

Foreword to the 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 et al. [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 [4–6] et al., would be a good start for DFT. χ theory [7–9] 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 are 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. The same is the case 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 (e.g., 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, along with some results. The analysis of one of the more promising techniques for studying adsorption, 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 chemists use, Chapter 1 could suffice. The results of the theories formulated will be used in a “cookbook” fashion in 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. It is hoped that 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 Brunaur et al. [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, which 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 time of writing 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 et al. [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 surface area, but it has some very serious flaws. The χ theory is a recent development that has not been tested thoroughly. 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 the 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 author’s 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 to the defining questions regarding the physical quantities. For example, what is the pore size for pores in the range of 2 nm diameters? Where is the inner boundary for these pores? Atomic sizes begin to have meaning in this range. How does one account for surface roughness on a nearly atomic scale (a classic fractal problem)? Again, there is 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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Foreword to the 2nd edition

It has been more than a decade since the first edition of the book. A promise was made to update the information presented, and this edition is intended 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 foreword ended with an implied question as to whether the situation described would change and become clearer in the future. The implication was somewhat hopeful. Sad to say, not many advancements have been 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 this 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 it right.” It is because of these questions that this book underplays 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

In my opinion, 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 more than a hundred isotherms available, mostly just empirical. The BET plot is an exception in that it does yield a value—albeit wrong—for the surface area and energy of adsorption. Several other isotherms are based on modifying the Langmuir isotherm. The assumptions made to derive the BET, as well as these other isotherms analysis, are very questionable. This was pointed out early in the development by Halsey [1] and others. Much of the literature is devoted to finding an alternative to the BET, but if the BET were valid, this question would be settled and the search for alternatives would have ended long ago. Furthermore, the BET is not reliable to within a factor of at least 4 for the surface area. It essentially yields meaningless values for energy, which are in stark contradiction to calorimetric values. Indeed, the value for the BET energy of adsorption is often a (mathematically) complex number. Both of these facts have long been known, in addition to seven other weaknesses as pointed out by Gregg and Jacobs [2]. However, until the 1980s, there was a lack of something better, and therefore the BET continued to be used. It is the surface area basis for most standard curves and DFT calculations. An extensive list of problems with the BET, both theoretical and practical, is available in a section

authored by Sing in 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. However, Multiple crystallographic planes are more common than variable composition.) The reason for this is given in the section entitled “Do isotherms for multiplane adsorption have anomalies?”, which demonstrates that the BET theory creates a mathematical anomaly as normally used. The phrase “normally used” indicates the practice of using statistics on a transform of the original equation. This anomaly problem 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 criticism in the previous paragraphs 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, Do NLDFT and Monte Carlo agree with experimental data?) It would be challenging 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 any instrumentation available today has multiplane analysis as a possibility.

In terms of theoretical developments, the analysis referred to as 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 if you had no idea what or where the brake pedal or the steering wheel were?” 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?

It is puzzling why ESW and the χ theory are not included as an option in these instruments, especially since the ESW has been used to support the NLDFT

calculations to determine a monolayer. The ESW and χ theories, which can be demonstrated as identical, are much simpler and more precise and versatile than NLDFT. Energy distributions and pore size distributions, such as they are, 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 are all that are 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 are all that are needed.

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

- both classical mechanical and classical statistical mechanics (ASP theory);
- both perturbation and WKB approximations quantum mechanics (χ); and
- 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, χ /ESW theory is well grounded theoretically. It neither resorts to “sites” or equilibrium between “sites,” Nor does it depend upon “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 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 are 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 populations 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 $\sim 2.5\%$. 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 so few isotherms follow not Henry’s Law¹ but rather

¹ I must make a comment here. Henry’s Law *cannot* 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.

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, "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 suitable for re-analysis. So what can one do? There are several places in this book where these older theories are compared to the χ theory. This is done for three reasons:

- as an explanation as to why the older theories almost fit the data (but never with an $r^2 > 0.990$);
- as an argument to convince the reader that the χ theory applies universally to the conditions specified (the liquid-like conditions); and
- 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.

