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README First - Organization of this Book

This book is organized with the most rudimentary material at the beginning and continues with the more sophisticated material at the end. In this sense it could be considered a textbook. As a fact it was originally designed to be a textbook. As with all textbooks it is very dangerous to start reading in the middle, or to use material at the beginning to do complex analysis that is described later in the book. For example, it would be very foolish to try to do pore size distribution calculations by simply skipping to chapter 6 without the background information about the quantum mechanically (QM) derived χ (ESW) theory¹. It would also not be very accurate to only use the standard curve method to determine porosity although it might be useful. (This would be taking advantage of the fact that the χ theory breaks the dependence of the standard curve method upon a matching non-porous standard. Thus, getting around the problem that it is nearly impossible to find a matching non-porous sample.) Thus if, as far as you go in this book is to use the χ theory in the standard curve method, then this is not sufficient today to publish your analysis in the open literature.

My advise, if you only want to use the QM derived χ theory, is to skip over those portions of the book dealing with the older theories and just study the relevant χ theory sections. Furthermore, if you are uneasy with QM, then simply trust the final χ equation that is derived and skip the QM portion. (When you get to this point, there is a note telling you to do this.)

¹ The χ theory (in a few reports listed as “CFS”), the Auto Shielding Physisorption (ASP) theory, the Disjoining Pressure Theory and the Excess Surface Work (ESW) theory are all fundamentally the same theory and will usually be referred to as simply χ theory. Each has approach the problem from a different view point but end up with the same isotherm equation. This makes it problematic if one searches using key words, one needs to use all of these terms.

Forward to 1st Edition

The objective of this book is to present the practice of measuring and interpreting physical adsorption. It is intended to be a practical guide and not an extensive review of either the literature or the theories involved with physical adsorption. Extensive reviews are available and the book by Gregg and Sing[1], though about 20 years old, is still highly recommended for specific details about a variety of adsorption experiments. Another recent book is the 2nd edition of the book by Rouquerol, Rouquerol, Sing, Llewellyn and Maurin[2]. A couple of more recent theoretical aspects are not covered in these books. These are density functional theory (DFT) and χ theory for which there are no comprehensive reviews. A review by Evans[3] and additional articles by Tarazona[4],[5],[6], et. al., would be a good start for DFT. χ theory[7],[8],[9] is rather simple and will be explained in detail throughout this book. (The one adsorbate-one energy of adsorption is easy, but needless to say, the more complicated the system, the more complicated is the resulting calculations.)

As with all scientific writing there are various levels that can be presented. For example, infrared spectroscopy could be used on simply the pattern recognition level or at the more sophisticated level of quantum mechanics. So it is with physical adsorption. One can use the data from physical adsorption measurements as a simple control device, i.e. “Does this powder have the right adsorption isotherm to meet production requirements?”, or on a different level “What is the meaning of the isotherm in terms of surface and pore structure and chemical attractions?” For most applications, the level of sophistication is somewhat intermediate.

In this book, the simple interpretations of the physisorption experiments are presented in chapter 1. Chapter 2 presents the important details on how to make the measurements usually associated with physical adsorption. If one already has a commercial instrument, this chapter may be irrelevant. Chapter 3 is designed to present step-by-step analysis of the isotherms by a few methods and to present other isotherm interpretations. It is generally not a good idea to rely upon manufacturers software supplied with the instruments. Although the programmers are quite knowledgeable about physisorption, it is still best to examine the data carefully. Chapter 4 presents extensive derivations of some theories of adsorption starting with the disjoining pressure approach. The derivations of most isotherms have been extensively reviewed in other books (for example see Gregg and Sing). After all, most have been used for more than 50 years. However, the more recent χ theory and DFT have not been reviewed. Therefore, more detailed descriptions of χ theory and DFT are presented and along with some results. The analysis of one of the more promising techniques for studying adsorption, that is, calorimetry, is not presented. A variety of others that are useful for porosity measurements such as X-ray, NM, FAIR, etc. are also not presented. There is a vast body of literature on these latter subjects which have been used extensively especially for the zeolites.

