m and ordinate intercept, b . From *Equation 3* the BET parameters, n_m and C are obtained. These parameters are then used to plot the theoretical fit by *Equation 1*.

The mixing of the dependent and independent variables creates mathematical problems for the analyses (and leads to anomalies.) An example is the determination of the “goodness of fit.” This is the reporting of the standard deviation of “fit,” and most often it the standard deviation of the linear regression of X versus y from *Equation 2* is used. This is incorrect, since the statistics should be extracted from the resultant fit from *Equation 1*. The differences between the original data point and the final fit should be used to obtain the standard deviation not from the linear regression.

$$y = mX + b \Rightarrow C = \frac{m+b}{b}, n_m = \frac{1}{m+b}$$

Equation 3 the method to determine the BET parameters

Some recent publications get around the uncertainties of this method by using non-linear least squares methods (NLLS.) This is especially useful for using summations of BETs or Langmuir isotherms^{26,27}. The transformed linear equations cannot be added since it leads to one of the types of anomalies.

Both methods, the transform method and the NLLS method, are addressed in this publication.

The BET does not perform well at higher pressures. The large breakdown happens near the inflection point of $X = 0.3678\dots$. A new criterion was recently created, the “Rouquerol criterion²⁸.” This states that only points less than the first maximum of the function, Q , calculated data-pointwise by *Equation 4* are used*.

$$Q = \max(n_a \{1 - X\})$$

Equation 4 The “Rouquerol criterion” for the upper limit of the BET calculation

The max is not likely to be past the inflection point.

* This criteria is an admission that the value of $n_a(1-X)$ tracks nearly linear over a range until it approaches the “magic point,” i.e. $X = 0.3678\dots$. Since it is approximately linear with X then $X = mX$ where m is a constant, so you are plotting a variable against itself. - Courtesy of Dr. John Kirkpatrick who also found an anomaly.

Section 2: An alternate hypothesis - Quantum Mechanics applied to Physisorption:

A) The QM Equations:

Just presenting the data and the BET fit is not sufficient to make a judgement about the fit. It needs to be compared to something. The “Gold Standard” for simulation in chemistry is quantum mechanics and a technique often used is perturbation theory. This technique is a very old method, used in mathematics that precedes quantum mechanics. This technique is combined with statistical thermodynamics, specifically the Grand Canonical Partition Function, to yield the equations presented here. Equation 5 is the QM equation for continuous “multilayers.”

$$\theta = \Delta\chi \mathbf{U}(\Delta\chi) \quad \Delta\chi = \chi - \chi_\zeta$$

$$\text{where } \chi = -\ln\left\{-\ln\left(P/P_{\text{vap}}\right)\right\} \quad \text{and} \quad \chi_\zeta = -\ln\left\{-\ln\left(P_\zeta/P_{\text{vap}}\right)\right\}$$

Equation 5 The multilayer equation for physical adsorption from Quantum Mechanical Perturbation Theory and the Grand Canonical Partition Function

Notice that the lowest pressure for which there can be data for the isotherm is slightly above χ_ζ . The unit step function, \mathbf{U} , is used to indicate that $\Delta\chi$ cannot be negative. P_ζ is referred to as the threshold pressure, indicating the phase transition for the onset of the surface liquid phase. $\Delta_l^a \bar{\mathbf{E}}$ is the molar* change in the internal energy function going from the liquid state (l) to the adsorbed state (a). Thus, $E_a < 0$ (exothermic.)† seen in Equation 6.

$$\chi = -\ln\left\{\frac{-\Delta_l^a \bar{\mathbf{E}}(-\theta)}{RT}\right\} \quad \text{or} \quad \Delta_l^a \mathbf{E}(-\chi) = E_a \mathbf{exp}(-\Delta\chi)$$

Equation 6 The thermodynamic energy function for adsorption for homogeneous, non-porous adsorbent. The standard state is the adsorptive liquid at the temperature of the adsorbent

Where T is the temperature of the adsorbent. The value $\Delta_l^a \mathbf{E}$ is the system internal energy function of the transition from the liquid to the adsorbed state. On the other hand $\Delta_g^a \mathbf{E} = \Delta_l^a \mathbf{E} + \Delta_g^l \mathbf{E}$, where $\Delta_g^l \mathbf{E}$ is the calorimetric system internal energy function referenced to 1 bar pressure. (Sometimes a superscript plimsoll symbol, \ominus , is used for this.)

These equations can be derived by another modern theoretical development, the Excess Surface Work theory (ESW) by Adolphs^{23,24,25,29,30}, et al. This approach uses the concept of disjoining pressure combined with classical thermodynamics to arrive at the same conclusion. The Polanyi-Fuller exponential decay of $\Delta_l^a \mathbf{E}$, the Dubinin “thermodynamic criterion,” and the assumption that the ESW maximum is at one monolayer equivalent justifies the match with the QM/ESW

* In this publication the used of the IUPAC alternative designation for “molar” is the overbar. This avoids the confusion between “molar” and “monolayer equivalence,” which is “ m ”. Both words “molar” and “molal” are defined in the IUPAC Gold Book in contradiction to the Green Book.

† The calorimetric heat of adsorption requires addition of the heat of vaporization due to shift from the reference state of the liquid adsorptive to the gas phase at 1 bar.

Equation 5. The two developments were formulated independently in the 1980s without communication between the two research groups, thus lending mutual support.

The next topic needs a new definition. This definition replace the normal word “layer” used classically. The implication of 1st “layer” is adsorbate molecules, or admolecules, deposit in a dense layer before a 2nd “layer” starts to form. The 2nd “layer” deposits a dense “layer” before a 3rd “layer” starts to form. Indeed, this seems to be the case for hard freezing but not for physisorption.

Thus, the word “schicht^{*}” (See appendix II) will be used to indicate that the position of the molecule is the important parameter. A molecule is in the 1st schicht if it is touching the adsorbent surface. A molecule is in the 2nd schicht if it is touching a molecule in the 1st schicht but not the surface. A molecule is in the 3rd schicht if it is touching a molecule in the 2nd schicht but not in the 1st schicht or the adsorbent surface, etc. This is like asking which floor one’s office is except the levels are determined by how the offices are touching.

Brunauer’s definition allowed did not have a definite specification of where the admolecules would be but were dependent upon the equilibrium specified by the constant “C,” which in practice could assume any value. The QM set the normal position according to the schicht equations.

In the application of the Grand Canonical Partition Function, the concept of “schicht areal relative density,” θ_n , where “n” is the ordinal value for the schicht where the adsorbate resides. These equations are shown in *Equation 7*.

$$\begin{aligned}\theta_1 &= 1 - \exp(-\Delta\chi) \\ \theta_2 &= 1 - \exp(-\Delta\chi + \theta_1) \\ &\vdots \\ \theta_{n+1} &= 1 - \exp\left(-\Delta\chi + \sum_{m=1}^n \theta_m\right) \\ \Rightarrow \theta &= \sum_{m=1}^{\infty} \theta_m \equiv \Delta\chi \geq 0\end{aligned}$$

Equation 7 The equations for the QM areal density in the schichten (pl). The subscript is the schicht ordinal value.”

The last equation after “ \Rightarrow ” yielding the total areal density is derivable from these equations.

The equation for θ_1 can be rearranged to yield the “log-law,” *Equation 8*, which is commonly observed for some isotherms. This indicates a steric restriction to single monolayer coverage.

* This is a word most Geologists are familiar with. The plural for “schicht” is “schichten” not “schichts.”

$$\theta_1 = 1 + \frac{RT}{\bar{E}_a} \ln \left(\frac{P}{P_{\text{vap}}} \right)$$

Equation 8 The "log-law." from the QM "schicht" equations.

With this background, tests of the BET against the quantum mechanical calculations is appropriate for comparison.

Conclusions from Part II concerning statistical comparisons

In part II of this series, the proof of invalidity of the BET and a demonstration of the statistical comparison was given. The conclusions were as follows:

In comparing the standard deviations, clearly the QM/ESW calculation is far superior to the BET (even discounting the high-pressure and low-pressure data for the BET) by a factor of >30. By any statistical test, this is off the charts. Also, a full isotherm is basically impossible for the BET and 2/3 of the isotherm is not used. Another statistical failure. This is consistent with a recent publication by Gómez-Gualdrón, Moghadam, Hupp, Farha, and Snurr³¹ between porous metal-organic frameworks which can be modeled from known structure to make a comparison. Their conclusion indicates that even with more restrictions, the BET is not reliable.

