

Title:

**Part II: Quantum Mechanics and Physisorption
BET vs QM plus heterogeneity**

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Part II: Quantum Mechanics and Physisorption BET vs QM plus heterogeneity

Abstract:

In this Part II the essence of part I, the proof of the “Henry’ law” isotherm, of which the BET belongs is shortly restated and additional evident is provided for the disproof.

This disproof and other phenomena are dependent upon very carefully performed experiments. What follows first is a list of the “**Big Errors**” and how to solve them. One must assume, when reading a report, that these errors are not prevented, and some features of the isotherm are distorted. For example, the first “**Big Error**” is not using at least a high vacuum system (HV) or, preferably, and ultra high vacuum system (UHV.) With low vacuum systems the threshold phenomenon is not observable, and the entire interpretation of the data could be wrong.

After the listing of the “**Big Errors**” the equation for the multilayer adsorption is presented and one modification, heterogeneity, is derived and used. This latter modification requires no knowledge of quantum mechanics (QM) and the QM derivation is put off to Part IV. The modifications for microporosity and mesoporosity are presented in subsequent parts.

An effect that has caused some confusion in isotherm analysis is presented early in this series. The effect is heterogeneity, that is where surface aliquots have differing low pressure starting energies of adsorption. This creates an early “artifact,” which could mislead a classical thinking researcher, but is quite normal in the QM calculation.

Introduction:

In Part I, it was demonstrated that all “Henry’s law” hypotheses as applied to physisorption* Henry’s law isotherms, which includes the BET, are proven here invalid. One characteristic of Henry’s law isotherms is that they are localized isotherm theories, that is they assume adsorption upon “sites,” and derive their origins from the Langmuir isotherm. In other words, they are attached to definite location, at least momentarily and chemical equilibrium, which uses only ratios is the basis for the derivation. The ratios reflect the bonding theory of adsorbent with adsorbate molecules and adsorbate with other adsorbate molecules. Under these postulate conditions, the adsorption must have a Henry’s law isotherm, and the isotherm must extend at low pressure to $P = 0$ and $n_a = 0$. For many experiments due to their pressure limitations, it is not possible to test the veracity of this rule. However, with the right equipment if one goes to low enough pressure, the amount adsorbed becomes zero at a finite pressure for many isotherms. If any isotherm for which $\theta \rightarrow 0$ when $P > 0$ contradicts Equation 2 in Part I, and it therefore unequivocally disproves Henry’s law hypothesis for physisorption.

Another major class of isotherms is the Dubinin class, which includes several, but all predict that the isotherm extrapolates to $[P, \theta] = [0, 0]$. The Freundlich isotherms also pass through $[P, \theta] = [0, 0]$. Thus, the Dubinin, et al., class and the Freundlich isotherms are also invalid.

* The wording “as applied to physisorption” should be understood as the default meaning of “Henry’s law,” since that is all that is being considered here, and not solution chemistry from which the phase came.

These hypotheses include the BET, the Langmuir, any linear combination or power weighted combination of these. Of course, one experiment could be claimed to be incorrect, false, faked, etc., so there must be multiple demonstrations of disproof, for which there are many. One detection problem is **Error 1** below, which makes the researcher blind to the disproof.

At this point, a look at experimental problems, which should be a serious concern for all researchers. Without attention to these details, it is highly likely that an experiment is invalid, and the conclusions could be misleading or simply false. So, a review of a list of errors is now in order in preparation for continued presentation of the modern hypotheses of physical adsorption.

Following the section on Errors some discussion will be presented on the QM fitting of a very well controlled isotherm created to be an IUPAC with a comparison to the BET provided.

Experimental Precautions – Conclusions are Only as Good as the Observations

It may seem strange that this section is included in a series that is mostly theoretical. However, theory must always come from the observations that scientists make and if the observations are faulty, it is likely the hypotheses formed will also be flawed. Sadly, this is what has happened in the field of physisorption. All the following errors have contributed to false assumptions and conclusions, but the one that is most problematic is **Error 1**.

It is extremely important to have good equipment and good technique when measuring the isotherm. one should not overlook this section. Measurement of the isotherm is the primary measurement made for physical adsorption and the easiest. The problem is that it may be too easy, and the pitfalls are ignored. Furthermore, there are two primary methods to measure the isotherm, either gravimetrically or volumetrically. A well-designed gravimetric system is less prone to error, but it is generally more expensive. The volumetric system on the other hand is usually more affordable but highly error-prone, some of the errors are built in. The first two common errors essentially yields useless data, although there may be ways to recover from disaster. The other errors can have similar disastrous results, but these are less common.

Error 1 vacuum requirements

Error 1 is using a system that does not pump down at least to the high vacuum, HV, and preferably into the ultrahigh vacuum, UHV. This has been thought of as unnecessary since originally the BET analysis ignored all data below an $X := P/P_{\text{vap}} = 0.01$, even if it existed*. (This perhaps may be because the isotherm starts to deviate from the expected trend^{1,2,3}.) In some of the older literature, the isotherm begins after a monolayer equivalence is already present. Furthermore, without these vacuum capabilities there is little assurance that the surfaces of the

* Interesting fact: the work for NASA for the Apollo moon specified the range of adsorptive pressures that the isotherm measurements on lunar soil. The researcher were require to present all data they had and the threshold pressure was detected, so the were several data points at $n_a = 0$. This was work by Fuller, et al., and is available in a US DOE- NASA government report: E. L. Fuller, Jr., F.A. Agron, "The reactions of atmospheric vapor with lunar soils," US Department of Energy Report DOE ORNL-5129 (UC-346), Department of Energy, Oak Ridge, TN (1976).

adsorbent are contaminant free. Capability does not seem to be the reason for the lack of attention, since the ability to obtain and measure these low pressures was available. At any rate, one seldom sees isotherm data below this limit until recently.

Why is this important? You will shortly learn the value of the quantity E_a , around which the entire calculation centers, is usually found in the HV or UHV range. Furthermore, the log-law, an important sub-law found in QM, is difficult to detect above $X = 0.01$. The log-law is also needed to determine if there is microporosity (as defined later) since it is more obvious with HV or UHV systems.

Another reason mentioned in the article by Silvestre-Albero, Silvestre-Albero, Llewellyn, and Rodríguez-Reinoso⁴ (SSLR) is that outgassing of the sample in HV appears to be a requirement for some adsorbent-adsorbate combinations. For volumetric systems, which require a deadspace calibrating gas, it is best to have a good vacuum system to reach these levels, HV or UHV.

