

Title:

**Part VII: Quantum Mechanics and Physisorption
Heats, Binaries, Final Conclusion**

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**Part VII: Quantum Mechanics and Physisorption
Heats, Binaries, Serie's Final Conclusion**

James Condon^{*†}

Abstract:

Two topics are discussed in this part:

1. How to calculate the heats of adsorption from the isotherm data without any new parameters (variable constants) and to compare this calculation with the calorimetric data if available.
2. Some hints about expanding the scope of the QM hypothesis to include the binary adsorption isotherms, that is, the adsorptions of two adsorbents on an adsorbent.

The first topic is relatively easy with at least one very good set of data by Dr. William Thomas Berg. Other calculations that support the conclusion are mentioned as being available in the literature but are not the quality of the data by Berg.

The second topic has a dearth of data available and there is, thus, very little confidence attached to the calculations. Indeed, some of the early data has obvious drift in the isotherms and a high degree of scatter. The main problem with this approach is the difficulty of the experiments and the low reproducibility. This obviously needs further research and a considerable number of researchers and finance to test and refine the approach to this problem. The traditional approach to this problem is to assume the Langmuir isotherm, due to its simplicity, however, the QM hypothesis is just as simple in the χ -space as the use of the Langmuir, perhaps simpler.

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Introduction:

Parts I through VI covered the most addressed topic in the literature by far. Beyond these topics the biggest failures of the classical theories has been to make sense of the heat of adsorption versus the isotherm data. Many attempts have been tried which inevitably lead to assuming the large deviation from the theoretical model to obtain the heat of adsorption involve fanciful assumption about the entropy of adsorption. Furthermore, the transition to full liquid density is left unexplained. Thus, these “theories” cannot reconcile the isotherm experiments with the calorimetric experiments.

What makes the reconciliation even more difficult is the lack of careful experimentation, with the experimental equipment measuring the calorimetry at the same time, on the same adsorbent sample, as the isotherm measurement. In addition, it is very rare to see adsorbate heat capacities measured. This is a requirement for careful calorimetry. The only data, that I know of, that was so carefully done was by William Thomas Berg and that data did not get fully publish in the literature probably for the usual reasons.

The theoretical aspects and the Berg data as the best supporting evidence is presented. However, other and cruder data will be cited in support.

The other topic addressed here is the binary adsorption isotherm. This is obviously a more difficult topic and there is even less data available to support the hypothesis for it. It is presented here to create interest in researching this very important and practical area. There is no claim that the calculation put forth are either correct or complete.

Heats of Adsorption - the Relationship to the Isotherm.

Heat of adsorption compared to the isotherm data by QM analysis

a) The Dubinin thermodynamic criterion

The Dubinin thermodynamic criterion predicts that the internal energies for the isotherm determination and the calorimetric determination are nearly equal for the simple case, that is:

$$\Delta_l^a \bar{\mathbf{E}}_{\text{isotherm}}(\chi) \cong \Delta_l^a \bar{\mathbf{E}}_{\text{calorimetry}}(\chi) \quad \text{Equation 1}$$

(Notice the sub-*l* on the right.) Provided there is no affect upon the internal vibrational and rotational modes in the adsorbate molecules, the only difference is the loss of one degree of translational freedom in the first “layer,” which is a relatively insignificant amount. The possibility of changes in internal vibrational and rotational modes is left open in future work.

b) Comparison of the $\Delta_l^a \bar{\mathbf{E}}_{\text{isotherm}}$ with $\Delta_g^a \bar{\mathbf{E}}_{\text{calorimetry}}$.

This section deals with comparison of the data from the isotherm and the data from calorimetry. In doing so, the one needs to keep in mind the different standard states being used. Calorimetry uses the conventional thermodynamic standard state, a comparison to 1 bar pressure. Isotherm representation uses the vapor pressure of the adsorptive at the temperature of the adsorbent (P_{vap}) as the reference pressure.

The agreement between the calorimetric data and the heats of adsorption using the isotherm is the objective. Normally, attempts to do this is performed by comparing the isosteric heat of adsorption, q_{st} , with the calorimetric data. In the case illustrated here the actual differential heat of adsorption, q_{d} , is compared. Theoretically, these two should be the same, but q_{st} is more difficult to obtain accurately due to the uncertainty of the differentiation between two temperature isotherms. even with minor scatter.

This comparison of q_{d} or q_{st} to the isotherm energy, $\Delta_l^a \bar{\mathbf{E}}(\chi)$, is something that other hypotheses cannot do well. Indeed, the BET does a terrible job of doing this. Usually, authors point out similarities in features for the two and not that the actual calculations match. The explanation for differences is usually attributed to entropy change without identifying what that is.

If one looks at the function $\Delta_l^a \bar{\mathbf{E}}(\chi)$ versus n_a on a homogeneous surface, it is an exponential decay from E_a to 0 with the decay constant of $\Delta\chi$. ($\Delta_l^a \bar{\mathbf{E}}(\chi) < 0$.) The ΔE^\ominus , which applies to calorimetry, adds the ε (which was found to be E_{vap}^\ominus or $\Delta_l^g \bar{\mathbf{E}}(\chi(T_a))$ the heat of vaporization.) The value of $\Delta_l^a \bar{\mathbf{E}}(\chi)$ is a function of χ and not $\Delta\chi$. That is:

$$\Delta_l^a \bar{\mathbf{E}}(\chi) = -RT \ln \left(\frac{P}{P_{\text{vap}}} \right) \Rightarrow \Delta_{g,1 \text{ bar}}^a \bar{\mathbf{E}}(\chi) = -RT \ln \left(\frac{P}{P_{\text{vap}}} \right) - \Delta_{g,1 \text{ bar}}^l \bar{\mathbf{E}} \quad \text{Equation 2}$$

Example 1) the W. Thomas Berg Data

A good example of an experiment, which used the same adsorbent sample for both the calorimetry (heat capacities and heats of adsorption) and the isotherm, are the experiments by

Dr. William Thomas Berg^{1 2 *}. Indeed, the same chamber and samples were used for both simultaneously. This experiment used Kr adsorption on anatase at 139K and 140K. The information was not accepted for publication for the usual reasons, but the data is available from the library of Case Northwestern University and listed on the web[†].

For the data by Dr. W. T. Berg presented here, the agreement between the isotherm data and the calorimetric data is excellent. In *Figure 1* are the isotherms and the calorimetric data by Berg. The calorimetric "fit" used only the parameters from the isotherm data to create the lines shown. Thus, absolutely NO adjustable parameters were used to make the calculation on the right side of *Figure 1*. Although the right graph is not a perfect fit, especially at low values, it is in stark contrast to other hypotheses that are unable to correlate the isotherm with the heats of adsorption at all.

