Adsorption by Powders and Porous Solids

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Principles, Methodology and Applications

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Principles, Methodology and Applications

Preface

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 the present 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 dynamics 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

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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.H. 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.

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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.

List of Main Symbols

As far as possible, the notation used here follows the recommendations of the International Union of Pure and Applied Chemistry.

a	specific surface area
A	surface area
	A(ext) or a(ext) external surface area
b	Langmuir adsorption coefficient
$b(B)$	molality of a solute B
B_m	second virial (molar) coefficient
c	concentration
C	BET constant
d	molecular diameter or particle diameter
E	energy
	E_0 adsorption molar energy at infinitely low coverage
	E_1 adsorption molar energy for the first layer
	E^l liquefaction energy
F	Helmoltz 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 pore
i	intercept
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
$\boldsymbol{n}$	specific surface excess amount
	n^σ surface excess amount (in the Gibbs representation)
	n^a adsorbed amount (in the layer representation)
	$\boldsymbol{n}_m$ monolayer capacity
	$\boldsymbol{n}_{(sat)}$ Specific surface excess amount corresponding to the saturation of pores
	n_p pore capacity

N number of elementary entities
p pressure
p° standard pressure (usually the saturation pressure)
Q heat
r pore radius
R gas constant
s slope
S entropy
t thickness of multimolecular layer
T thermodynamic temperature
U internal energy

U^σ surface excess (internal) energy

$u^\sigma = \dfrac{U^\sigma}{n^\sigma}$ molar surface excess (internal) energy

$\dot{u}^\sigma = \left(\dfrac{\partial U^\sigma}{\partial n^\sigma}\right)_{T,A.}$ differential surface excess (internal) energy

V volume

$v^\sigma(\mathrm{STP}) = \dfrac{V^\sigma(\mathrm{STP})}{m^s}$ specific gas volume (STP) corresponding to the specific surface excess amount n^σ.

w effective pore width
W work
x mole fraction
y mole fraction
z distance from surface

α polarizability
ε pairwise interaction energy
γ surface tension
Γ surface excess concentration defined as n^σ/A
θ surface coverage, defined as the ratio of two surface excess amounts, one of which is used as a reference
θ Celsius temperature
μ chemical potential
Π spreading pressure
ρ mass density
σ molecular cross sectional area
φ potential energy
ϕ heat flow

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1.1. Importance of Adsorption

Adsorption occurs whenever a solid surface is exposed to a gas or liquid: it is defined as the enrichment of material or increase in the density of the fluid in the vicinity of an interface. Under certain conditions, there is an appreciable enhancement in the concentration of a particular component and the overall effect is then dependent on the extent of the interfacial area. For this reason, all industrial adsorbents have large specific surface areas (generally well in excess of $100\,m^2\,g^{-1}$) and are therefore highly porous or composed of very fine particles.

Adsorption is of great technological importance. Thus, some adsorbents are used on a large scale as desiccants, catalysts or catalyst supports; others are used for the separation of gases, the purification of liquids, pollution control or for respiratory protection. In addition, adsorption phenomena play a vital role in many solid state reactions and biological mechanisms.

Another reason for the widespread use of adsorption techniques is the importance now attached to the characterization of the surface properties and texture of fine powders such as pigments, fillers and cements. Similarly, adsorption measurements are undertaken in many academic and industrial laboratories on porous materials

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