Error 2 temperature control and measurement:

Error 2 is poor measurement and control of the adsorbent temperature and the adsorptive gas immediately over it. This is a very common error, especially with inexpensive volumetric systems. The solution that is commonly advertised is the dual hang-down tubes. This is better but not as good as it could be. The reasons for this are:

There is usually radiative heating problems, especially for a cryogenic bath. Even though the sides of the cooling chamber are well above the sample, there is room temperature radiation from above. Shielding using metal foils will help, but usually, unless there are bends in the tubes, there could still be some heat gain.

If the adsorbent is a dark color or black this radiative heating problem would be worse.

It is insufficient to assume that a cryogenic bath is at a constant temperature*. The temperature of the bath is dependent upon the atmospheric pressure and not taking this into account, which the dual tubes should do, the answer can be wildly wrong.

Even if attempts are made to measure the temperature for the isotherm, it may vary with time. This is especially true with cryogenic cooling since the atmospheric pressure changes also change the bath temperature. Keeping track using a liquid-gas thermometer reading is advised for a post experiment correction†.

The temperature effect has not been fully researched. However, it was recognized as a problem early in the work by deBoer and Zwikker⁵, but since they were in general “discredited,” almost no one paid attention to this publication (until recently.) Given little guidelines, it is best to play it safe and do everything possible to control and correctly measure P/P_{vap} . The control and measurement of the temperature to 0.01K is minimal for a liquid nitrogen temperature. If a liquid cryostat is being used, selection of a nice steady weather day to get data is advised. Also, keeping an eye on the barometer and recording the uncorrected atmospheric pressure. This is another quality control. Uncorrected changes in P_{vap} causes a wavy χ -plot

* Some system use modern cryo-freezers. There is still a need for good control to cool (or heat) the sample and precise temperature measurement and good heat shielding.

† Keeping track allows modification of the value of P_{vap} . Although this is strictly mathematical incorrect, but for small changes in P_{vap} it is a practical and valid method.

If temperature control can be maintained but with questions about the actual pressure, then one can use an extra parameter to find the P_{vap} value. That was the technique that deBoer and Zwikker used. However, it is best to use a liquid-gas thermometer in good contact or close to the adsorbent.

Error 3 Knudsen Effect:

Error 3 is a problem for the low end of the HV pressures. This is the point where liquid nitrogen temperature measurements have a problem with the Knudsen effect. This is very hard to handle with a volumetric system where the tube size cannot be arbitrary of the sample size. One would have to use adsorbent sample sizes of kilograms instead of typically milligrams. Langmuir⁶ solved this problem by calibrating each individual hang-down tube. Characteristic of this error is the occurrence of a “double dogleg^{*}” at the lowest pressures. For the best information on this problem see the Vacuum Technology book by Roth⁷. With gravimetric systems the hang-down tube diameter and length can be increased to eliminate the problem.

Error 4 Attention to residual dead space gas or buoyancy gas:

Error 4 is residual dead space/buoyancy probe gas in the sample. This is especially bad with porous samples. It appears to be a common cause of hysteresis, but not the only one. An excellent paper on this subject is the one by SSLR. In this publication they emphasize the importance of

either a high temperature outgas of the dead space gas or
doing the dead space calibration last or

repeating the isotherm measurement two times. (For proper analytical analysis, by convention a measurement should be repeated thrice and if one of the three measurements disagrees, one continues to repeat more times for reproducibility or attempt to resolve the problem and correct it.)

The SSLR publication is very important for several reasons and reading it is advised.

Error 5 kinetics:

Error 5 is kinetic problems.: This problem varies with the sample – porous versus nonporous, tightly packed versus loosely packed and other factors. Most instruments are automatic, but the researcher should not go automatic. Set the wait time for different settings and see if it makes a difference. The length of time to settle “enough” depends upon where in the isotherm the measurement is being made, so keep track of this phenomenon throughout the measurement to get an indication of the wait time versus pressure. The criteria based on the exponential advance to a constant pressure used in some instrument might yield more consistent results, but multiple

* A relatively sharp bend in an initially straight line to the right/left followed by a sharp turn to the left/right ending up in a parallel straight section.

runs using different decay constants for a particular adsorbate-adsorbent pair is advised. This will give an indication of how long one should wait.

Speculated Error Gravitation:

There is speculation in the literature that gravity can cause significant errors. For example, gravity by having placed small spaces between particles can lead to the false indication of large pores or it may cause an error by excluding areas of the particles that are touching. These are referred to bed porosity and surface exclusion. Even though many publications speculate that these effects exist, there has not been much work on this question. It has been assumed that the energy of adsorption exceeds the energy of gravitational force, and no surface is excluded. This is an unsettled question and maybe NASA could help with these questions.

Fluidized beds are the norm in industry to overcome this last problem.

Gravimetric versus volumetric:

Most of the above problems are much worse with volumetric systems than they are with gravimetric systems. For example, temperature control and measurement, Knudsen problem, UHV use, are easily handled in a gravimetric system.

For gravimetric, the biggest experimental problem is ground noise, especially small earthquakes. Ground noise is a problem of location and to minimize this, a firm concrete slab foundation and sturdy well-anchored metal (machine) table can handle it. Avoid close truck noise - that is, if possible, find a nice quiet side street to avoid the annoyance. Earthquakes can happen almost anywhere on earth, but it is not usually a big problem. It may require redoing an isotherm because of an isolated quake. If there is a big one strong enough to damage the system, it would probably damage a volumetric system as well. Nearby blasting could also be a problem, but one may be able to arrange to know when the blasts occurs and schedule accordingly.

The derived equations for QM explaining physisorption.

So far it must be that quantum mechanics predicts that there is a threshold pressure and violates “Henry’s Law” for physisorption. This further implies a phase change due to the observation of the Dubinin “Thermodynamic criterion,” which indicates that the entropy of adsorption from the liquid state to the adsorbed state is close to zero. This is the phase change to the liquid state must be at the threshold pressure. Thus, there is no requirement for a “break,” according to Guillet-Nicolas, Wainer, Marcoux, Thommes and Kleitz⁸, in the isotherm at higher pressure. However, such a break will be seen for mesoporosity where these “simple conditions” of no porosity are not met*.