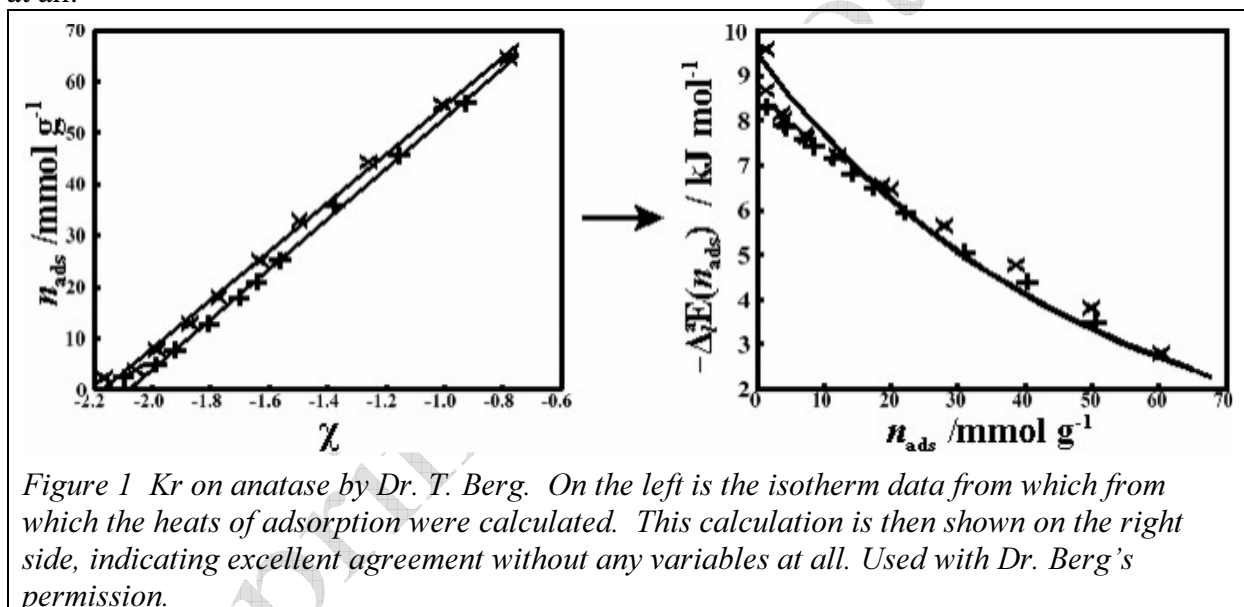


Figure 1 Kr on anatase by Dr. T. Berg. On the left is the isotherm data from which the heats of adsorption were calculated. This calculation is then shown on the right side, indicating excellent agreement without any variables at all. Used with Dr. Berg's permission.

The reasons for the deviations at low pressure could be 1) when taking differences for the differential there is a loss of one data point at the beginning of the resultant plot 2) there is obviously some heterogeneity in the anatase as seen by the rounding at the low pressures.

In Figure 4 and Figure 2 of reference 2 the isosteric energy of adsorption is listed with the 140 K data is corrected to 130 K using the heat determined heat capacity. The difference between the

* Since the only way at that time to measure surface area was using the BET equation. This led to problems and Dr. Berg knew something was amiss, so he never mentioned the precise sample size except about "50 g." He left the data in terms of moles, so his data for adsorption and energy is OK, but his specific heat capacities of the adsorbate are off by a bit, since the calorimetry includes the heat capacity of the adsorbate. There is some other data in the report the one can use to calculate the true value of the monolayer equivalence by comparing the QM calculation with the BET. See a new upcoming publication on this conversion that is to be published.

† There is no reason to be suspicious of this data. It was performed well before this author could have provided information to Dr. Berg. The only reason that I knew about this data is that Dr. Berg and I taught together at the same college in the 1990's. He published his work when I was 15 years old (1955,) so it is a real stretch to accuse me of being disingenuous. He makes no mention of deBoer-Zwicker nor Polanyi. I do not know if he knew Loren Fuller, but it would have been well after he wrote this thesis, since he spent many years working in Canada before arriving in Oak Ridge. The web listing is in ResearchGate.com under James Condon since Dr. Berg is deceased.

measurements at the two temperatures disappears to within the significance of the data. This is another piece of supporting evidence.

Dr. Berg's data is not the only publication that shows the consistency between data from the isotherm and calorimetric data, although it is undoubtedly the best. In a publication³ about this subject, there are several other examples given, including a very early measurement by Hawkins and Jura⁴, which can be calculated by *Equation 2*.

However, this does not work for mesoporosity. Two changes occur for mesopore analysis. In the mesopore range a large portion of the adsorbate is not contributing to the first schicht energy after a very short burst to complete the first schicht as well as other schichten. There is an extra release of energy due to the formation of a complete gas-liquid interface. However, the external surface continues to be a source of energy release usually at a very low amount.

There is a good deal of uncertainty about these speculations, but the analysis is certainly much better than any other analysis of energy versus isotherm. More tests are recommended.

Conclusion About the Isotherm comparison to Heats of Adsorption:

The QM description reconciles the values for energy between the isotherm calculations and the calorimetric measurements. It is not just the data by Berg that indicate this but other publications that do and are presented in another publication³. The calculations that have been performed have been restricted so far to the "simple" case of adsorption. The extension to microporous adsorption would seem to be a simple step. It may even be possible to extend this calculation to include mesoporosity once the mechanism is settled and the proper values of γ for adsorptive at adsorption temperatures are measured.

The calculation that is possible with the QM hypothesis is, at this time, the only hypothesis that can do this. This bodes favorably for the QM/ESM hypotheses and unfavorably to all other hypotheses that have come before.

Adsorption of Two Adsorptives Simultaneously:

The last topic is the application to binary adsorptives. It is highly speculative for two reasons, There is not very much appropriate literature data on the subject to use for testing. There is plenty of engineering data with the purpose of solving a particular problem, but very little well controlled, wide ranging data collection on ideal materials suitable for making appropriate calculations.

There are some assumptions and approximations needed to use on what data there is available, which, even though they seem reasonable, may not be appropriate^{5,*}.

It is difficult to find appropriate literature on binary adsorption that is useful to make calculations using the QM/ESW hypotheses. The approach to this is simple, but mathematics could become tedious. It seems obvious, that if two adsorbates have about the same E_a , then the mixture is likely to behave like a single adsorbate in the first schicht. However, schichten above the 1st schicht might to start to approximate the behavior of the bulk liquid adsorptive.

The isobaric binary phase diagram dominated by the first schicht:

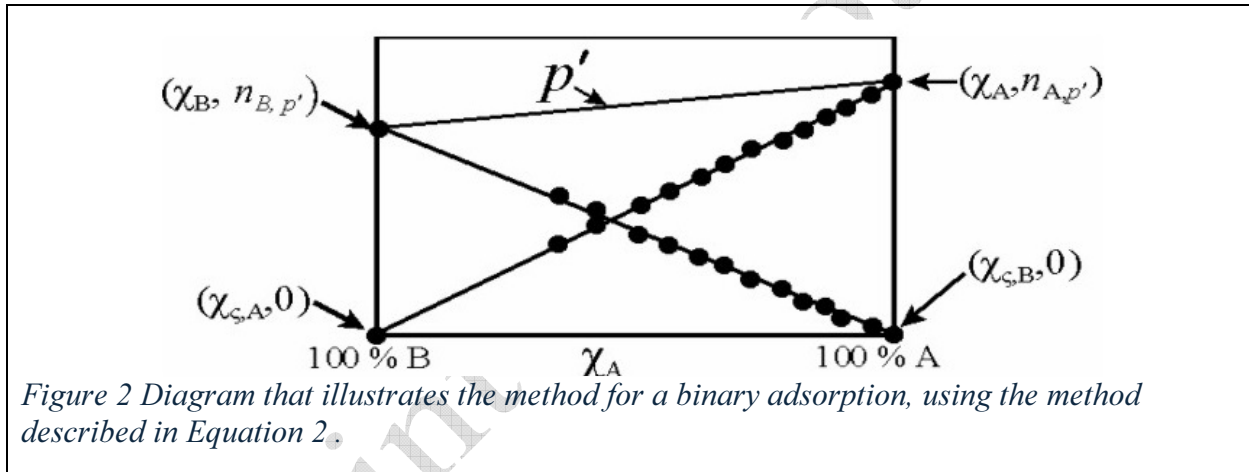
If there is a big difference between the two $E_{a,s}$, the one that is the most exothermic (call it "A") will fill most of the first schicht before the least exothermic one (designated "B") has an opportunity. Thus, the B will have little influence on the adsorption of A in the first schicht. In subsequent schichten the ratio of A to B should eventually approach the bulk liquid composition. There is probably an exponential decay going into the liquid in a similar fashion as predicted by the Debye-Hückel theory. This has been demonstrated for the Debye-Hückel theory in other systems using Darken's equations and Poisson's equation to obtain equilibrium⁶. Something similar may be the case here. If there are mesopores, then this is also true after the pore filling has started. Which should lead to Raoult's law behavior with increased pressures.

Thus, one should be able to calculate the binary adsorption curve given only the isotherms of the two adsorbates and the adsorptive binary phase diagrams, which are probably available. (If the adsorptive binary phase diagrams are not available, many binary mixtures can be approximated with a regular-solution theory calculation.) This would save considerable effort and should be quite useful at least for screening studies. The effort saved could be considerable. For X adsorptives and P pressures, the number of experiments that are needed $(1-X)XP$ plus X single isotherms, whereas, using the single isotherms requires only X isotherms to determine E_a . and n_m , although it always advisable not to depend upon a single isotherm run.