Thus, in a practical application, there is no question that the BET yields poor information. Of course, its n_a answer is within a factor of ± 3 of the answer, but the old "B" point³² method was as good. This magnitude throws the rest of the parameters off, for example pore. As a fact, one could use the inflection point and get an approximate answer which is usually high but within an order of magnitude. (The quickest way is to get an approximate answer is to do a $\Delta\chi$ -plot and take the value at $\Delta\chi = 1$. For accurate answers, measurements to $n_a = 0$ is needed to check for microporosity. This might require a UHV system.)

There is another advantage using the χ -plot. It has already been mentioned that $\Delta\chi$ -plots have the advantage are spread out according to θ , which is the experimental increments normally used. The χ -plots scales directly with $\ln(-E^p/RT)$ which is handy in calculating the onset of mesoporosity and the ESW notation scales the hysteresis forces

Section 3 - The Threshold Pressure: QM hypothesis and BET disproof.

In Part II two examples of the threshold pressure was presented. This phenomenon is proof of the invalidity of the BET and a couple more examples are presented here.

Example 4) Thompson's hydrogen cleaned diamond data.

Data by Thompson³³ on hydrogen cleaned diamond is presented. The original purpose of this research was to characterize synthetic diamond powders. The most prevalent surface contamination on diamond surfaces is graphite. To eliminate the graphite without destroying the diamond, one heats it in a low pressure of hydrogen gas. This research was done to optimize the conditions to create a clean surface. Using natural diamond powders as a standard, he observed

the startling result, that is, the observation of the threshold pressure. The results of argon adsorption are in *Figure 1*. Here the measurements were specifically started in the UHV region.

Notice, the threshold pressure is in the low-pressure range at about 6.2×10^{-4} bar or 0.47 torr. This could be observed by almost any commercial instrument. However, the cleaning process is critical, and the preparation temperature is above the softening point for most glasses.

Other authors have selected another adsorption isotherm from the original publication to indicate the threshold was not present. This latter selection was disingenuous, since it was the exception rather than the rule and probably had some residual surface graphite. Indeed, the presence of a sharp threshold pressure became an analytical sign that the diamond surface was graphite clean. (The cleaning process is dependent upon the temperature and pressure used. At too high a temperature, the surface of the diamond is graphitized and too low a temperature the graphite is not converted to methane fast enough. Thus, it is a balancing act to obtain the right conditions.)

Indeed, the QM/ESW predicts a round-off if the sample surface is heterogeneous, that is, it has a distribution of surface energies. This is present in other isotherm in his publication but slightly if at all in *Figure 1*. Furthermore, a round-off is not disproof of the QM/ESW as some critics have indicated, but rather is a sensitive indication of heterogeneity. Some other QM/ESW prediction needs to be found to establish a disproof.

The data extracted from the data in *Figure 1* are provided in **Table 1**

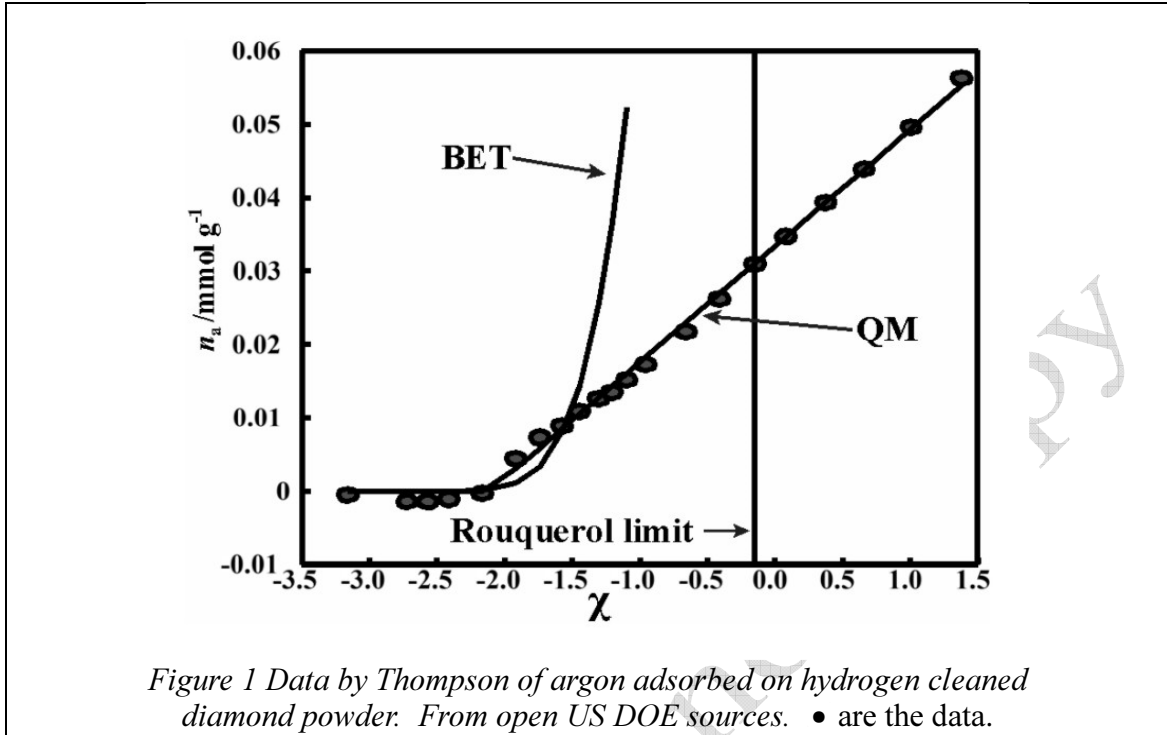


Figure 1 Data by Thompson of argon adsorbed on hydrogen cleaned diamond powder. From open US DOE sources. • are the data.

