Using Quantum Mechanics to interpret the output of the BET analysis

with Tables to convert *A* and *C* to *n*m and *E*a,

James B. Condon[[1]](#footnote-1)

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Using Quantum Mechanics to interpret the output of the BET analysis

Tables to convert *A* and *C* to *n*m and *E*a,

James B. Condon[[2]](#footnote-2)

**Abstract:**

The Brunauer-Emmitt-Teller[[3]](#endnote-1) (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 II and III. These *should* suffice to eliminate the BET and its derivatives as the standard characterization theory. However, other evidence 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, **E**(*n*ads) = *E*a **exp**(*n*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*ads(1-*P*/*P*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.

**Introduction:**

The Brunauer-Emmitt-Teller1 (BET) theory has long been known to be deficient and difficult theoretically to deal with. In part I through III of this paper, only two theoretical and 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’ rule[[4]](#endnote-2) that considers the adsorbate amount, *n*ads, 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 postulate[[5]](#endnote-3).

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*?”[[6]](#footnote-3) 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. 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[[7]](#footnote-4). 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. (The 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.)[[8]](#footnote-5)

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 parts this publication consists of three parts:

 Part I Two problems with the BET

 Part II An alternate hypothesis - Quantum Mechanics applied to Physisorption

 Part III The weak spot for BET – Henry’s Law applied to physisorption.

 Part IV Reconciling the BET with the Quantum Mechanics

This publication is limited in scope to addressing only the simplest cases of adsorption. It only mentions microporosity for 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.

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 2024) is covered in a review for this purpose.[[9]](#endnote-4) 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.[[10]](#endnote-5) There are multiple publications dealing with the QM implications[[11]](#endnote-6),[[12]](#endnote-7),[[13]](#endnote-8),[[14]](#endnote-9),[[15]](#endnote-10),[[16]](#endnote-11),[[17]](#endnote-12),[[18]](#endnote-13),[[19]](#endnote-14),[[20]](#endnote-15),[[21]](#endnote-16),[[22]](#endnote-17),[[23]](#endnote-18) as well as a related companion subject Excess Surface Work (ESW[[24]](#endnote-19),[[25]](#endnote-20),[[26]](#endnote-21),[[27]](#endnote-22)[[28]](#endnote-23).) 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 designated by QM/ESW From here on. Another place to obtain information is the lesson plan created for University of Tennessee’s surface science group[[29]](#footnote-6).

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

**Some basic concepts and definitions:**

1. 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 layer equation.

Chemisorption changes the topography of the adsorbate, whereas physisorption does not. This is the important distinction between the two. In the 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 Clark[[30]](#endnote-24). This explains what most chemist understand about the difference between “intermolecular forces” and “chemical bonds.”

**Part I Two problems with the BET theory.**

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

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| *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*vap, and the ordinate, *y*, a mixture of the dependent and independent variables as given in *Equation 2*:

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

This graphing method is widely used way to arrive at the output parameters *n*ads and *C*. This mixing of the dependent and independent variables creates mathematical problems for the analyses (and leads to anomalies.) The normal method of determining the standard deviation of the curve fit is to use the statistics provided from the linear regression of the transform over the BET range. This is incorrect, since the statistics should be extracted from the resultant untransformed fit.

Some recent publications get around the uncertainties of this transform with the use of non-linear least squares methods (NLLS.) This is especially useful for using summations of BET or Langmuir isotherms[[31]](#endnote-25),[[32]](#endnote-26). Both the transform method and the NLLS method are addressed in this publication.

*A) “Henry’s law” applied to physisorption?*

*Equation 3* is implied by *Equation 1* and is referred to as Henry’s Law in analogy (not derived from) the law for solutions at low concentration. In solutions, Henry’s Law is thermodynamically linked with Raoult’s Law, and Raoult’s Law is impossible for physisorption[[33]](#footnote-7). The Henry’s law requirement is delt with in **Part III** as the fatal error that the BET produces.

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| Equation 3 The statement of Henry's Law |

The other problem with the BET that was obvious very early is the fit was very bad, even though the shape of the predicted isotherm had the same features as the experimental isotherms. The fit is especially bad at pressure above *X =* 0.378.

To solve this problem, only points below *X* = 0.35 were allowed in the calculation. The unusual ordinate transform contains both the dependent and independent variables and as the data approaches *X* = 0, it tends to “blow-up.” Apparently, the reason for this at the time was not known, so, a lower limit of use was picked to be *X* = 0.01 (sometimes *X* = 0.05) with advice to extrapolate from the last point to [0,0]. In other words, the “Henry’s law” region is ignored, but assumed.

There were obvious problems with the BET, especially with the introduction of porosity into the BET-plot. Standard isotherm plots were then developed based upon adsorbent that were thought to match the material of interest but were non-porous. The assumption being that isotherm should be the same for the surface of the porous materials. This turns out to be a big leap of faith, because the creation of the non-porous material is unlikely to be identical to the fully dense material with respect to their surfaces, otherwise their geometry could not be different.

It was also discovered that the original upper limit of the plot was also not reliable. A new criterion was recently created, the “Rouquerol criterion[[34]](#endnote-27).” This states that only points less than the first maximum of the function, ***z***, calculated data-pointwise by *Equation 4* are used.

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

The max is not likely to be past the inflection point, since the energy of adsorption would be very low. The inflection point is also were the BET starts to vier off from the expected curve. Thus, the portion of the overall isotherm suitable for a BET analysis is ≤ 37% of the total range. However, this is often considerably less using the “Rouquerol criterion.” The rest of the isotherm is ignored for the determination of the monolayer equivalent, *n*m (thus *A*) and the *C* constant.

