

Cambridge University Press

978-1-107-62142-8 - The Adsorption of Gases on Solids

A. R. Miller

Frontmatter

[More information](#)

CAMBRIDGE MONOGRAPHS ON PHYSICS

GENERAL EDITORS

N. FEATHER, F.R.S.

Professor of Natural Philosophy in the University of Edinburgh

D. SHOENBERG, PH.D.

Fellow of Gonville and Caius College, Cambridge

THE ADSORPTION OF GASES
ON SOLIDS

Cambridge University Press

978-1-107-62142-8 - The Adsorption of Gases on Solids

A. R. Miller

Frontmatter

[More information](#)

Cambridge University Press
978-1-107-62142-8 - The Adsorption of Gases on Solids
A. R. Miller
Frontmatter
[More information](#)

THE ADSORPTION OF GASES ON SOLIDS

BY

A. R. MILLER

*Imperial Chemical Industries Research Fellow
at the Royal Society Mond Laboratory,
Cavendish Laboratory, Cambridge*

*A sequel to the Cambridge Physical Tract
written in 1939 by J. K. Roberts and entitled
Some Problems in Adsorption*



CAMBRIDGE
AT THE UNIVERSITY PRESS

1949

Cambridge University Press
978-1-107-62142-8 - The Adsorption of Gases on Solids
A. R. Miller
Frontmatter
[More information](#)

CAMBRIDGE UNIVERSITY PRESS
Cambridge, New York, Melbourne, Madrid, Cape Town,
Singapore, São Paulo, Delhi, Mexico City

Cambridge University Press
The Edinburgh Building, Cambridge CB2 8RU, UK

Published in the United States of America by Cambridge University Press, New York

www.cambridge.org
Information on this title: www.cambridge.org/9781107621428

© Cambridge University Press 1949

This publication is in copyright. Subject to statutory exception
and to the provisions of relevant collective licensing agreements,
no reproduction of any part may take place without the written
permission of Cambridge University Press.

First published 1949
First paperback edition 2013

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

ISBN 978-1-107-62142-8 Paperback

Cambridge University Press has no responsibility for the persistence or
accuracy of URLs for external or third-party internet websites referred to in
this publication, and does not guarantee that any content on such websites is,
or will remain, accurate or appropriate.

Cambridge University Press

978-1-107-62142-8 - The Adsorption of Gases on Solids

A. R. Miller

Frontmatter

[More information](#)

GENERAL PREFACE

The Cambridge Physical Tracts, out of which this series of Monographs has developed, were planned and originally published in a period when book production was a fairly rapid process. Unfortunately, that is no longer so, and to meet the new situation a change of title and a slight change of emphasis have been decided on. The major aim of the series will still be the presentation of the results of recent research, but individual volumes will be somewhat more substantial, and more comprehensive in scope, than were the volumes of the older series. This will be true, in many cases, of new editions of the Tracts, as these are republished in the expanded series, and it will be true in most cases of the Monographs which have been written since the War or are still to be written.

The aim will be that the series as a whole shall remain representative of the entire field of pure physics, but it will occasion no surprise if, during the next few years, the subject of nuclear physics claims a large share of attention. Only in this way can justice be done to the enormous advances in this field of research over the War years.

N. F.

D. S.

Cambridge University Press

978-1-107-62142-8 - The Adsorption of Gases on Solids

A. R. Miller

Frontmatter

[More information](#)

CONTENTS

AUTHOR'S PREFACE *page ix*

CHAPTER 1

Experimental Methods

1.1. General introduction, p. 1. **1.2.** The measurement of accommodation coefficients, p. 7. **1.3.** The measurement of the heat of adsorption, p. 13. **1.4.** The amount of hydrogen adsorbed on tungsten, p. 16. **1.5.** Variation of heat of adsorption of hydrogen on tungsten with fraction of surface covered, p. 18.

CHAPTER 2

The Theory of Heat of Adsorption with Interaction between Adsorbed Particles

2.1. Langmuir's theory of adsorption on definite sites, p. 20. **2.2.** Mobile and immobile adsorbed films, p. 21. **2.3.** The equilibrium distribution of particles on the surface in a mobile film, p. 24. **2.4.** The variation of heat of adsorption with fraction of sites occupied for simple adsorption into a mobile film, p. 27. **2.5.** Variation of heat of adsorption with fraction of sites occupied in a mobile film for adsorption with dissociation, p. 29. **2.6.** The theory of heat of adsorption for an immobile film, p. 30.