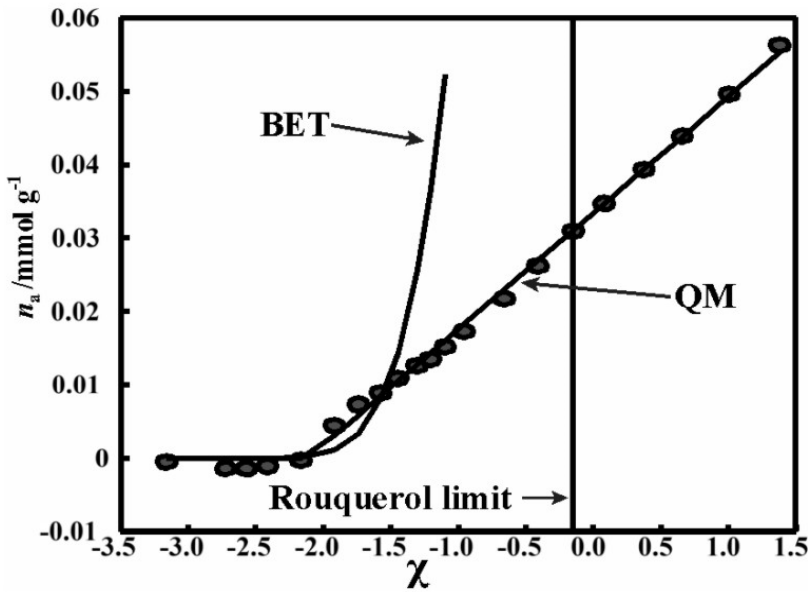


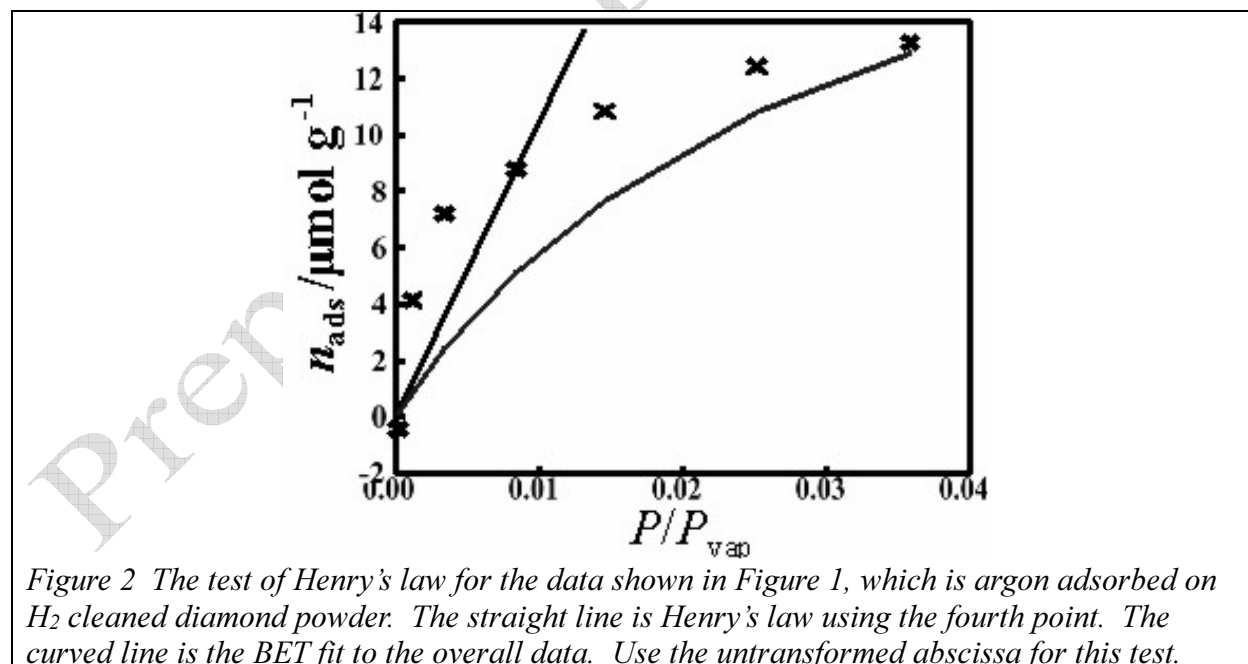
Table 1 The physical quantities extracted from the data shown in <i>Figure 1</i>					
Quantity	QM value	/units	Quantity	BET value	/units
$n_a =$	0.0158	mmol g ⁻¹	$n_a =$	0.0221	mmol g ⁻¹
$\sigma (n_a) =$	2×10^{-3}	mmol g ⁻¹	$\sigma (n_a) =$	0.278	mmol g ⁻¹
$\sigma (n_a)$ FDR =	0.43%		$\sigma (n_a)$ FRD =	658%	
$\chi_s =$	-2.1076		$C_{\text{BET}} =$	40.6	
$E_a =$	-6.03	kJ mol ⁻¹	$\Delta_l^a E = -RT \ln(C) =$	-2.71	kJ mol ⁻¹

A second Henry's Law test

Figure 1 suggest there is also a second test, other than the threshold pressure, to disprove "Henry's law." This test overcomes the low-pressure positive curvature argument for "Henry's" Law. This is illustrated in *Figure 2*. The sequence of this disproof is:

1. Select any low-pressure point, below $X = 0.01$ if the data is available
2. For whatever abscissa transform of X only is used, create a straight line as a function of X using a single point, $(X, n_a) =$ arbitrary, and $(X, n_a) = (0,0)$.
3. The line will go through only two points (unless you happen to pick the tangential point, in which case it is one point) one of which is the selected point.

Below is a graph, *Figure 2*, of this technique.



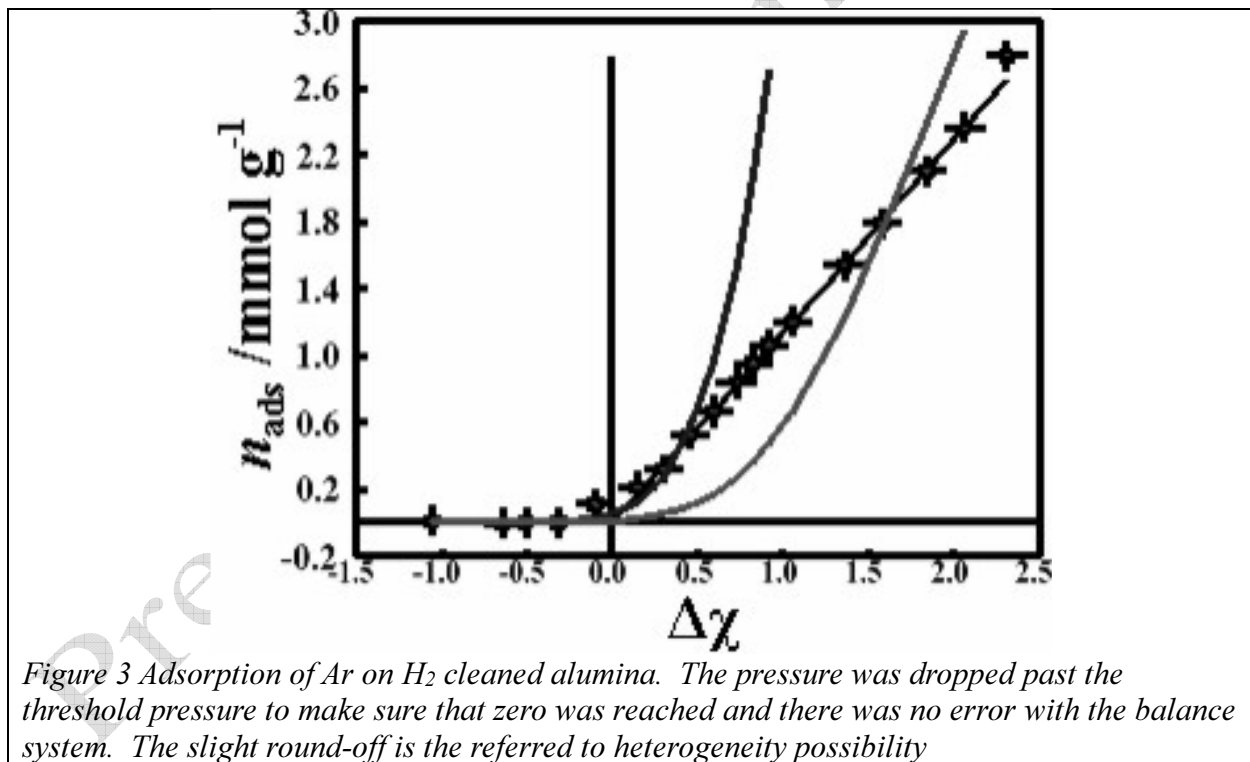
Notice that Henry's law line does not line up with any points other than those mentioned above. The low-pressure line crossing is hidden in the scale of this graph at 0.00032 bar or 0.25 torr. For comparison, the fitted BET to the data is shown using the "Rouquerol criterion." This

criterion uses, in this case, the pressures between $X = 0.00113$ and $X = 0.312$. It does not matter if a low-pressure limit for the BET is used, the “Henry’s Law” stays the same in this test.

Example 5) Data by Thompson of argon on hydrogen cleaned alumina^{34}:*

When Thompson discovered that cleaning diamond powders revealed a threshold pressure, he decided to try the same thing on other materials. The thought was that “dirty” adsorbents have contamination on the surface that yield an energy distribution, in accord with the QM equation for heterogeneity.

The data by Thompson for argon adsorbed on H₂ cleaned 8571 alumina is shown in *Figure 3*. The comparison to the “Henry’s Law” test is given in the two curved lines. One could argue that the two points that are off the projected χ -plot indicates there is no threshold. This argument only holds by ignoring that the QM/ESW predicts that the heterogeneity of a surface such as Al₂O₃ should be present and should show up as a positive curvature. Furthermore, there is no counter argument that can explain how the “Henry’s law” extrapolations are so miserable for the data.