There is one other criterion: the BET *C*constant cannot be below 50. If it is below 50 then the position of the valid linear range must be adjusted so that it is above 50. In practice this does not seem to be followed. The reason for the criterion is uncertain. There seems to be no theoretical reason that it must be above 50, except, perhaps, results by other research did not make sense when it was below 50. Obviously, the *C* constant is an equilibrium constant, it cannot be negative, or one obtains an imaginary adsorption energy. However, if the *C* constant is negative the investigators probably would not report this, there are many older publications where only *A* is reported.

*B) What is wrong with the BET?*

There is a long list of problems with the BET. The early arguments were set aside since there was no alternative to obtain an answer for surface area. An entire section of this has been covered in the previous publication4 along with a section in a book5 and its Appendix III with a list by Gregg and Jacobs, which present many of these arguments. Provided here are two arguments not presented early in the 20th century. One is a definite disproof; another is an argument for the practical question, “How good does the BET fit the data?” This latter is a statistical disproof, not a QED like the first, but it does not make sense to fit data to a function if it does not match.

First, is the question of standard deviation of the fit. To be fair, only the data in the “BET range” will be compared statistically; even though there are very few areas of science where it is permissible to discard ⅔ of the data because it disagrees with theory. The simplest case, that is, a homogeneous, non-porous adsorbent is selected to avoid complications. It turns out that the first requirement is difficult to fulfill, but there are some examples that come close[[35]](#footnote-8).

The question of “fit” is a question of comparison. Does a theory fit the data well enough that no other theoretical formulation can match or exceed the goodness of fit, and does the alternative yield the same or fewer output parameters that have physical meanings. Thus, there must be an alternative hypothesis to make a comparison. In this case, the other hypothesis is the quantum mechanical and excess surface work hypotheses (QM/ESW.) In their simplest forms, both the BET and the (QM/ESW) yield *n*m and an energy parameter. However, as indicated in the example below, the BET over its limited range has a standard deviation that is 1.6 × 105 greater than the standard deviation of the QM/ESW fit over the entire data range. This is an almost unbelievable advantage, even given the cautionary statements above. It seems it would be hard to ignore this difference.

For a QM/ESW analysis, the normal acceptable error limit has been arbitrarily set to less than 1% of the entire data range. This is a criterion that the BET seldom fulfills, provided the *n*a amount observed, is compared to the calculation *n*a from the transform calculation, even over the selected BET restricted range.

**Part II: An alternate hypothesis - Quantum Mechanics applied to Physisorption:**

*A) The QM/ESW 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 equation presented here. Equation 5 is the QM/ESW equation for continuous “multilayers.”

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| 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 χς. The unit step function, **U**, is used to indicate that Δχ cannot be negative. *P*ς is referred to as the threshold pressure, indicating the phase transition for the onset of the surface liquid phase. Δ*la***Ē** is the molar[[36]](#footnote-9) change in the internal energy function going from the liquid state (*l*) to the adsorbed state (a.) Thus, *E*a < 0 (exothermic.)[[37]](#footnote-10) seen in *Equation 6.*

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| 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 Δla**E** is the energy function of the transition from the liquid to the adsorbed state. On the other hand Δga**E =** Δla**E +** Δgl**E**, whereΔgl**E** is the calorimetric internal energy function referenced to 1 bar pressure. (Sometimes a superscript plimsoll symbol, ⦵, is used for this.)

These equations can be derived by another modern theoretical development, the Excess Surface Work theory (ESW) by Adolphs20,21,22,[[38]](#endnote-28),[[39]](#endnote-29), 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 Δla**E**, the Dubinin “thermodynamic criterion,” and the assumption that the ESW maximum is at one monolayer equivalent, which justifies the match with the QM/ESW *Equation 5*. The two developments were formulated independently in the 1980s without communication between the two research groups, thus, lending mutual support.

In the application of the Grand Canonical Partition Function, the concept of “layer density” is derived. These equations are shown in *Equation 7.*

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| Equation 7 The equations for the QM “layering.” |

The subscripts on the θs designate the position of the “layers.”[[40]](#footnote-11) The last equation after “⇒” is derivable.

The equation for θ1 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.

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| Equation 8 The “log-law.” from the QM "layering" eqautions. |

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

*B) Statistical Demonstration of QM*/*ESW versus BET for Physisorption:*

*Example 1) Data by Krug, Jaroniec and Olivier[[41]](#endnote-30):*

Probably the best performed experiment to determine a standard curve was conducted by Krug, Jaroniec and Olivier (KJO.) with N2 adsorption on LiChrospher Si-1000 Silica. The silica sample was apparently very pure with little heterogeneity. The calculated heterogeneity for the energy distribution, <*E*a>, is 640 J mol-1 out of 8.84 kJ mol-1 total value of *E*a. Although this may seem like a big uncertainty, it really is not as the following graphs will illustrate.

1. Four graphs below illustrate how good the QM/ESW theory fits the overall data and how the BET strays at high and very low pressures.
2. The BET range is, showing the upper and lower limits in *Figure 2*.
3. How the BET in the allowed range fits to the data compared to the how QM/ESW fits to the data over the full isotherm.
4. What the effect of the energy distribution has on the curve near <χς> (*Figure 4*.)

The plots are all based upon the χ-transformation of the independent variable. Some may object to this as being biased, but it is not. This is because the significant errors that exist are in the dependent variable and the analysis is only of the dependent variable. One of the advantages of the χ-plot is that it “stretches out” the data for presentation in both the very high and very low pressures ranges. This became obvious with its early use.[[42]](#endnote-31),[[43]](#endnote-32) Also, the Δχ-plot is a direct reading of the monolayer equivalence on the abscissa making interpretation easier.

