

Cambridge University Press

978-0-521-11519-3 - The Concepts of Classical Thermodynamics

H. A. Buchdahl

Frontmatter

[More information](#)

*CAMBRIDGE MONOGRAPHS ON PHYSICS*

GENERAL EDITORS

A. HERZENBERG, Ph.D.

*Reader in Theoretical Physics in the University of Manchester*

J. M. ZIMAN, D.Phil.

*Professor of Theoretical Physics in the University of Bristol*

THE CONCEPTS OF  
CLASSICAL THERMODYNAMICS

Cambridge University Press

978-0-521-11519-3 - The Concepts of Classical Thermodynamics

H. A. Buchdahl

Frontmatter

[More information](#)

# THE CONCEPTS OF CLASSICAL THERMODYNAMICS

BY

H. A. BUCHDAHL

*Professor of Theoretical Physics,  
School of General Studies,  
Australian National University*



CAMBRIDGE  
AT THE UNIVERSITY PRESS

1966

Cambridge University Press  
978-0-521-11519-3 - The Concepts of Classical Thermodynamics  
H. A. Buchdahl  
Frontmatter  
[More information](#)

---

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

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](http://www.cambridge.org)  
Information on this title: [www.cambridge.org/9780521115193](http://www.cambridge.org/9780521115193)

© Cambridge University Press 1966

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 1966  
This digitally printed version 2009

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

*Library of Congress Catalogue Card Number: 66-10176*

ISBN 978-0-521-04359-5 hardback  
ISBN 978-0-521-11519-3 paperback

## CONTENTS

*Preface**page ix*

## CHAPTER 1

## Introduction

**1.** The nature of physical theory and related notions, p. 1. **2.** Presupposition of mechanical concepts. Motivation of thermodynamic theory, p. 5. **3.** Terminal conditions. Thermodynamic systems, p. 6. **4.** Equilibrium, p. 7. **5.** Coordinates, p. 9. **6.** States. Transitions, p. 10. **7.** Pseudo-static, quasi-static, and reversible transitions, p. 10. **8.** Adiabatic enclosures and partitions, p. 13. **9.** Concerning the character of thermodynamic theory, p. 14. **10.** Standard systems, p. 18. **11.** Representative spaces, p. 20. **12.** The notations of mathematics and physics, p. 23. **13.** Outline of following chapters, p. 26.

## CHAPTER 2

## The Zeroth Law

**14.** The mutual equilibrium of two systems, p. 27. **15.** The Zeroth Law, p. 29. **16.** The empirical temperature, p. 30. **17.** Isothermals, p. 31. **18.** Temperature as coordinate. Equation of state, p. 32. **19.** Thermometers, p. 33.

## CHAPTER 3

## The First Law

**20.** Laws of conservation, p. 38. **21.** The First Law, p. 40. **22.** The energy, p. 41. **23.** Heat, p. 43. **24.** Additivity of the energy, p. 44. **25.** On certain properties of the energy function, p. 45. **26.** Energy and empirical temperature scale, p. 46. **27.** Calorimetric experiments, p. 48. **28.** Perpetual motion of the first kind, p. 49. **29.** Two-sided and one-sided conservations laws. Laws of impotence, p. 50. **30.** Quasi-static adiabatic transitions, p. 51. **31.** Reversibility of quasi-static transitions, p. 52.

## CHAPTER 4

## Integrability

**32.** Introductory remarks, p. 55. **33.** The two classes of linear differential forms, p. 56. **34.** Sufficiency of integrability conditions, p. 59. **35.** Character of solutions, p. 60. **36.** The Theorem of Carathéodory, p. 62.

Cambridge University Press

978-0-521-11519-3 - The Concepts of Classical Thermodynamics

H. A. Buchdahl

Frontmatter

[More information](#)

vi

CONTENTS

## CHAPTER 5

## The Second Law (I)

**37.** Adiabatic inaccessibility, p. 66. **38.** The Second Law, p. 67. **39.** The Second Law and integrability, p. 69. **40.** The empirical entropy, p. 70. **41.** The absolute temperature, p. 71. **42.** The metrical entropy, p. 73. **43.** Additivity of entropy, p. 74. **44.** The principle of increase of entropy, p. 75. **45.** Sign of the absolute temperature, p. 77. **46.** Entropy principle for non-standard systems, p. 79. **47.** Perpetual motion of the second kind, p. 82. **48.** Empirical determination of  $S$  and  $T$ , p. 83. **49.** Concerning the definition of absolute temperature, p. 86. **50.** Other formulations of the Second Law, p. 89.