Logic above would indicate that the onset of adsorption and its continuation is governed by the more exothermic of the two adsorbates. In **Table 1** is a procedure to take advantage of this for binary mixtures where the $E_{a,s}$ are different enough. This procedure would apply to a given total pressure and variation of stoichiometry. Notice that only the χ -values associated with the lowest χ_c value, listed as the "A" adsorbate, is used for plotting.

* These assumptions, however, are more reasonable than the Henry's law assumption use in the classical explanation. See the book by Prof. Diran Basmadjian for these.

Table 1 - Steps to calculate the binary diagrams when $\chi_{\zeta}(A) \ll \chi_{\zeta}(B)$	
1)	Do the χ -plot for both adsorbates
2)	Determine what total pressure you wish to have the phase diagram for. (call this p' .)
3)	From the χ -plots, determine which adsorbate has the lowest value for χ_{ζ} . It may be difficult to do this, so try determining the value of χ_{ζ} from the log-law plot. (This adsorbate with the lowest χ_{ζ} is adsorbate "A," labelled " $\chi_{\zeta}(A)$ ")
4)	Determine the value of n_a from both isotherms of the adsorbates at pressure p' . Designated these $n_A(p')$ and $n_B(p')$
5)	Draw straight lines for A from $(\chi_{\zeta,A}, 0)$ to $(\chi(p'), n_A(p'))$ and for B from $(\chi_{\zeta,B}(A!^*), n_B(p'))$ to $(\chi(p'(A!^*)), 0)$
The "!" is placed here to emphasize that one uses only the χ values for A.	



The diagram in *Figure 2*, illustrates the method. In the single adsorbate isotherms, component A has the lowest χ_{ζ} (largest exothermic adsorption energy) so the abscissa is specified by it. The four points needed are shown in parenthesis.

The data points are matched pairs in the binary experiment. The abscissa is χ_A , which is the species with the highest value of $|E_a|$. If, χ_B is used for abscissa a straight line is not obtained. (This phenomenon is referred to as the "strong Henry's law" species in classical calculation⁵.)

Isobaric by Danner and Wenzl - Illustrating the method:

The data by Danner and Wenzl⁷ is reasonably precise to make some tests. The data being analyzed by Danner and Wenzl was for the gases CO, N₂ and O₂ on 5A and 10X zeolite. The temperature was 144.3 K. The P_{vap} was calculated from data by Clayton and Giaque⁸ for O₂ and CO, which has some uncertainty. For N₂ the Dortmund data base⁹, mentioned previously, was used.

There are, however, some uncertainties about the extrapolated χ_{ζ} , but they are good enough to tell which one is dominate. The binary phase diagrams were obtained at 1 atm, which is probably within the range where a one monolayer equivalent is being adsorbed. Thus, to find the

χ_s s, a log-law might be useful. Therefore, both the χ -plot and the log-law were used and a judgement as to which is clearer in the determination was made.

The graph in Figure 3 used the real data from Danner and Wenzl for N₂ and O₂ on 5A zeolite for illustration. Other combinations were similar. The binary diagrams were created at one atmosphere, but P_{vap} for the adsorptives were quite high:

$$P_{\text{vap}}(\text{O}_2) = 29.96 \text{ atm}$$

$$P_{\text{vap}}(\text{N}_2) = 55.28 \text{ atm}$$

$$P_{\text{vap}}(\text{CO}) = 45.97 \text{ atm}$$

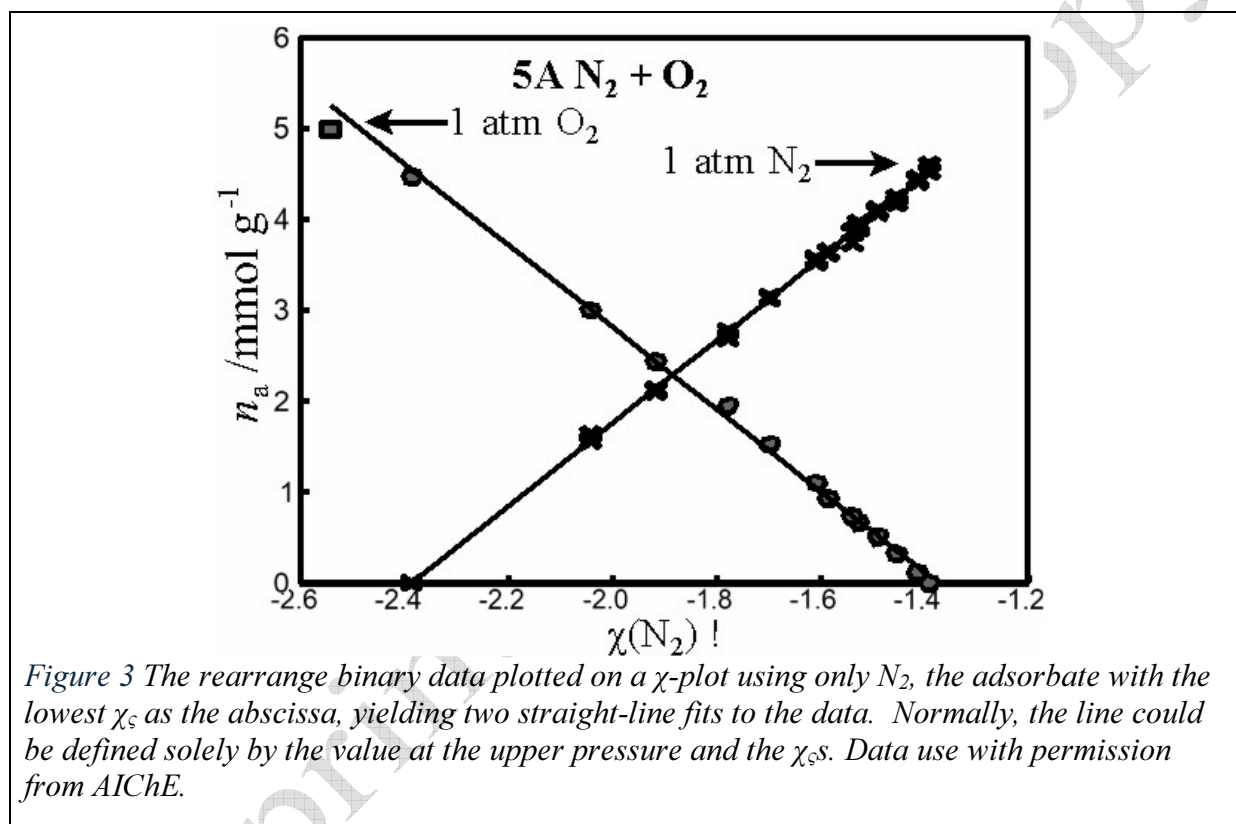


Figure 3 The rearrange binary data plotted on a χ -plot using only N₂, the adsorbate with the lowest χ_s as the abscissa, yielding two straight-line fits to the data. Normally, the line could be defined solely by the value at the upper pressure and the χ_s s. Data use with permission from AIChE.

Thus, this data was undoubtedly below mesopore considerations and there was no indication of observed mesoporosity. Indeed, the isotherms up to 1 atm is for only about one monolayer equivalence. In Figure 3 the straight lines are determined by a linear regression to the data, however, this is not the normal method but rather that illustrated by Figure 4.

Figure 4 is the full experimental method using the 5A zeolites and adsorbing O₂ and N₂. The lowest χ values are left off in this figure, but the high and low values are all that is needed to yield the straight line, as evident in Figure 4. Thus, the only points that need to be measured is the adsorption at the designated pressure, in this case 1 atm, and the determination of the χ_s s. However, these points are difficult to determine with just the observation without the isotherm, especially the χ_s s. Probably, the extrapolation of several data points in the low-pressure region is needed. (Although, there might be a yet-to-be-exploited experimental method to find these values quicker. Up to now, there does not seem to be a reason to do so.)

