

# Surface Area and Porosity Determinations by Physisorption

## Measurements and Theory

Second Edition

**James B. Condon**



Elsevier  
Radarweg 29, PO Box 211, 1000 AE Amsterdam, Netherlands  
The Boulevard, Langford Lane, Kidlington, Oxford OX5 1GB, United Kingdom  
50 Hampshire Street, 5th Floor, Cambridge, MA 02139, United States

© 2020 Elsevier B.V. All rights reserved.

No part of this publication may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or any information storage and retrieval system, without permission in writing from the publisher. Details on how to seek permission, further information about the Publisher's permissions policies and our arrangements with organizations such as the Copyright Clearance Center and the Copyright Licensing Agency, can be found at our website: [www.elsevier.com/permissions](http://www.elsevier.com/permissions).

This book and the individual contributions contained in it are protected under copyright by the Publisher (other than as may be noted herein).

#### Notices

Knowledge and best practice in this field are constantly changing. As new research and experience broaden our understanding, changes in research methods, professional practices, or medical treatment may become necessary.

Practitioners and researchers must always rely on their own experience and knowledge in evaluating and using any information, methods, compounds, or experiments described herein. In using such information or methods they should be mindful of their own safety and the safety of others, including parties for whom they have a professional responsibility.

To the fullest extent of the law, neither the Publisher nor the authors, contributors, or editors, assume any liability for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions, or ideas contained in the material herein.

#### Library of Congress Cataloging-in-Publication Data

A catalog record for this book is available from the Library of Congress

#### British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library

ISBN: 978-0-12-818785-2

For information on all Elsevier publications  
visit our website at <https://www.elsevier.com/books-and-journals>

Publisher: Susan Dennis  
Acquisition Editor: Susan Dennis  
Editorial Project Manager: Theresa Yanetty  
Production Project Manager: Omer Mukhtar  
Cover Designer: Miles Hitchen

Typeset by SPi Global, India



Working together  
to grow libraries in  
developing countries

[www.elsevier.com](http://www.elsevier.com) • [www.bookaid.org](http://www.bookaid.org)

# Contents

README first—Organization of this book .....	xi
List of figures .....	xiii
List of tables .....	xxiii
Foreword to the 1st edition .....	xxvii
Foreword to the 2nd edition .....	xxxi
<b>CHAPTER 1 An overview and some uninteresting history of physisorption .....</b>	<b>1</b>
Introduction.....	1
What do you want?.....	1
Scope and terminology .....	2
General description of physisorption .....	6
Measuring the surface area by physisorption .....	8
Preliminary analysis .....	10
Classical classifications of adsorption isotherm types.....	10
Single point methods .....	14
The inflection point method .....	16
Quantum mechanical classifications of isotherms using $\chi$ plots.....	22
Measuring the surface area from the isotherm .....	27
What is the “Henry’s law” assumption? .....	28
Implications of the Henry’s law disproof .....	30
The BET theory (Brunauer, Emmett, and Teller) .....	32
The “absolute method” by Harkins and Jura .....	36
$\chi$ and ESW theories that do yield monolayer equivalence $n_m$ .....	36
Relating $a$ and $A_s$ to $n_m$ .....	38
The advantages of the $\chi$ theory formulation.....	41
Summary for introduction to Chi and ESW theories .....	42
Using standard curves to obtain the $n_m$ .....	42
Determining porosity by physical adsorption .....	43
Micropore analysis .....	43
Ultramicropore analysis.....	46
Mesopores .....	47
Macropores .....	52
Statistical treatment of isotherms—Error analysis .....	53
Summary of this chapter .....	54