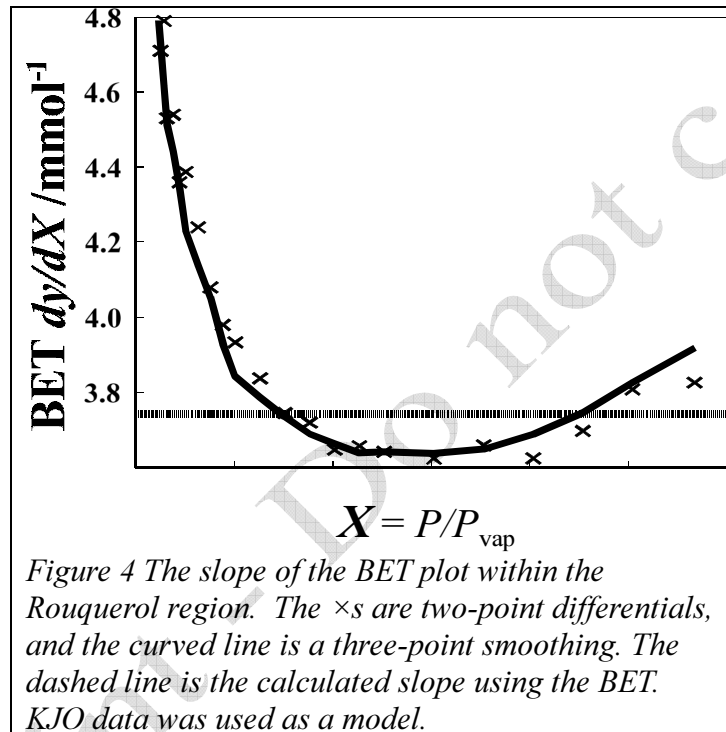


A Third “Henry’s law” test:

There is one additional comment about the BET and the method of analysis. When one plots *Equation 2* against X to plot that one obtains in the Rouquerol region looks very straight and one

* (I was not involved in the experiment nor the writing of this report. A lot of the theoretical basis is presented so maybe he felt that I should have some credit. I also did not attend the conference and I no longer worked for DOE.)

is inclined to assume that the slope is the overall slope through this region. This is an optical illusion. Using the KJO data in Part II one can two pointwise differentiate or three pointwise smoothing to obtain an indication of the instantaneous slope. This is shown in *Figure 4*. The range of answers could be from ~ 4.8 to ~ 3.6 , a range of $\sim 30\%$. However, the KJO data is very precise with an overall standard deviation of better than 0.0059% of the full range of data in the χ -plot. Very few isotherms are that precise.



Conclusion about “threshold quantities” – a disproof of “Henry’s Law”:

Presented in parts II and III there are three tests to determine if ‘Henry’s law’ for physisorption is valid, and it is not. There are four examples presented that invalidate the isotherm “theories” that predict this. These examples should be convincing concerning the threshold pressure and the invalidity of “Henry’s Law” for physisorption. There are other examples cited in reference 6, with adsorbents such as thoria, beryllia, Teflon® and lunar soils. It is difficult to find examples in the literature for two reasons: 1) the phenomenon occurs usually in the high vacuum or ultra-high vacuum range and 2) if one had submitted a report mentioning this phenomenon for journal publication, rejection was automatic*.

* That has been the case for JBC for the last 40 years. During that time there have been many failed attempts to “improve” the BET, the Langmuir and other isotherm equation producing junk. Think how much better the discipline would be if this had not been the case. There are surely more advances to be made beyond this series. Keeping the great mistake is approaching a century – a long time for a totally false theory to survive.

It was important to review the material in this section, which is overwhelming evidence of the threshold pressure. This was to illustrate that any valid theory of physical adsorption that is a denial of this phenomenon is at best incomplete and probably totally false. Indeed, the IUPAC convention should be that any valid theory of physical adsorption should allow for the possibility of threshold pressure.

The puzzle that Brunauer could not rectify about the phase change is solved. The phase change to the liquid state, though not fully dense, is at the threshold pressure – thus fulfilling the Gibbs' phase rule expanded for surfaces. Another puzzle is solved.

Thus, three tests have been provided between the publication Part I and in this. They are:

1. The presence of a threshold pressure
2. The two-point check compared to a Henry's law line
3. digital check for a consistent slope at low pressures

All three require at least a high vacuum system to perform.

Section 4 Correlation between BET results and the quantum mechanical expected results:

In this section the exercise is to compare the calculation of the BET to QM/ESW results. In the BET theory, the constant "C" does not seem to have any meaning other than an arbitrary constant*. The E_a from QM/ESW has the meaning of the starting adsorption energy as defined by *Equation 6*. Thus, \bar{E}_a does have a physical meaning, it is the pre-exponential constant for the $\Delta_f^{\ddagger} \bar{E}$ function.

There are two widely used conventions for the BET that specify the allowed pressure. A third, less common new convention, is to use a nonlinear-least-squares fit. This latter method also requires a specific pressure range. It is important to know what the allowed pressure range is, since the BET answer is dependent upon the choice. (A Renaissance scientist would be horrified by this inconsistency.)

The method simulates the normal transform method with $\{X/[n_{\text{ads}}(1-X)]\}^{\ddagger}$ as the ordinate transform. The QM/ESW results in a χ -plot are linear and the BET plot is calculated from this. The equations used to do this are derived from *Equation 1* and *Equation 5* to yield the values for [x,y] for the BET. The value of n_a for the QM/ESW is selected as 1 and thus the answer is the ratio: $n_m(\text{BET})/n_m(\text{QM/ESW})$. The equations used are (x on abscissa and y on the ordinate) are *Equation 9*.

* Brunauer argued that the constant "C" was an equilibrium constant. The problem is that it does not match the calorimetric heats of adsorption regardless of attempting to make up for the difference with entropy. Such attempts yield ridiculous answers that cannot be justified, but researchers continue to report these answers.

† Recall: $X'' = P/P_{\text{vap}}$

$$\frac{n_{a,BET}}{n_m} = -\ln\{-\ln(X)\} - \chi_\zeta$$

$$[x, y]_{BET} = \left[X, \frac{X}{(-\ln\{-\ln(X)\} - \chi_\zeta)(1-X)} \right]$$

Equation 9 conversion equation for QM/ESW to BET.

There are three tables presented. They are:

Table II - The BET is found the traditional way with the ordinate transform and limited to the range $X = 0.01$ to 0.35 , called Sing, et.al. (or “old”) criterion

Table III - The BET is found using the traditional ordinate transform but uses the “Rouquerol” criterion for the upper pressure. Specifies the high pressure is at **max** [$n_{ads}(1-X)$]. There is no lower pressure specified. However, the traditional $X \geq 0.01$ is implied. Most commercial instruments do not measure below this value anyway.

Table IV - The BET is fit using a non-linear least square routine (NLLS) normally with the same criterion as in **III** above. Some researchers expand the parameter count with multiple additional BET fits or other modifications, which maintain the BET or Langmuir framework.*

The limit $X > 0.01$ obviously excludes the high (HV) and ultrahigh vacuum (UHV) and thus misses all the important energy information needed to make a thorough analysis. This means, according to QM/ESW, porosity onset of any type is questionable, except for Gurvitsch rule, if there is no external surface, in which case a QM analysis is required anyway.

How to read the tables:

In **all tables**, the 1st and 2nd columns are χ_ζ and $-\bar{E}_a/kJ\ mol^{-1}$. The 3rd is the ratio of $n_m(BET):n_m(\chi)$. Since χ_ζ is not available when using the BET, then the value of the “C” constant in 4th column is used to look up the first two items. The 5th column is the standard deviation of the BET versus the QM/ESW only over the range specified.

The range specified for **Table II** is $X = 0.01$ for the low value and $X = 0.35$ for the high value. This convention is referred to here as the Sing or “old” convention.

In **Table II** the 6th column is the standard deviation of the BET versus QM/ESW divided by the data range as specified by the Sing criterion.

* Some suggested fits have had as many as 10 parameters. Other fits add parameters that speculate different effect to justify a fit in the post inflection area. Just as an exercise, I have tried polynomial fits up to the 8th power in both the normal isotherm, the log-law and the χ -plot just to see what it would take to make a fit. All three worked out acceptably but not surprisingly the χ -plot did best. These fits had absolutely no meaning for reality and the extrapolation from most of them outside the ranges used was terrible...and, of course, there was no threshold pressure.

for **Table III** and **Table IV** in the 6th column is the limit for the “Rouquerol” rule, the 7th column is the standard deviation of the BET versus the QM/ESW only over the range specified, the 8th column is the standard deviation of the BET versus QM/ESW divided by the data range as specified by being useable.

Conversions Old below $X = 0.35$ and the Rouquerol convention.

The “new” criterion for the high pressure limit is by Rouquerol, et al.²⁸, that is, the range is below the maximum value for $Q = n_{\text{ads}}(1 - P/P_{\text{vap}})$. There is no lower range specified for this, but obviously it will start to break down at pressures below $P/P_{\text{vap}} = 0.01$ as does the “old” analysis. It is assumed that systems with HV and UHV are still rare in the present literature and such a requirement is either not noticed or ignored. Furthermore, the BET cannot handle data that does not approximate Henry’s law, so the threshold pressure is not included.

An interesting question is, “How did Sing figure out that $X \geq 0.01$ needed to be a required or things would break down without using QM/ESW?”

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Table II Comparison of the BET versus χ monolayer equivalences using the “old” BET convention and traditional linear fit for the range selection, $0.01 < P/P_{\text{vap}} < 0.35$. (χ is full range.)