For most practical applications using commercial instruments, and given that one is accustomed to analysis that physical chemist use, chapter 1 could suffice. The results of the theories formulated will be used in a “cook book” fashion in the chapter 1 with little explanation. The

caveat to the simplified treatments is that occasionally a simple explanation for the behavior of the adsorption is not appropriate. Hopefully, by recognizing patterns in the original or transformed isotherms most misinterpretations can be avoided. The pattern recognition utilized the set of isotherm “types” as originally presented by deBoer and modified by Brunauer, Deming, deming and Teller[10],[11] and later expanded by Gregg and Sing[1] and by χ plot features. Recognition of the possibilities of the complicating features beyond the simple isotherm is important for physical adsorption to be of value. Such features may be interpreted in terms of multiple surface areas, pore sizes and volume, energies of adsorption and the distribution of pore sizes or of adsorption energies. The isotherms are generally interpreted in terms of these features and these features have associated with them physical quantities that in many cases would be useful to know.

Unfortunately, the physical quantities associated with the physical features listed above must be extracted using some theoretical assumptions and the associated mathematical manipulations. It is not at all certain at this time that any generalized theory is capable of this. The theories available yield quite different values for these quantities and at the moment there has not been resolution as to which interpretation, if any, is correct. Most theories of adsorption do not even yield values for these physical quantities and some that claim to do so in reality do not. For example, the only theories that have a theoretical basis for calculating surface area of unknown samples are the BET (Brunauer, Emmitt and Teller[12]) and the χ theory. Both of these will be explained in the theoretical portions of this book. The BET is unquestionably the most widely used theory to calculate the surface area but it has some very serious flaws. χ theory is a recent development that has not been thoroughly tested. Another possibility is the continuing development of DFT, which has so far not been successful in calculating the surface area independent of the BET results or from assumed equations of state. There are numerous theories and methods for determining pore volume, both microporosity and mesoporosity. However, To determine the pore radius, most methods rely upon BET. Furthermore, the BET is used as a correction in these methods as well. Most theories yield approximately the same answer, within a factor of 10, due to an obvious feature in the isotherm that would allow an educated guess to be correct.

It is this authors hope that in the future some of these questions will be resolved, but for the moment there is a need for some answer even if only approximate. It is unlikely that any theory will yield answers with the precision which chemists or physicists are used to, say better than 1%, due not just to the uncertainties of the theories and the associated calculations, but also due to the defining questions regarding the physical quantities. For example, what is the pore size for pores in the range of two nm diameters? Where is the inner boundary for these pores? Atomic sizes begin to have been meaning in this range. How does one account for surface roughness on a nearly atomic scale (a classic fractal problem?) Again, the same uncertainty in definition. Luckily, these questions may not be of practical importance in many applications. If a pore is large enough to allow, say, methanol to adsorb but not ethanol, there is a parameter that one could possibly extract to yield the distinction. If a catalyst’s activity is proportional to the surface area, whatever that means, there is probably a parameter that is proportional to the surface area to

make a relative distinction. So, in spite of the theoretical uncertainties the measurement of physical adsorption is a very useful tool and promises to be more so in the future.

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Forward to the 2nd Edition

It's been more than a decade since the first edition of the book. The promise was made to update the information presented and this editions is meant to fulfill that promise. Not much has changed theoretically but, of course there have been changes in the availability and capabilities of the instrumentation.

The first forward ended with an implied question as to whether the situation described would change in prior paragraphs would change. The implication was somewhat hopeful. Sad to say, there has not been much advance made. Much of this is due to attempts to calculate from the adsorption isotherm the physical properties of the adsorbent. It is my belief that is is missing the major points, theoretically and practically. It seems that much of the tweaking being performed with the DFT type theories is in response to this drive to "get is right." It is because of these questions that this book under-plays the importance of "surface area" and "pore dimensions" and emphasizes the "monolayer equivalence" and uses the word "layer" with a new meaning.