Usually, one obtains an upturn in the data toward the end of the χ-plot. This is normally interpreted as an incorrect temperature reading and a distortion in the data. An upturn in the χ-plot indicates that the temperature of the adsorbent is higher than the authors believe, which is the most common cause and is attributed to unbaffled radiative heating, which warms the adsorbent. A negative curvature near the end χ-plot has also been observe. This is usually attributable to a temperature being colder than believed to be the case. This is a special problem for liquid N2 or other refrigerants being used at pressures lower than 1 bar atmospheric pressure, for example at higher elevations or during a strong low-pressure weather system.

In the KJO case, the temperature from the data was calculated to be less than 0.01 K too warm, which creates little problems and changes the output parameters very little. It must be that they took special care to guard against this error, since, normally in the past, Micromeritics instruments lacked such control[[44]](#footnote-12). The vacuum system was UHV capable of ~1 × 10-10 bar and the first data point was *P*/*P*vap = 5.55 × 10-7. The last two data points in KJO’s publication, presented in parenthesis in their data listing, were not used. These data points were obtained from a different adsorbent sample which was characterized as being physically, and probably chemically, different. The residual of these two points were well out of the range for the other data points, but even so, the effect was to change the standard deviation only by about 8.4 x 10-6 mmol/g out of 1.3 mmol/g total or 6.5 × 10−4 % FDR (of Full Data Range[[45]](#footnote-13).)

In *Figure 1* through *4* are the fits of the KJO data with at different magnifications with the BET and the QM/ESW fits. The following fits were calculated and presented in **Table 1.**:

1. a QM/ESW calculation assuming no heterogeneity
2. a QM/ESW calculation assuming heterogeneity
3. a BET calculation with the high pressure Rouquerol criterion and *X* = 0.10 for the low.
4. a BET calculation with the high pressure Rouquerol criterion and no lower limit.

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| A graph of a function  Description automatically generated*Figure 1 Plot of data by KJO, the QM*/*ESW fit and the BET fit. The line through the data points,* X*s, is the QM*/*ESW fit. The BET line is very high at high pressure* (*High* Δχ) *and very low at low P* (*low* Δχ.) | *Figure 2 Plot of Data by KJO for the BET Rouquerol range. QM*/*ESW fit closely follows the data. The best fit in the BET Rouquerol range, which is the vertical lines, is the curved line.* |

The QM/ESW fit is the nearly straight line passing through the data points. The BET fit is the line that for most of the isotherm is far from the data points. For perspective, mesoporosity begins near χ = 0 which in this case is at Δχ = 2.6, therefore there is no mesoporosity to contend with.

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| *Figure 3 Lower pressure plot of data by KJO, the QM*/*ESW fit and BET fit. The line through the data points is the QM*/*ESW fit. The curved line is the BET fit line*. | *A graph of a function  Description automatically generated**Figure 4 Low pressure plot of data by KJO, the QM*/*ESW fit and BET fit. The straight line is QM*/*ESW linear fit, the upper curved line is NLLS QM*/*ESW fit and the line at the bottom is the BET fit line.* |

*Figure 1* shows the overall fit which for the QM/ESW model is very good, but for the BET is very far off except for the range specified for the BET. The high pressure has always been discounted for the BET, although there is no theoretical reason other than it does not work. The low pressure was normally not measured partly due to instrument limitations, but also by tradition.

*Figure 2* expands the BET range and why it gives an indication of a straight line. The two vertical lines are the criteria, *X* = 0.01 and *X* = “Rouquerol criterion.” Perhaps by serendipity, the range is selected so that the negative deviation and positive deviation cancel somewhat. However, in this case, the deviation is 0.0604 mmol g-1 or 4.7 % FDR. Without the lower limit this increases to 15.5 % FDR. These deviations are for *n*a and not for the BET transformed ordinate, which is traditional since usually a linear regression is used on the transformed plot.

In *Figure 3* is another magnification for the BET range. It also shows more clearly how good the QM/ESW fit is.

In *Figure 4* is the very low-pressure data with the correction for heterogeneity. This normally shows up only in the High Vacuum (HV) or even Ultra HV (UHV) pressure range. The *Equation 5* is modified by the statistical “area” function, which normally has the symbol ***Z***and is the double integral of the normal distribution. Here there are no theoretical reason for the normal distribution, other than nature favors it. Arriving at the **Z** distribution takes a bit of explaining, which is provided in the textbook4. Notice at this point the BET equation predicts nearly no adsorption compared to the experimental data. This is why the BET transform fit “blows up” at low pressure.

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| **Table 1 C**omparison of the QM model and the BET parameters for KJO data. |
| **BET with lower limit (0.01):** | ***n*ads /mmol g-1:** | **0.265** |
|  | *A* /m2 g-2 (IUPAC) | 25.9 |
|  | **BET *C* /\* unitless** | **130.1** (-3.2 kJ mol)-1) |
|  | **Standard deviation of fit:** | **0.0604** |
|  | Deviation/full data range  | 4.7 % |
| **BET with no lower limit:** | ***n*ads /mmol g-1:** | **2.56** |
|  | *A* /m2 g-2 (IUPAC) | 25.1 |
|  | **BET *C* /\*unitless**  | **393** (3-9 kJ mol-1) |
|  | **Standard deviation of fit:** | **1.05** |
|  | Deviation/full data BET range  | 15.5 % |
| **QM output parameters** | ***n*ads /mmol g-1:** | **0.157** |
| **with *T* correction - no limits** | *A* /m2 g-2 (IUPAC) | 15.3 |
| **4 parameters** | **<μς> (heterogeneity)**  | **-2.6123** |
|  | *E*a /kJ mol-1 | -8.84 |
|  | **Std deviation fit /mmol g-1:** | **7.63 × 10-5** |
|  | Deviation/full TOTAL data range | 0.0059 % |
|  | **σ (heterogeneity)** | **0.2048** |
|  | **<Δ*Ē*a>** /kJ mol-1 | **0.64** |
|  | ***P*vap adsorptive /bar** | **1.0089** |
|  | **Δ*T***  | **≤+0.01 K** |
| **QM output parameters** | ***n*ads /mmol g-1:** | **0.156** |
| **without *T* correction and**  | *A* /m2 g-2 (IUPAC) | 15.2 |
| **no heterogeneity- no limits** | **μς = χς** | **-2.6115** |
| **2 parameters** | *E*a /kJ mol-1 | -8.92 |
|  | **Std deviation fit /mmol g-1:** | **9.12 × 10-4** |
|  | Deviation/full data range | 0.089 % |
| **Ratio of *n*BET/*n*QM** |  | 1.69 |

The output parameters for both the QM/ESW model and the BET model are given in **Table 1.**  The *C* in terms of units is problematic. However, it would officially be unitless.