χ_c	$-\bar{E}_a$ /kJ mol ⁻¹	$n_m(\text{BET})/ n_m(\chi)$	C	σ of fit	σ % FDR
-4.0	35.41	2.680	-289.7	0.435	29.5%
-3.9	32.04	2.611	-334.5	0.378	25.6%
-3.8	28.99	2.542	-401.1	0.326	22.1%
-3.7	26.23	2.474	-510.5	0.279	18.9%
-3.6	23.73	2.405	-723.6	0.236	16.0%
-3.5	21.48	2.337	-1321.4	0.197	13.3%
-3.4	19.43	2.269	-13003.2	0.163	11.0%
-3.3	17.58	2.201	1503.2	0.133	9.0%
-3.2	15.91	2.132	676.2	0.107	7.2%
-3.1	14.40	2.065	421.0	0.085	5.7%
-3.0	13.03	1.997	297.0	0.067	4.5%
-2.9	11.79	1.929	223.6	0.054	3.7%
-2.8	10.66	1.862	175.1	0.047	3.2%
-2.7	9.65	1.794	140.6	0.044	3.0%
-2.6	8.73	1.728	114.8‡	0.044	2.9%
-2.5	7.90	1.661	94.8‡	0.045	3.0%
-2.4	7.15	1.595	78.8‡	0.046	3.1%
-2.3	6.47	1.530	65.7‡	0.046	3.1%
-2.2	5.85	1.466	54.7‡	0.044	3.0%
-2.1	5.30	1.403	45.3	0.041	2.7%
-2.0	4.79	1.343	37.2	0.036	2.4%
-1.9	4.34	1.286	30.1	0.029	1.9%
-1.8	3.92	1.235	23.6	0.019	1.3%
-1.7	3.55	1.197	17.6	0.009	0.6%
-1.6	3.21	1.205	11.3	0.022	1.5%
-1.5*	2.91	0.781	-49.1*	6.336	428.5%

*Above $\chi_c = -1.527\dots$ the analysis breaks down.

‡These are approximately the stated range of validity by Sing.

Table III: The ratio and relationship between χ monolayer equivalence and the BET monolayer equivalence. The traditional transform method and the “new” (Rouquerol) criterion are used. Lower limit is set at $X = 0.01$

χ_c	$-\bar{E}_a/\text{kJ mol}^{-1}$ $T=77.35\text{ K}$	$\frac{n_m(\text{BET})}{n_m(\chi)}$	C	σ of BET	P_{\max}/P_{vap}	σ of BET % FDR	X_{high} of new criterion
-4.0	35.41	2.910	385.2	0.036	0.1315	1.1%	0.132
-3.9	32.04	2.823	356.0	0.038	0.1325	1.2%	0.132
-3.8	28.99	2.737	328.2	0.040	0.1386	1.3%	0.139
-3.7	26.23	2.651	301.7	0.042	0.1449	1.4%	0.145
-3.6	23.73	2.566	276.7	0.045	0.1513	1.5%	0.151
-3.5	21.48	2.482	252.9	0.047	0.1579	1.6%	0.158
-3.4	19.43	2.398	230.5	0.049	0.1646	1.7%	0.165
-3.3	17.58	2.315	209.3	0.051	0.1714	1.9%	0.171
-3.2	15.91	2.233	189.5	0.053	0.1783	2.0%	0.178
-3.1	14.40	2.152	170.9	0.055	0.1853	2.1%	0.185
-3.0	13.03	2.072	153.4	0.056	0.2003	2.2%	0.200
-2.9	11.79	1.992	137.2	0.057	0.2079	2.3%	0.208
-2.8	10.66	1.914	122.0	0.058	0.2155	2.5%	0.215
-2.7	9.65	1.837	108.0	0.059	0.2232	2.6%	0.223
-2.6	8.73	1.761	95.0	0.058	0.2401	2.6%	0.240
-2.5	7.90	1.687	83.1	0.057	0.2483	2.7%	0.248
-2.4	7.15	1.614	72.1	0.056	0.2566	2.7%	0.257
-2.3	6.47	1.544	62.0	0.053	0.2749	2.6%	0.275
-2.2	5.85	1.475	52.9	0.049	0.2939	2.4%	0.294
-2.1	5.30	1.409	44.5	0.044	0.3029	2.3%	0.303
-2.0	4.79	1.345	37.0	0.037	0.3228	2.0%	0.323
-1.9	4.34	1.286	30.1	0.029	0.3320	1.6%	0.332
-1.8	3.92	1.234	23.7	0.020	0.3527	1.1%	0.353
-1.7	3.55	1.192	17.8	0.010	0.3739	0.6%	0.374
-1.6	3.21	1.184	11.7	0.025	0.3954	1.5%	0.395
-1.5	2.91	1.703	3.0	0.150	0.4053	9.4%	0.405
-1.4*	2.63	1.665	2.5	0.140	0.4272	9.0%	0.427
-1.3*	2.38	1.195	4.0	0.098	0.4493	6.5%	0.449
-1.2*	2.15	0.855	9.2	0.165	0.4716	11.2%	0.472

* χ_c is above the $X = 0.01$, which creates a conflict with Henry’s Law perception.

As can be seen from **Table III**, the results are, in the main, much better and there is no negative “C” values. At higher (exothermal) energies, which is $\chi_c < -1.53$, this new criterion breaks down. Below -1.527... the fit introduces sporadic errors.

Non-Linear Least Squares fit:

Non-linear least squares fit (NLLS) to the BET is unusual. There are some exceptions, noteworthy is that by Buttersack³⁵ who compared several isotherm fits in a statistical “bake-off.” The traditional transform method was used to get around the problem of a non-linear fit in the early 20th century. However, NLLS is today quite simple with computers and proper programs.

Table IV: The ratio and relationship between χ monolayer equivalence and the BET monolayer equivalence. The fitting uses a non-linear least-squares fit. This also uses the “new” criterion, but lower limit $P/P_{\text{vap}} = 0.01$ or $P = P_c$, whichever is greater.

χ_c	$-\bar{E}_a/\text{kJ mol}^{-1}$ $T=77.35\text{ K}$	$n_m(\text{BET})$ $n_m(\chi)$	C	σ of BET	$P_{\text{max}}/P_{\text{vap}}$	σ of BET % of range	X_{high} of new criterion
-4.0	35.41	2.883	467.4	0.027	0.0103	3.4%	0.128
-3.9	32.04	2.803	408.3	0.024	0.0140	3.1%	0.133
-3.8	28.99	2.713	385.2	0.027	0.1389	3.2%	0.139
-3.7	26.23	2.625	360.9	0.029	0.1449	3.4%	0.145
-3.6	23.73	2.538	335.7	0.031	0.1512	3.5%	0.151
-3.5	21.48	2.452	309.9	0.033	0.1580	3.6%	0.158
-3.4	19.43	2.367	283.8	0.034	0.1652	3.7%	0.165
-3.3	17.58	2.283	257.8	0.036	0.1729	3.8%	0.173
-3.2	15.91	2.201	232.2	0.037	0.1810	3.8%	0.181
-3.1	14.40	2.120	207.3	0.037	0.1896	3.7%	0.190
-3.0	13.03	2.041	183.5	0.037	0.1987	3.7%	0.199
-2.9	11.79	1.955	172.0	0.043	0.2082	4.0%	0.208
-2.8	10.66	1.880	149.0	0.042	0.2183	3.9%	0.218
-2.7	9.65	1.807	127.8	0.041	0.2288	3.7%	0.229
-2.6	8.73	1.727	114.9	0.045	0.2399	3.9%	0.240
-2.5	7.90	1.651	101.5	0.047	0.2514	3.9%	0.251
-2.4	7.15	1.585	83.8	0.044	0.2635	3.6%	0.263
-2.3	6.47	1.515	71.4	0.045	0.2760	3.5%	0.276
-2.2	5.85	1.449	59.6	0.043	0.2891	3.3%	0.289
-2.1	5.30	1.388	48.7	0.041	0.3026	3.0%	0.303
-2.0	4.79	1.331	38.9	0.036	0.3166	2.6%	0.317
-1.9	4.34	1.280	30.4	0.028	0.3310	2.0%	0.331
-1.8	3.92	1.234	23.3	0.019	0.3565	1.3%	0.356
-1.7	3.55	1.194	17.7	0.010	0.3716	0.7%	0.372
-1.6	3.21	1.161	13.1	0.016	0.3870	1.1%	0.387
-1.5*	2.91	1.128	9.9	0.031	0.4128	1.9%	0.413

*Indicates the low pressure is above 0.01 and at P/P_c

Table IV is the results of a non-linear least squares fit of the BET equation compared to the QM/ESW equation. The range is the $X\{\mathbf{max}(0.01, \chi_c^*)\} \leq X \leq X\{\mathbf{max}[n\{1-X\}]\}$. This range gets smaller as the energy term, $-E_a$, gets higher. It could be expanded by lowering the low limit. This is not done here. The program used is more versatile than a polynomial routine and can handle any equation that is monotonic and more. The NLLS approach yields better statistical results than the transformation method and is perhaps more reliable. To avoid negative values for n_a the lower limit on the range must be increased. Thus, the calculation is adjusted to terminate at χ_c instead $X = 0.01$.

