Equilibrium thermodynamics

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THIRD EDITION

CAMBRIDGE UNIVERSITY PRESS
Cambridge
London New York New Rochelle
Melbourne Sydney

PUBLISHED BY THE PRESS SYNDICATE OF THE UNIVERSITY OF CAMBRIDGE
The Pitt Building, Trumpington Street, Cambridge CB2 1RP, United Kingdom

CAMBRIDGE UNIVERSITY PRESS
The Edinburgh Building, Cambridge CB2 2RU, United Kingdom
40 West 20th Street, New York, NY 10011–4211, USA
10 Stamford Road, Oakleigh, Melbourne 3166, Australia

First published by McGraw Hill Book Company (UK) Ltd 1968
Third edition published by Cambridge University Press 1983
Reprinted 1984, 1985, 1986, 1989, 1991, 1994, 1997

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

ISBN 0 521 25445 0 hardback
ISBN 0 521 27456 7 paperback

Transferred to digital printing 2003

To Tessara

Cambridge University Press
978-0-521-27456-2 - Equilibrium Thermodynamics, Third Edition
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Preface

This book is intended as a thorough but concise course on the fundamentals of classical thermodynamics. My overriding objective in writing has been to achieve a clear and stimulating exposition: to give an account of the subject that is easy to learn from.

There are many ways of writing a textbook on thermodynamics because the subject is relevant to so many branches of science. The terms of reference of *Equilibrium thermodynamics* are primarily those of the undergraduate physicist; but it is also suitable for use in materials sciences, engineering and chemistry. The subject is usually taught in the first or second year of a UK undergraduate course but the book takes the student to degree standard and beyond. Prerequisites are a knowledge of elementary mechanics, calculus and electromagnetism, and a familiarity with school-level thermal physics. In overseas universities, thermodynamics may be taught somewhat later in an undergraduate course to allow more time for preparatory work.

Many books and courses on thermal physics attempt to develop classical thermodynamics and statistical mechanics side by side. Although it is essential that the relationship between the two be established at some stage of a scientific undergraduate's education, it is best to teach classical thermodynamics first and separately, for the ability to use it well depends largely on knowing what it can achieve *without* appealing to the microscopic nature of things. On the other hand, while it might be an interesting intellectual exercise to develop thermodynamics without reference to microscopic structure, it would be obscurantist and educationally foolish to do so. Therefore, in this book, I make free use of microscopic ideas to illuminate the subject and to bring out its relevance to modern physics; but I do not include any statistical mechanics nor any irreversible thermodynamics: hence the title.

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Many current undergraduate courses tend to neglect classical thermodynamics in favour of time spent on statistical mechanics because the concern of the latter with microscopic models makes it appear more 'fundamental'. This is educationally unfortunate. It also places the student at a serious disadvantage when he seeks to take the statistical approach beyond the most elementary level since the techniques of classical thermodynamics become essential for the manipulation of statistical results. By the time it is needed, the classical mode of argument should be as readily called to hand as the techniques of elementary mathematics.

In writing any book on classical thermodynamics there is the problem of deciding how to develop the second law. The advocates of a traditional approach based on the classical statements of Clausius or Kelvin argue that these are such simple generalizations of everyday experience that the experimental basis of the law is clearly displayed and it is therefore easy to accept it. However, within the structure of the subject, the essential function of the second law is the introduction of entropy, and to arrive at entropy from the Clausius or Kelvin statements requires a long chain of argument involving heat engines, cyclic processes and the rest. The advantage that may be gained by giving insight at an early stage into the functioning of thermal machines is counterbalanced by the deviousness of the route by which one arrives at entropy.

At the opposite extreme are the approaches by which the existence and properties of entropy are set out in a set of axioms. This has the advantage of introducing entropy directly, but it is too far abstracted from the experimental foundations for my liking.

Between the extremes lies the statement of Carathéodory which is based directly on the essential physical facts and leads quickly to entropy. The arguments are necessarily more abstract than those associated with the classical statements, but I have found them quite acceptable to the average student when treated via the idea, introduced by Buchdahl, of empirical entropy.

In this book I first give the traditional treatment and then break off in chapter 6 to develop the second law from the statement of Carathéodory. Chapter 6 may be omitted without disturbing the basic narrative, but I hope it will not be, for to reassemble the structure of the second law from the statement of Carathéodory after having first followed through the traditional development is a great help to a proper understanding of entropy.

At the end of the book, I have gathered together a number of problems which I hope will prove both instructive and stimulating. Many are based on old Cambridge University examination questions. Throughout the book I have, of course, used SI units. As regards choice of symbols and conventions used for showing units, I have generally followed the recommendations of the Symbols Committee of the Royal Society and current British Standards. Technical details of temperature scales and thermometry are in line with current decisions of the International Committee of Weights and Measures.

It would be unwise to write something in the nature of a textbook without drawing on the experience of those who have tackled the task before and it would be impossible to acknowledge all those who have contributed indirectly to its making. Of books I referred to often I should mention the classic texts of Zemansky and Pippard, and Wilks' book on the third law was a great help as I set about writing chapter 12. I also owe much to members of this laboratory, in particular to Dr John Ashmead and Professor Sir Brian Pippard for helpful comments and profitable arguments. Finally, I must thank generations of undergraduates and other readers of earlier versions of this book who, by their questions, comments and suggestions have contributed in no small measure to this text.

C. J. Adkins
Cambridge 1983