2nd Edition

ADSORPTION
by Powders and Porous Solids
Principles, Methodology and Applications

F. Rouquerol J. Rouquerol K.S.W. Sing
P. Llewellyn G. Maurin

Adsorption by Powders and Porous Solids

Principles, Methodology and Applications

Second edition

*F. Rouquerol, J. Rouquerol, K.S.W. Sing, P. Llewellyn and G. Maurin**

Aix Marseille University-CNRS-IUSTI/DIRE-Laboratory, Marseille, France
**University of Montpellier 2, Institute Charles Gerhardt, Montpellier, France*

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Preface to the First Edition

The growing importance of adsorption (e.g. in separation technology, industrial catalysis and pollution control) has resulted in the appearance of an ever-increasing volume of scientific and technical literature on novel adsorbents and catalysts. Also, various new procedures have been introduced over the past few years for the interpretation of adsorption data – particularly for micropore and mesopore size analysis. It is hardly surprising that it is becoming increasingly difficult to obtain a well-balanced view of the significance of the recent developments in such fields as adsorption energetics, network percolation and density functional theory against the background of the more traditional theories of surface coverage and pore filling.

In writing this book, we have endeavoured to give an introductory survey of the principles, methodology and applications of the adsorption of gases and liquids by powders and porous solids. In particular, we hope that this book will meet the needs of all those students and non-specialists who wish to undertake adsorption measurements. In addition, we believe that certain sections of the book will be of interest to those scientists, engineers and other technologists who are already concerned, either directly or indirectly, with the characterization of finely divided or porous solids.

We are conscious of the fact that few people now have the time or inclination to read a scientific volume from cover to cover. Furthermore, we know that some readers are looking for concise information on the general principles or methodology of adsorption while others are more interested in the adsorptive properties of, say, carbons or oxides. For these reasons, we have not adopted the more orthodox arrangement of material in which the description of each theory is immediately followed by a lengthy discussion of its application. Instead, the format of this book is as follows. First, a general treatment of the theoretical principles, thermodynamics and methodology of adsorption is given in Chapters 1–5. Secondly, the use of adsorption methods for evaluating the surface area and pore size is discussed (also in general terms) in Chapters 6–8. Thirdly, some typical adsorption isotherms and energies obtained with various adsorbents (carbons, oxides, clays, zeolites) are presented and discussed in Chapters 9–12. Finally, our general conclusions and recommendations are summarized in Chapter 13.

Throughout this book, the main emphasis is on the determination and interpretation of adsorption equilibria and energetics. We are not concerned here with the dynamic or chemical engineering aspects of adsorption – both are very important topics which we must leave to other authors! Since we have set out to provide useful guidance to newcomers to adsorption science, our approach is to some extent didactic. In a book of this nature, it would be impossible to achieve a comprehensive review of all aspects of adsorption by powders and porous solids, and the inclusion of material is necessarily selective. By drawing attention to certain publications and overlooking other excellent pieces of research, we risk the displeasure of some members of the international adsorption community. In defence of this approach, we can only plead that the choice of material was dictated by the need to explain and illustrate the general principles which are summarized in Chapter 13.

Many of the ideas expressed in this book have been developed as a result of collaborative research over the past 30–40 years. It would be invidious to name all our co-workers here but they can be identified in the references listed at the end of each chapter. Our cordial thanks are extended to all those authors and publishers who have readily agreed to the reproduction of published material. For the sake of clarity and consistency of units, etc., most figures have been either redrawn or restyled.

We wish to express our grateful thanks to the following people for information supplied privately: D. Avnir, F.S. Baker, F. Bergaya, M. Bienfait, R.H. Bradley, P.J. Branton, P.J.M. Carrott, J.M. Cases, B.R. Davis, M. Donohue, D.H. Everett, G. Findenegg, A. Fuchs, P. Grange, K.E. Gubbins, K. Kaneko, N.K. Kanellopoulos, W.D. Machin, A. Neimark, D. Nicholson, T. Otowa, R. Pellenq, F. Rodriguez-Reinoso, N.A. Seaton, J.D.F. Ramsay, G.W. Scherer, W.A. Steele, F. Stoeckli, J. Suzanne, J. Meurig Thomas, K.K. Unger and H. Van Damme.

Special thanks are due to our colleagues Y. Grillet, R. Denoyel and P.L. Llewellyn for their forbearance and encouragement, to P. Chevrot for the quality of the artwork and to Madame M.F. Fiori for her unfailing dedication in processing the manuscript.

Last but not least we should like to pay tribute to the leadership of Dr. S. John Gregg, whose many contributions to adsorption and surface science were made over a period of more than 60 years.

Preface to the Second Edition

The principal aim of the second edition of this book remains essentially the same as that of the first: to provide an introductory survey of the principles, methodology and applications of the adsorption of gases and liquids by powders and porous solids.

As before, special attention is given to the determination and interpretation of experimental data, particularly in relation to the characterization of adsorbents of technological importance. Over the past 14 years, considerable progress has been made in the development of ordered pore structures and computer modelling of well-defined adsorption systems. However, a number of problems remain unresolved – notably in the assessment of the surface area and pore-size distribution of disordered adsorbents. The discerning reader will detect different shades of opinion in certain chapters and we hope that this will serve to stimulate further discussion and research.

