

Equilibrium thermodynamics



# **Equilibrium** thermodynamics

C.J.ADKINS

Lecturer in Physics in the University of Cambridge and Fellow of Jesus College, Cambridge

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

© McGraw Hill Book Company (UK) Ltd 1968, 1975 © Cambridge University Press 1983

This book 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 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



# Contents

	Preface	xi
1	Introduction	1
1.1	Origins of thermodynamics	1
1.2	The macroscopic approach	2
1.3	The role of the laws	2
1.4	Systems, surroundings, and boundaries	3
1.5	Thermodynamic variables	5
1.6	Thermodynamic equilibrium	6
1.7	Thermodynamic reversibility	8
1.8	Degrees of freedom	10
1.9	Some useful mathematical results	12
2	The zeroth law	17
2.1	The zeroth law	17
2.2	Temperature	18
2.3	Scales of temperature	20
2.4	The perfect gas scale	20
2.5	Thermodynamic temperature	21
2.6	The Celsius scale	23
2.7	Some common thermometers	23
2.8	The International Practical Temperature Scale	28
3	The first law	30
3.1	Background to the first law	30
3.2	The first law	31
3.3	Internal energy	32
3.4	Heat	32
3.5	Work in various systems	35

vii



/i	ii	Contents	
	3.6	Heat capacities	42
	3.7	Enthalpy	45
	3.8	Flow processes	46
	4	The second law	50
	4.1	The function of the second law	50
	4.2	Cyclic processes and heat engines	50
	4.3	Statements of the second law	53
	4.4	Hotness and temperature	55
	4.5	Carnot's theorem	56
	4.6	Thermodynamic temperature	58
	4.7	Uniqueness of reversible adiabatics	60
	4.8	Refrigerators and heat pumps	62
	4.9	Real heat engines	64
	5	Entropy	68
	5.1	Clausius' theorem	68
	5.2	Entropy	71
	5.3	Entropy in irreversible changes	72
	5.4	The entropy form of the first law	74
	5.5	Entropy and the degradation of energy	76
	5.6	Entropy and order	77
	6	The Carathéodory formulation of the second law	87
	6.1	Introductory remarks	87
	6.2	Empirical entropy	88
	6.3	Empirical entropy and heat	93
	6.4	Thermodynamic temperature and entropy	93
	6.5	Irreversible changes	95
	6.6	Subsequent development	97
	7	Thermodynamic potentials	100
	7.1	The potential functions	100
	7.2	The Legendre differential transformation	103
	7.3	Maxwell relations	104
	7.4	General conditions for thermodynamic equilibrium	106
	8	Applications to simple systems	112
	8.1	Some properties of specific heat capacities	112
	8.2	The perfect gas	116
	8.3	Behaviour of real pure substances	120
	8.4	The elastic rod or filament	124
	8.5	The reversible electric cell	125
	8.6	Surface tension	128



	Contents	iz
8.7	Piezoelectricity	132
8.8	The magnetocaloric effect	134
8.9	Thermal radiation	144
8.10	Fluctuations	157
9	Applications to some irreversible changes	162
9.1	The Joule expansion	162
9.2	The Joule–Kelvin expansion	165
9.3	Liquefaction of gases	168
9.4	Thermoelectricity	172
10	Change of phase	180
10.1	Systems of more than one phase	180
10.2	The condition for equilibrium between phases	180
10.3	The Clausius-Clapeyron equation	182
10.4	Integration of the Clausius-Clapeyron equation	184
10.5	Gibbs functions in first order transitions	186
10.6	Critical points	188
10.7	Higher order change of phase	193
10.8	Some examples of higher order phase changes	194
10.9	Interpretation of second order transitions	203
10.10	The fountain effect with liquid helium	205
10.11	Surface effects	208
11	Systems of several components	213
11.1	Mixtures of ideal gases	213
11.2	Increase of entropy in diffusion	216
11.3	Chemical potential	218
11.4	Conditions for equilibrium	221
11.5	Ideal solutions	224
11.6	Ideal gas reactions	228
11.7 11.8	Solubility gaps in binary mixtures  Equilibrium between liquid and solid mixtures	231
11.0	Equilibrium between iiquid and solid iinxtures	236
12	The third law	241
12.1	The third law	241
12.2	Elementary physical consequences of the third law	242
12.3	Unattainability of absolute zero	245
12.4	Allotropic transformations	247
12.5	Glasses The aquilibrium constant	249
12.6	The equilibrium constant	251



## x Contents

Appendix. Magnetic energy	253
Useful data	256
Problems	257
References	278
Index	281



# 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.



### xii Preface

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.



Preface xiii

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