The latter point might not work well, since the fitting data of the older theories may cover only 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 a range for one 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 are taken today by most investigators. It is very unusual for isotherm data be collected below 0.01 P/P_{vap} . As will become obvious while reading this book, this limit is insufficient to obtain 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 solve. It is relatively easy to use equipment that has a high vacuum capability or even an ultrahigh vacuum to measure in the low pressure range. It is also important to obtain 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 is 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 are also usually lacking. One should 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 are 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 experimental 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, which considers 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 the molar area, \bar{A} , or monomolecular, a . This uneasiness is not new; it is evident from the earliest days of the BET development. Along with this comes the question, "What is meant by surface area?" It is no secret that with adsorption experiments, one obtains a variety of answers depending on the conditions of the adsorbent and especially on the adsorbate used. The concept and visualization of surface area are quite simple, but can also be misleading. In this book, I have put forward the concept of a specific monolayer equivalent, n_m , as the physical property that is important to tabulate. It is acceptable to list the surface area, provided that the specific monolayer equivalent, which is more fundamental, is supplied. 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 \bar{A} or a , as preferred by the reader, is always possible.

On a more practical note, the symbolism in this edition has been changed to be more in alignment with the 3rd edition of the IUPAC's book, *Quantities, Units and Symbols in Physical Chemistry*. There have been many changes since the 2nd edition that apply here. However, superscript notations have been avoided as much as possible, since these may easily be 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 differentiations. (The only distinguishing superscript used is the standard symbols, "⁰" or "**", which are so unique that there is little chance for confusion.) This is done as some of the advanced mathematical treatments are difficult enough without such a notation confusion. Even for those who are reasonably 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 that chemists normally use—that is, with units of g mol^{-1} . This is given the symbol (capital bold) “**M**” versus “ \overline{M} ” which is with units of kg mol^{-1} , as explained in the symbol list. (The IUPAC alternative bar-over designation is used for molar quantities.) Furthermore, the word “molar,” meaning per mole of material, is used throughout and not the word “enplethic,” which the IUPAC recommends. Most scientists today recognize the word “molar” and not “enplethic.”² In my opinion 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 the IUPAC’s Green Book, or in texts discussing terminology that quote the Green Book.)

Where are all the thermodynamics?

Many books present very long explanations about the thermodynamics of adsorption. Examples include the 2nd edition of the Elsevier book *Adsorption by Powders and Porous Solids: Principles, Methodology and Applications* [3], starting with Section 2.3 on page 33, or even throughout A. Adamson’s book *Physical Chemistry of Surfaces* [4], in particular section XVI-12, starting on page 633. It might be interesting reading for some, but most of it is unnecessary. There are 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 *cannot* derive any isotherm or any other phenomena in this book using only the four laws of thermodynamics. What one really needs is the equation of state for the material with which one is working. Given the equation of state, the phenomena are usually explainable without using thermodynamics. Furthermore, without equations of states, thermodynamics is not very useful. The assumption that the thermodynamics alone yield 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 is obvious that without a pressure of adsorbent, the adsorbate goes to 0 as P goes to 0), then the lower limit of P for the integral

² It seems that the IUPAC committee has a problem with the words “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 unsuccessful because these terms are so widely used and understood.

would drop 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 obtain the equation of state correctly. The thermodynamics that can be used to make relationships have been known for a very long time and it is assumed that the reader is aware of this very old and pervasive tool. To obtain 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, very few assumptions are made going into the QM derivation, especially for the determination of the amount of adsorption.

Some final advice if you're in a hurry

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

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 scientists³ were furious whenever the theory was mentioned. Loren finally promised one of these scientists, out of great and deserved respect, 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, which is a considerable advantage in being straightforward.

Shortly before Loren's death, I noticed that the χ -plot always passed through a common point, and I mentioned this to him. His immediate reaction 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.

³ I will not name these scientists here, but I assure you that most scientists would immediately recognize them.

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