**In Table I, values in bold type are output parameters from the calculation;** whereas values in non-bold are quantities derived from these parameters. The stated IUPAC convention is the conversion of *n*m to surface area, *A*. The conversion for nitrogen this is 0.162 nm2 molecule-1 or 9.77 × 104m2 mol-1.

The elimination of the temperature parameter for the QM/ESW calculations makes no significant difference in the output parameters. This is encouraging that a temperature difference of about 0.01 K at 78K makes little practical difference. It does, however, increase the standard deviation of the fit by nearly a factor of ~15.

*Conclusions concerning statistical comparison*

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 for 88 degrees of freedom. By any statistical test, this is off the charts. Also, a full isotherm is basically impossible for the BET.

Thus, in a practical application, there is no question that the BET yields poor information. Of course, it is within a factor of ±3 of the answer, but the old “B” point[[46]](#endnote-33) method was as good. 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 Δχ-plot and take the value at Δχ = 1. For accuracy measurements to *n*a = 0 to check for microporosity is needed.)

An anticipated accusation concerning this treatment is, “the Δχ-plot or χ-plot introduces a transform that distorts in the picture. This distortion probably favors the analysis of your proposed theory.” The argument is bogus since for the QM/ESW Δχ-plot or χ-plot there is *no transformation in the dependent variable*, and the calculated deviation is in the amount adsorbed and not the relative pressure. The BET line was performed using the IUPAC method convention and makes no difference how it is displayed, so long as the dependent is *n*a or *v*a data and not the transform.

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

**Part III The weak spot for BET – Henry’s Law applied to physisorption***:*

The presence of a threshold pressure is a *definitive*, not a statistical, disproof of BET and similar “Henry’s Law” theories. These “theories” include multiple additions of BET or Langmuir isotherms or using powers of these representations. Obviously, the addition of Langmuir isotherms cannot work past the inflection point since there is none. Some combination use multiple BET or Langmuirs and add to them functions that simulate the high-pressure data with some justification, but summation still predicts “Henry’s Law.” This approach is also disproved.

To detect the threshold pressure, the equipment normally needs to be capable of at least HV. (There are some rare exceptions.) Therefore, it is usually not routinely observed. Very often, the analysis starts after the first monolayer equivalent is already adsorbed. However, there are several laboratories that have HV or UHV systems. The following illustrate that it is possible to observe the threshold pressure.

*Example 2)* *Data by Silvestre-Alberto, Silvestre-Alberto, Llewellyn and Rodríguez-Reinoso:*

The data of N2 absorbed on microporous activated carbon (LMA233.) by Silvestre-Albero, Silvestre-Albero, Llewellyn, and Rodríguez-Reinoso[[47]](#endnote-34) (AALR) evidences the threshold pressure at 2 x 10-7 bar. In *Figure 5* is a graph of data obtain for the referred to AALR paper.

They also observed a threshold pressure for the adsorption of N2 absorbed on ordered mesoporous silica SBA-15 at ~2 x 10-6 bar and on activated carbon DD52 at ~6.5 x 10-6 bar.

Although the purpose of this paper was to warn researchers how to handle “dead space” gas out-gassing, as a side issue it clearly shows the threshold pressure in the HV range. (This publication is extremely important, for reasons other than the threshold pressure, and all researchers in the area should read it.)

The graph by AALR shows the isotherm as the log-law. This law is predicted from the QM model for adsorption that is physically restricted to one monolayer. (See *Equation 8* above.) Notice that the data points not the [*n*ads, X] = [0, 0], but to [0, ~2×10-7].

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| *Figure 5 Data by AALR on microporous carbon illustrating 1) effect of dead space gas and 2) clearly shows the threshold pressure. This uses the QM transform from Equation 8 indicating restriction to a monolayer. Used with permission from American Chemical Society.* |

*Example 3) The Nguyen and Du Data*.

The threshold pressure can be seen from the data by Nguyen and Du[[48]](#endnote-35), of argon adsorbed on microporous carbon. This is shown in *Figure 6* or directly in their figure 4. From the data one can obtain the monolayer coverage for the pores, the volume of the pores, the parameter *E*a and the external monolayer equivalence:

* *n*m = 8.25 ± 0.019 mmol g-1 (0.24 % FDR)
* χς = -2.7118 → *E*a = -9.76 kJ mol-1
* *n*pore = 6.91 ± .028 mmol g-1 (0.34 % FDR)
* *n*m,ext = 0.26 ± .0077 mmol g-1 (0.094 % FDR)

By the self-imposed criteria of σ < 1 % full range used for QM/ESW fits, these values of 0.24 % are relatively precise.

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| *Figure 6 Date by Nguyen and Du of nitrogen adsorbed on microporous carbon. The grey line in the log-law fit (1st layer) the black line in the Δχ plot is the external area line. The vertical line in the log-law plot is approximately where the external line fit. Used by permission from Elsevier Publishers.* |

In the graph on the left, there appears to be a very slight start of the 2nd layer, which does not form fully due to the lemma that the first layer must be complete even at the expense of an already forming 2nd layer if need be. This is referred to as cannibalization. However, in this case, there is not a long enough linear portion at the beginning of the Δχ plot to be certain of this conclusion. Never-the-less, the point of the threshold pressure is clearly demonstrated.

