5) **Modern theoretical developments for replacements of “Henry’s Law” isotherms.**

The development of alternatives to the “Henry’s Law” isotherms is not to continue modifying the BET or Langmuir, which used acceptable theory 100 years ago, but to use more advanced physical theory and mathematics. This more advance methods include QM and ESW, even though it is about 100 years the foundational development. Almost every other field of chemistry references back to QM. Physical adsorption is an exception. This has been the case for many years[[1]](#footnote-1).

The most common objective presented by that most chemists, engineers, and some physicist is that the adsorbate molecules are “too big and massive” to behave according the quantum mechanics. This is, of course, nonsense. The QM model assumes that adsorbate molecules are not affected by irregularities in potential variations on the order of atoms. The argument against this is that molecules are too big to behave like a wave. This argument is widely disputed by the physics literature. Firstly, why would QM for high mass molecules, not apply? Physics dictates, today, that all matter is controlled by QM. Secondly, this argument has been proven false by several Young’s experiments[[2]](#endnote-1),[[3]](#endnote-2),[[4]](#endnote-3). These molecules include He molecules, I2 molecules (molar mass 254), C60 “buckyballs”[[5]](#endnote-4),[[6]](#endnote-5) (molar mass 720) and a series of molecules over 10000 amu. Indeed, quantum interference has been observed with several fluorinated thiol chains with masses above 10,000[[7]](#endnote-6). If this had not been true it would have disproved the linearity of QM, something at this time would be a big shock to physics. Thus, the wave nature of adsorbate molecules is expected and is made the first assumption of the derivation. This is a firm assumption, no exceptions

Thus, the following formulation is totally correct according to fairly early developments in quantum mechanics which includes perturbation theory, a method developed before quantum mechanics.

*The Models:*

There are two methods to arrive at the same overall equation for adsorption. These include:

* A quantum mechanical (QM) derivation using perturbation theory. This followed by using the Grand Canonical Partition Function (GCPF)
* A method that uses the Disjoining Pressure Theory inserted into Thermodynamic Functions. This second method utilizes Disjoining Pressure Theory that was developed at about the same time as QM, but was generally ignored. Its principles can be derived from QM.

Other interesting inputs to this process are those by Polanyi, Dubinin and Fuller in their insight.

The derived equations are simple and have simple macroscopic explanation, although it is best to keep in mind that the behavior is QM dependent, so to overdo the macroscopic explanation is dangerous. There are Lemmas to provide some guidance. There will be three graphic representations based on transforms of the abscissa, that is the pressure value, only. The isotherm plot untransformed yields surprisingly little information.

Some addition terms need to be defined here:

* The monolayer (total) equivalence, *n*m: It is the amount of adsorbate molecules that would cover the adsorbent to saturation as IF they all WERE in direct contact with the adsorbent in the same orientation for molecules that can be in direct contact, that is, [*def*] the first “layer” molecules.
* The total coverage, θ = *n*ads/*n*m
* The first “layer” coverage, θ1
* The nth “layer” coverage, θn

*The three standard states*

As the QM derivation proceeds to the final overall answer, there are three energy states that are used as reference states or standard states.

1. The particle in the box model, the unperturbed reference state is the bottom of the box (= 0) that has infinite sides. Since this model is a very big box and the particle is very small the first approximation for the increase in energy from this unperturbed state is assumed correct, although this is not necessary and for more complex systems higher approximation may be needed. This is the so-called “big box approximation.”
2. The second reference state is 1 bar adsorptive pressure. This turns the perturbation calculation upside down. It is also the normal thermodynamic reference state and is used for calorimetry.
3. The third reference state is the vapor pressure of the adsorptive at the temperature of the adsorbent. This is the so-called relative pressure used in isotherm representations.

It also makes a difference if the perturbation is of a higher energy or lower energy than the energy of vaporization of the adsorptive. Only the case where[[8]](#footnote-2):

|  |  |  |
| --- | --- | --- |
|  |  | *Equation 1* |

Is considered here, which is the most common case. This equation indicates that the heat of adsorption is greater, exothermically, than the heat of vaporization. There are some cases with adsorptives with high molar heat of vaporization, such as water or benzene, where there may be the need to remodel.