What's next? .....	55
References.....	56
<b>CHAPTER 2 Measuring the physisorption isotherm .....</b>	<b>59</b>
Introduction—Equipment requirements .....	59
The volumetric method .....	60
Equipment description.....	60
Determination method .....	62
Error analysis for the volumetric method .....	65
Advantages and disadvantages of the volumetric technique .....	68
The gravimetric method .....	69
Equipment description.....	69
Determination method .....	71
Error analysis for the gravimetric technique .....	73
Advantages and disadvantages of the gravimetric technique .....	73
General error analysis—Common to both volumetric and gravimetric .....	74
Pressure and temperature measurements .....	74
Kinetic problems.....	76
Sample density problems.....	77
Calorimetric techniques.....	77
Adiabatic calorimetry .....	77
Measuring the isosteric heat of adsorption .....	79
The thermal “absolute” method .....	79
Differential scanning calorimetry.....	82
Arnold’s adsorptive flow system.....	83
Carrier gas flow method.....	86
Engineering aspects: Carrier gas flow method .....	87
Summary of methods.....	91
References.....	92
<b>CHAPTER 3 Interpreting the physisorption isotherm.....</b>	<b>93</b>
Interpreting the isotherm .....	93
Objectives in interpreting isotherms .....	95
Surface area determination from isotherms .....	100
The BET analysis .....	100
$\chi$ plot analysis .....	102
Strategy of the non-local density functional theory .....	104
Strategy of the $\chi$ /ESW theory .....	105

Dubinin et al. method of determining surface area .....	106
Tóth T-equation isotherm.....	107
The Harkins-Jura absolute/relative method .....	107
Porosity determinations from the isotherm.....	108
Approximate pore analysis method.....	109
Micropore analysis .....	109
Mesoporosity analysis .....	112
Isotherm fits which yield relative numbers for the surface area .....	118
Langmuir isotherm .....	118
Freundlich isotherm .....	120
Polanyi formulations.....	121
deBoer-Zwikker formulation.....	122
The Frenkel, Halsey, Hill (FHH) isotherm .....	122
Analysis using standard isotherms .....	123
Principal problem with standard curves.....	124
Standard isotherms .....	124
Tables of standard isotherms.....	128
What about those Type VI isotherms?.....	138
Summary of interpreting the physisorption isotherm .....	140
References.....	143
<b>CHAPTER 4 Theories behind the <math>\chi</math> plot .....</b>	<b>145</b>
Introduction—A short historical background .....	146
Theory behind $\chi$ plots.....	147
The quantum mechanical derivation of the “simple” $\chi$ equation.....	147
A Particle in a box with a “Tooth”—Perturbation theory for adsorption on a surface with a molecule present.....	150
Continuing the derivation .....	156
Converting $\chi_s$ to different conditions .....	160
Summary .....	162
What is $a$ ? ... and is the hard sphere approximation appropriate? .....	162
The hard sphere geometry and Lennard-Jones correction....	167
Summary .....	168
In summary of $\chi$ theory so far .....	169
The disjoining pressure derivation (ESW).....	169
The meaning of $\Gamma_m$ in the hard sphere model .....	174
Relationship to $\chi$ -theory .....	175
Heterogeneous surfaces .....	177

The additive principle of $\chi$ plots.....	177
Insensitivity for $\chi \geq \max \chi_c$ .....	178
Reformulation for a distribution of $E_a$ values.....	179
Heats of adsorption.....	180
Isosteric heat of adsorption, $q_{st}$ .....	180
The integral heats of adsorption.....	181
Heats of adsorption from BET plot.....	183
Depth profiles and n-layer calculations with $\chi$ theory .....	184
Assumptions used to calculate the Normal Direction	
Profile.....	185
#3 The QMHO approximation for the LJ 6–12 potential .....	186
#4 The packing problem uncertainty .....	188
Combining the normal direction distributions with	
the $\chi$ -n layer results .....	189
Simulations of the isotherm using n-layer .....	194
Adsorption of binary adsorptives—More than	
one adsorbate .....	195
Method 1: Adjusting the grand canonical ensemble .....	196
Method 2: Binary adsorbate using the n-layer analysis .....	205
Is the $\chi$ plot compatible with the Freundlich and Dubinin	
isotherms? .....	208
The thermodynamics and spreading pressure .....	210
Gibbs' phase rule in systems with surfaces .....	211
The Olivier monolayer criterion .....	213
Summary of this chapter .....	213
References.....	215
<b>CHAPTER 5 Comparison of the <math>\chi</math> and ESW equations</b>	
<b>to measurements .....</b>	<b>217</b>
Comparison to standard isotherms .....	217
Cranston and Inkley standard $t$ -curve .....	218
deBoer's standard $t$ -plots.....	218
The $\alpha$ -s standard plots .....	221
Standard thoria plots.....	223
Standard curves for lunar soils.....	224
Isotherms by Niclán and Teichner .....	227
Isotherms by Bradley.....	228
McGavack and Patrick .....	232
Data by Bray and Draper .....	233
Conclusion and some comments about carbon.....	233
Summary with regards to standard curves.....	234
The observation of $\chi_c$ .....	235