An opinion concerning BET and other similar models

It is my opinion that it is time to discard the BET theory and other isotherms analysis based on the "Henry's Law" assumption. Firstly, these "Henry's Law" isotherms do not yield the correct value for the surface area or the energy of adsorption, nor do they have any basis for measuring porosity. This latter point has become obvious to almost every investigator in the field and is the driving force for the continued development of DFT theories. Most of the "Henry's law" methods do not yield values for surface area or porosity at all and are essentially empirical fits to the isotherm. There are probably over a hundred isotherms available, mostly just empirical. The BET plot is an exception in that it does yield a value, although wrong, for the surface area and energy of adsorption. There are several others that are based on modifying the Langmuir isotherm. The assumptions made to derive the BET and these other isotherms analysis are very questionable. This was pointed out early in the development by Halsey[1] and others. There is much literature devoted to finding an alternative to the BET, but if the BET were valid, this question would be settled and the search for alternative would have ended long ago. Furthermore, the BET is not reliable within at least a factor of 4 for the surface area. It essentially yields meaningless values for energy, which are in stark contradiction to calorimetric values. Indeed, often the value for the BET energy of adsorption is a (mathematically) complex number. Both of these facts have been long known along with seven other weaknesses as pointed out by Gregg and Jacobs[2]. However until the 1980s, there was a lack of something better, therefore the BET continued to be used. It is the surface area bases for most standard curves and DFT calculations. A rather extensive list of problems with the BET both theoretical and practical is available in a section authored by K. S. W. Sing in of a book on adsorption[3]. Such an extensive discussion is not presented here but some additional problems are pointed out in this book. Today there are better theories and techniques.

Another problem, with most of the older theories, including the BET, is that they cannot be used

for analyzing isotherms for adsorbents that have more than one energy of adsorption present, referred to here as “multiplane adsorption.” (This is sometimes referred to as “heterogeneous.”) This designation seems to indicate a surface of variable composition rather than multiple crystallographic planes which is more common.) The reason for this is given in a section on this in the section “Do isotherms for multiplane adsorption have anomalies?”, which demonstrates that the BET theory creates a mathematical anomaly as normally used. By “normally used” is the practice to use statistics on a transform of the original equation. This anomaly problems is also true for any isotherm analysis that uses a transform which mixes the pressure and the amount adsorbed.

An opinion on the way around the BET problems

The exceptions to the previous paragraphs criticism arise by use of the standard curve methods and the χ theory along with the disjoining pressure theory. Presumably this applies to the NLDFT (non-local density functional theory) and the Monte Carlo technique. (Although there is usually agreement between NLDFT and Monte Carlo, this should not be surprising since they use the same classical assumptions. The real test is, “is there agreement to experiment?”) It would really be hard to imagine that either one of these latter techniques would produce an anomaly, although the use of the BET precondition would invalidate this statement. In terms of normal practice, it is doubtful that instrumentations available today have multiplane analysis as a possibility.

In terms of theoretical developments, the analysis referred to a NLDFT analysis is now included in several of the instruments. This is quite handy since the calculations are, for most users of these instruments, confusing at best. The imbedded NLDFT along with the value for the surface area might yield the porosity correctly, especially in a comparison mode. However, the question for such “black box” analysis is, “Specifically, how does it work and what problems might crop up that yield incorrect answers, for a variety of systems?” An analogy that is relevant today is, “Would you be willing to drive a self-driving car (in 2019) if you had no idea what or where the brake peddle or the steering wheel is?” For example, does NLDFT account for multiple energies of adsorption or a distribution of energies? Does it really use the disjoining pressure theory (or the χ theory, but using χ makes the DFT irrelevant) to calibrate? What combination of pore analysis is used and does it take into account the thermodynamic limits that are now well known?