The particle in the box looks as follows:

**Assumptions:**

The assumption for the quantum mechanical (QM) description is reasonable for any theoretical chemist. The following is the simple case for only one type of adsorptive being measured. (Going to binary mixtures gets a little more complicated although there are examples of simple binary cases.) The derivation first must consider the “simple case”, that is, a homogeneous, flat non-porous surface. Expansion to the more complex cases will use the “simple case” and add to it “features” or modifications. The underlying theory remains with these added features.

The only assumption, other than the validity of quantum mechanics, is a common technique used int QM, called separation of variables. The assumption is that the wave function of an adsorbate particle may be separable into two geometrical parts as:

Part 1 is parallel to the plane of the surface (*x,y*). This is the most important part and generates the isotherm. It specifies the amount of adsorbate molecules directly in contact with the surface and the amount in subsequent “layers.” This latter term is in quotes because the word is a classical interpretation, but molecules are indistinguishable, which is an important concept in QM. It yields *n*m, the monolayer equivalence from the isotherm directly without modeling or the use of standard plots. Furthermore, the heats of adsorption obtained from the equations are in excellent agreement with those obtained by calorimetry.

Part 2 is the wave function normal to the surface (*z*). From the “layer” amounts, one obtains an estimate of the amount that fills the pores from each “layer.” For actual vertical distance from the surface, one needs to assume an intermolecular potential, such as a Lennard-Jones potential to get the distribution between the “layers.”

The only difference between this the normal QM treatment is that the xy-plane is treated differently from the z direction, whereas, normally for this type of problem all three dimensions are treated the same. Notice that neither Part 1 nor the Part 2 involve input parameters. However, once the basic outputs are obtained, cross-sectional area and diameter of the adsorbate is needed to get physical dimensions. These measurements are not as easy as the BET or IUPAC formulation naively assumes.

The calculation was originally based on non-localization, that is, the specifics to the potentials of individual atoms and molecules on the surface is not detected, but rather the overall potential. This assumption is used for liquids versus solids, where the local potential becomes important. This assumption has also become common in other physisorption calculations such as NLDFT, where NL stands for Non-Local. Thus, the energy is not localized either by the surface atoms nor the admolecules. Once a molecule is adsorbed, it becomes part of the system, as defined above.

For a nonporous homogeneous surface, if the resulting equations are fit to the isotherm, then there are two output parameters, *n*m, and *E*a. The fit for these simple cases is a linear regression, which is quite simple. (Adding features require non-linear least squares routines.) If porosity exists, Part 2 is used to convert the extra output parameters to radii and volumes.

*Perturbation of the “particle in the box”[[9]](#footnote-3):*

To start a potential box with infinite walls (in potential) and a particle is placed in this box. The various dimensions will allow certain approximations that are not strictly need but makes the presentation easier. These dimensions are that the adsorbate molecule is extremely small compared to the adsorbate aliquot. These approximations have been referred to as the “big-box” approximation in the original publications[[10]](#endnote-7),[[11]](#endnote-8).

A one directional box is used here to illustrate, but this can be extended to 2 dimensions (2D – *x.y*) yielding a similar answer. A generalized quick derivation using the Hellmann-Feynman theorem will demonstrate this. The answer to this without a perturbation is very easy. QM calculation for particle in the box yields for the lowest (ground) state a value given by the one-dimensional (1D) equation:

|  |  |  |
| --- | --- | --- |
|  |  | *Equation 2* |

For argon the energy for a 1 micrometer in 1D is ~0.5 × 10-6 or in 2 dimensions (2D) is about 1 × 10-6J mol-1. One needs to be on the nanometer range to be perhaps significant, since a 2D surface of 1 nm yields an energy of 1.0J mol-1. This is still small compared to a typical physisorption energies of about 3 to 10 **k**J mol-1. Thus, one can ignore the difference between the base energy and the ground state with little error. This is merely a simplification, if there is a need, this can be altered.