The next few examples are from work by the Oak Ridge DOE Analytical Divisions.

*Example 4) Thompson’s hydrogen cleaned diamond data*.

Data by Thompson[[49]](#endnote-36) 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 7*. 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.)

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| *Figure 7 Data by Thompson of argon adsorbed on hydrogen cleaned diamond powder. From open US DOE sources.* |

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There was a very short round-off and the start of the isotherm, but just because an isotherm has a low-pressure round-off is not disproof of the QM/ESW, contrary to some statements in the literature. 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 illustrated in *Figure 4*. Thus, a round-off is not disproof of the QM/ESW, but rather is a sensitive indication of heterogeneity. Some other QM/ESW prediction needs to be found that is incorrect to establish a disproof.

On the other hand, it only takes one verifiable threshold pressure observation to disprove the BET or any other isotherm that predicts “Henry’s law” as applied to physical adsorption.

A second Henry’s Law test

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 8*. 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*ads) = arbitrary, and (*X*, *n*ads) = (0,0).
3. The line will go through only two points (unless you happened to pick the tangential point, which is then one point) one of which is the selected point.

Below is a graph, *Figure 9*, of this technique.

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| *Figure 8 The test of Henry’s law for the data shown in figure 8, which is argon adsorbed on H2 cleaned diamond powder. The straight line is Henry’s law using the fourth point. The curved line is the BET fit to the overall data.* |

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 the 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[[50]](#endnote-37)[[51]](#footnote-14):*

When Thompson discovered that cleaning diamond 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/ESW equation for heterogeneity.

The data by Thompson for argon adsorbed on H2 cleaned 8571 alumina is shown in *Figure 9*.

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.

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| *Figure 9 Adsorption of Ar on H2 cleaned alumina. The pressure was dropped past the threshold pressure to make sure that zero was reached and there was no error with the balance system. The slight round-off is the referred to heterogeneity possibility* |

*Example 6) Alternate “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 is inclined to assume that the slope is the overall slope through this region. This is an optical illusion. Using the KJO data one can point-wise or piece wise differentiate to obtain an indication of the instantaneous slope. This is shown in *Figure 10.* The range of answers could be from ~4.8 to ~3.6, a range of ~30%. This is with extremely good data with an overall standard deviation of better than 0.0059 % of the full range of data in the χ-plot.

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|  | *Figure 10 The slope of the BET plot within the Rouquerol region. The ×s are two-point differentials, and the curved line is a three-point smoothing. The dashed line is the calculated slope using the BET. KJO data was used as a model.* |  |

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

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 4, 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.

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.

**Part IV 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[[52]](#footnote-15). The *E*a from QM/ESW has the meaning of the starting adsorption energy as defined by *Equation 6.* Thus, *E̅*adoes have a physical meaning, it is the pre-exponential constant for the **Δ**la**E̅** 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*ads(1-*X*)]} 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(BET)/ *n*m(QM/ESW). The equations used are (*x* on abscissa and *y* on the ordinate) are *Equation 9.*

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| 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 is specified. However the traditional *X* ≥ 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 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, which does not correct for external surface.

*How to read the tables:*

In **all tables**, the 1st and 2nd columns are χς and *E̅*a/kJ mol-1. The 3rd is the ratio of *n*m(BET)**:** *n*m(χ). Since χς 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 =* 0.01to 0.05 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 being useable.

for **Table III** and **Table IV** in the 5th column is the limit for the “Rouquerol” rule, the 6th column is the standard deviation of the BET versus the QM/ESW only over the range specified, the 7th column is the standard deviation of the BET versus QM/ESW divided by the data range as specified by being useable.

*Conversion: - the Rouquerol convention*.

The “new” criteria are by Rouquerol, et al.27, that is, the range is below the maximum value for *n*ads(1-*P*/*P*vap .) There is no lower range specified for this, but obviously it will start to break down at pressures below *P*/*P*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 yield Henry’s law, so the threshold pressure is not included.

An interesting question is, “How did Sing figure out that *X* ≥ 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*vap < 0.35. (χ is full range.) |
| χς | *-Ē*a /kJ mol-1 | *n*m(BET)/ *n*m(χ) | *C* | σ of fit | σ/full data range |
| -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 χς = -1.527… the analysis breaks down. |
| ‡These are approximately the stated range of validity by Sing. |

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| **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 |
| χς  | *-* *Ē*a /kJ mol-1*T=77.35 K* | *n*m(BET).  *n*m(χ) | *C* | σ of BET | *P*max/*P*vap | σ of BET% of range | *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 |
| \*\*χς is above the *X* = 0.01, which creates a conflict with Henry’s Law. |

As can be seen from **Table III**, the results are, in the main, much better and there is no negative “*C*” values. At lower energies, which is χς  < -1.53, this new criterion begins to break down. Above -1.572… 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 Buttersack[[53]](#endnote-38) 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.

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| **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*vap = 0.01 or *P = P*ς., whichever is greater. |
| χς  | *-* *Ē*a /kJ mol-1*T=77.35 K* | *n*m(BET).  *n*m(χ) | *C* | σ of BET | *P*max/*P*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*ς |

**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*{**max** (0.01, χς)} ≤ *X* ≤ *X* {(**max** [*n* {1- *X*}]}. 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 transform 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 χς instead *X* = 0.01.

The ratio of the *n*m(BET)**:** *n*m(χ) is nearly linear with *r*2 = 0.9997 between χ = -4.0 and -2.0 It then transitions to another linear portion from about χ = -1.5 to -0.6. Comparing T**ables III and IV** the *n*m(BET)**:** *n*m(χ) 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 paper, which was to demonstrate under certain conditions that the information needed from the BET can be recovered with 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 excess for the final equations. However, a thorough understanding requires a paradigm shift in thinking once one gets deeper involved.