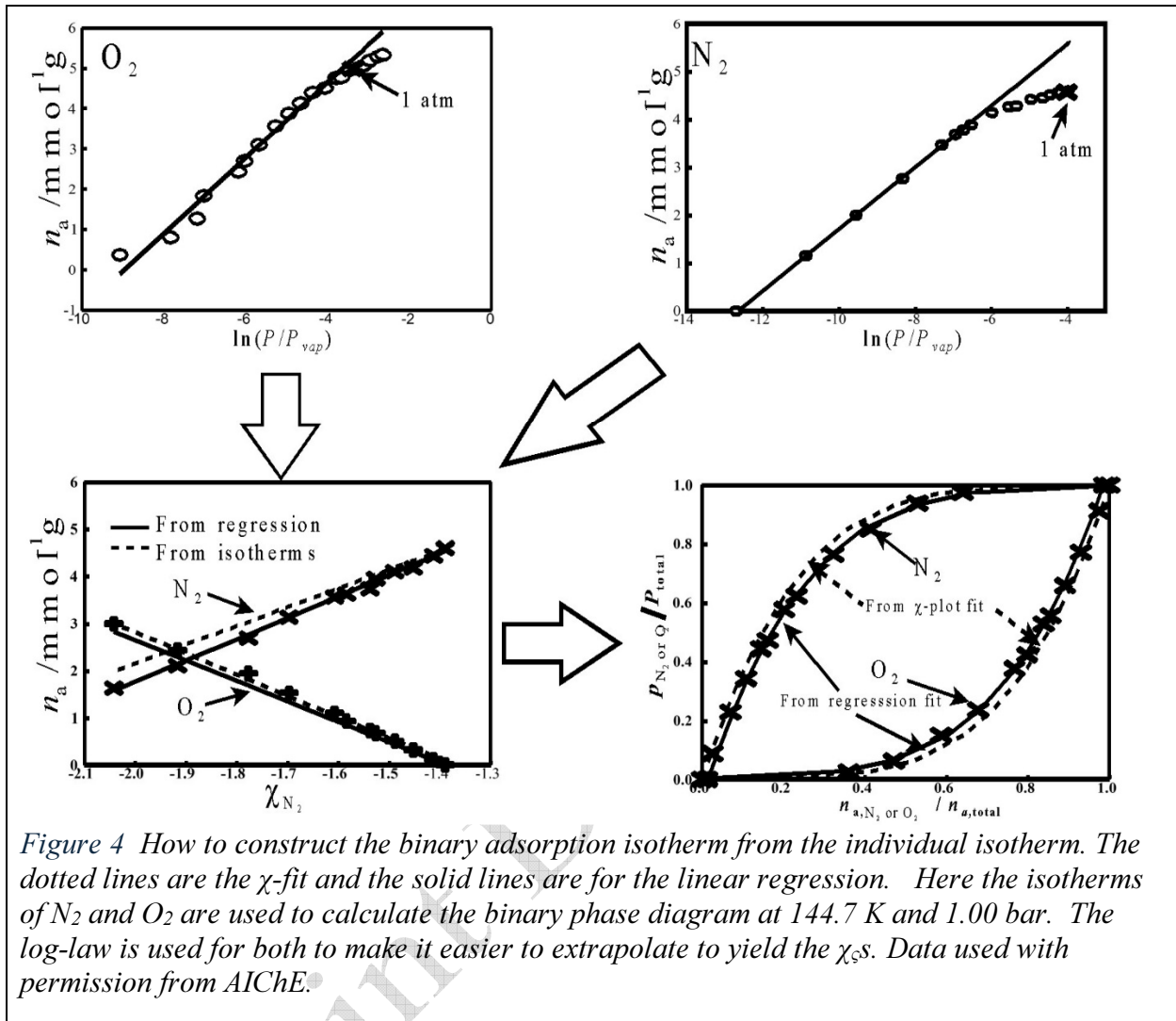


Figure 4 How to construct the binary adsorption isotherm from the individual isotherm. The dotted lines are the χ -fit and the solid lines are for the linear regression. Here the isotherms of N_2 and O_2 are used to calculate the binary phase diagram at 144.7 K and 1.00 bar. The log-law is used for both to make it easier to extrapolate to yield the χ_{ζ} s. Data used with permission from AIChE.

In Figure 4 the six steps are shown for the method to measure the isotherms for N_2 and O_2 . Using the maximum and minimum points (dotted lines) one extracts the values, pressures and amount (as in Figure 3 and Figure 4) and plot them on the binary diagram. If one has the full isotherms plotted for the lower left, one can get a more accurate binary diagram by using a regression analysis for this figure. However, this may not be available, so the final high and low points must suffice, that is, the 4-point method, is used.

Notice that in Figure 3 the χ -plot values for the 4-point binary diagrams are normally a little imprecise when combined to the binary. On the other hand, the linearity of both regression plots on the bottom-left are fair, with a standard deviation of about 1.3 % FDR. This is slightly out of the χ imposed criterion of 1.0 % FDR, but it is certainly an advance over past efforts. There is, however, considerable data scatter, especially for the O_2 isotherm as is evident in Figure 4 upper left. One would not expect high precision starting with low precision data. Without high resolution with the starting individual isotherms, the results are only crudely approximate.

However, the improvement in the scatter when the binary plots are made is an interesting phenomenon, which provides hope for improvement.

Example – Analysis of Danner and Wenzl Data:

The six preliminary binary diagrams and the binary adsorptions diagram for 1 atm are presented in *Figure 5* and *Figure 6* for the 5A zeolite. In these preliminary diagrams, the linear regression for the binary mixtures is shown as solid lines. The data calculated from the individual isotherms are the dashed lines. Obviously, a better fit could be obtained with such fits from the binary mixture, although it is only within about 3%. However, notice that the fit to both adsorbates is linear. Other than the QM model, there is no reason that this linearity should exist. that would increase the amount of work needed. However, if one wanted to construct a series of diagrams of different pressures, that would have to be done anyway. An alternative would be the two point per isotherm method mentioned above and illustrated below.

Using the four point method, two of the binary phase diagrams were excellent, but the CO-O₂ diagram is not. The reason may be the previously mentioned data scatter, but intuitively, at least one of the other diagrams should be off as well. This effect needs more investigation.

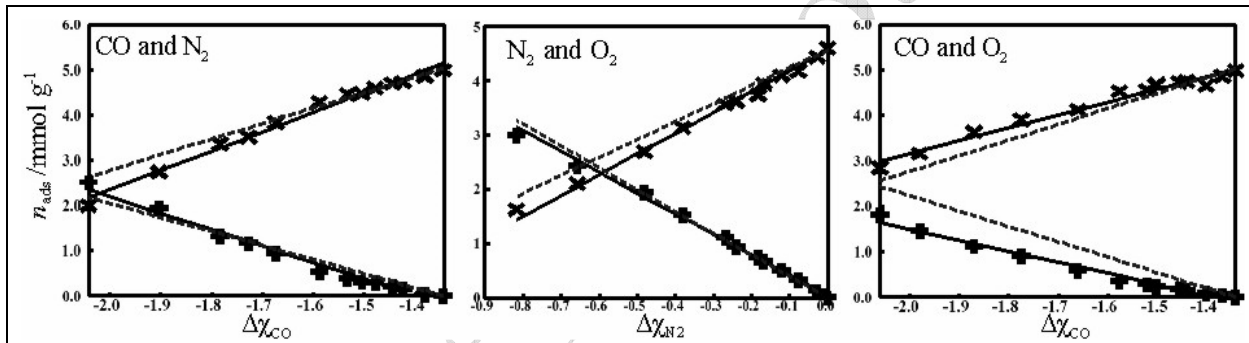


Figure 5 The $\Delta\chi$ intermediate plots of the binaries CO-N₂, N₂-O₂ and CO-O₂ on 5A zeolite. The dashed lines in are the resultants from the 4-point method and the solid lines are the results of regression through the data.