After the first molecule enters the box, with the energy given by *Equation 2* the box now contains a perturbation. (This was called a particle in the box with a “tooth,” rather than a hole.) Normally, this perturbation, which is for the second adsorbate molecule, yields the following equation in the modified Schrodinger equation:

|  |  |  |
| --- | --- | --- |
|  |  | Equation 3 |

It is not necessary to use time dependent wave vector (or function.) Addition of the perturbation would be:

|  |  |  |
| --- | --- | --- |
|  |  | *Equation 4* |

Thus, multiplying both side by :

|  |  |  |
| --- | --- | --- |
|  |  | *Equation 5* |

So:

|  |  |  |
| --- | --- | --- |
|  |  | *Equation 6* |

(Normally, renormalizing is not needed due to the smallness of the perturbation, but it is OK to do so.) The increments designated with δ are very small so one should be able to use Hellmann-Feynman Theorem[[12]](#footnote-4):

|  |  |  |
| --- | --- | --- |
|  |  | *Equation 7* |

And since **H** is a function of space only and not time:

|  |  |  |
| --- | --- | --- |
|  |  | *Equation 8* |

However, to be clear, the δ*E*' will vary as the adsorption continues as a function of **E**(θ) and the energy of vaporization. At this point a diagram would be useful. [The notation is changed from previous notations[[13]](#footnote-5).] For the one dimension, *a* is the length of the perturbation (looking forward to 2 D) and *A* is the length of the 1D box. The is shown in *Figure 1* for the perturbation after the first admolecule is on the surface. The ground state and the bottom of the box are approximately the same value (~0.) The energy of the perturbation is β and the length of the box is *A.* The energy of β is referenced against *E*0. The perturbation changes as more admolecules are physiosorbed thus changing the base energy *E*0 to *E*1, *E*2, *E*3….

|  |  |  |
| --- | --- | --- |
| Figure the energy diagram for the particle in the box with a perturbation formed from the first admolecule present. | Figure The energy diagram after the first adsorbed particle; showing how the constant β is modified by the perturbation. | Figure Energy diagram showing the further decrease in β due to the second admolecule |

The perturbation, called particle-in-box-with-a-tooth to describe *Figures 1 to 3*, is then:

|  |  |  |
| --- | --- | --- |
|  |  | Equation 9 |

However, according to *Equation 9* the normalization is limited to the distance *A* and outside this space it is zero, since the walls of the box are infinite. Thus, since **H'** is a function distance only and the integral over the area *A* is the same as the integral over all space then equation becomes:

|  |  |  |
| --- | --- | --- |
|  |  | Equation 10 |

Thus, *E*1is given by:

|  |  |  |
| --- | --- | --- |
|  |  | Equation 11 |

However, since *E*0 ≈ 0 then:

|  |  |  |
| --- | --- | --- |
|  |  | Equation 12 |

*E*1 is the energy that the second admolecule will experience upon adsorption. In *Figure* 2 the admolecule provides a perturbation for the third molecule of:

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | |  | *Equation 13* | |
| So: | |  | *Equation 14* | |
| Competing the “square:” |  | | | *Equation 15* | |

This begins the sequence based on the binomial lemma with *y*n = *E*n/β:

|  |  |  |
| --- | --- | --- |
|  |  | *Equation 16* |
|  |  | *Equation 17* |
|  |  | *Equation 18* |
| Back substituting and using traditional *N* in place of *n*: |  | *Equation 19* |

Typically. the cross-section of a simple molecule is about 0.2 to1nm and the adsorbent surface aliquots are in the range of micrometers. Squaring these numbers and dividing one gets a factor of at least 1 × 106 so an approximation of an exponential function for the second term in the brackets may be made provided there is a relationship between *n* and *x*. This relationship is called the monolayer equivalence, θ, or classically, the coverage:

|  |  |  |
| --- | --- | --- |
|  |  | *Equation 20* |

Apologizes are in order for the next step, which should be simple, but there has been in the past strong opposition to the approximation that follows, so there may be information that one does not care to read since it should be obvious.

|  |  |  |
| --- | --- | --- |
| *Let:* |  | *Equation 21* |
| *Then:* |  | *Equation 22* |
| *But for large x:* |  | Equation 23 |
| So, *Equation 18 or19 becomes* |  | Equation 24 |

The question is how big *x* needs to be. The follow are calculations.

