**2)**

**2) A short explanation of traditional physical adsorption theory analysis**

The traditional way of analyzing the physical adsorption isotherm is to determine which Type of isotherm it is according to its appearance. There are at least 6 Types of isotherms specified by IUPAC and some researchers have expanded this by using sub-Types to 9. Type 6 isotherm has steps in it that are attributed to distinct monolayers. However, this seems to be restricted to isotherms performed below the freezing point of the adsorptive. After Typing, analysis leads to the BET for Types II and IV and to other analysis for the other types. Type I used to be considered a subset of Type II but is no longer officially so. This is probably due to the unnatural attempt to make it fit. It has also been analyzed with the Langmuir isotherm, which seems more reasonable since it does not curve positive at *P*/*P*vap = 0.38 as require by the BET. Very often the BET is used for everything, but this is not the official position of IUPAC.

The BET had to be restricted in use. The first restriction is the “Sing” criteria[[1]](#endnote-1), the lower limit which was implied in the original statement. It restricts the analysis to the relative pressure range of 0.01 to 0.35. Initially, the lower limit was a natural result that the pressure readings would be inconsistent with readings above this limit. Additional qualifications are added to this to determine the linear portion of the transformed BET plot.

The problem with this restriction is that the presence of porosity interrupted this range. Sing’s, et al., recommendation[[2]](#endnote-2) to get around the problems, is the use of the α-s plots. They are standardized plots to which one can compare a non-ideal plot to. These plots make sense, only if the surface area assessment is correct which is in turn dependents upon the BET analysis. However, the selection of the linear portion in the transformed BET is often translocated by the porosity.

A further criterion, called the “Rouquerol” criterion, for the upper limit is requiring, which states that (at least 10) data points below the maximum of the function *n*ads(1 - *P*/*P*vap) be used. Here *n*ads is the moles adsorbed and *P*vap is the vapor pressure at the temperature of the powder sample. In most cases, this limit is usually less than 0.35 *P*/*P*vap.

A positive C is another criterion. If the use of restrictions it is unusual that the *C* constant is negative. A requirement widely ignored in several publications is the use a minimum of 10 points to fulfill the “Rouquerol” criterion.

Given all the requirements, less than 1/3 of the data of a particular isotherm is used without violating at least one requirement. Many isotherms do not fit the requirements at all.

There is another isotherm transform that is recommended by IUPAC for micropore analysis. Micropores are defined by IUPAC as pores of diameters 2 nm or less. (This definition is not used by the Modern Hypothesis.) For micropore analysis the recommendation is to use the Dubinin-Radakovich (DR) equation[[3]](#endnote-3),[[4]](#endnote-4) to extrapolate the *n*ads to *P*/*P*vap = 1. This is really a stylized way of using the Gurvitsch rule. If there is significant external surface area, which sometimes occurs, the more appropriate equation would be a different Dubinin, et al., equation. A generalize equation would be[[5]](#endnote-5):

|  |
| --- |
| Equation 1 is the class of Dubinin equations |

Thus, where *k* is a constant. *k* varies, but it is 2 for the DR equation. The Gurvitsch approximation yields the volume of the pores only. It cannot yield the surface area inside the pores or, for that matter, outside the pores.

For the most part, this is the situation up to today. There has been other developments, notably work by M. Polanyi[[6]](#endnote-6),[[7]](#endnote-7),[[8]](#footnote-1),[[9]](#footnote-2) deBoer and Zwikker[[10]](#endnote-8),[[11]](#footnote-3)and by E. L. Fuller[[12]](#endnote-9). Polanyi’s proposals were unfortunately opposed by Einstein and Brunauer and were not just ignored but generally scoffed at. Fuller avoided controversy by disguising what he published by plotting opposite to the Polanyi method and, although giving him credit, did not make a point of acknowledgement.

In the mid 1980’s the physical basis for Polanyi’s equation was firmed up with the discovery of the quantum mechanical (QM) reason for the observations. However, it could not be clearly stated due to classification problems. The word “quantum” tripped alarm bells, even though it had nothing to do with security. A classical explanation analogy was concocted to yield the same equation. However, in the first publications[[13]](#endnote-10),[[14]](#endnote-11) there are a hint to the true derivation with the statement that the derivation was a “big box” approximation. For quantum physicist this clearly means “first order perturbation theory.” Perturbation theory in the open literature also turned out to be a publication killer. Later, the theory made it into the literature with the WKB approximation[[15]](#endnote-12), which very few chemists have heard of.

This, then, is a short history of attempt to formulate a reliable and theoretically sound hypothesis of physical adsorption. It is an interesting and sad history with continued sallying forth despite some very serious questions. There has not been so far any disproof of the BET presented in the literature, nor for that matter the Langmuir and other Henry’s Law theories, of which there are many. There are plenty of indications that the BET is false, but these indicators, although numerous, are rationalized in one way or another. There is no sense to formulate any new hypothesis without a disproof by the criteria presented earlier. Specifically, the BET will be addressed, but for the curious one should also look at the publication that Langmuir received the Nobel Prize for with a critical eye and some calculations to understand that it too is troublesome[[16]](#endnote-13).