Why the ESW and the χ theory are not included as an option in these instruments is puzzling, especially since the disjoining pressure theory has been to support the NLDFT calculations to determine a monolayer. ESW and χ theories, which can be demonstrated to be identical, are much simpler and more precise and versatile than NLDFT. Energy distributions and pore size distributions, such as it is, are easy to analyze. The transformed χ plot is intuitive in interpretation once one knows what to look for. In most cases a simple χ plot and a calculator with **ln** function is all that is needed for a complete analysis. For more sophisticated analysis, simply good data (necessary for all methods) and a computer program to take the first and second derivative of the χ plot is all that is needed.

As the reader will find out, the χ theory and disjoining pressure theory have been demonstrated to be identical. This one theory has been derived from three different approaches:

- from both classical mechanical and classical statistical mechanics (ASP theory)
- from both perturbation and WKB approximations quantum mechanics (χ)
- and from continuum mechanics of the liquid-solid surface and classical thermodynamics (disjoining pressure theory or ESW) with an assumed one monolayer potential decay constant.

From this point of view, it is well grounded theoretically. It does not resort to “sites” or equilibrium between “sites” or between “sites” that are on top of other adsorbate molecules (the primary Halsey criticism.)

Given the solid theoretical grounding and the simplicity of analysis, it seems strange that the χ -ESW method is not used more often. It may be that researchers are not familiar with the derivations of either one, because if they were, they would realize how powerful a few reasonable assumptions can be. For example, the disjoining pressure theory relies upon the concept of disjoining pressure, Π , which is not really widely known by adsorption investigators, even though it is standard in many courses on surface chemistry. For the χ theory there may be some confusion about the separation of variables that is used. The direction normal to the surface is treated differently than the plane of the surface. The normal direction uses the stand-by Lennard-Jones (6-12) potential similar to most DFT, whereas the plane of the surface uses a modified version of the “particle-in-the-box.” The population of the various “layers” are calculated from the result obtained from the plane-of-surface calculation, which then allows one to calculate the distributions normal to the surface. The method predicts that for most temperatures of adsorption and adsorbates, the error introduced by some geometrical factors should be only ~2.5%. In this revision of the book, the philosophy behind this method will be explored in more detail, and hopefully in a convincing fashion. It will also be pointed out that the theories resolve some problems that Brunauer continued to puzzle over, such as where the transition to the liquid phase is and why there are so very few isotherms that follow “Henry’s Law²” but rather the Freundlich isotherm at low pressures. (Just because the isotherm appears to intersect at the origin does not mean it is following “Henry’s Law”!)

Comments about problems with many publications

Given the discussion above one would be justified in asking the question, “Why are you presenting the older theories? Why not just stick to NLDFT, ESW and χ theories? Why do I have to wade through all these other mathematical presentations?” The answer is that unfortunately most of the literature is analyzed based on these theories. Furthermore, many articles do not present the original data in a form proper for re-analysis. So, “What can one

² I just have to insert a comment here. Henry's Law can not be derived from the laws of thermodynamic as some authors and books claim. For that matter neither can the ideal gas law. For solution chemistry, it is an extremely reasonable assumption and observed almost all of the time, but even for this there are some rare exceptions. Although there are reasons for this, they are still exceptions.

do?” There are several places in this book where these older theories are compared to the χ theory. This is done for two reasons.:

- as an explanation as to why the older theories almost fit the data (but never with an $r^2 > .990$.)
- as an argument to convince the reader that the χ theory applies universally to the conditions specified (the liquid-like conditions.)
- to demonstrate that one can obtain the parameters of the χ theory by refitting the old data, even if it is only available in the form of the fitting parameters of the older theories.

This latter point might not work well since the fitting data of the older theories may only cover a portion of the isotherm. For example, the BET is usually fitted over the pressure range from 0.05 to 0.35 of P/P_{vap} . This is much too short of a range to have any confidence in the answers. Unfortunately, some of the “standard curves” have been biased toward the BET fit with the original data not available.