The equations for the QM hypotheses are given here without derivation (available in Part IV.)

The solution for θ as a function of pressure is:

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

Where if $\theta = 0$ then:

$$\ln \left(-\frac{\bar{E}_a}{RT} \right) = \ln \left\{ -\ln \left(\frac{P_\zeta}{P_{\text{vap}}} \right) \right\} \quad \text{Equation 2}$$

Then:

$$\theta = -\ln \left\{ -\ln \left(\frac{P}{P_{\text{vap}}} \right) \right\} + \ln \left\{ -\ln \left(\frac{P_\zeta}{P_{\text{vap}}} \right) \right\} \quad \text{Equation 3}$$

It is convenient to write this in a short form with the substitutions:

$$\chi = -\ln \left\{ -\ln \left(\frac{P}{P_{\text{vap}}} \right) \right\}, \quad \chi_\zeta = -\ln \left\{ -\ln \left(\frac{P_\zeta}{P_{\text{vap}}} \right) \right\} \quad \text{Equation 4}$$

Interpretation of χ and $\Delta\chi$ from the derivation-

So that the linearly transformed equation is obtained:

$$\theta = \Delta\chi \quad \text{where} \quad \Delta\chi := \chi - \chi_\zeta \quad \text{Equation 5}$$

Both the plot of amount versus χ and $\Delta\chi$ present meaningful and easy interpretation of the data. The $\Delta\chi$ plot is a plot of the amount adsorbed versus the monolayer equivalence, whereas the χ plot yields the energy function, $\Delta_1^a \mathbf{E}(n_a)$, the system internal energy change with adsorption from the liquid state to the adsorbed state at the temperature of the adsorbent.

* Whether this liquid phase is only in patches or is less dense microscopically than the bulk liquid cannot be determined from this derivation. (Indeed, quantum mechanics implies one cannot distinguish either between molecules or position. Only when the molecules are “frozen” due to the disturbance of an observation, will there be a distinction.) Regardless of details, it is obvious that macroscopically the areal density is less than the bulk liquid. This is an interesting question that needs more research.

$$1) \Delta_l^a \bar{E} = -RT \exp(-\chi) \quad \text{or:} \quad 2) \Delta_l^a \bar{E} = -RT \ln(P/P_{\text{vap}}) \quad \text{Equation 6}$$

(The line “ $\bar{\text{—}}$ ” is the alternative IUPAC embellishment symbol for “molar.”) Thus, we arrive at the empirically supported isotherms by Polanyi-London^{5,9,10,11,12}, by DeBoer and Zwikker^{5,13}, and by Fuller^{14,15,16,17,18,19,20,21}.

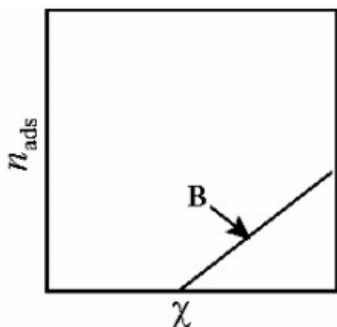
Equation 7

Heterogeneity – The First Added Feature.

Heterogeneity is an easy modification to account for by using the χ equations. Graphically, the abscissa, χ , is a function of pressure only, and the ordinate is a function of the amount adsorbed only. Thus, if there are two energy plains, their χ -plots simply add*. It is not rare to have two energies or type of plots to be represented in the same sample. For example, one could have a sample that has large external surface area, and the porosity is “microporous,” which follows the log-law. Although this sounds complicated, one simply determines the log-law fit for the “microporous” part and use the χ -plot for the external area and add n_a s which have common energies. This combination is optimized with a non-linear least squares routine (NLLS.) Such a fit will be illustrated later, but first some mathematical logic.

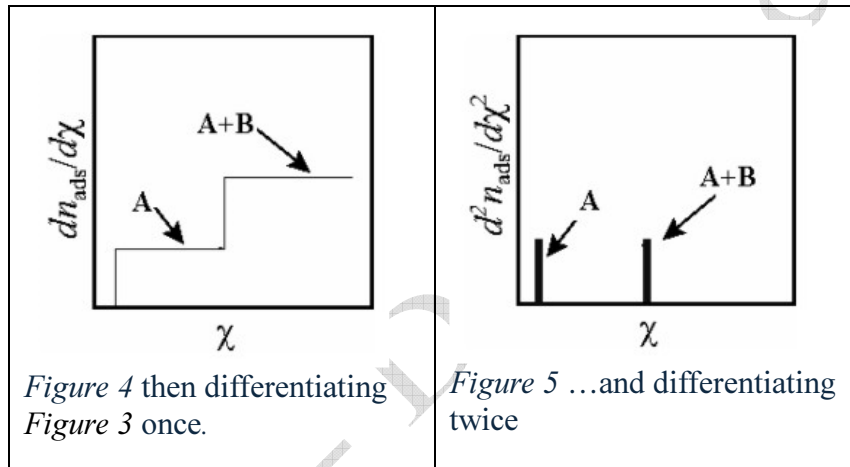
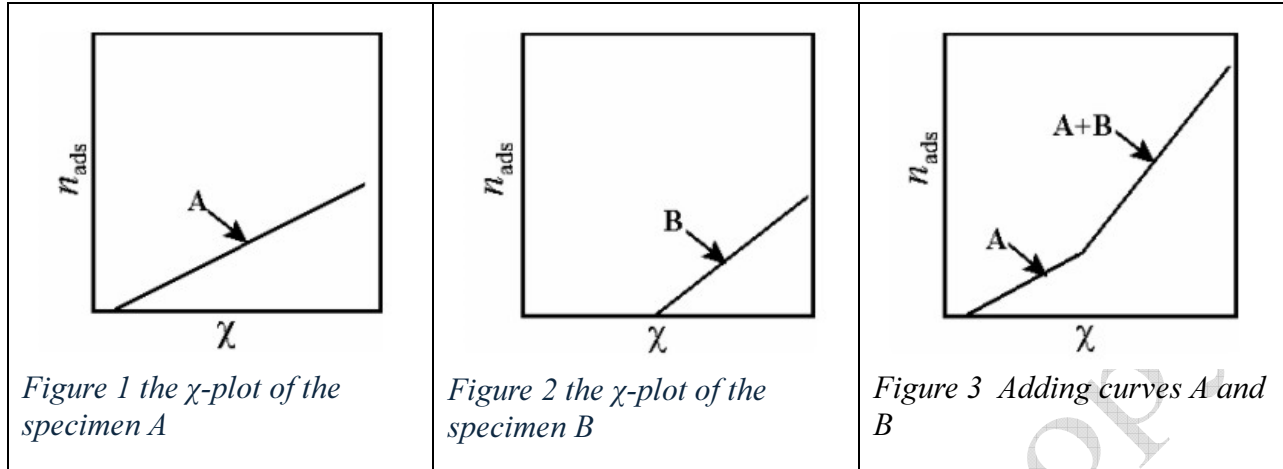
An advantage of QM/ESW: The chi plots are simply additive