CHAPTER 3

Variation of the Potential Energy over the Surface

3.1. Introduction, p. 38. **3.2.** Physical model, p. 40. **3.3.** Variation of the heat of adsorption with the fraction of the surface covered for a mobile film, p. 44. **3.4.** The relation between the heat of adsorption of an immobile film and the fraction of the surface covered by it, p. 47. **3.5.** Application to experiment, p. 48. **3.6.** States of minimum energy, p. 51.

CHAPTER 4

The Process of the Formation of Adsorbed Films

4.1. The kinetics of the formation of immobile adsorbed films with dissociation, p. 55. **4.2.** Some properties of oxygen films, p. 59. **4.3.** The kinetics of the formation of mobile films with dissociation, p. 61.

CHAPTER 5

Evaporation Processes and the Production of Atomic Hydrogen

5.1. The production of atomic hydrogen by hot tungsten, p. 65. **5.2.** Groups of processes occurring at the surface, p. 66. **5.3.** Fundamental assumptions, p. 67. **5.4.** Theory of equilibrium and of production of atomic hydrogen including effect of interactions, p. 70. **5.5.** True and apparent heats of evaporation of adsorbed films, p. 76. **5.6.** The adsorption isotherm, p. 82.

Cambridge University Press

978-1-107-62142-8 - The Adsorption of Gases on Solids

A. R. Miller

Frontmatter

[More information](#)

viii

CONTENTS

CHAPTER 6

Some Other Types of Adsorption

6.1. The distribution of particles in a mobile film when each adsorbed particle precludes occupation of neighbouring sites, p. 85. **6.2.** The kinetics of adsorption and evaporation in a mobile film on the 110 plane of tungsten when each adsorbed particle precludes occupation of neighbouring sites, p. 89. **6.3.** Properties of immobile films on tungsten in which each adsorbed particle precludes occupation of neighbouring sites, p. 91. **6.4.** General summary, p. 94. **6.5.** Experimental method, p. 95. **6.6.** The different types of oxygen film, p. 95. **6.7.** The kinetics of the adsorption of oxygen, p. 100.

CHAPTER 7

Dipole Interactions between Adsorbed Particles

7.1. Introduction, p. 104. **7.2.** The electrostatic field, p. 107. **7.3.** The partition function for the system, p. 109. **7.4.** The variation of the heat of adsorption, p. 111. **7.5.** Numerical calculations, p. 114. **7.6.** The treatment of long-range forces, p. 124.

REFERENCES

page 126

INDEX

129

Cambridge University Press

978-1-107-62142-8 - The Adsorption of Gases on Solids

A. R. Miller

Frontmatter

[More information](#)

AUTHOR'S PREFACE

Kinetic theory calculations can be carried out exactly when the dimensions of the apparatus used are small compared with the free path of the molecules in the gas. The discrepancies between such calculations and experiments on the exchange of energy between a metal surface and a gas at a different temperature suggested that the metal surfaces which had been used were all covered with adsorbed layers of impurity. To obtain results which would refer to known systems, it was necessary to work with surfaces kept free from impurities. This formed the starting-point for the experiments initiated by the late J. K. Roberts in 1931. These experiments, together with the theory so far as it had been developed by the end of 1938, were described in a Cambridge Physical Tract entitled *Some Problems in Adsorption*. The series of physical tracts were designed to provide interim reports of research work in progress, and it was intended that they should be replaced, as the development of their subject-matter demanded, by revised editions which would contain accounts of subsequent research. The present monograph is such a revision of Roberts's tract on adsorption. When the original tract was written statistical theories had not been developed to describe either the behaviour of immobile films (which had been studied by empirical methods) or of the effect of dipole-dipole, in addition to van der Waals, interactions; nor had account been taken of the continuous variation of the potential field provided by the adsorbing surface. In considering a revision of the original tract it seemed desirable to rewrite it so that these matters could be dealt with adequately. To do this it was necessary to discard much of the original text and to rearrange the presentation of the remainder to conform to the new material which was to be introduced. In the result, about half of the present book consists of new material, which is contained mainly in Chapters 2, 3 and 7, with important additions also to Chapters 4 and 5.

A. R. MILLER

Royal Society Mond Laboratory
University of Cambridge

21 MAY 1947