Observations of the energy implications of $\chi_c$ .....	236
Direct observation of $\chi_c$ (threshold pressure) .....	237
Summary and conclusion concerning $\chi_c$ .....	246
Multiplane adsorption.....	246
Examples of two plane adsorption.....	246
The Freundlich, Dubinin-Polanyi, and Tóth isotherms .....	247
Summary of comparisons to some other isotherms.....	251
Do isotherms for multiplane adsorption have anomalies? ....	251
Conclusion concerning multiple energies .....	255
Heats of adsorption.....	255
Data by Harkins and Jura—The absolute method .....	256
Data by T. Berg, Kr on Anatase—Simultaneous measurements.....	258
Data by Kington, Beebe, Polley, and Smith on anatase.....	260
Summary of heats of adsorption .....	261
Adsorption of more than one adsorbate.....	261
Adsorption on non-porous surfaces.....	262
Binary adsorption in micropores.....	267
Conclusions regarding binary adsorption.....	274
Statistical comparisons of other isotherms to the $\chi$ -plot .....	275
General conclusions.....	277
References.....	277
Further reading .....	279
<b>CHAPTER 6 Porosity calculations.....</b>	<b>281</b>
Introduction to porosity calculations.....	281
Ultramicropore analysis.....	284
Micropore analysis .....	291
The BDDT equation .....	291
The DR and DA equations .....	292
Standard curve analysis using distributions.....	293
$\chi$ theory interpretation of the distribution fit .....	298
Analysis of mesoporosity—Classical.....	308
Comments about the standard plot of determining mesoporosity .....	309
What $\chi$ theory says about prefilling.....	318
Is it microporous or mesoporous and does it matter? .....	319
Combined mesopore/micropore equation $\chi$ .....	319
Using an arbitrary function to determine porosity .....	320
Interpretation of mesopore equation using standard curve.....	321
The boundary between mesopores and micropores.....	322

Should one use a micropore or a mesopore analysis?.....	323
Real data examples.....	324
What does $\chi$ theory say about hysteresis? .....	328
$\chi$ theory n-layer simulation .....	329
Conclusions and summary.....	330
References.....	333
<b>CHAPTER 7 Density functional theory (DFT).....</b>	<b>335</b>
Introduction.....	335
What is a functional?.....	337
The functional derivative .....	339
Correlation functions .....	340
A quick trip through some partition functions .....	341
Direct correlation functions.....	344
The hard rod approximations .....	345
Hard rods between two walls .....	347
Percus-Yevick solution expansion for hard spheres.....	349
Thiele analytical approximation.....	351
The Carnahan-Starling approximation .....	351
Helmholtz Free Energy from the CS Approximation.....	352
Non-local density functional theory (NLDFT) .....	353
Modeling with the presence of a surface .....	355
A note about the Monte Carlo technique.....	357
$\chi$ theory versus NLDFT, what are the practical differences? ..	358
References.....	360
Appendixes .....	361
Acknowledgments .....	401
In Memory of Dr. E. Loren Fuller .....	403
Author Index .....	405
Subject Index .....	409

# 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, and in fact it was originally designed to be such. As with all textbooks, it is not recommended 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 ill-advised to try to do pore size distribution calculations by simply skipping to Chapter 6 without the background information about the quantum mechanically (QM) derived  $\chi$  (ESW) theory.<sup>1</sup> It would also not be very accurate to use only the standard curve method to determine porosity, although this might be useful. (This would be taking advantage of the fact that the  $\chi$  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 you only read enough of this book to use the  $\chi$  theory in the standard curve method, then this will not be sufficient today to publish your analysis in the open literature.

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

---

<sup>1</sup> The  $\chi$  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  $\chi$  theory. Each has approached the problem from a different viewpoint but ends up with the same isotherm equation. This makes it problematic if one searches using keywords, and one therefore needs to use all of these terms.