Looking at two separate energy-function pre-exponentials, E_a . The high $|E_a|$ curve has the lowest value of χ , so one starts at that point. Assume two ideal χ -plots with different χ_s s, with differing E_a s, as in *Figure 1* and *Figure 2*. These can be added directly without any problem to yield *Figure 3*. This is something the BET is not able to do, without some difficult mathematical manipulations. If one differentiates one obtains *Figure 4* and if one differentiates again, one



obtains *Figure 5*.

* This is conveniently a lot easier than trying to "add" BETs or Langmuirs together, which can lead to anomalies. Oops!



Looking at the first and second derivative of Figure 3 one first gets two step functions and then two δ functions. The δ functions together is the $\langle E_a \rangle$ distribution. But what if there is a different type of distribution other than two discrete peaks? If one has a normal distribution of E_{as} then the second integral of this is the original χ -curve. This is just the same steps in reverse. Starting with the normal distribution* used for statistics, the equation† double integration yields the proper equation, Equation 1 Equation 8:

$$G(x, \mu, s) = \frac{\exp(-\{x - \mu\} / 2s^2)}{\sqrt{2\pi}s} \quad \text{Equation 8}$$

Here x is the independent value, μ is the mean or peak value and s is the distribution. So, for the 1st integral one obtains the cumulative normal distribution, **D** Equation 9

* It is not necessary to use a normal distribution, but it seems to be nature's way to scatter things. Other distributions might be justified, indeed for mesoporosity distribution there is a theoretical alternative for uniform pores.

† The statistical functions are used here because they are available in most spread sheets, except for **Z**. One could obviously use the Gaussian and its integrals just as well.

$$\mathbf{D}(x, \mu, s) = \int_0^x \mathbf{G}(x, \mu, s) \quad \text{Equation 9}$$

and for the 2nd integral, one obtains the “statistical area function,” or \mathbf{Z} function, Equation 10 :

$$\mathbf{Z}(x, \mu, s) = (x - \mu) \mathbf{D}(x, \mu, s) + \frac{2s^2}{\sqrt{\pi}} \mathbf{G}(x, \mu, s) \quad \text{Equation 10}$$

The function \mathbf{G} is for a “reduced” value for n_a , in other words for θ , therefore, Equation 10 needs multiplying by n_m for the isotherm:

$$\begin{aligned} n_{\text{ads}} &= n_m \mathbf{Z}(\chi, \langle \chi_\zeta \rangle, \zeta) \\ &= n_m \left\{ (\chi - \langle \chi_\zeta \rangle) \mathbf{D}(x, \langle \chi_\zeta \rangle, \zeta) + \frac{2\zeta^2}{\sqrt{\pi}} \mathbf{G}(\chi, \langle \chi_\zeta \rangle, \zeta) \right\} \quad \text{Equation 11} \end{aligned}$$

The value $\langle \chi_\zeta \rangle$ is the mean value for the χ_ζ s and is the peak for the distribution, \mathbf{G} , Equation 8. The Greek letter final-sigma, ζ , indicates the spread of $\langle \chi_\zeta \rangle$ with the same units as χ . This will be seen again for mesoporosity.

The output parameters are n_m , $\langle \chi_\zeta \rangle$ and ζ . So, the fitness is expanded from 2 to 3. This is the first feature to expand the simple isotherm description. In doing so, one parameter has been replaced and one added.

If $\zeta = 0$ this equation would yield the original χ linear equation. If one wished to see what a homogeneous fit would be using a non-linear, least squares routine that has ζ as a variable, one cannot set it to zero since that generates an error. One must set ζ to an extremely low value to simulate zero.

Thus, this equation was used to fit the KJO data along with the test to see if there is a temperature problem. To do this one lets the value of P_{vap} be another parameter. If the temperature were well measured and controlled, the fit might be better but the other parameters do not change.

To what is the parameter count taking in the heterogeneity and the P_{vap} error, and assuming no other error is present? This count would be 5: n_m , $\langle \chi_\zeta \rangle$, $\langle E_a \rangle$, ζ and P_{vap} or T .

An Example: A well-controlled experiment by Krug, Jaroniec and Olivier:

There have been many attempts to create a very well controlled and mistake free standard curve for physisorption. The most prominent being by Cranston and Inkley²², Sing²³, t-curve by Lippens, Linsen and deBoer²⁴, Standard UIPAC for silica and carbon²⁵ and many more listed in the textbook²⁶. This has been driven in part by the frustration of the BET analysis and its unreliability. It has also been driven by the desire to have some standard curve for determining the properties of porous materials. The assumption has been that once one has a “universal” standard, then all the isotherms could be compared to this sample and calculate the surface area by ratios. This ignores the idea that not all materials have the same interaction with the adsorbate, never-the-less, maybe if one has, say a nonporous silica sample, it could be used for all silica samples especially porous silica to find the surface area and the areas inside the pores*.

* This seems to assume that one can find the surface area of the standard somehow.

Most standard curves have problems with reproducibility. This is because one curve cannot standardize all or even similar materials since the E_a of the material depends on the chemistry. Furthermore, there is the problem of the **Big Errors**, especially temperature measurement for the reasons mentioned above. DeBoer and Zwicker⁵ **Error! Bookmark not defined.** recognized this problem and had to make P_{vap} a third parameter.

These problems, however, seems to have been overcome by a recent publication provided in the example 1)

Example 1) Data by Krug, Jaroniec and Olivier²⁷:

Probably the best performed experiment to determine a standard curve was conducted by Krug, Jaroniec and Olivier (KJO) with N_2 adsorption on LiChrospher Si-1000 Silica. The silica sample was apparently very pure with little heterogeneity. The calculated heterogeneity for the energy distribution, $\langle E_a \rangle$, 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. The 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 in Figure 6
2. The BET range is, showing the upper and lower limits with vertical lines in Figure 7.
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 in Figure 8
4. What the effect of the preexponential energy term distribution mean, $\langle E_a \rangle$, has on the curve near $\langle \chi_c \rangle$ (Figure 9.)