This latter statement brings up another problem with archived data and even data that is taken today by most investigators. It is very unusual for isotherm data be collected below 0.01 P/P_{vap} . As will become obvious in reading this book, this limit is insufficient to get accurate results in terms of adsorption energies and distributions, surface areas and their distribution and pore sizes and type. Experimentally, this problem is easy to cure. It is relatively easy to use equipment that has high vacuum capability or even ultrahigh vacuum to measure in the low pressure range. It is also important to get accurate data as one approaches P_{vap} ($P > 0.9P_{\text{vap}}$ at least). This problem seems to have been ignored in early data, as evident from the deviations between various investigators for the high pressure data. It is harder, however, to extend the pressure range to approach P_{vap} . It requires very careful temperature control of the sample, something that most instruments commercially available do not have. Proper baffling and attention to the kinetic/laminar flow transition is also usually lacking. One should make an attempt to push the experimental limit ever closer to P_{vap} . This requires better vacuum system design, better temperature controls and particular attention to the areas of the instrument that affect temperature control using baffles and awareness of the laminar to turbulent transition zone. It is naive to assume that the sample has the same temperature as the refrigerant and that the pressure is the same in the cold zone as it is in the rest of the vacuum system.

What's new in this edition?

In this book there is one change on the theoretical side for the χ theory. There is enough data available to make a decision about how the adsorbed molecules are organized on the surface, whether as individual molecules or as patches of molecules. It seems obvious now, from both theoretic considerations and experiment data, that the molecules must cluster, at least in patches. If this is the case, then the previously questionable geometric factor, f , listed as in the first edition has a value of nearly 1. This makes sense from the classical point of view that there are lateral forces. It is also consistent with the assumption used to derive the ESW. However, this has not yet been specifically addressed and confirmed with experimental data.

There is general uneasiness for those dealing with the theory of adsorption and assigning a value to molar area, \bar{A} , or monomolecular area, a . This uneasiness is not new and is evident from the earliest days of the BET development as well. Along with this is the question, “What is meant by surface area.” It is no secret that with adsorption experiments one obtains a variety of answers depending upon conditions of the adsorbent and especially on the adsorbate used. The concept and visualization of surface area is quite simple but can also be misleading. In this book I have put forward the concept of specific monolayer equivalent, n_m , as the physical property that is important to tabulate. It is fine to list the surface area, provided the specific monolayer equivalent, which is more fundamental, is provided. Therefore, for now, the important quantity that is not in question, that is the monolayer equivalence n_m will be tabulated. The conversion to surface area with the reader’s favorite \bar{A} or a is always possible.

On the more practical side, the symbolism in this edition has been changed to be more in alignment with the 3rd edition of the IUPAC “Quantities, Units and Symbols in Physical Chemistry” (the Book). There have been many changes since the 2nd edition that apply here. However, superscript notations have been avoided as much as possible, since superscript notations are easily confused with exponents. The IUPAC convention that numbers and quantities be *italic*, whereas distinguishing letters be roman type, does not seem to be sufficient to keep things straight. Therefore the quantities that use superscript for distinction are not used here. Other methods, usually distinct subscripts, are used to make the distinctions. (The only distinguishing superscript used is the standard symbol, “[⊖]” or “*”, which are so unique that there is little chance for confusion.) The reason this is done is that some of the advanced mathematical treatments are difficult enough without such a notation confusion. Even for those somewhat familiar with the subject, it would be wise to make a quick survey of the symbol list before starting in order to check what equivalent symbols and names apply in this book. You may want to go to www.genchem.net/symbolist.pdf and print out the symbol list and keep it handy as a reference. There are several subtle distinctions for some quantities, such as energies and heats, that are important to recognize. A further modification in this book is to use the molar mass the chemists normally use, that is, with units of g mol^{-1} . This is given the symbol (capital bold) “**M**” versus “ \bar{M} ” which is with units of kg mol^{-1} , as explained in the symbol list. (The IUPAC alternative bar-over designation are being used for molar quantities.) Furthermore, the word “molar,” meaning per mole of material, is used throughout and not the word “enplethic” which IUPAC recommends. Most scientist today recognize the word “molar” and not “enplethic.”³ My opinion is that it seems unlikely that the word “enplethic” will catch on any time soon (if ever?) since it does not appear in any dictionary. (It only appears in the 3rd edition of IUPAC Green Book or places discussing terminology quoting the Green Book.)