For the non-porous, homogeneous isotherm the BET calculation usually has a very high standard deviation in the comparison of the calculation versus the actual *n*a. This is assuming the discard of ⅔ 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. I

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*, 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. Neither the BET nor the χ-plot can are valid for this, only the QM *Equation 8* 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 how the mesopore range lies on the χ-plot. Mesoporosity is expected at χ values above 0 where the energy of adsorption has drop below the energy of capillarity. Thus, assuming χς ≤ ~−2 where there is enough volume of adsorbate to start forming “layer” 3. 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 a 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. There is no scientific basis for the prohibition and there have been multiple observations of this phenomenon. Whatever the reasons were behind this declaration, they are outside of scientific logic. Polanyi discussed this rigid point of view in his last article in Science[[54]](#endnote-39)[[55]](#footnote-16). This article should be read by all who are tempted to block information contained in this publication[[56]](#footnote-17). A person who claims to be a scientist, or even an engineer, is required to keep an open mind.

The problems with the BET calculation 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
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 project[[57]](#endnote-40). 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[[58]](#footnote-18) (or σ = 24% to 57%), but application also varied. The BETSI program which attempts to optimizes the individual data sets with *point selection* (?) is more consistent from 0.01% to ~8 % (or σ = 1% to 28%.) (For comparison, acceptable deviation for the QM/ESW acceptability is σ < 1%. of the full range of all data.)

The rationale for the BETSI considers two reasons 1) the “Rouquerol” criteria are indeterminate and 2) They are too cumbersome to use. (The use in this present report disputes the latter claim. The reaction to the first reason is, “What?”[[59]](#footnote-19) Did they observe the threshold pressure and not report it? Indeed, perhaps creating a low-pressure limit could resolve their reproducibility problem.) This report reputes both arguments, unless the material is microporous, in which case the BET is invalid anyway. It also cannot usually be used for mesoporosity since to total surface is not available with the onset of mesoporosity, usually a little above χ = 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 the quality control to the level of zero certainty.

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

*The question of nm 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**ga function and perhaps other considerations. However, this step is probably more for psychological reasons, not for scientific reasons.

*General Recommendations*

What is the recommendation from present investigation? It is not to switch from the BET to the QM/ESW method, today. 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:

* 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 the 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 Langmuir[[60]](#endnote-41).

**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 “warrants more assertion[[61]](#footnote-20)”. 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 have been performed to support the QM/ESW approach. The is enough 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 the 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. It would be best, if possible, to repeat the experiment and report the data. Given today’s uncertainty, it would be best to report the data and not just the parametric output, to ensure lasting value.

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[[62]](#footnote-21) program called BETSI to set in concrete something which cannot be so solidified without any solid theoretical backing[[63]](#footnote-22). 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. See the slopes for *Figure 1* through *4* to get a feel for the reason.

There is a second problem, which is common to both the 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 ±20% difference.

However, for all adsorbate molecules the question from QM/ESW is, “What distortions are in play with fields that go as high at 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.

**Acknowledgements:**

I would like to thank Dr. Jürgen Adolphs for his consultation and acknowledge his continued work in improving the ESW.

Several researchers have kindly supplied me with data, without which I would have had nothing to compare the theoretical aspects with. This is because I have not had, after developing the equipment, the instruments in my control to make the measurements. For this help I am thankful.

**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, Δχ. However, subscripted θs, Example θ2, θ3, ... are the areal densities with subscripts indicating the “layer.”

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, Σ*Atotal =* 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

**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

**E**(θ) or **E**(*n*a) or Δla**E**(θ)= 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

**E**aϴ = Δla**E**(θ) + ε,

*E*n, n = 1. 2.... = base energy after adsorption of the 1.,2. ... n. molecule

*ħ* (*h* bar) = the reduced Plank’s constant = *h/*2π

*h* = the Plank’s constant = 6.62607015×10−34 J⋅Hz−1

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

**G =** the normal distribution

**Ĥ** = 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,↓ = 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*vap(*T*) = The vapor pressure of the adsorptive at temperature *T*.

*Pς* = threshold pressure

*̃* = fugacity

*r =* pore radius

*R* = the gas constant

*r*core *=* (*h* – *t*) the “core” radius

*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 absorptive

*T*c = the critical temperature of absorptive

*T*MP = The melting point temperature of absorptive

U = Unit step function.

*͞*$\overbar{V}$ *=* molar volume

*X = P/P*vap the "relative pressure"

**Z** = the statistical area function. *Equation 66*

*Starting with a Greek letter*

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

βD = the Dubinin, et al., scaling factor

γ = Surface tension of the adsorbate

ΔlaS = the entropy of adsorption with standard state of the liquid state at the *T* of the adsorbent

Δ*l*aμ = change in chemical potential from liquid phase at adsorbent *T* to the adsorbate.

Δχ = χ-χς

Δχp = the position on the Δχ-plot where the peak for σp is.

Δχ-plot = a plot of *n*ads versus χ-χς

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

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

θ1 = or relative areal density of “layer” 1 compared to *n*m = 1

θMT = classically the area not covered by θ. In QM: = 1 – θ1

θn = or relative areal density of “layer” n compared to *n*m = 1

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

λ*Z =* the canonical partition function of absorptive

μ = chemical potential (molar quantity)

μa = 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

Π(*t*) = Excess Surface Work – a function of adsorbate “thickness.”

σ = the spread of values of multiple χςs

σfit = the standard deviation of *n*a calculated values versus *n*a experimental values.