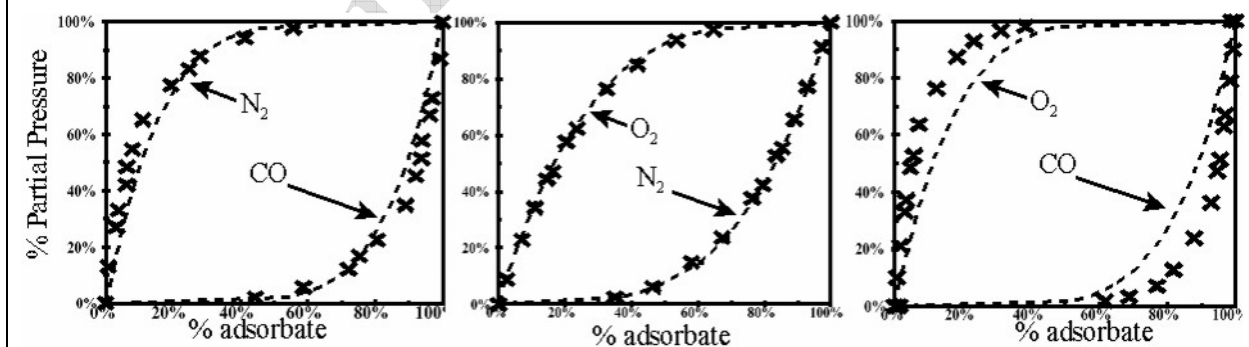
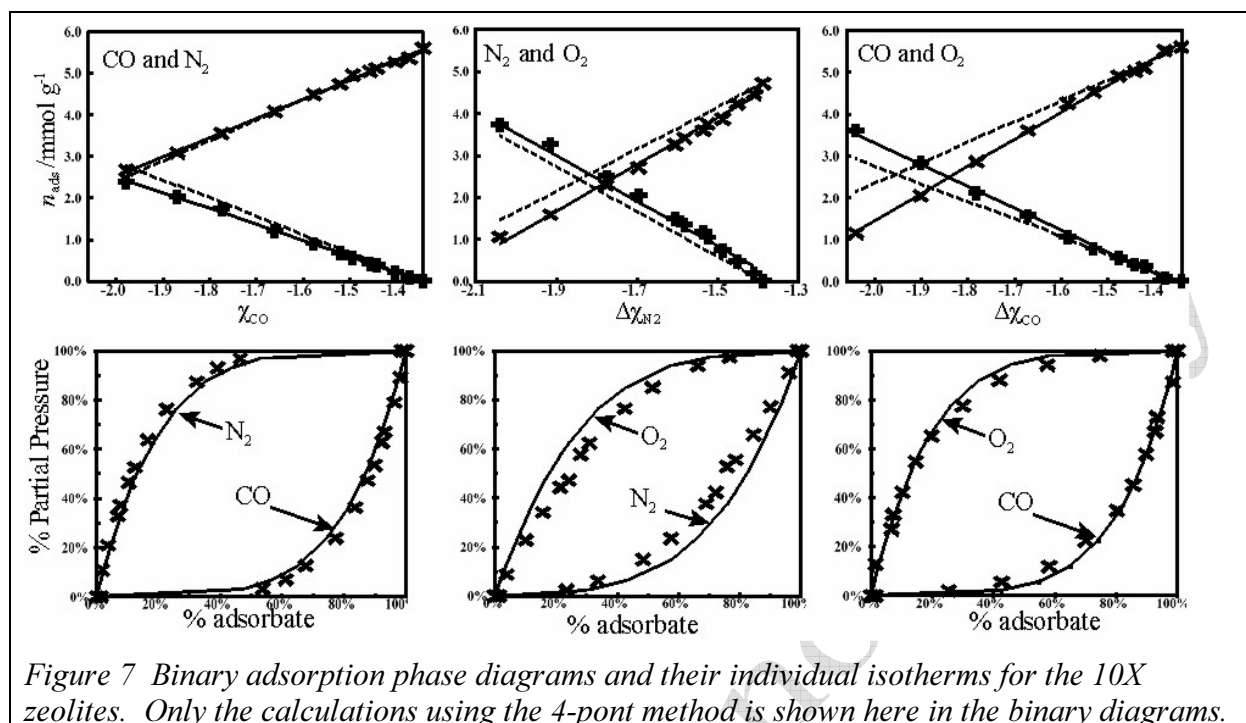


Figure 6 The $\Delta\chi$ binary plot of the binaries CO-N₂, N₂-O₂ and CO-O₂ on 5A zeolite (top) and the binary adsorbate diagrams formed from the individual isotherms above. The dashed lines in are the resultants from the 4-point method.



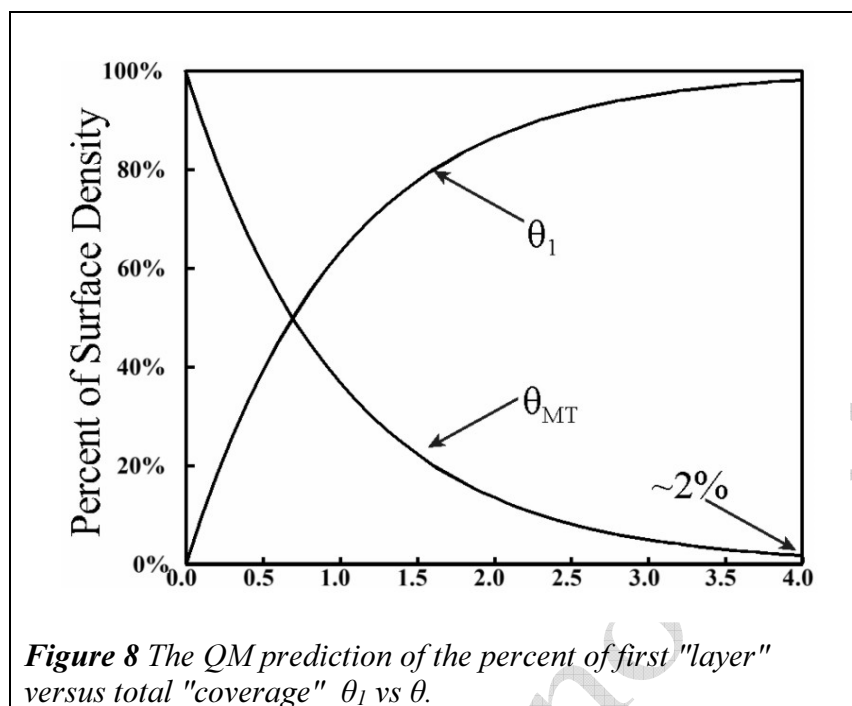
Similar graphs for 10X zeolite analysis and the resulting diagrams are shown in Figure 7. The 10X is a little better than the 5A. Both, however, are not as accurate as one would like them to be. They are, however, good enough to determine if the combinations are suitable for further study. In Figure 7 10X phase diagrams, only the calculation from the individual isotherms, the four point method) is shown as a solid line. The linear regression fits in the binary are left off to diminish the confusion.

Example – Isothermic data by Arnold, O₂-N₂ mix on anatase:

One might expect that as the adsorption proceeds to ever higher monolayer equivalency that the binary adsorption would begin to resemble the liquid phase binary diagram. This could apply to the case with the various mixtures of O₂ and N₂ adsorbed on anatase as measured by Arnold¹⁰.

Classically, one would assume that the first layer adsorbs well before any second “layer” does, after all, one cannot have a 2nd “layer” without a complete 1st. The ratios are then arbitrary set by adjusting the equilibrium constants*. The reasoning seems correct. The problem with this idea is that quantum mechanics predicts there is a finite and designated fixed ratio of the 2nd schicht filling and other schichten fillings to the areal densities in the 1st schicht. (The 1st schicht does not need to be completely filled before the 2nd schicht starts to fill.) Thus, there is a relationship between the overall areal density, θ , and the areal density in the 1st schicht, θ_1 .

* Some DFT calculations show steps that indicate this problem.



The point is that the quantum effect continues to fill the higher ordinal numbered schichten and a classical concept of Raoult's law may not apply. This is due to the occupancy of the 1st schicht is at 95% filled, not 100% even when the overall coverage is 3 monolayers (*Figure 8*). Even at 4 monolayers there is still an amount in the 1st schicht, ~2%, that is available for further filling. This extent of adsorption is approaching the end of most practical experimental isotherm measurements, especially volumetric, without special surface treatments or material selection for the reaction chamber to make it adsorptive-phobic. (For gravimetric the hang-down wires and pans must be special, but not the balance itself since it is outside the cold zone. This is much less problematic since one could use pans made of Teflon® and the wires can be coated.)