## CHAPTER 6

## The Second Law (II)

**51.** The ordering of states, p. 93. **52.** Existence of  $s(x)$  when the First Law is presupposed, p. 95. **53.** Principle of increase of empirical entropy, p. 97. **54.** The integrability of  $dQ$ , p. 97. **55.** Consequences of integrability reviewed, p. 98. **56.** Existence of  $s(x)$ , given a weak substitute for the First Law, p. 99. **57.** On a strengthened version of the Second Law, p. 101.

## CHAPTER 7

## The Third Law

**58.** On the behaviour of systems as  $T \rightarrow 0$ , p. 104. **59.** The problem of the attainability of zero temperature, p. 106. **60.** The Third Law, p. 107. **61.** Further remarks concerning the Third Law, p. 110.

## CHAPTER 8

Potentials, Constitutive Coordinates, and  
Conditions of Equilibrium

**62.** Thermodynamic potentials, p. 113. **63.** The system as a black box, p. 117. **64.** The system not as a black box, p. 118. **65.** Constitutive coordinates. External and internal states, p. 119. **66.** A single inert phase as open system. Chemical potentials, p. 121. **67.** The active heterogeneous system, p. 125. **68.** Conditions for physico-chemical equilibrium: unnatural states not admitted, p. 126. **69.** Conditions for physico-chemical equilibrium: unnatural states admitted, p. 130. **70.** Stability, p. 134.

Cambridge University Press

978-0-521-11519-3 - The Concepts of Classical Thermodynamics

H. A. Buchdahl

Frontmatter

[More information](#)

## CONTENTS

vii

## CHAPTER 9

## Miscellaneous Topics

**71.** Ideal and super-ideal gases, p. 137. **72.** Behaviour under Lorentz transformations, p. 141. **73.** Systems in the terrestrial gravitational field, p. 143. **74.** Remark on surface effects, p. 147. **75.** Thermal conduction. Localization of energy and of entropy production, p. 150. **76.** Fluctuations considered phenomenologically, p. 155.

## CHAPTER 10

## Applications (I)

**77.** Classification of applications, p. 160. **78.** Consequences of the existence of an equation of state, p. 161. **79.** Virial coefficients, p. 162. **80.** Consequences of the existence of the energy function, p. 164. **81.** Consequences of the existence of  $S$ . Thermodynamic identities, p. 165. **82.** Thermodynamic functions of gases and gas mixtures, p. 169. **83.** Miscellaneous results of type  $I_2$ , p. 174. **84.** The Third Law invoked, p. 190.

## CHAPTER 11

## Applications (II)

**85.** The critical region, p. 193. **86.** Heterogeneous equilibrium of systems of one constituent, p. 197. **87.** The phase rule for inert systems, p. 199. **88.** Phase rule for chemically active systems, p. 202. **89.** Further remarks on the stability of general systems, p. 203. **90.** Law of Mass Action for ideal gases: one reaction, p. 205. **91.** Law of Mass Action for ideal gases: several reactions, p. 207. **92.** Ideal systems and their equilibrium constants, p. 208. **93.** The equilibrium condition for real gases, p. 211. **94.** Calorimetric determination of equilibrium constants. The Nernst Heat Theorem, p. 213.

*Bibliography* *page 218*

*Index* 219

Cambridge University Press

978-0-521-11519-3 - The Concepts of Classical Thermodynamics

H. A. Buchdahl

Frontmatter

[More information](#)

ix

## PREFACE

There exist today many excellent treatises on classical thermodynamics such as those of Guggenheim, Landsberg, Pippard, and Wilson, to mention but a few. It is not my purpose to supplant them, even were I competent to do so. On the contrary, this small volume is intended merely to present the basic ideas of classical thermodynamics on a purely phenomenological level, against a general background of physical theory. This is done in a way which should give the reader a feeling of easy familiarity with the laws to be introduced and the concepts to be defined. It is just this feeling which the student so often lacks after a first study of the subject. In a sense, therefore, my aim is very circumscribed. There will be no attempt at completeness or generality, and all manner of simplifying assumptions will be introduced from time to time. This procedure is, I think, likely to enhance the reader's chances of getting a basic understanding of the subject, and any required generalizations can be undertaken at a later stage.