χ = -ln(-ln(*P*/*P*vap))

χ*ς* = the threshold χ = -ln(-ln(*P*ς/*P*vap))

<χς> = the mean of the addition of several manifolds of χ-plots and their χςs

χ-1 = the inverse chi function = exp(-exp(-(x-μ)/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

σp = the normal distribution spread of the pore dimensions

χp = the position on the χ-plot where the peak for σp 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*:

 ͞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 - 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 0.01 |

|  |
| --- |
| **“Rouquerol” criteria** |
| The Rouquerol transform *n*ads (1-*P*/*P*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/(√*C* + 1) ≈ *P*/*P*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 Polanyi[[64]](#endnote-42) where almost all isotherms start near or after this. (See reference 4 pages 109 301 - 304.)

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

# **Appendix III - What did Arthur Adamson write?**

I believe it is worth-while to look at the progression of physical adsorption through the eyes of one of the premier investigators, Professor Arthur Anderson. I was at the American Chemical Society (ACS) meeting when Professor Arthur Anderson made a very strong case against how closed minded the members of the Surface and Colloids Division had become with respect to physical adsorption. Although the QM hypothesis was in the literature, it was not an acceptable hypothesis to anyone except for two people, Loren Fuller and James Condon. I doubt that Professor Anderson was aware of the development but had plenty of evidence that the empirical equation associated with “polarization theory” was superior to all other formulations. Looking into his books, it is hard not to come to the following conclusions about “polarization theory,” today QM/ESW.

Arthur Adamson[[65]](#endnote-43) left open the judgement about the BET versus other descriptions of the adsorption isotherm. However, he did make direct comparisons between the following descriptions apparently based on the data fit at the time. These were:

1. The BET over the relative pressure range of *X* = 0.05 to 0.30
2. The Harkin-Jura over the relative pressure range of *X* = 0.2 to 0.5
3. The potential theory over the relative pressure range of *X* = 0.003 to 0.93
4. The polarization theory over the relative pressure range of *X* = 0.25 to 0.93

The polarization theory, although the energies and amounts are incorrect, is functionally identical in the final equation to the QM/ESW equation for the multiple layers. The potential theory is similar, but the log term is raised to a fractional power, in the case here it is to ½ power.

Adamson’s strongest argument is the comparison of each using the same adsorbent but differing gases to check consistency between the adsorbate answer. The results provided in terms of variation for three adsorbents were as follows:

|  |
| --- |
| Variations for each contenting theory to decide the most reliable |
| adsorbent | BET | Harkin-Jura | potential theory | polarization theory |
| egg albumin | 15 % | 12 % | 2 % | 6 % |
| TiO2/KCl | 10 % | 13 % | 1 % | 0 % |
| SiC/Sterling C | 4% | 11 % | 7 % | 4 % |

Overall, the potential theory and polarization theory were equal in their reproducibility and superior to the BET and Harkin-Jura. Professor Adamson did not write so but given the limited range and poor reproducibility of the BET compared to the potential/polarization equation it would normally be no contest.

However, his conclusion was that, despite the poor performance of the BET that researchers prefer it since the area of the surface is specifically given a value based on some simple assumptions. These are the sites of adsorption are spaced in a close packed arrangement, and the area taken up by a molecule is that which is expected from the liquid density of the adsorptive. This is a psychological advantage for the BET even if it is incorrect, and even if more than 2/3 of the data must be ignored. Despite these problems, he did not provide a conclusion. He wrote in the first edition:

“There is thus little to choose from between the various models, but partly because of tradition and familiarity and partly because *v*m enters in it so explicitly, the BET equation is in fact almost exclusively used.”

Later 5th edition:

Thus, a plot of log(log(*P*o/*P*))versus *n* should give a straight line, and indeed Eq. XVI-92 is quite successful. The polarization theory was severely criticized by Brunauer on the grounds the effect was not large enough and the theory has been largely ignored.

[However,] returning to multilayer adsorption, the potential model [**lnln** model] appears to be fundamentally correct.

He then dismisses all theories that have energies that are dependent not only on the adsorbate but also upon the adsorbent. This was based on the belief that all *t*-plots are the same regardless of adsorbent, which is incorrect. There is no experiment nor theoretical reason for that to be true. There is a great difference between the starting energy on a silica sample and a Teflon®[[66]](#footnote-23) sample. It also makes no sense from a chemical standpoint. Theoretically, however, since the ln(ln(*P*o/*P*)) is a straight line then at *t*-plots are identical except for an abscissa translation that might be difficult to detect if data begins at *X =* 0.01 and any *n*a offset is ignored.

He does not mention Einstein’s attack at the Berlin Conference, which probably carried more weight. The Brunauer criticism essentially dismissed any serious discussion of physical intermolecular attractions on the basis that they are too weak. Although the BET assumes that some of the surface initially either remains free of adsorbate or the attractions are chemical bonds. Since the energies can be quite high, Brunauer came down on the side of chemical bonding, eliminating a phase transition from the first layer, thus his response to Fuller3 that the phase transition is at *P*o, a response that is thermodynamically unsatisfying.

One of the items that Professor Adamson surely knew, since there seems to be qualification to this, the percentage of error should be taken from the plot of the calculated values of the moles absorbed versus the real values. Normally, what is reported is the linear regression of the BET transform. Such a calculation of standard deviation yielded values is not only meaningless but deceptive, after all one would think that a plot of *X×*(a content) versus *X* would be very good since the denominator has counter-weighting terms yielding a nearly linear value. (Indeed, the Rouquerol criterion nearly requires this to be the case.) A rework of the data that he uses by Keeton and Holmes[[67]](#endnote-44) illustrates this. In the *Table 1* below, this data is reworked to yield the BET answer and the quantum mechanical (QM) answer. In *Table 1* the range all the data points were used for the QM calculation, whereas only the points in the range *P/P*vap = the lowest recorded (there were none below 0.01) to the highest recorded but not greater than 0.35 were used for the BET. Outside this range, the BET fit was extremely bad.