Thus, the first step in the calculation is to determine the χ_c values for each adsorbate. This determines the dominant (or classically, "Henry's law") adsorptive. In *Figure 9* are the calculations from the pure adsorptive isotherms that Arnold determine. There were considerable deviations above $\chi \approx 0$. Probably this is a large T error. However, this is the value where mesoporosity would start, but here does not seem to be any evidence of mesoporosity. Furthermore, Berg did not observe this deviation with Kr adsorption on anatase.

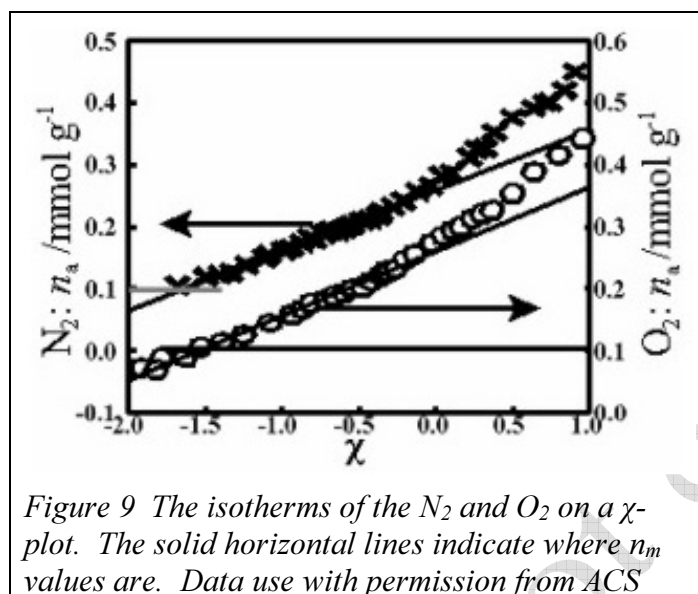


Figure 9 The isotherms of the N_2 and O_2 on a χ -plot. The solid horizontal lines indicate where n_m values are. Data use with permission from ACS

In **Table 2** are the output parameters χ_c and n_m along with other output values of interest.

Nitrogen adsorption:		Oxygen adsorption:	
$\chi_c =$	-2.992	$\chi_c =$	-2.494
$n_m =$	0.0808 mmol g ⁻¹	$\chi_c =$	0.0911 mmol g ⁻¹
$\sigma_{fit} =$	0.0012 mmol g ⁻¹	$\sigma_{fit} =$	0.0025 mmol g ⁻¹
$\sigma_{fit} \% FDR^* =$	0.73 %	$\sigma_{fit} \% FDR^* =$	0.60 %

The fits were made from n_a at the lowest given value and to their highest values less than $\chi = 0$. Obviously, a problem with temperature control existed. (See an attempted correction in Appendix I) However, the only need at this point is which adsorbate has the lowest χ_c and the selection of the range of the fit leaves the ratios of the χ_c approximately constant. Thus, the determination of the dominate adsorptive does not change with the fit range. The standard deviation relative to the data range is good with the imposed criterion of <1 % FDR. If values above $\Delta\chi = 0$ were included both would be out of the criterion without a pressure correction. The reason for this deviation could be solved by repeating the experiment. The problem is typical of an estimate of P_{vap} being too low, which also creates an error in the n_m , but it may be an unusual mesoporosity. However, the deviation seems to start at too low a χ value for mesoporosity.

Using this as a starting point, the binary isotherms are analyzed. The data scatter in the binary isotherm were much worse. However, it was noted by Arnold that the paired data points for the N_2 and the O_2 tended to correlate. So, the following strategy could be used to compensate. For each pair data points the error is due to the same relative experimental error, for example, not

* FDR over the range used, not necessarily the total full range. True in the Appendix I as well.

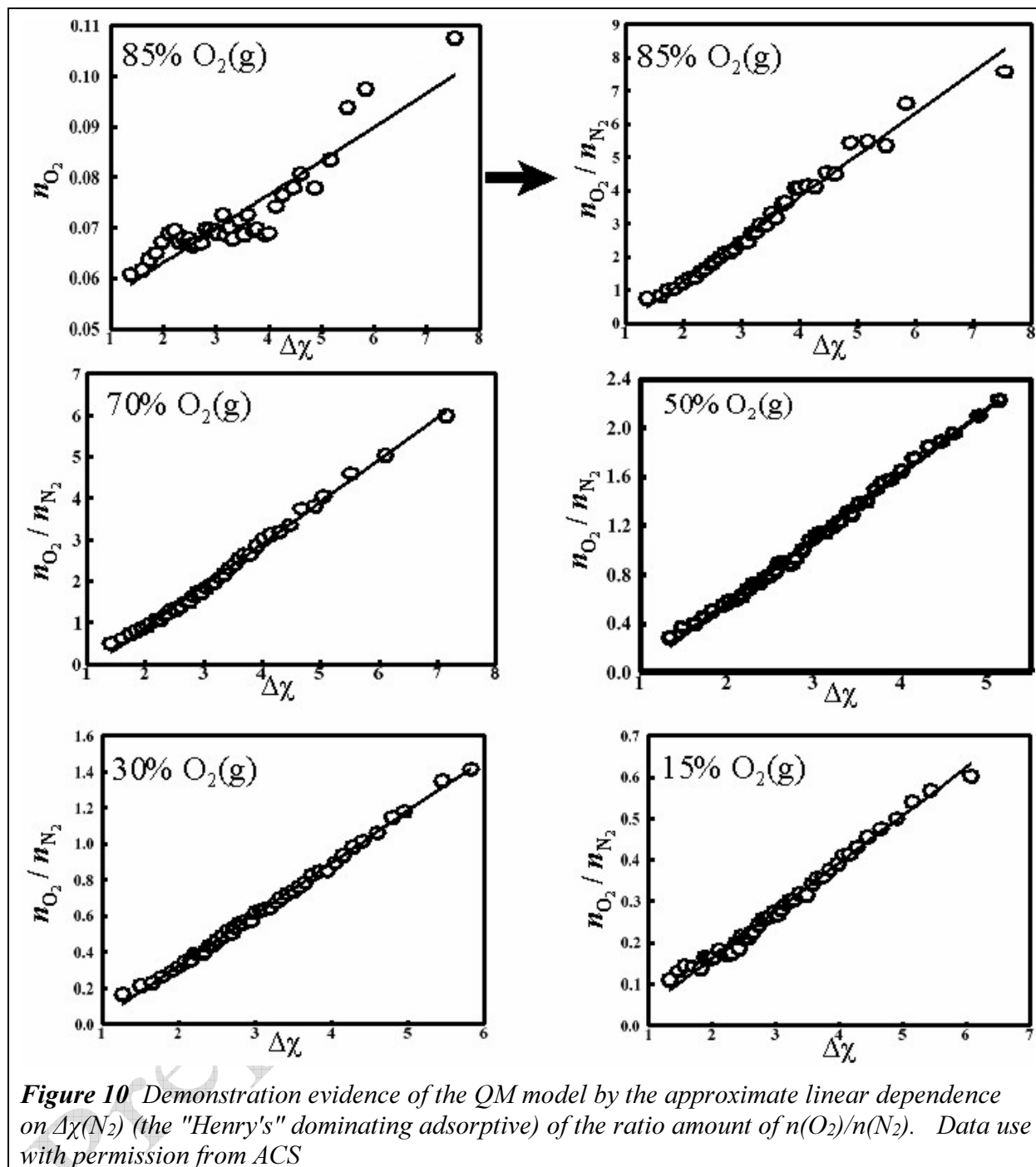
waiting long enough for equilibrium or a shift in the temperature, that is, the P_{vap} . These problems would be random relative* errors as far as the investigator is concerned, without additional information. This additional information is that the two adsorbates are being randomized due to the same experimental disturbance. Thus, the division of the n_{ad} for oxygen by the value of n_{ad} for the nitrogen should have less experimental random error. This is illustrated in **Figure 10** in the upper left panel versus the upper right panel with the isotherm of 85% O₂ and 15% N₂.