The plots are all based upon the χ -transformation of the independent variable. Some may object to using the χ -plot as introduction of bias, but this is incorrect. 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.^{18,28} Also, *Equation 5* indicates that $\Delta\chi$ -plot is a direct reading of the monolayer equivalence on the abscissa making interpretation easier. On the other hand, *Equation 6* indicates the χ -plot is a direct measurement of $\Delta^a \bar{E}/RT$. It is quite convenient to have two plots to directly yield the quantities sought*.

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 un baffled radiative heating, which warms the adsorbent. A negative curvature near the end χ -plot has also been observed. This is usually attributable to the temperature being colder than believed to be the case. This is a special problem for liquid N_2 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.

* This statement is for nonporous samples. A similar statement be made for the log-law. However, mesoporosity is a little more complicate after its onset.

In the KJO case, the temperature from the data was calculated to be less than 0.01 K too high, which creates little problems and changes the output parameters very little. It must be that the authors took special care to guard against this error, since, normally in the past, Micromeritics instruments lacked such control*. The vacuum system was UHV capable of $\sim 1 \times 10^{-10}$ bar and the first data point was $P/P_{\text{vap}} = 5.55 \times 10^{-7}$. 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, LiChrospher Si-5000 Silica, 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 8.4×10^{-6} mmol/g out of 1.3 mmol/g total or 6.5×10^{-4} % FDR (of Full Data Range†.)

In *Figure 6* through *Figure 9* are the fits of the KJO data at different magnifications with the BET and the QM fits. The following fits were calculated and presented in these figures.

- 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.

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

Figure 6 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 7 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 in n_a is 0.0604 mmol g⁻¹ or 4.7 % FDR. Without the lower limit this increases to 15.5 % FDR.

* 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.

† A question is, "How does one compare the standard deviation 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 versus low data scatter. It also helps separate good versus bad hypotheses.

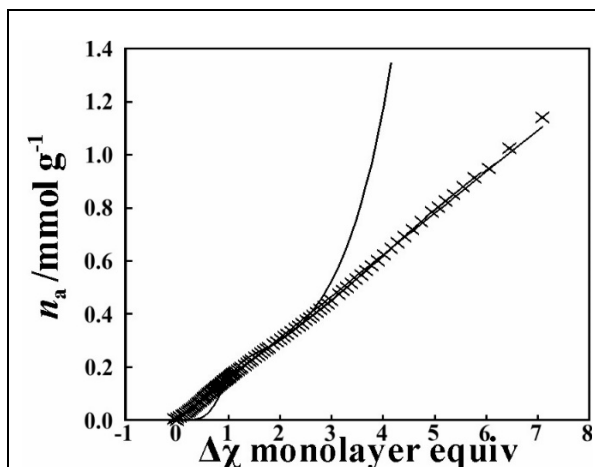


Figure 6 Plot of data by KJO, the QM/ESW fit and the BET fit. The line through the data points, Xs, is the QM/ESW fit. The BET line is very high at high pressure (High $\Delta\chi$) and very low at low P (low $\Delta\chi$.)

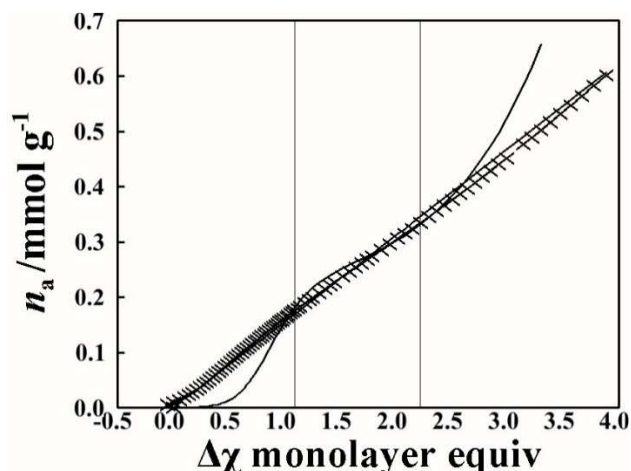


Figure 7 Plot of Data by KJO for the BET Rouquerol range. QM/ESW fit closely follows the data. The best fit in the BET Rouquerol range, which is the vertical lines, is the curved line.

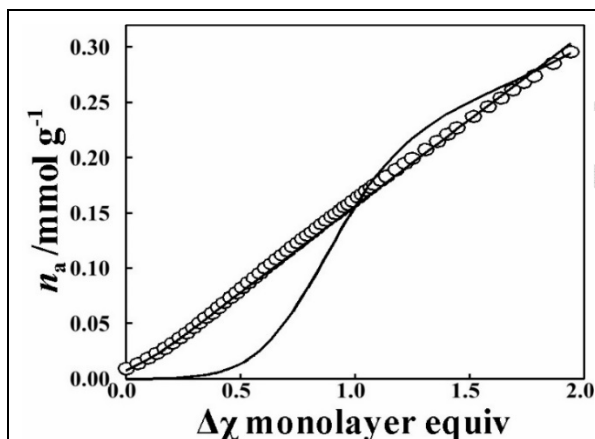


Figure 8 Lower pressure plot of data by KJO, the QM/ESW fit and BET fit. The line through the data points is the QM/ESW fit. The curved line is the BET fit line.

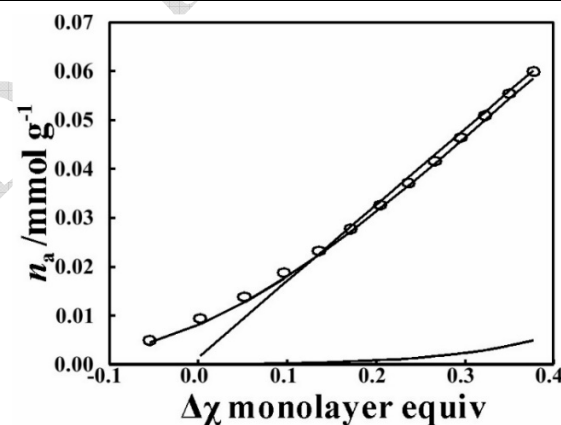


Figure 9 Low pressure plot of data by KJO, the QM/ESW fit and BET fit. The straight line is QM/ESW linear fit, the upper curved line is NLLS QM/ESW fit and the line at the bottom is the BET fit line.