Table 1 Rework of the Keeton and Holmes data of N2, Ar, and O2 on KCl powder at different temperatures. Data is available from the original publication.

|  |  |  |  |
| --- | --- | --- | --- |
| Isotherm | Nitrogen | Argon | Oxygen |
| /K | 78 | 84 | 84 | 85 | 90 | 83 | 85 | 90 | 85 | 90 |
| QM real | 0.55% | 0.56% | 0.54% | 0.46% | 0.58% | 1.8% | 2.0% | 1.5% | 1.9% | 1.8% |
| transform | 0.89% | 0.78% | 0.49% | 0.64% | 0.80% | 1.7% | 0.40% | 0.31% | 0.48% | 0.42% |
| BET real | 86% | 68% | 37% | 36% | 40% | 13% | 16% | 22% | 10% | 16% |

Notice that the transform fit seems to be very good for the BET. Indeed, it is competitive with the QM calculation. However, when the answers for nm and the BET constant, C, are used to calculate the fit to the real data, *n*a the standard deviation is very high. In some case the deviation increases by a factor of nearly 100. Below are two graphs, one for the BET transform and another to calculate the fit to real data. This example uses the data from the Nitrogen 78 K physically adsorbed on KCl. Similar results were obtained for the other data sets.

|  |  |
| --- | --- |
| A graph of a positive curve  Description automatically generated with medium confidence | A graph with a line and numbers  Description automatically generated with medium confidence |
| Figure 1 Data points from Keenen and Holmes of nitrogen on KCl at 78 K. The Xs are data points, and the line is the calculation from the BET equation. On the left is the BET transform and on the left is the real physical quantities plotted using the parameters from the transform. This illustrates that a regression analysis of the BET transform plot is unlikely to yield a good fit to real isotherm plot. The upturn in the calculation at the beginning of the fit going to ∞.  |

**Conclusion:**

The method of using the BET transform method is a poor technique and can lead to deceiving results. It is convenient but mathematically incorrect. The mathematical treatment is especially egregious since the transform dependent variable is a function of the isotherm dependent and independent variables. The best technique is to use a non-linear least squares routine to fit the original isotherm. Alternatively, one may transform the abscissa so long as it remains a function of pressure.

There were two reasons that Prof. Arthur Adamson did not back the polarization theory more vigorously. These are mentioned in his quote above. Firstly, the value of *v*m is explicit in the theory. There was much doubt about that at the time. The assumption that was made is the value of the calculated *v*m was indeed connected to the surface through the liquid density. Thus, although to avoid other problems, it was assumed that the adsorbate did not act like the liquid and Brunauer said the phase change was a *P*vap.

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email: Physisorption@genchem.net [↑](#footnote-ref-1)
2. Professor Emeritus from Tennessee Regents’ College and University System.

email: Physisorption@gencem.net [↑](#footnote-ref-2)
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5. Personal conversation between S. Brunauer and E. L. Fuller, Jr. at the request of J. B. Condon. [↑](#endnote-ref-3)
6. This portion of discussion to the very heart of the definition of science that has firmed up in the 20th century. [↑](#footnote-ref-3)
7. Investigators should not leave reasoning and logic of physics behind a let statistics dictate decisions. For example, correlation is not the same as cause. [↑](#footnote-ref-4)
8. 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. [↑](#footnote-ref-5)
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35. To keep from being accused of bias by presenting data that I generated, I have used other investigators data, open in the literature where possible, to make points. For the “Henry’s Law” section there are difficulties propagated by a (temporary) IUPAC decision effectively banning any publication mentioning the threshold pressure. Thus, in the open literature, there are publications that show the threshold pressure, but is not mentioned. However, many examples were observed by Dr. Fuller’s group in the Oak Ridge DOE Analytical Laboratory. I was also employed by the Oak Ridge labs, under a totally a different vice president and had no control over the experiments. I did not work in these groups, nor did I supervise any employees of either Fuller’s, Thompson’s or anyone else’s who worked in the Analytical Labs. I was the instrument developer and worked in the area of corrosion. Once an instrument was developed and tested, it was transferred to the Analytical Laboratories, and I no longer had any control what-so-ever over the operation of the instrument. [↑](#footnote-ref-8)
36. 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”. [↑](#footnote-ref-9)
37. The calorimetric heat of adsorption requires addition of the heat of vaporization due to shift from standard state of the liquid adsorptive to the gas phase at 1 bar. [↑](#footnote-ref-10)
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44. In communication with Micromeritics, this uniform temperature between the sample hang-down and the comparison tube was accomplished by wrapping the tubes together in copper foil. This was a clever solution, but there is still radiative heating from above the tubes. This also would have a simple solution. However, if the sample and the simulated sample have about the same color, it may be OK. It would be great if someone would make a study of this. [↑](#footnote-ref-12)
45. A question is, “How does one compare the std dev. of one isotherm fit to another since the amount adsorbed might be different. The way this has been done is to divide each by the full range of the data and express it as a percent.

This FDR may not be a perfect way, but its approximate and one can designate what a good fit is using this value. A FDR < 1% seems to separate isotherms with high data scatter and low. It also divides good versus bad hypotheses [↑](#footnote-ref-13)
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51. (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.) [↑](#footnote-ref-14)
52. 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. [↑](#footnote-ref-15)
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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. [↑](#footnote-ref-16)
56. This has been happening periodically for the last 40 years. [↑](#footnote-ref-17)
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58. 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? [↑](#footnote-ref-18)
59. 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.) [↑](#footnote-ref-19)
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61. John Dewey’s phrase for closer to truth. [↑](#footnote-ref-20)
62. 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. [↑](#footnote-ref-21)
63. 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?” [↑](#footnote-ref-22)
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