The ratio of the $n_m(\text{BET})$: $n_m(\chi)$ is nearly linear with $r^2 = 0.9997$ between $\chi = -4.0$ and -2.0 It then transitions to another linear portion from about $\chi = -1.5$ to -0.6 . Comparing **Tables III and IV** the $n_m(\text{BET})$: $n_m(\chi)$ values are very close, but comparing to **Table II**, there is a significant

difference as the energy preexponential constant, E_a , gets higher. Thus, it makes very little difference if one uses **Table III** or **Table IV**, but it does make a difference if one uses **Table II**, so it is important whether one uses the “old” Sing criteria or the “Rouquerol” criteria in the original publication.

Discussion:

What this paper reveals:

It is fortunate for most practical purposes that the BET and QM/ESW are monotonic. One can use the “C” constant as a look-up on the tables. Thus, the original object of this Part III paper, which was to demonstrate under certain conditions that the information needed from the BET can be recovered with the modelling of some with the simple equations determined by Quantum Mechanical/Statistical Dynamics (QM) as well as Excess Surface Work (ESW.) These equations are easy to apply and require no knowledge of QM/ESW to access the final equations. However, a thorough understanding requires a paradigm shift in thinking once one gets deeper involved.

The ratio of the BET to QM determined surface areas is between 1.5 and 3.0, with most ceramic oxides having an $\bar{E}_a \sim 10 \text{ kJ mol}^{-1}$. This agrees with some classical mechanical calculations that determine the surface area of pore by geometry (NASA method) and the BET by Gómez-Gualrón, Moghadam, Hupp, and Farba³¹.

For the non-porous, homogeneous isotherm the BET calculation usually has a very high standard deviation in comparison to the calculation versus the actual n_a . This is assuming the discard of $\frac{2}{3}$ of the data. The fact that it might yield a linear region in the BET transform is a matter of the choice of the transform, which has a high component of pressure versus relative pressure. Most mathematicians today would agree that the BET transform and the misuse of linear regression is on very shaky grounds.

The use of the BET to find the surface area on microporous adsorbent is obviously not valid. This is obvious from the information extracted from *Figure 1* through *Figure 4* of Part II, since for the BET range either by the “old” criterion or the “Rouquerol” criterion does not yield a linear region of the BET plot. In fact, the isotherm is a log function in P/P_{vap} which is associated with microporosity. Neither the BET nor the χ -plot are valid for this, only the QM *Equation 7* is valid. This means that the QM formulation is only hypothesis that can handle both forms.

For mesoporosity, it is questionable if the conversion is valid, depending on how the mesopore range lies on the χ -plot. Mesoporosity is expected to be at values above 0 where the energy of adsorption has dropped below the energy of capillarity. Thus, assuming $\chi_\zeta \leq \sim -2$ where there is enough volume of adsorbate to start forming a 3rd schicht. Thus, the conversion may by chance work for the total surface area below that value, but never for the external area. Since the BET does not give the correct value for the monolayer equivalence it may fit mesoporosity but most likely yields the wrong answer for the dimensions of the pores. The volume of most mesopores may be approximately correctly using Gurvitsch rule, provided there is an insignificant external area.

Attempts to Standardize – the BETSI project.

The SIO/IUPAC had declared a certain feature that as being impossible, that is the presence of a threshold pressure in the isotherm. At least the requirement has been dropped. There is no scientific basis for the prohibition and there have been multiple observations of this phenomenon. Whatever the reasons behind this declaration, they are outside of scientific logic. Polanyi discussed this rigid point of view in his last article in *Science*^{36*}. This article should be read by all who are tempted to block information contained in this publication[†]. A person who claims to be a scientist, or even an engineer, is required to keep an open mind.

The problems with BET calculations has been plaguing the field since 1930. The response has been to periodically issue another IUPAC publication on how to

- 1) get consistent results
- 2) how to treat the results or view them once they are obtained, and...
- 3) keep using the BET and discourage any other approach, apparently because we are stuck with a backlog of results.

Probably the most recent attempt to resurrect the BET for an IUPAC/SIO[‡] standard is the BETSI project³⁷. The publication uses a lot of criteria for an acceptable fit and many researchers participated in the round-robin experiments. In summary it was found that the result of using the “Rouquerol” criteria from the researchers vary from 6 % to 32% variation coefficient[§] (or $\sigma = 24\%$ to 57%), but application also varied. The BETSI program which attempts to optimize the individual data sets with *point selection* (?) is more consistent from 0.01% to ~8 % (or $\sigma = 1\%$ to 28% .) (For comparison, acceptable deviation for the QM/ESW acceptability is $\sigma < 1\%$. of the

* Polanyi referred to BET as “orthodoxy.” He quotes Bertrand Russell, “The triumphs of science are due to the substitution of observation and inference for authority. Every attempt to revive authority in intellectual matters is a retrograde step. ... And it is part of the scientific attitude that the pronouncements of science do not claim to be certain, but only the most probable [based on] present evidence. One of the great benefits that science confers upon those who understand its spirit is that it enables them to live without the delusive subjective authority.”

Unfortunately, the authority has not only been within governments, churches, or society but also within the scientific community itself. Lysenkoism is alive and well and practiced by scientists.

[†] This has been happening periodically for the last 40 years.

[‡] The question of n_m conversion to A: A final weak assumption for the BET is the conversion of monolayer equivalence to surface area. The SIO/IUPAC convention is widely used but it surely cannot be accurate. This step has not been officially taken by the QM/ESW and thus recent publications have stopped at the monolayer equivalence. (Sometimes for the comfort of the reader words such as “according to the IUPAC convention” a surface area is quoted.) This step will require QM/ESW calculations that depend upon E_g^a function and perhaps other considerations. However, this step is probably more for psychological reasons, not for scientific reasons.

[§] Reevaluation here indicates these numbers are overly optimistic. Perhaps the values are 1 sigma. Furthermore, there is some question about what the comparison is to. It’s also not made clear what the dependent variable is and if all the investigators are following the same mathematical protocol. The 0.01% variation seems bogus. So what is the explanation? Did they use the transformed plot and obtain their standard deviation from it. See the previous comment about this math error.

full range of data, with no exclusions without a valid reason. In other words, one doesn't ignore any datum because it does not fit some preconceived notion or "theory.")

The rationale for the BETSI considers two reasons 1) the "Rouquerol" criterion is indeterminate and 2) it is cumbersome to use. (The use in this present report disputes the latter claim. The reaction to the first reason is, "What?*" Did they observe the threshold pressure and not report it? Indeed, perhaps creating a low-pressure limit could resolve their reproducibility problem. That is, delete the troublesome data.) This report repudiate both arguments, unless the material is microporous, in which case the BET is invalid anyway. It also cannot usually be used for mesoporosity since the total surface is not available with the onset of mesoporosity, usually a little above $\chi = 0$, which is a discussion for another publication. The selection of a few "valid" points is also a troubling problem after all the "Rouquerol" criteria requires 10 points minimum.

The scatter reported is not of n_m but rather the reproducibility from Laboratory to Laboratory. One would predict that all the laboratories should all get the same answer, even if the answers are wrong, especially if the same samples are used. Unfortunately, it appears that this is a very uncontrolled experiment.

For the BETSI project it appears to allow very loose criteria for the experiments. For example, there is no mention of temperature control nor is the Knudsen effect checked or why it is not. Are the instruments gravimetric or volumetric and are the cautionary notes about each followed? Some supply the commercial model, but were there any modifications? Since probably most used the volumetric technique the concerns about the temperature and the Knudsen effect are especially relevant, however, it is unlikely most instrument measured into the HV or UHV. The only mention of quality control was "...60 Laboratories with expertise in adsorption science ...". This leaves quality control to the level of zero certainty.