In Figure 8 is another magnification for the BET range. It also shows more clearly how good the QM/ESW fits. However, notice that there is a slight positive curvature, not big enough to be “Henry’s law,” but is due to heterogeneity which is modification or additional feature that will now be explained.

In Figure 9 is the very low-pressure data magnified with the correction for heterogeneity. This normally shows up only in the High Vacuum (HV) or even Ultra HV (UHV) pressure range. This requires a bit of explanation:

Table 1 Comparison of the QM model and the BET parameters for KJO data. is a summary of the parameters for the BET and the QM/ESW fits.

<i>Table 1 Comparison of the QM model and the BET parameters for KJO data.</i>		
BET with lower limit (0.01):	$n_a / \text{mmol g}^{-1}$:	0.265
	$A / \text{m}^2 \text{ g}^{-2}$ (IUPAC)	25.9
	BET C /* unitless	130.1 (-3.2 kJ mol)
	Standard deviation of fit /mmol g⁻¹:	0.0604
	Data Range	0.01 – 0.27 (Rouquerol)
	Deviation/full data range BET	4.7 %
BET with no lower limit:	$n_a / \text{mmol g}^{-1}$:	2.56
	$A / \text{m}^2 \text{ g}^{-2}$ (IUPAC)	25.1
	BET C /*unitless	393 (-3.9 kJ mol ⁻¹)
	Standard deviation of fit /mmol g⁻¹:	1.05
	Data Range	0 – 0.27 (Rouquerol)
	Deviation/full data range BET	15.5 %
QM output parameters with T correction - no limits 4 parameters	$n_a / \text{mmol g}^{-1}$:	0.157
	$A / \text{m}^2 \text{ g}^{-2}$ (IUPAC)	15.3
	$\langle \mu_\varepsilon \rangle$ (heterogeneity)	-2.6123
	$E_a / \text{kJ mol}^{-1}$	-8.84
	Std deviation fit /mmol g⁻¹:	7.63×10^{-5}
	Deviation/full data range*	0.0059 %
	σ (heterogeneity)	0.2048
	$\langle \Delta \bar{E}_a \rangle / \text{kJ mol}^{-1}$	0.64
	$P_{\text{vap}} / \text{bar}$	1.0089
	ΔT	$\leq +0.01 \text{ K}$
QM output parameters without T correction and no heterogeneity- no limits 2 parameters	$n_a / \text{mmol g}^{-1}$:	0.156
	$A / \text{m}^2 \text{ g}^{-2}$ (IUPAC)	15.2
	$\mu_\varepsilon = \chi_\varepsilon$	-2.6115
	$E_a / \text{kJ mol}^{-1}$	-8.92
	Std deviation fit /mmol g⁻¹:	9.12×10^{-4}
	Deviation/full data range*	0.089 %
Ratio of $n_{a,\text{BET}}/n_{a,\text{QM}}$		1.69

Conclusion to Part II

The BET has other problems other than being disproved in Part I. One problem is it yields the wrong answer. This solves the problem that the physical area and the physisorption area do not match. In the Rouquerol range, which is only about 1/3 of the data, the BET yields an answer to high and, as Hobson found, but did not believe, it yields an answer below $X = 0.01$ that is a factor low by 1/3. Other researchers claimed that the surface roughness is to blame for the discrepancies. Also, it is obvious, looking at this standard-curve data by KJO, that it does not match up with the BET prediction.

* Full data range for QM analysis means all the LiChrospher Si-1000 Silica data points only, not the Si-5000 points.

In Part III the relationship between the BET two parameters and the QM/ESW two parameters for the ideal non-porous, homogeneous adsorbent with nitrogen as adsorbate are related.

For additional comments, there is a summary of what Prof. Arthur Adamson reports in his 2nd and 5th addition of his book on physisorption. This is contained in Appendix I.

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Appendix I - What did Arthur Adamson write?

I believe it is worthwhile 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 presented 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 Adamson²⁹ 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 multiple “layers.” The potential theory is similar, but the log term is raised to a fractional power, in the case here it is to $\frac{1}{2}$ 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:

<i>Variations for each contenting theory to decide the most reliable</i>				
<i>adsorbent</i>	<i>BET</i>	<i>Harkin-Jura</i>	<i>potential theory</i>	<i>polarization theory</i>
<i>Range X =:</i>	<i>0.05 – 0.30</i>	<i>0.2 – 0.8</i>	<i>0.1 – 0.8</i>	<i>0.1 – 0.8</i>
<i>egg albumin</i>	<i>±15 %</i>	<i>±12 %</i>	<i>±2 %</i>	<i>±6 %</i>
<i>TiO₂/KCl</i>	<i>±10 %</i>	<i>±13 %</i>	<i>±1 %</i>	<i>±0 %</i>
<i>SiC/Sterling C</i>	<i>±4%</i>	<i>±11 %</i>	<i>±7 %</i>	<i>±4 %</i>

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 $\log(\log(P^0/P))$ 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.” [...]s are inserted for clarity.

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®* sample. It also makes no sense from a chemical standpoint. Theoretically, however, since the $\ln(\ln(P^0/P))$ 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 Fuller **Error! Bookmark not defined.** that the phase transition is at P^0 , 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 $X \times (\text{a content})$ 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 Holmes³⁰ illustrates this. In the Figure 10 below, this data is reworked to yield the BET answer and the quantum mechanical (QM) answer. In these graphs the range of all the data

* ® duPont trade name.

points were used for the QM calculation, whereas only the points in the range $P/P_{\text{vap}} =$ 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.

In Table 2 is the results of analysis of the Keeton and Holmes data. The analysis is for

- 1) the QM analysis and how it compares to the reals data
- 2) The BET analysis and how it compares to the data as transposed, and
- 3) The BET analysis using the transform but comparing the answers to the real data.

Table 2 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	
	78	84	84	85	90	83	85	90	85	90
QM σ_{FDR}	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 n_a vs. X	86%	68%	37%	36%	40%	13%	16%	22%	10%	16%

Notice that the transform fit versus transformed data seems to be very good for the BET. Indeed, it is competitive with QM calculations. However, when the answers for n_m 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.