* For a 1% error *x*= 50.
* For 0.1% error this is *x* = 500.
* For 0.01% error this is *x* = 5000.

Thus, the ratio of *A* to *a* is unlikely to present a significant error in this approximation.

The final result for the QM derived energy:

|  |  |  |
| --- | --- | --- |
|  |  | *Equation 25* |

Thus, we arrive at the empirically supported isotherm by Polanyi[[14]](#endnote-9), by DeBoer and Zwikker[[15]](#endnote-10) and by Fuller[[16]](#endnote-11).

One would tend to think that the upper limit would be the saturating energy, in other words the Δla**E**(*T*ads) = Δlg**E**(*T*ads) = β. However, at this point β is an arbitrary constant. The proof of this comes with the Grand Canonical Partition Function along with the proof of the Dubinin “thermodynamic criterion.”

There is one more observation to be made from these equations. Notice that the greater the coverage, slower the coverage becomes by the exponential function. Looking at it another way, how is the “open surface” being depleted. The answer is obvious:

|  |  |  |
| --- | --- | --- |
|  |  | Equation 26 |

Where θ*MT* is the remaining surface that can be filled, patches of zero areal density or less density[[17]](#footnote-6) < 1. If that is the case than the first “layer” θ1 is given by:

|  |  |  |
| --- | --- | --- |
|  |  | *Equation 27* |

Subsequent “layers” can be calculated by assuming the first layer is fixed and acts as part of the surface, then the following equation is obtained for the 2nd layer:

|  |  |  |
| --- | --- | --- |
|  |  | *Equation 28* |

This can be repeated over and over so:

|  |  |  |
| --- | --- | --- |
|  |  | *Equation 29* |

*Equation 27* leads to the so-called log-law:

|  |  |  |
| --- | --- | --- |
|  |  | *Equation 30* |

Which is common in the literature and a few examples have already been presented in this report.

**Grand Canonical Partition Function**

In the above equations, β is an arbitrary constant and the functional relationship to pressure is not

obvious. The meaning for β and the pressure dependence will now be determined using the Grand Canonical Partition Function (GCPF). The system, the adsorbate and adsorbent, is an open system therefore the GCPT is an appropriate technique to determining the thermodynamics

First recall that the base energy for the calculations for β was the bottom of the well. The surrounding energy however is not defined by this energy but by the standard thermodynamic convention, designated with the symbol “⦵,” as shown in *Figure 4.* This figure shows the shift in the reference energy to 1 bar for the adsorptive.

|  |  |  |
| --- | --- | --- |
|  | Figure The shift in reference energy to the standard thermodynamic reference of 1 bar for the adsorptive. |  |

The energy is changed in an open system by changes due to the release of energy by the adsorption:

1. From the adsorbate surface interaction with adsorbate molecules
2. By adsorbate-adsorbate interaction and
3. The energy indicated by the change of state for the adsorptive

The first of these energies is what the particle-in-box-with-a-tooth provides. The second one must be the interaction between the adsorbate molecule, and it must be between all of the molecules or:

|  |  |  |
| --- | --- | --- |
|  |  | Equation 31 |

Where here the quantity ε is defined as an independent quantity from the reference state. The third quantity is given by the canonical partition function for the adsorptive gas, in other words, what the gas loses the system obtains. So, these three quantities are the energies that go into the GCPF. At this point a conversion to a new standard state becomes convenient. This is to the standard pressure as the vapor pressure of the adsorptive as designate by the energy value ε, whose meaning is yet to be discover in the derivation.

|  |  |  |
| --- | --- | --- |
|  |  | *Equation 32* |

It is shown in the following that this equation is correct.

|  |  |  |
| --- | --- | --- |
|  |  | *Equation 33* |

It is assumed that there are no changes in rotational or internal vibration for the adsorptive-adsorbate molecule change. This can obviously be change with the determination that these are present. There is a fourth term added here of ½*N*θ1*kT* which account for the loss of one translational mode for molecules touching the surface. This quantity is extremely small compared to normal energies observed with physisorption, so it also is ignored here.