**Theories based on a “force field”:**

In recent years there has been a revival of the Polanyi and DeBoer-Zwikker idea of a force field approach. The idea was put forth by Tarazona[[17]](#endnote-14),[[18]](#endnote-15) and calculations were made for confined geometries for liquids. The approach was referred to as Functional Density Theory DFT (applied to physisorption.) Theoretically the problem is that one can bring back the old arguments that Brunauer used. What is this force field that has a decay constant of one monolayer thickness. None of the intermolecular attractions contain this field, but never-the-less it has been used.

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It has been used mostly unsuccessfully so there have been several variations of it. The problem is that to get high enough energies, one needed to use localized attractions, which in turn created adsorption curves that were stepped as if adsorption were with a solid and not a liquid. Freeing up the localization, of course, caused other problems. The main problem remains, where does the exponential decay force come from?

DFT and its variants, however, create a very pleasing spectral analysis for porosity, but it is being disputed today in the literature[[19]](#endnote-16). Even so, the final analysis relates back to measuring the surface area using the BET, which we are here in the process of disproving. Perhaps, the use of the QM analysis for the surface area would work better, but there is an alternative already in place for porosity measurement using the QM approach.

* Next: **The Langmuir and BET theories**

References:

1. K. S. W. Sing, in “Adsorption by Powders and Porous Solids – Principles, Methodology and Application” by F. Rouquerol, J. Rouquerol, K. S. W. Sing, P. Lliewellyn, and G. Maurin, eds, (2014) Chapter 7 p263-264. [↑](#endnote-ref-1)
2. J, B. Condon, “Surface Area and Porosity Determinations by Physisorption - measurements. Classical Theories and Quantum Theory, 2nd Edition,” Elsevier Publishers, Amsterdam, NL (2021) ISBN:978-0-12-818785-2See Reference 1, Chapter 7, pages 297-298 [↑](#endnote-ref-2)
3. See Reference 2, Chapter 9, pages 317-318, [↑](#endnote-ref-3)
4. M. M. Dubinin, L V. Radushkevich. Proc. Acad. Sci. USSR, **55** (1947) 331. [↑](#endnote-ref-4)
5. M. M. Dubinin, V.A. Astakhov, Adv. Chem. Soc. **102** (1970) 69 [↑](#endnote-ref-5)
6. M. Polanyi as quoted by S. Brunauer, “The Adsorption of Gases and Vapors, Vol. 1” (1945) Princeton University Press, Princeton, NJ mentioned in ref. 9. [↑](#endnote-ref-6)
7. M. Polanyi. Science **141** (1963) 1010. [↑](#endnote-ref-7)
8. Adamson referred to the Polarization Theory as “fundamentally correct. It accounts for the empirical fact that systems at the same value of *RT***ln**(*P/P*o) [“o” means “vap”] are in essentially corresponding states.” He also stated “There is thus little to choose between the various models, but partly because of tradition and familiarity and partly because *v*m [“m” for monolayer] enters in it so explicitly, the BET equation is in fact almost exclusively used.” This latter reason no longer applies due to QM. [↑](#footnote-ref-1)
9. In his Science article Polanyi referred to BET as “orthodoxy.” He quotes Bertrand Russell, “The triumphs of science are due to the substitution of observation and inference [the mathematical meaning] for authority. Every attempt to revive authority in intellectual matters is a retrograde step. …And it is part of the scientific attitude that the pronouncements of science do not claim to be certain, but only the most probable [based on] present evidence. One of the great benefits that science confers upon those who understand its spirit is that it enables them to live without the delusive subjective authority.” ([]s are added for clarity.)

   Unfortunately, the authority is not within governments, churches, or society but rather within the scientific community itself. Lysenkoism is alive and well and practiced by scientists. [↑](#footnote-ref-2)
10. J. H. deBoer, C. Zwikker, Zeitschrift für Physikalische Chemie, **3B(1)** (1929) 407. [↑](#endnote-ref-8)
11. deBoer and Zwikker had very little success of advancing the isotherm for two reasons, 1) they had a poor theoretical reason for their observation and 2) their adsorbent was at a higher temperature than the presumed temperature of their bath and an additional parameter was required; although they, like many others were not aware of how serious this temperature problem can be. [↑](#footnote-ref-3)
12. E. L. Fuller, Jr. [↑](#endnote-ref-9)
13. J. B. Condon, “The Derivation of a Simple, Practical Equation for the Analysis of the Entire Surface Physical Adsorption Isotherm.” (Oct. 1988) US DOE report Y-2406. [↑](#endnote-ref-10)
14. E. L. Fuller, J. B. Condon, [↑](#endnote-ref-11)
15. J. B. Condon, Microporous mesoporous Mat., Appendix B, **38** (2000) 373. [↑](#endnote-ref-12)
16. I. Langmuir, J. Am. Chem. Soc., **40** (1918) 1361-1403. [↑](#endnote-ref-13)
17. P. Tarazona, Phys. Rev.A, **31**(1985) 2672. [↑](#endnote-ref-14)
18. P. Tarazona, R. Evans,Mol. Phys. **52** (1984) 847. [↑](#endnote-ref-15)
19. G. Kupgan, T. P. Liyana-Arachchi, C. M. Colina, *Langmuir,* **33**(42) (2017) 11138–11145. [↑](#endnote-ref-16)