The improvement in the data scatter is such that the σ_{fit} changed from 1.7% to 1.27% FDR. However, of importance, the r^2 went from 0.834 to 0.981. Such improvement in r^2 was also noted for the other mixes. The improvements in the other binaries were even better, enough that $\sigma_{\text{fit}} < 1\%$ FDR. In **Table 3** are the output parameters and uncertainty of the measurements for the data shown for the data in **Figure 10**.

Table 3 - parameters of the ratio $n(\text{O}_2)/n(\text{N}_2)$ as in regression with $\Delta\chi(\text{N}_2)$				
%O ₂ :	Statistics	$n(\text{O}_2)/n(\text{N}_2)$	Values	$n(\text{O}_2)/n(\text{N}_2)$
85%	σ % FDR = r^2 =	1.27% 0.9819	line slope = $\Delta\chi$ intercept =	1.265 -1.248
70%	σ % FDR = r^2 =	0.80% 0.9922	line slope = $\Delta\chi$ intercept =	1.009 -1.130
50%	σ % FDR = r^2 =	0.90% 0.9942	line slope = $\Delta\chi$ intercept =	0.530 -0.494
30%	σ % FDR = r^2 =	0.18% 0.9972	line slope = $\Delta\chi$ intercept =	0.287 0.016
15%	σ % FDR = r^2 =	0.35% 0.9886	line slope = $\Delta\chi$ intercept =	0.115 0.250

The other ratios from the isotherms are also shown. These plots should be linear versus $\Delta\chi(\text{N}_2)$. The slopes and $\Delta\chi$ intercept of these graphs track the O₂%. Indeed, the values of the slope plotted against O₂% is very close to linear. The regression for the slopes has an r^2 of 0.995 for the 5 points. The intercepts also trend with O₂% but the r^2 is only 0.86 with no obvious functionality.

* Definition of a relative error is a multiplicative error, versus an absolute error which is an additive error.



Only one of the fits fails the criterion for acceptability, the 85% set. and that was close. On the other hand, the pure isotherms adsorptives are also not well fitted and that is needed as the basis of the calculation.

There is even a linear relationship between the slope of the fits in **Figure 10** and the percent adsorptive of O_2 with an $r^2 = 0.995$ (good for 5 points). The intercepts followed the trend without a break in the trend at a $r^2 = 0.964$ with no obvious fitting function.

It is quite apparent that there might be some truth to the two approaches taken here, but it is also apparent that more critical experiments on binary adsorption are needed. The derivation is not particularly clear, and one should be very skeptical about what has been presented above.

The experiment was, indeed, a very difficult one and with modern equipment the situation might improve. Unfortunately, such modern equipment is not available commercially today. Not using equipment that does not fulfill the advice to avoid the **Big Errors** mentioned previously, may not yield useful answers. Obtaining inaccurate experimental results is always a problem if one wishes to check theoretical formulations. Here is where some graduate students could make a big impact.

Conclusion – binary adsorption:

It was demonstrated in this section that the calculation of the binary adsorption isotherms from the individual isotherm outputs is probably possible. Two example publications were presented and calculated. One publication the concentration of the adsorptives are set at 1 bar and the composition varied. In the other study, the concentration of the adsorptives are fixed and the pressure varied. Ideal solutions were assumed for both cases and the adsorbate that yields the highest exothermic energy, that is the lowest χ_G , rules the calculation. (This Energy assumption has been called Henry's law binary adsorption rule in classical adsorption theory⁵⁵.) With these assumptions, the QM model yields reasonable answers for the experiments.

If the adsorption energies of the two adsorptives are about the same, there might be significant amounts of the lower energy adsorbate in the first layer. This, then, needs to be accounted for. However, energy also depends on the adsorptive vapor pressure, P_{vap} , so it may be hard to find a near perfect match to test this glitch.

Hardly any binary isotherm is ideal and in real situations the adsorption will need to take into consideration the binary bulk isotherm. Thus, the first layer might be solved using the isotherm output parameters and the subsequent layers will probably require partially the information from the bulk liquid diagrams mixed with first layer concentration enhancement. Although, the above examples do not seem to indicate this idea.

At any rate, by accounting for the quantum nature of binary adsorption seems to be a step forward, but much work is yet to be performed, both theoretically and experimentally.

Overall Conclusion for the Series

The first thought is the approach to science. No theory, law or hypothesis should be thought of as settled. This psychological problem is a trap for advancement of science. When this happens, the field 1) shuts down to new ideas and 2) becomes an art rather than what should be a science. Exceptions to old theories are incorporated and rationalized at the expense of reliability. The advancement and innovation of theoretical models is preempted. The goal to advanced theories that simplify calculations and to obtain better results more quickly* is stifled.

Will AI solve these problems? What do you suppose AI would do for physical adsorption? Obviously, it would start with the BET and go downward from there. Use of QM or ESW seem very unlikely, since the literature on these subjects is too small in comparison. It is even less likely to invent a theory that is thought out and tested, after all, how would it test it, by comparison to BET, Monti Carlo and perhaps some version of DFT? How would AI construct a critical experiment?

BET is one of those theories that has served science in a negative way by stifling innovation and squelching presentation of new hypothesis for adsorption. It is true that the BET might yield a faux value for surface area, which is psychologically pleasing but of little practical use. It is doubtful that it can be an unbiased certification benchmark since the faux values vary from experimental setup and where the data points are taken. At least in the last half century, critical analyses by other investigators have not been performed, or if they have been, were probably not allowed in the literature especially if a problem with BET was indicated. The IUPAC study named BETSI^{†11} yielded some answers where the uncertainty value was greater than the mean value. However, it was well known that BET is a poor fit for the entire isotherm and that the answers obtained are statistically very poor. Thus, the uselessness for certification. This latter problem is hidden by using the BET transform, which in the "linear" range produces values that are specifically dependent upon the independent (abscissa) value. The "fits" are often quoted as

* This psychological barrier is just not a science "thing." It is also important for engineering and for practical production. Here are two stories from my experience one had a bad outcome, if you wish to call a bad outcome the waste of \$8,000,000,000 is bad, but the other had a good outcome at literally the last day. This other project that cost about the same as the first, and it had very large implications for the safety of USA. The first one could have been avoided, had they taken my advice. But the engineering concept was already set, and they tried for another 10 years to make it work with failure after failure. Eventually, the politicians got involved and pulled the plug. The second one was solved on the deadline. The DoD was about to scrap an entire missile system that was already built except for this last part. They finally called upon the scientists, one day before the deadline. We provided a simple fix that solved the problem literally, yes literally, the next day with one experiment.