Where is all the thermodynamics?

³ It seems the IUPAC committee has a problem with the word molar and molarity. I believe they want to eliminate any confusion for molar quantities and molar solution. I do not see how anyone with a chemistry background would be confused between, for example, molar volume of 18 ml and a 10 molar solution. Their attempt to ban the words molar, molarity and percent have been unsuccessfully because they are so widely used and understood.

Many books present very long explanations about the thermodynamics of adsorption. Examples include the 2nd edition of Elsevier book “Adsorption by Powder and porous Solids - Principles, Methodology and Applications[3],” starting with section 2.3 on page 33, or even throughout the book by A. Adamson’s book on “Physical Chemistry of Surfaces[4],” and in particular the section XVI- 12 starting on page 633. It might be interesting reading for some but most of it is unnecessary. There is some thermodynamic derivations included when needed, but other than heats of adsorption and disjoining pressure, thermodynamics is a minor part of this book.

You may wonder why this is. The reason is simple. One can not derive any isotherm or any other phenomena in this book using only the four laws of thermodynamics. The thing one really needs is the equation of state for the material one is working with. Given the equation of state, the phenomenon are usually explainable without using thermodynamics. Furthermore, without equations of states, thermodynamics is not very useful. The assumption that the thermodynamics alone yields answers for physical adsorption is a dilution. Take, for example. the integral often used to justify the postulate of “Henry’s” law-like behavior of:

$$\Pi = \frac{RT}{A} \int_0^P \frac{n_{\text{abs}}(P)}{P} dP \quad (1)$$

The implied assumption is that the number of moles of adsorbate material $n(P) > 0$ when $P > 0$. If this were the case (and it’s obvious that without a pressure of adsorbent that the adsorbate goes to 0 as P goes to 0) then the lower limit of P for the integral drops out using L’Hospital’s rule. This may not be, and generally is not, the case.

The most important point, as the reader will discover, is to get the equation of state correctly. The thermodynamics that can be used to make relationships has been known for a very long time and it is assumed that the reader is aware of this very old and pervasive tool. To get the equations of state theoretically correctly and not by measurements, the gold standard is quantum mechanics (QM) linked with statistical mechanics for which there is a long history of success. For the χ theory, there are very few assumptions made going into the QM derivation especially for the determination of the amount of adsorption.

Penultimate Finally:

To understand the full implications and the theory of χ , you need to read all the sections on χ -theory in chapters 1 through 6, in other words, you can skip the sections of all the more established theories. If you would like the background in DFT then chapter 7 is appropriate.

Finally, A Tribute to Loren Fuller

This is a final history note. Dr. Loren E. Fuller, Jr., worked very diligently on the ASP (χ) theory for many years, working against the odds, but was able to publish several papers. Indeed, some

very prominent scientists⁴ were furious whenever the theory was mentioned. Loren finally promised one of these scientist, out of great respect that was due, not to publish the theory until that scientist's passing. The basis and use of the ASP theory was usually downplayed in order to make the publications acceptable. I was resolved to be open about the theory and therefore was not very successful in my publications record. However, I have worked in situations where publications did not matter, a considerable advantage in being straight forward.

Shortly before Loren's death I notice that the χ -plot always passed through a common point and mentioned this to him. He reaction immediately was, "Yes, the point of the relative pressure of 0.368 (1/e) is the magical point from which one can extract a lot of information!" Indeed, this is a jaw-dropping point along with the early data points in the isotherm. By itself this point yields the energy of adsorption and surface area for a flat surface or as Loren would indicate for a fractal factor of 1. Together with the early part of the isotherm it yields the fractal factor other than 1, usually porosity but maybe very low particle sizes. This will become clear when you read about the inflection point technique in Chapter 1 with details in Appendix III.

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⁴ I will not name these scientist here, but I assure you that most scientist would immediately recognize them.