The usual method is to take the **natural log** of **Ξ** (which yields the grand canonical potential) and then differentiate with respect to *N* the maximum term[[18]](#footnote-7), designated here by **Ξ**max, obtained from the **natural log**, the grand potential**.**  This maximum is found by setting the resultant equation to 0. The canonical ensemble term λZ is replaced by the fugacity[[19]](#footnote-8), *̃*, which is equal to simply *P* at low pressures, which is typical for physisorption. Ignoring the first layer translation then:

|  |  |  |
| --- | --- | --- |
|  |  | *Equation 34* |

In place of *̃* substitute use *P* and using molar quantities[[20]](#footnote-9)*.*

|  |  |  |
| --- | --- | --- |
|  |  | Equation 35 |

Now to evaluate ͞ε. As θ goes to infinity then *P* must go to *P*vap. Thus, ε is the thermodynamic internal energy of vaporization at the temperature of the adsorbent (as well as the Gibbs’ free energy, but ΔlaS = 0) so ͞ε is *RT***ln**(*P*vap), which defines a new the standard pressure, *P*vap.

|  |  |  |
| --- | --- | --- |
|  |  | *Equation 36* |
|  |  | *Equation 37* |

\*\*\*What happens if θ goes to zero? In limiting case, *P* must be finite. This is referred to as the threshold pressure with the symbol *P*ς. Thus, quantum mechanics predicts that there is a threshold pressure, and violates “Henry’s Law” which makes it difficult to release in publications. This further implies a phase change as discussed above. This is the phase change must be to the liquid state and there is no requirement for a “break” in the isotherm at higher pressure. However, as will be seen in the mesoporosity where these “simple conditions” are not met. 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 obviously macroscopically less dense than the bulk liquid. This is an interesting question that needs more research.

The solution for θ as a function of pressure is easy to obtain:

|  |  |  |
| --- | --- | --- |
|  |  | *Equation 38* |

Where if θ = 0:

|  |  |  |
| --- | --- | --- |
|  |  | *Equation 39* |

Then:

|  |  |  |
| --- | --- | --- |
|  |  | *Equation 40* |

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

|  |  |  |
| --- | --- | --- |
|  |  | *Equation 41* |

So that the linearly transformed equation is obtained:

|  |  |  |
| --- | --- | --- |
|  |  | *Equation 42* |

Both the plot of amount versus χ and Δχ present meaningful data. The **χ** plot is a plot of the amount adsorbed versus the monolayer equivalence; whereas, the Δ**χ** plot yields the energy function, Δla**E**(θ) as −*E*a*RT***exp**(−Δ**χ**).

A note about the energies. All the energies are negative, i. e. adsorption is exothermic and the energies are leaving the isothermal system in the form of heat. Another point is that the heat of adsorption in the calorimetry is Δla**E**(θ) + ε, so it is offset from the heat calculated from the isotherm (−*E*a*RT***exp**(−Δ**χ**).)

The heat calculated is unlikely to be the isosteric heat of adsorption, where attempts are made to differentiate two or more isotherms to get the values. This should be OK if one were to do a fit of very good data to the equations described here, but, of course, no one has done this[[21]](#footnote-10).

Thus, for the “simple case” everything is now define:

1. For the monolayer coverage, one obtains *n*ads as a function of Δ**χ** whose slope yields the *n*m the monolayer.
2. The energy of adsorption as a function of χ through the starting energy *E*a and the function −*E*a*RT***exp**(−Δ**χ**)

A note of caution, even if θ = Δ**χ**, they are not the same thing. This is like the familiar equilibrium expression *K(T) =* ***Q****(C).* It is important to keep this in mind when one start use restricted geometries. The **χ** values are areal densities, not amounts, a difficult QM concept to keep in mind.

This also means that the total θ value is Equations 25 to 28 in the exp function is actually Δ**χ**. More about this is presented for microporosity.