† Committee consisted of Johannes W. M. Osterrieth, James Rampersad, David Madden, Nakul Rampal, Luka Skoric, Bethany Connolly, Mark D. Allendorf, Vitalie Stavila, Jonathan L. Snider, Rob Ameloot, João Marreiros, Conchi Ania, Diana Azevedo, Enrique Vilarrasa-Garcia, Bianca F. Santos, Xian-He Bu, Ze Chang, Hana Bunzen, Neil R. Champness, Sarah L. Griffin, Banglin Chen, Rui-Biao Lin, Benoit Coasne, Seth Cohen, Jessica C. Moreton, Yamil J. Colón, Linjiang Chen, Rob Clowes, François-Xavier Coudert, Yong Cui, Bang Hou, Deanna M. D'Alessandro, Patrick W. Doheny, Mircea Dincă, Chenyue Sun, Christian Doonan, Michael Thomas Huxley, Jack D. Evans, Paolo Falcaro, Raffaele Ricco, Omar Farha, Karam B. Idrees, Timur Islamoglu, Pingyun Feng, Huajun Yang, Ross S. Forgan, Dominic Bara, Shuhei Furukawa, Eli Sanchez, Jorge Gascon, Selvedin Telalović, Sujit K. Ghosh, Soumya Mukherjee, Matthew R. Hill, Muhammed Munir Sadiq, Patricia Horcajada, Pablo Salcedo-Abraira, Katsumi Kaneko, Radovan Kukobat, Jeff Kenvin, Seda Keskin, Susumu Kitagawa, Ken-ichi Otake, Ryan P. Lively, Stephen J. A. DeWitt, Phillip Llewellyn, Bettina V. Lotsch, Sebastian T. Emmerling, Alexander M. Pütz, Carlos Martí-Gastaldo, Natalia M. Padial, Javier García-Martínez, Noemi Linares, Daniel MasPOCH, Jose A. Suárez del Pino, Peyman Moghadam, Rama Oktavian, Russel E. Morris, Paul S. Wheatley, Jorge Navarro, Camille Petit, David Danaci, Matthew J. Rosseinsky, Alexandros P. Katsoulidis, Martin Schröder, Xue Han, Sihai Yang, Christian Serre, Georges Mouchaham, David S. Sholl, Raghuram Thyagarajan, Daniel Siderius, Randall Q. Snurr, Rebecca B. Goncalves, Shane Telfer, Seok J. Lee, Valeska P. Ting, Jemma L. Rowlandson, Takashi Uemura, Tomoya Iiyuka, Monique A. van derVeen, Davide Rega, Veronique Van Speybroeck, Sven M. J. Rogge, Aran Lamaire, Krista S. Walton, Lukas W. Bingel, Stefan Wuttke, Jacopo Andreato, Omar Yaghi, Bing Zhang, Cafer T. Yavuz, Thien S. Nguyen, Felix Zamora, Carmen Montoro, Hongcai Zhou, Angelo Kirchon, and David Fairen-Jimenez

the fit to the transform and not to the dependence of amount of adsorbate versus pressure. The measurement of surface area is also in doubt, as the recent “effective surface area” handle (whatever that means) attests to. (At the Oak Ridge labs, measurement by electron transmission microscopy modified with a computer to act as tomography always disagreed with the BET. It always yielded an answer that was too low in comparison to the BET. So, the technique was abandoned and funding ceased. That shows how blind the belief in BET was correct.)

It must also be pointed out that the Langmuir isotherm for chemisorption has also been a stumbling block for several scientific areas and has not been tested adequately. It has been assumed correct in many publications with no indication of validity.

The disproof of the “Henry’s law” for physisorption, should be the death nail for the BET and Langmuir and all other “Henry’s law” isotherms, including multiple addition, multiplications and exponentiations of these two. The only isotherm forms that are excluded from this class are those of the Dubinin types, and these can be approximated by the QM approach^{12,13}. They yield the approximately correct pore volume, but yield neither the low pressure information nor other properties of the isotherm correctly.

All theoretical formulations except the QM/ESW are incapable of correlating the heats of adsorption with calorimetric heats without invoking some impossible entropy changes. The calculation of the heats of adsorption from the QM/ESW is straight forward and accurate without any arbitrary parameter (adjustable input constants) for the small number of experiments in the literature that make the measurements with the same adsorbate-adsorbent system¹⁴

What about the future? Of course, no one can tell how things will fare for physisorption. It is my belief that the QM/ESW approach promises to be a step forward. However, in the rush to “improve” QM/ESW, the discipline may be steered again in the wrong direction by propping up a hypothesis whose validity is in question. It should be encouraged to attempt to disprove this hypothesis, and indeed this is a noble thing to do even if there is no replacement, at least it will be known that a replacement is needed.

As noted in the various sections, the testing of the QM/ESW hypothesis and the collection of data related to such tests is very meager. Testing of adsorptives on well-known adsorbents is still in order, especially if the HV or, if needed, UHV had been lacking. Data is required down to the threshold pressure, which yield the correct energies upon which the rest of the analysis hinges. For example, the data by Goldmann and Polanyi¹⁵ has been analyzed in the forementioned book¹⁶, but the low-pressure data is missing. This is no comment on their technique. The ability may not have been possible for them. This would be an obvious group of isotherms to redo with modern equipment from which the “**Big Errors**” have been eliminated.

Finally, the statement by Bertrand Russell¹⁷ should be repeated as a mantra, as Polanyi¹⁸ stated: “The triumphs of science are due to the substitution of observation and inference for authority. Every attempt to revive authority in intellectual matters is a retrograde step. And it is part of the scientific attitude that the pronouncements of science do not claim to be certain, but only the most probable on the basis of present evidence. One of the great benefits that science confers upon those who understand its spirit is that it enables them to live without the delusive support of subjective authority.”

Sadly, I add: “Unfortunately, the authorities are not so much within governments, churches, or society but rather within the scientific community itself. Lysenkoism is alive and well. It is practiced by the science ‘authorities.’”

Looking Forward:

There is no question that the QM/ESW hypothesis is far superior to any other formulated “theory” or proposal presented so far to date. The disproof of the “Henry’s law” “theories” eliminates these older theories as being false. These include all combinations of the BET and Langmuir presentations, including multiple additions and multiplications and exponentiation of these forms. Even though the Dubinin types of isotherms are not “Henry’s Law” isotherm, they also predict extrapolation to [0,0]. Thus, except for total pore volume under certain conditions, they do not yield other properties of the isotherm correctly.

Thus, the only proposed hypothesis that yields both the isotherm fit and yields the heats of adsorption consistent with the isotherm, is the QM/ESW hypothesis. This proposal fits the isotherm usually within 1% FDR (Full Data Range) from $P = 0$ to at least 98% of $P = P_{\text{vap}}$.

Although these features are consistent with the QM and ESW derived equations as presented here, what proof is there that this is correct? This is not a question that the scientific method can provide. It can only be stated that these hypotheses do the best job so far of calculating the isotherm and the calorimetric data. In contrast, all other “theories” have either been disproved, that is all the “Henry’s law” isotherms or have some other weakness.

The success of the QM has been accomplished, in principle, with one derived set of equations and modifications to account for additional features beyond the “simple” case. The results is confirmed in agreement with ESW and compatible with calorimetry. These are some things that all other formulations fail to do.

There has not been much testing of these hypotheses (QM and ESW.) This is especially the case if one excludes the papers mentioned as the pioneering authors* and referenced herein. There has also not been much fundamental advance in the theories for the past 40 years. Since these hypotheses have generally been either ignored or excluded from scientific literature, critical experimentation by others is lacking. Such experiments are very appropriate now.

If QM/ESW stands up to testing and confidence becomes solid, that is not the end of the research needed. The modelling is very crude, using symmetrical ad molecules and simple surfaces that fulfill certain conditions. For example, these conditions include the energy of adsorption must be greater than the exothermicity of vaporization. Some work has been attempted to address this latter problem, without clear results at the moment. What new insights might this lead to? Another example includes making the “big box” smaller and smaller. What happens if the big box is on the nanoscale or even the atomic scale, for example interactions with biomolecules. Indeed, there is some indication that some channel controls are due to a QM effect. So, there appears to be much innovative work ahead, if the validity of the QM/ESW hypothesis is supported.

* That is, Polanyi, London, Fuller, Condon, Adolphs and coauthors.

Appendix I

he Arnold data had an obvious temperature problem. However, in attempting to correct for P_{vap} three data each for both exceeded the P_{vap} which is not allowed unless there is a reason (unknown) for it.

Here are the revised values for **Table 2**.

Table 4- Parameters for the O_2 and N_2 isotherms on anatase by Arnold.			
Nitrogen adsorption:		Oxygen adsorption:	
$\chi_c =$	-2.322 ± 0.2	$\chi_c =$	-2.446 ± 0.2
$n_m =$	$0.1111 \text{ mmol g}^{-1}$	$n_m =$	$0.1046 \text{ mmol g}^{-1}$
$P_{\text{vap}} =$	1.077 bar	$P_{\text{vap}} =$	1.12 bar
$\sigma_{\text{fit}} =$	$0.0015 \text{ mmol g}^{-1}$	$\sigma_{\text{fit}} =$	$0.0014 \text{ mmol g}^{-1}$
$\sigma_{\text{fit}} \% \text{ FDR} =$	0.25%	$\sigma_{\text{fit}} \% \text{ FDR} =$	0.22%

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

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