My general approach tries to couple simplicity with reasonable sophistication. It should be clearly understood from the outset that, superficial appearances to the contrary, this is *not* an axiomatic treatment of the subject. Undeniably useful though an axiomatic treatment of a physical theory may be, it too easily gives the appearance of a logical exercise, and were this to be the case here the whole purpose of this work would be vitiated. Moreover, to carry through a valid axiomatic development is likely to require at times assumptions so restrictive as to put its relevance to *physical* theory in doubt. This point of principle seems to be sometimes overlooked. At any rate, frankly pragmatic though the character of the present approach may be on occasion, it is constantly governed by the main aims of simplicity and clarity, however much I may in fact have failed to achieve these.

Though this volume is reasonably self-contained, it might well be read alongside one of the standard treatises already referred to. I adhere strictly to the phenomenological point of view, not least in order to counter the widely held opinion that one can gain an understanding of the concept of entropy, for instance, only on a

Cambridge University Press

978-0-521-11519-3 - The Concepts of Classical Thermodynamics

H. A. Buchdahl

Frontmatter

[More information](#)

x

## PREFACE

statistical basis. In the first place, it might be reflected that the theoretical foundations of statistical thermodynamics are difficult to a degree which makes it doubtful whether the belief in question can be sustained. Be that as it may, it involves an obvious logical difficulty: a statement of the kind ‘the results of statistical thermodynamics must not lead to contradictions with the laws of phenomenological thermodynamics’ becomes meaningless if the latter can be ‘understood’ only on the basis of the former: to grant that it is meaningful is to grant that the conceptual frameworks of both theories are *separately* well defined.

After some general remarks concerning physical theories as such, the subject is developed in a manner which does not place undue verbal emphasis on terms characteristic of the realm of engineering. Moreover, the introduction of ideal gases into the basic parts of the theory is avoided, for there is a didactic weakness inherent in an early appeal to the properties of a class of substances whose existence in nature is later denied by one of the principal laws of thermodynamics. The four main laws are stated in their traditional order even though, from a pedagogic viewpoint, there are advantages in stating the second before the first. With regard to the former, Carathéodory’s formulation has been adopted, since this allows one to achieve a clearer separation between the mathematical and the physical content of the theory, even if, contrary to a widely held view, its supposed greater logical economy appears to be somewhat illusory. The concept of entropy is introduced in various alternative ways, with a certain emphasis on the idea of an ordering of states. Some redundancy is of little account: I have not aimed at the greatest possible brevity. Indeed, as a result of closely scrutinizing points which are often scarcely examined at all, this exposition may appear somewhat old-fashioned in its discursiveness. It may not be out of place to emphasize that it is intended to be of an elementary character, though here and there it may reveal itself as being a little more sophisticated than most elementary treatments of the subject; an occasional reference to an unfamiliar branch of physics may simply be left unread.

The systematic development of the general theory has been kept unencumbered by discussions of specific applications. These have been relegated to the last two chapters, where they are presented



## PREFACE

xi

in an orderly fashion on the basis of a classification which assigns to any particular application a certain character. It will be appreciated that the material of these chapters is mainly intended to serve a methodological purpose. Bearing in mind at the same time that this work will mostly be used as collateral reading, the absence of numerical examples should occasion no surprise.

My warmest thanks go to Professor Arthur Hambly and to Dr Daniel Greenberg for reading the whole manuscript, and to Mr Malcolm Urquhart for reading the first three chapters. Their advice has been of great value to me. The responsibility for any errors and omissions which remain is of course entirely mine. To Mrs Myrene Hickey I wish to express my appreciation of the excellence and patience she displayed in typing the manuscript.

Finally I should like to thank the Cambridge University Press most warmly for their unfailing care and courtesy.

*Canberra*  
*6 June 1965*

H.A.B.