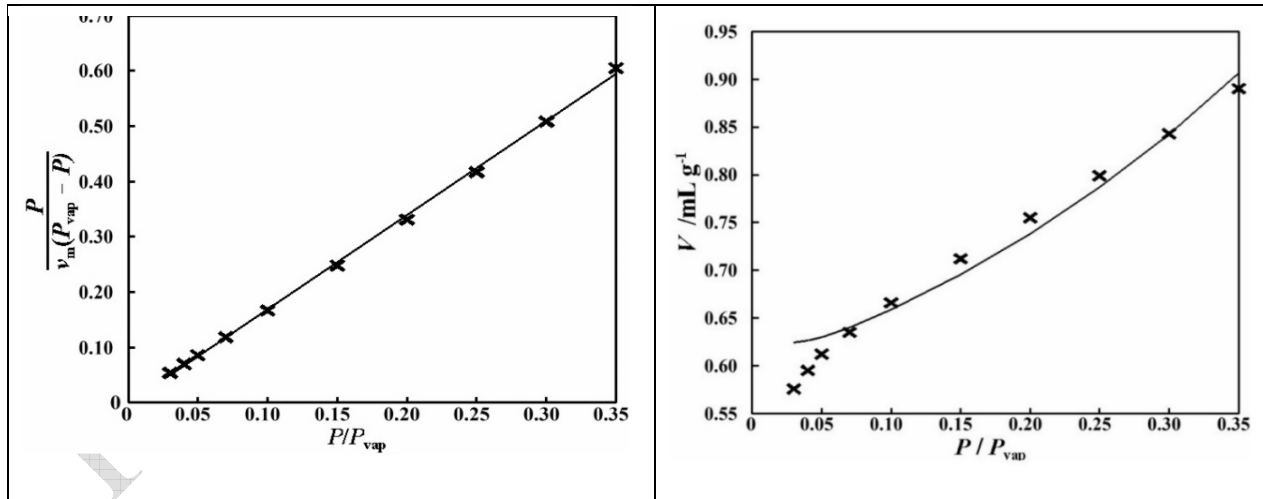


Figure 10 Data points from Keenen and Holmes of nitrogen on KCl at 78 K. The Xs are data points, and the line is the calculation from the BET equation. On the left is the BET transform and on the right is the real physical quantities plotted using the parameters from the transform. This illustrates that a regression analysis of the BET transform plot is unlikely to yield a good fit to the real isotherm plot. The upturn in the calculation at the beginning of the fit is going to ∞ .

The above graphs yields a cautionary tail, that dependent variable transforms, and especially mixing the dependent and independent quantities for a transform is likely to be misleading. It is amazing that no one reported this mathematical problem in the literature.

Conclusion about Prof. Adamson's critiques:

The method of using the BET transform method is a poor technique and can lead to deceiving results. It is convenient but mathematically incorrect. Mathematical treatment is especially egregious since the BET-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. However, due to occasional anomalies with the BET equation as well as negative C constants, this is impossible. Alternatively, one may transform the abscissa so long as it remains a function of pressure, which is what the QM treatment does.

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 BET 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 (a bit of a contradiction) and Brunauer said the phase change was at P_{vap} (which has never been observed.)

Both the polarization and potential hypothesis fit the isotherm quite well. Of course, not as well as the total development of QM/ESW, but these forementioned hypotheses have the advantage of recognizing the experimental data had problems and the theoretical bases were not quite correct.

Symbol list:

English:

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

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

$X := P/P_{\text{vap}}$

Greek:

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

θ = the classical coverage of the QM relative areal density compared to n_m

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

Embellishments

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

Abbreviations

BET = Brunauer, Emmitt and Teller

ESW = Excess Surface Work

HV = high vacuum

KJO = Krug, Jaroniec and Olivier

NASA = National Aeronautics and Space Administration.

QM = quantum mechanics

UHV = ultrahigh vacuum

Acknowledgements:

I am thankful for the guidance received from Dr. E. Loren Fuller, Jr., who was a kind mentor to me and passed on the knowledge that started with Polanyi. I am grateful to W. Thomas Berg who provided me with his excellent thermodynamic data that provided a significant breakthrough. I also wish to thank Dr. Jürgen Adolphs for his encouragement, multiple discussions and confirmatory evidence for the theoretical developments.

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Data and materials availability:

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

The important points to mention from Table 1:

The BET is a very poor fit even when much is ignored by using the Rouquerol criterion of proper data fitting.

- 1) For the best BET fit, the convention lower limit of $X = 0.01$. If this limit is ignored, the standard deviation of the fit is 3 times or more worse
- 2) There is no question that the QM/ESW fit is far superior to the BET even though the entire data set, other than the two LiChrospher Si-5000 Silica data were used for the QM.
- 3) The use of the temperature correction, left little change in the output parameter, however,
- 4) The precision improved by over a factor of 10 using the temperature correction, indicating it is probably very important to compensate for this. ...
- 5) However, the P_{vap} correction is less than 0.01 bar. Better control than this is very difficult.
- 6) The BET is off by a factor of about 1.7, which is closer than for many other calculations on ceramic materials. The energy, of course, from the BET has little meaning. Here the values of -3 to -4 kJ mol⁻¹ are off by a factor of at least 2 - well, at least it isn't an imaginary number.

Although, this is only one comparison, one can make many comparisons, and the answer usually comes out the same. In Part III, you will find out that there is a correlation between the BET and QM/ESW that might be used to obtain the approximate values for the real meaningful physical parameters, assuming quantum mechanics is correct.

Acknowledgements:

I am thankful for the guidance received from Dr. E. Loren Fuller, Jr., who was a kind mentor to me and passed on the knowledge that started with Polanyi. I am also grateful to W. Thomas Berg who provided me with his excellent thermodynamic data that provided a significant breakthrough. I also wish to thank Dr. Jürgen Adolphs for his encouragement and multiple discussions and confirmatory evidence for the theoretical developments.