In writing this second edition, we are aware that it is becoming increasingly difficult for the non-specialist to appreciate the scope and limitations of recent advances in adsorption science against the background of 'classical' work. We have therefore endeavoured to summarize and explain the significance of the more important developments in relation to the characterization of the surface properties of porous and non-porous materials.

The new chapter on modelling of physisorption in porous solids should be of particular interest to those experimentalists who wish to understand the purpose and application of computational procedures. Another new chapter is on the adsorptive properties of metal-organic frameworks, which have received much attention in recent years. It will be evident that other parts of the book have been substantially revised; much of the subject matter is now rearranged and expanded so that each chapter is to a large extent self-contained.

We set out to provide useful guidance in the interpretation and application of adsorption methods, and to this end, we have selected particular examples of our own research and other related studies to illustrate the principles expounded in the various chapters. In fact, the amount of new work on adsorption published over the past 14 years is far too extensive to discuss properly in a book of this size. Unfortunately, we have had to omit any reference to a number of excellent research papers by distinguished scientists.

Many of the ideas expressed in the book have originated indirectly from the numerous fruitful – and always enjoyable – discussions with our colleagues and friends. Of course, all directly related pieces of work are indicated by the appropriate references to be found in the list at the end of each chapter. There are other people who deserve special thanks for their help. In addition to the names in the preface to the first edition, we must extend our grateful thanks to the following for their continued help and encouragement: Peter Branton, Donald Carruthers, Renaud Denoyel, Tina Düren, Erich Müller, Alex Neimark, Jehane Ragai, 'Paco' Rodriguez-Reinoso, Randall Snurr, John Meurig Thomas, Petr Nachtigall, Matthias Thommes, Klaus Unger and Ruth Williams.

List of Main Symbols

As far as possible, the notation used here follows the recommendations of the International Union of Pure and Applied Chemistry (Cohen et al., 2007)

a	specific surface area
A	surface area
a(ext)	external specific surface area
b	Langmuir adsorption coefficient
B	structural constant D–R (Dubinin–Radushkevich)
B_m	second virial (molar) coefficient
$c(B)$	amount concentration $\left(=\frac{n(B)}{V}\right)$
C	BET constant (Brunauer, Emmett and Teller)
d	molecular diameter or particle diameter
l	single linear dimension
D	D–R constant (Dubinin–Radushkevich)
E	energy
E_o	adsorption molar energy at infinitely low coverage
E_1	adsorption molar energy for the first layer
E_L	liquefaction energy
F	Helmholtz energy defined as $U-TS$
G	Gibbs energy defined as $H-TS$
H	enthalpy defined as $U+pV$
H	distance between the nuclei in the parallel walls of a slit pore
i	intercept
k	Boltzmann constant
k_H	Henry's law constant
K	equilibrium constant
K	Kelvin, SI unit
L	Avogadro constant
m	mass
M	molar mass
n	amount of substance
n	specific surface excess amount
N	number of elementary entities
N	number of layers
p	pressure
$p^\ominus$	standard pressure
p°	saturation pressure
P	probability
q	electric charge
Q	heat

r pore radius
r curvature radius
R gas constant
s slope
S entropy
t thickness of multimolecular layer
T thermodynamic temperature
U internal energy
V volume
w pore width
W work
x mole fraction
y mole fraction
z distance from surface
α polarisability
α_S ratio of two adsorbed amounts which one is used as a reference in the α_S-method
ε porosity
ε pairwise interaction energy
φ potential energy
ϕ heat flux, defined as dQ/dt
γ surface tension
γ(S0) or γ^s surface tension of the clean solid
γ(SG) or γ surface tension of the solid in equilibrium with a gas
γ(SL) surface tension of the solid in equilibrium with a liquid
Γ surface excess concentration defined as n^σ/A
μ chemical potential
π spreading pressure, defined as $\gamma(S0) - \gamma(SG)$ or $\gamma^s - \gamma$
ρ mass density (or volumic mass)
σ molecular cross-sectional area
τ distance to the surface in the adsorption space
θ surface coverage, defined as the ratio of two surface excess amounts, one of which is used as a reference
θ Celsius temperature

Superscripts

g gas or vapour
l liquid
s solid
aq aqueous solution
a adsorbed (in the layer model)
σ surface excess (in the Gibbs representation)
i interfacial
$\ominus$ standard
* pure substance
∞ infinite dilution

Subscripts

m related to a complete monolayer
p pore

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Any symbol of a state variable (e.g. T, V, p, A, n) can be used as a subscript of a physical quantity to denote that this variable is kept constant (e.g. $G_{T,p}$; $V_{T,p}$; $H_{298.15}$)

Use of operator Δ

The symbol Δ followed by a subscript is used to denote the *change of an extensive quantity* associated with a physical or chemical process. The main subscripts used in this book are:

vap vaporisation
liq liquefaction
sub sublimation
fus fusion
trs transition (between phases)
mix mixing of fluids
sol solution (of solute in solvent)
dil dilution (of a solution)
ads adsorption
dpl displacement
imm immersion

Reference

Cohen, E.R., Cvitas, T., Frey, J.G., Holmström, B., Kuchitsu, K., Marquardt, R., Mills, I., Pavese, F., Quack, M., Stohner, J., Strauss, H.L., Takami, M., Thor, A.J., 2007. Quantities, Units and Symbols in Physical Chemistry, third ed. RSC Publishing, Cambridge, UK.

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