Considering the QM/ESW, in order to assure that the same answer is obtained, one would need to specify the common set of data, $\{n_{a,1}, n_{a,2}, n_{a,3}, \dots n_{a,10}\}$, otherwise the waviness of the inverse BET transform is too great.

Aside from the control questions, the digital data might be useful and are available from the corresponding author.

General Recommendations

What is the recommendation from the present investigation? The answer is not to switch from the BET to the QM/ESW method today. However, if the BET results are reported, then the QM results should also be reported. The QM/ESW formulation has not been tested enough, nor for that matter any other of many proposals put forth. (...and why are there so many others?) So, the recommendations are:

* During the creation of this report no indeterminates were found in the mathematics. Perhaps the author is referring to the transformed equation and very low pressures, but even at low pressures, if $n_a > 0$, there should not be indeterminates. If they measured an amount of zero, as predicted by QM/ESW, then the transform would yield an indeterminate, but there is no indication in the report of such a finding. (Perhaps, it is because that would disprove the BET.)

- More experimental data is needed with critical tests being the goal rather than simply accumulating more, perhaps useless, data.
- Publish all the raw data obtained as is from instruments. That is, all the data that the researcher needs to do an analysis, including dead space and what dead space gas was used, etc. In other words, all the data that goes into the research notebook of record.
- Special attention should be paid to temperature control. Use radiative shielding and liquid-gas thermometer.
- Make corrections for the Knudsen effect by calibrating the sample tubes as recommended by Langmuir³⁸.

Conclusion:

The BET has several problems, but never-the-less, there is a good chance to convert the BET values of n_m , or A , the monolayer equivalence and the C constant to n_m and E_a of the QM/ESW calculation. The BET is too incomplete and has too many fallacies in comparison to QM/ESW hypotheses. Thus, the latter “warrants more assertion^{*}”. Although quantum mechanics seems by today’s standards to be more fundamental, there are some problems. The remaining problems include, for example, not enough critical experiments which have been performed to support the QM/ESW approach. There is evidence that QM/ESW is more accurate than other choices that this paper and others like it are warranted and worthy of critical testing.

The conversion herein described depends upon the original conventions used to make the BET calculation. The most important being what range of data is used for BET calculation. Unfortunately, many investigators simply hunt around for a linear portion and use that. As can be seen from the different values in the BET-to-QM/ESW conversion tables, this is not a trivial problem. If the publication does not state the convention used, then the date of submission might supply a hint. Given today’s uncertainty, it would be best, if possible, to repeat the experiment and report the data.

Before the specification of these data range conventions, wildly differing results were obtained by various authors with little explanation. A recent round-robin is attempting to made to further standardize beyond the “Rouquerol” of “Sing” conventions with a semi-AI[†] program called BETSI to set in concrete something which cannot be so solidified without any solid theoretical backing[‡]. Apparently, the program used decides which points to use to make a calculation. (Even though the IUPAC recommendation is to use at least 10 points in the Rouquerol range, this does not appear to be a requirement.) This is a problem since selecting certain points in the Rouquerol range versus other points can lead to wildly different answers.

^{*}John Dewey’s phrase for closer to truth.

[†] What is meant by AI here. Probably, AI would attempt to give consistent answers, regardless of whether the method is scientifically justified. Given the overwhelming presence of publications that use BET, undoubtedly the BET would be cited, but the decision how to apply it is left up to chance.

[‡] This is from a recent round-robin attempt to “standardize” the BET based on an “impartial” application of the “Rouquerol” criteria. (The application of the criteria seems to be very well outlined except for the low pressure limit, so the meaning of addition “impartiality” is not clear.) The results were anything but sterling. A lot of effort, many laboratories and researchers were involved in this effort. You might have expected someone among those 60 would have asked, “Wait! This does not seem to be working – is there something else that can be done?”

There is a second problem, which is common to both BET and the QM/ESW, that is the conversion of n_m to a measure of surface area. This has not been treated here, but what is normally used is simply the IUPAC convention, which is clearly flawed. Certainly, for nitrogen, the unsymmetrical nature of the molecule is a problem. Is it standing up or prone? This makes at least a $\pm 20\%$ difference. But the outstanding question is, "Is this conversion necessary?"

However, for all adsorbate molecules the question from QM/ESW is, "What distortions are in play with fields from energies that go as high as 30 kJ mol^{-1} ?" One would expect a "flattening" of the molecule, but how great is this? For nitrogen, one expects under high fields that nitrogen would tend to be prone, but is there a distribution of orientations? This phenomenon needs some research to determine if it exists, what is the energy dependence, and can it be correlated to the surface energy?

Another question is, how much of the surface is excluded from the measurement due to the adsorbent particles touching. Are points of contact masked from adsorptive or is the adsorption energy high enough to separate the adsorptive particles? For the latter question, is there a dependence upon energy? It would be desirable to settle this latter question by experiments in the absence of gravity. This might be a difficult task without the cooperation of NASA. Even so, in general practice it is unlikely that all samples can be sent to space.

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Appendix I - Symbol List:

This list applies to this publication and others produced by the author. The IUPAC conventions are followed as much as possible. However, there are some exceptions. For example, the molar quantities are written with an overbar instead of an m which is used for “monolayer. An italic lowercase L (l) is used for liquid state at the temperature of the adsorbent. θ (coverage) is used for the actual amount compared to a monolayer equivalent, that means any physical obstruction will lower the value from the flat surface areal density, that is, $\Delta\chi$. However, subscripted θ s, Example $\theta_2, \theta_3, \dots$ are the relative areal densities with subscripts indicating the “schicht.”

It is assumed that the reader understands that all adsorbed amounts, n_{as} or n_m , are reported on a basis of 1 g of adsorbent as normally reported.

English Symbols

A = 2D box dimension in the plain of the surface

A = the area of the surface aliquot, ΣA_{total} = total area (given as specific quantity if unstated.)

a = the cross-sectional constant for the admolecule.

A = the Polanyi-Dubinin “Adsorption Potential”

c = an arbitrary constant in the Dubinin class of isotherms. $c = 2$ is the Dubinin-Radakovich

C = The BET constant

D = a constant is the Dubinin class of isotherms

D = The Dubinin, et al., exponent

\mathbf{D} = the normal cumulative distribution

E = energy (matrix value) from bottom of well (box)

E' = resultant energy change due to perturbation

$E(n=1)$ = ground state energy in a 1 D box

$\mathbf{E}(\theta)$ or $\mathbf{E}(n_a)$ or $\Delta_l^a \mathbf{E}(\theta)$ = The energy of internal energy as a function of θ or n_a referenced against liquid state at the temperature of the adsorbent.

E_a = The threshold energy, the pre-exponential constant for the internal energy function, E

$\mathbf{E}_a^\ominus = \Delta_l^a \mathbf{E}(\theta) + \varepsilon$,

E_n , $n = 1, 2, \dots$ = base energy after adsorption of the 1., 2. ... n. molecule

\hbar (h bar) = the reduced Plank's constant = $h/2\pi$

h = the Plank's constant = $6.62607015 \times 10^{-34} \text{ J}\cdot\text{Hz}^{-1}$

h = radius of the pore (core plus “thickness”) measured from the adsorbent surface.

\mathbf{G} = the normal distribution

$\hat{\mathbf{H}}$ = the Hamiltonian (matrix) operator

H' = the operator for the perturbation. Here it is time independent.

H_o = Pre-exponential for the excess surface work function

$H_{o,\downarrow}$ = Pre-exponential for the excess surface work function for desorption

k = Boltzmann constant

L = the 1D box length

m (if alone) = mass of a particle

m = A number used in the Kelvin equation to account for geometry.

n_m = the quantity of molecules in a monolayer equivalence.

n_p = the quantity of molecules in a pore.

P = pressure of adsorptive (over adsorbent and at adsorbent temperature.)

P_p = pressure of mesopore onset.

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

$P_{\text{vap}}(T)$ = The vapor pressure of the adsorptive at temperature T .

P_{ζ} = threshold pressure

\tilde{p} = fugacity

$\mathbf{Q}(n_a, P)$ = The Rouquerol criterion function

r = pore radius

R = the gas constant

$r_{\text{core}} = (h - t)$ the "core" radius

s = The "spreading" constant for the \mathbf{G} function, normal distribution

T = temperature in K

t = the adsorbent "thickness"

T_a = meaning at the temperature of the adsorbent

T_{BP} = The standard boiling point temperature of adsorptive

T_c = the critical temperature of adsorptive

T_{MP} = The melting point temperature of adsorptive

U = Unit step function.