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References:

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- ¹ J. P. Hobson, First adsorbed layer of nitrogen on Pyrex at 77.4 K. *Can. J. Phys.* **37(10)** 1105-1113 (1959).
- ² J. P. Hobson, A study of physical adsorption at very low pressures using ultrahigh vacuum techniques. *J. Phys. Chem.* **67(10)** 2000-2007 (1963).
- ³ J. P. Hobson, R. A. Armstrong, Physical adsorption isotherms extending from ultrahigh vacuum to vapor pressure. *J. Phys. Chem.* **73(8)** 2720-2727 (1969).
- ⁴ A. M. Silvestre-Albero, P. L. Silvestre-Albero, Llewellyn, F. Rodríguez-Reinoso High-Resolution N₂ Adsorption Isotherms at 77.4 K: Critical Effect of the He Used During Calibration. *J. Phys. Chem. C* **117** 16885–16889 (2013).
- ⁵ J. H. deBoer, C. Zwikker, Adsorption als Folge von Polarisierung: Die Adsorptionsisotherme. *Z. Phys. Chem.* **3B(1)** (1929) 407-418.
- ⁶ I. Langmuir, the Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum. *J. Am. Chem. Soc.* **40** (1918) 1361-1403.
- ⁷ A. Roth, "Chapter 3" in *Vacuum Technology, 3rd updated and enlarged edition* (North Holland – Elsevier Publishing, Amsterdam, ed.3, 1998) ISBN:0 444 88010 0
- ⁸ R. Guillet-Nicolas, M. Wainer, L. Marcoux, M. Thommes, F. Kleitz, Exploring the confinement of polymer nanolayers into ordered mesoporous silica using advanced gas physisorption. *J. Colloid and Interface Sci.* **579** 489–507 (2020).
- ⁹ M. Polanyi, "Über die Adsorption vom Standpunkt des dritten Wärmesatzes. *Verh. Dsch. Phys. Ges.* **16** 1012-1016 (1914).
- ¹⁰ M. Polanyi, Adsorption von Gasen (Dampfen) durch ein festes nichtflüchtiges Adsorbens. *Verh. Dsch. Phys. Ges.* **B18** 53-80 (1916),
- ¹¹ M. Polanyi, K. Welke, Adsorptionswärme und Bindungscharakter von Schwefeldioxyd an Kohle bei geringen Belegungen. *Z. Phys. Chem.* **132U (1)** 371-383 (1928).
- ¹² M. Polanyi as quoted by S. Brunauer "Chapter VI, pp143-144" in *The Adsorption of Gases and Vapors, Vol. 1* (Princeton University Press, Princeton, NJ, 1945.)
- ¹³ J. H. deBoer Die Adsorption von Jod an vakuumsublimierten Bariumchloridschichten und ihre Temperaturabhängigkeit. *Z. Phys. Chem.* **14B(1)** 457-470 (1931).
- ¹⁴ E. L. Fuller, Jr., H. F. Holmes, C. H. Secoy, Gravimetric Adsorption Studies of Thorium Oxide. II. Water Adsorption at 25.00°C. *J. Phys. Chem.* **70** (1968) 1633-1636.
- ¹⁵ R. B. Gammage, E. L. Fuller, H. F. Holmes, Uniform nonporous thorium: The effect of surface water on adsorptive properties. *J. Colloid Interface Sci.* **34(3)** (1970) 428–435.
- ¹⁶ R. B. Gammage, H. F. Holmes, E. L. Fuller, Jr., D. R. Glasson, Pore structure induced by water vapor adsorbed on nonporous lunar fines and ground calcite. *J. Colloid Interface Sci.* **47(2)** (1974) 350–363.
- ¹⁷ E. L. Fuller, Jr., Interaction of gases with lunar materials (12001): Textural changes induced by sorbed water. *J. Colloid Interface Sci.* **55(2)** (1976) 358–369.
- ¹⁸ E. L. Fuller, Jr., F. A. Agron, "The reactions of atmospheric vapor with lunar soils" (US Department of Energy Report DOE ORNL-5129 (UC-346), Oak Ridge, TN, 1976).
- ¹⁹ E. L. Fuller, Jr., "Surface chemistry and structure of beryllium oxide" (US Department of Energy Report DOE Y/DK-282, Oak Ridge, TN, 1982).
- ²⁰ E. L. Fuller, Jr., N. R. Smyrl, J. B. Condon, M. H. Eager, Uranium oxidation: Characterization of oxides formed by reaction with water by infrared and sorption analyses. *J. Nucl. Mater.* **120(2/3)** (1984) 174–194.
- ²¹ E. L. Fuller, Jr., J. B. Condon, **Error! Main Document Only.** Statistical mechanical evaluation of surface area from physical adsorption of gases. *Surf. Colloid.* **37(1)** (1989) 171–182.

-
- ²² R.W. Cranston, F.A. Inkley, The Determination of Pore Structures from Nitrogen Adsorption Isotherms. *Adv. Catal.* **9** (1957) 143-154.
- ²³ K. W. S. Sing, *Surface Area Determinations* in (D. H. Everett, R. H. Ottwell (eds) Butterworth, London, UK , 1970) p25.
- ²⁴ B. C. Lippens, G. G. Linsen, J. H. deBoer, Studies on pore systems in catalysts II. The shapes of pores in aluminum oxide systems. *J. Catalysis* **3(1)** (1964) 32-37.
- ²⁵ D. H. Everett, G. D. Parfitt, K. S. W. Sing, R. Wilson The SCI/IUPAC/NPL project on surface area standards. *J. of Appl. Chem. and Biotech.* **24(4-5)** (1974) 199-219.
- ²⁶ J. B. Condon, *Surface Area and porosity Determinations by Physisorption* (Elsevier Publishing, Amsterdam, Netherlands, ed. 2, (2020) ISBN 978-0-12818785-2.
- ²⁷ M. Krug, M. Jaroniec and J. Olivier, Standard Nitrogen Adsorption Data for Characterization of Nanoporous Silicas. *Langmuir* **1516** (1999) 5410-5414. (#1a990136e)
- ²⁸ J. H. Deboer and C. Zwikker, Adsorption als Folge von Polarisation Die Adsorptionsisotherme. *Z. Phys. Chem.* **B3** (1929) 407-418.
- ²⁹ Arthur W. Adamson, "Chapter XIII sections 7-9 595-607" in *Physical Chemistry of Surfaces* (Interscience Publishers, John Wiley and Sons, New York, ed. 2, 1967)
- ³⁰ A. G. Keeton, J. M. Holmes, The Adsorption. of Nitrogen, Argon, and Oxygen on Potassium Chloride at 78-90°K. *J. Phys. and Colloid Chem. (J. Phys. Chem.)*, **53** 1309-1320 (1949).