The next questions are:

* How does one take heterogeneity into account?
* How does one calculate the heterogeneity?
* How does one determine if there is microporosity and how much?
* How does one determine if there is mesoporosity and how much and big?

These topics are next. But here’s a tip for heterogeneity. The **χ** plots have as the ordinate moles (or number of things) and can straight out add multiple plots.

Lemma 1: The first “layer” will always get filled by the log-law, even if other “layers” might start to form. If, for example, if the second “layer” begins to form and the first “layer” requires more admolecules to follow the straight-line filling in the log-law, then the second “layer” will release some admolecule to fulfill the law. This is referred to as “cannibalization.”

Here there is reference to the log-law which the first layer must follow all the way to saturation. This can be derived from *Equation 25* by taking the **ln**.

The use of θ is for the simple case where there is no physical barrier

1. For at least 63 years in my experience. Perhaps one could mark it beginning with Pauling’s first edition of the “Nature of the Chemical Bond.” [↑](#footnote-ref-1)
2. O. Carnal, J. Mlynek, Physical Reviews, **66** (1991) 2689. [↑](#endnote-ref-1)
3. I2 scattering paper. J. Can. Phys. [↑](#endnote-ref-2)
4. O. Nairz, M. Arndt, A, Zeilinger, Am. J. Phys., **71** (2003) 319. [↑](#endnote-ref-3)
5. M. Arndt, O. Nairz, J. Vos-Andreae, C. Keller, G. van der Zouw & A. Zeilinger, “Wave–particle duality of C60 molecules” *Nature* **401**, 680–682 (1999). <https://doi.org/10.1038/44348> [↑](#endnote-ref-4)
6. A. M. I. Rae, Review in Nature Magazine, **401** (14 OCT 1999) pp 680-682). See *Eur. J. Phys.* **23**, 615-621 (2002) [↑](#endnote-ref-5)
7. S. Eibenberger, S. Gerlich, M. Arndt, M. Mayor and J. Tüxen, Phys. Chem. Chem. Phys., **15** (2013)14696. [↑](#endnote-ref-6)
8. The actual mathematical proof of the definition of “ε” comes later. [↑](#footnote-ref-2)
9. There is a short-cut taken using the Hellmann-Feynman theorem. For a more complete derivation see the 2nd edition of “Surface Area and Porosity Determination by physisorption 2nd edition” by J. B. Condon, Elsevier Press, Netherlands ISBN 978-0-12-818785-2. [↑](#footnote-ref-3)
10. J. B. Condon, US Government Repot. Y- [↑](#endnote-ref-7)
11. E. L. Fuller, J. B. Condon, [↑](#endnote-ref-8)
12. This is the easiest way. You can take the long way by referencing some QM textbook. For example, “Introduction to Quantum Mechanics by Chambers W. Sherwin, from Holt, Rinehart and Winston, New York. Thus, I have presented three different ways of coming to the same answer. [↑](#footnote-ref-4)
13. This is being done to avoid confusion with look-alike character, for example Italic “*a*” and Greek “α”. Another reason the “threshold” symbol subscript “c” is replace with Greek “ς” since “c” is used by IUAC for the critical *P*cand *T*c. [↑](#footnote-ref-5)
14. Polanyi [↑](#endnote-ref-9)
15. DeBoer, Zwikker [↑](#endnote-ref-10)
16. Fuller [↑](#endnote-ref-11)
17. QM does not specify which it is. Good question. Does it even matter? [↑](#footnote-ref-6)
18. In other words, “What happens to the energy as one changes the amount incrementally?” [↑](#footnote-ref-7)
19. ̃ is the latest IUPAC symbol for fugacity. Ideal gas and other ideal quantities are used throughout for simplicity. Obviously, these assumptions can be changed. [↑](#footnote-ref-8)
20. The alternate IUPAC symbolism or overline for molar quantities is used throughout due to confusion with subscript “m” which also stands for “monolayer (equivalence,)” [↑](#footnote-ref-9)
21. To my knowledge, at least. [↑](#footnote-ref-10)