\bar{V} = molar volume

$X = P/P_{\text{vap}}$ the "relative pressure"

\mathbf{Z} = the statistical area function.

Starting with a Greek letter

β = a constant that is dependent upon the number of adsorbate molecules

β_D = the Dubinin, et al., scaling factor

γ = Surface tension of the adsorbate

$\Delta_l^a S$ = the entropy of adsorption with standard state of the liquid state at the T of the adsorbent

$\Delta_l^a \mu$ = change in chemical potential from liquid phase at adsorbent T to the adsorbate.

$\Delta\chi = \chi - \chi_{\zeta}$

$\Delta\chi_p$ = the position on the $\Delta\chi$ -plot where the peak for σ_p is.

$\Delta\chi$ -plot = a plot of n_{ads} versus $\chi - \chi_{\zeta}$

ε = [internal] energy of vaporization at the adsorbent temperature (determined)

θ = classical "coverage." QM relative areal density compared to 1 monolayer equivalence

θ_1 = relative areal density of adsorbate in the 1st schicht compared to 1 monolayer equivalence

θ_{MT} = classically the area not covered by θ . In QM: = $1 - \theta_1$

θ_n = relative areal density of adsorbate in the n^{th} schicht compared to 1 monolayer equivalence

λ = the position of the minimum in the ESW, shown to be at 1 monolayer equivalent.

λZ = the canonical partition function of adsorptive

μ = chemical potential (molar quantity)

μ_a = chemical potential of the adsorbate

μ_l = chemical potential of the liquid phase at the temperature of the adsorbent.

Ξ = Grand Canonical Partition Function GCPF

$\Pi(t)$ = Excess Surface Work – a function of adsorbate "thickness."

σ = the spread of values of multiple χ_{ζ} s

σ_{fit} = the standard deviation of n_a calculated values versus n_a experimental values.

σ_{FDR} or σ (% FDR) = the standard deviation of error compared to the **Full Data Range**.

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

χ_{ζ} = the threshold $\chi = -\ln(-\ln(P_{\zeta}/P_{\text{vap}}))$

$\langle \chi_{\zeta} \rangle$ = the mean of the addition of several manifolds of χ -plots and their χ_{ζ} s

χ^{-1} = the inverse chi function = $\exp(-\exp(-(x-\mu)/s))$

Ψ = the time dependent portion of the particle wave function(s)

ψ = the time independent portion of the particle wave function(s)

ψ^* = the complex conjugate of ψ (redundant in bra-kets)

Subscripts and Superscripts

_m = monolayer, not used for molar which is the overbar (ISO/IUPAC alternate method)

^o = _{vap} to follow tradition

_{pore} = of the pores, varies as to type but there should be no ambiguity.

_p = of mesopores

_{vap} = of vaporization

_ς = a threshold quantity

σ_p = the normal distribution spread of the pore dimensions

χ_p = the position on the χ -plot where the peak for σ_p is.

↑ = for adsorption versus ↓

↓ = for desorption versus

“:=” = equal by definition (the def over the equal sign is not yet Unicode.)

^l or _l = superscript to liquid state, subscript from liquid state (at adsorbent T)

^a or _a = superscript to adsorbate state, subscript from adsorbate state (at adsorbent T)

^g or _g = superscript to gas state, subscript from gas state (at adsorbent T)

Other marks:

\bar{x} (over line) = per mole of x, see preemptive _m,

Abbreviations:

AALR = Silvestre-Albero, Silvestre-Albero, Llewellyn, and Rodríguez-Reinoso

BET = Brunauer, Emmett and Teller

DD52 = a microporous activate carbon

DFT = Density Functional Theory (non-QM)

DoD = Department of Defense

DOE = Department of Energy

ESW = Excess Surface Work

FDR = of the Full Data Range

GCPF = Grand Canonical Partition Function

HV = High Vacuum between 10^{-3} and 10^{-7} mbar

IUPAC = International Union of Pure and Applied Chemistry

LMA233 = a microporous activate carbon

NASA = National Aeronautics and Space Administration

NLLS = Non-Linear Least Squares

QM = Quantum Mechanics

SBA-15 = a microporous activate carbon

STD = Standard Temperature and Pressure

UHV = Ultrahigh Vacuum between 10^{-7} and 10^{-12} mbar

WKB = Wentzel–Kramers–Brillouin (Jeffreys) QM Approximation

XXDFT = DFT modified by letters standing for various modifications, For example, if XX is
NL = non-local, or
QS = quenched solid

Appendix II Some basic concepts and definitions:

1. A thermodynamic system consists of the adsorbent and adsorbate only. It is an open system.
2. Adsorptive = the gas species that is in contact with the adsorbent and adsorbate. The adsorptive is not part of the open thermodynamic system.
3. Adsorbate = the same component as the adsorptive except it is adhered to the solid material and is part of the thermodynamic system. This is measured in both the volumetric and gravimetric experiments as part of the system.
4. Adsorbent = the solid material (part of the thermodynamic system.)
5. Compound = a chemically bonded entity which cannot be separated by evaporation, freezing, centrifuging or other low energy processes.
6. Component consists of a single compound.
7. Phase = A homogeneous grouping of a component or components, such as a liquid, a solid, a solution, or a gas
8. Chemical reaction = is the energetic interaction between components or within a component which changes the topography of the compounds' electrons. A reaction can be an attractive or repulsive force.
9. Physical forces = these include dipolar-dipolar, dipolar-induced dipolar, London forces, "hydrogen bonding," or other non-chemical forces. Physical forces do not change the topography of the involved electrons, although it may distort the geometry of system components.
10. Microporous = pores that can be explained by a fit to the log-law of first schitch equation.
11. Schicht: a new definition. The position an admolecule is in relative to the adsorbent surface in terms of the shortest chain of touching admolecules.

Chemisorption changes the topography of the adsorbate electrons, whereas physisorption does not. This is the important distinction between the two. In the physisorption literature other distinctions are made, but this one has no exceptions. For a complete discussion of the difference, see chapter VI for physical forces and chapter VII for chemical forces, or bonds, in the book by Clark³⁹ or the IUPAC report dealing with this⁴⁰. This explains what most chemist understand about the difference between "intermolecular forces" and "chemical bonds."

Appendix II - the “Sing” and “Rouquerol” criteria:

Both the Sing and Rouquerol criteria assume the BET transform plot for application.

The “Sing” criteria:
The BET can be used for Type II and Type IV (IUPAC/SIO designation)
The following condition must be met, otherwise the range must be adjusted to do so:
The “C” constant must be between 50 and 150
The upper limit remains $X = 0.35$ and the lower limit – not listed but 0.01- 0.05 traditional*
“Rouquerol” criteria
The Rouquerol transform $n_{\text{ads}} (1-P/P_{\text{vap}})$ must increase with P/P_{vap} for the data selected to calculate the BET parameters.
The monolayer capacity - n_m (obviously according to the BET) should be within the limits of data that were used to fit the BET parameters.
There must be 10 points in the Rouquerol range that are used to make the calculation
The lower limit is $X = 0.01$ (not stated but obviously needed.)
The value of $1/(\sqrt{C} + 1) \approx P/P_{\text{vap}}$ at the monolayer capacity.

The last requirement is a problem. The question is where is the monolayer capacity? Many isotherms start at one or even more monolayers capacity since the vacuums are not good enough to obtain lower levels. For example, see the data by Goldmann and Polanyi⁴¹ where almost all isotherms start near or after this. (See reference 6 pages 109 301 - 304.)

Additional requirement would be the lower limit, rather than $X = 0.01$, that if $\chi_c > \chi (X = 0.01)$, then χ_c be used for the lower limit. This would apply to the lowest energy. However, this requires a χ -plot to determine this, or one of the tables could yield the answer.

The BET method approaches the inflection point and if there is no mesoporosity, the slope at that point is proportional to the surface area. This is the basis of the χ -“single” point method⁴² and takes advantage of the Fuller magic point lemma. The slope of the basic isotherm at the magic point yields the monolayer equivalence by the formula:

	$n_m = \frac{dn_a}{dX} e^{-1} \quad X = P/P_{\text{vap}}$	<i>Equation 10</i>
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Of course, obtaining the slope requires data at least at the magic point and ideally points equally spaced on either side of that point. It might just be easier to do the χ -plot.

* The lack of a lower pressure along with the fact that there is specified set of points to be taken $\{n_{a,1}, n_{a,2}, n_{a,3}, \dots\}$ every time the same, explains why there is high variability between researchers' data.

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