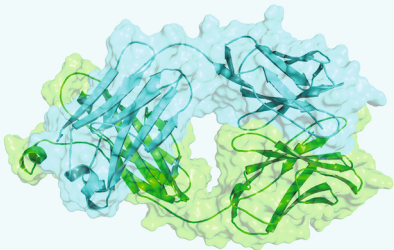


OXFORD

MODERN THERMODYNAMICS FOR CHEMISTS AND BIOCHEMISTS



DENNIS SHERWOOD AND PAUL DALBY

Modern Thermodynamics for Chemists and Biochemists

Modern Thermodynamics for Chemists and Biochemists

Dennis Sherwood and Paul Dalby

OXFORD
UNIVERSITY PRESS

OXFORD
UNIVERSITY PRESS

Great Clarendon Street, Oxford, OX2 6DP,
United Kingdom

Oxford University Press is a department of the University of Oxford.
It furthers the University's objective of excellence in research, scholarship,
and education by publishing worldwide. Oxford is a registered trade mark of
Oxford University Press in the UK and in certain other countries

© Dennis Sherwood and Paul Dalby 2018

The moral rights of the authors have been asserted

First Edition published in 2018

Impression: 1

All rights reserved. No part of this publication may be reproduced, stored in
a retrieval system, or transmitted, in any form or by any means, without the
prior permission in writing of Oxford University Press, or as expressly permitted
by law, by licence or under terms agreed with the appropriate reprographics
rights organization. Enquiries concerning reproduction outside the scope of the
above should be sent to the Rights Department, Oxford University Press, at the
address above

You must not circulate this work in any other form
and you must impose this same condition on any acquirer

Published in the United States of America by Oxford University Press
198 Madison Avenue, New York, NY 10016, United States of America

British Library Cataloguing in Publication Data
Data available

Library of Congress Control Number: 2017932407

ISBN 978-0-19-878295-7 (hbk.)

ISBN 978-0-19-878470-8 (pbk.)

Printed and bound by
CPI Group (UK) Ltd, Croydon, CR0 4YY

Links to third party websites are provided by Oxford in good faith and
for information only. Oxford disclaims any responsibility for the materials
contained in any third party website referenced in this work.

Foreword

Thermodynamics has evolved dramatically since the precursor of this book, Dennis Sherwood's *Introductory Chemical Thermodynamics*, was published in 1971. This development is completely reflected in the new text, which is really an entirely new book. The title has also very aptly been changed in order to emphasise that one of the most important new areas where thermodynamics can make a major impact is within the bio world: biochemistry and molecular biology. This is emphasised by chapters on the bioenergetics of living cells, macromolecular conformations and interactions, and even an outlook toward where thermodynamics seems to be headed in the future, such as the self-assembly of large complexes.

The sequence of chapters cleverly escalates from everyday experiences to precise definitions, to ideal modelling and then real adjustments. Spontaneity, time, order and information follow naturally, and from these the more complicated chemical and electrochemical reactions, ending up with reactions and structure formation in the living environment – a very long staircase, but with comfortable small steps.

While the content has been brought fully up-to-date and the focus adjusted to fertile modern areas, the old friendly writing style has been preserved. In particular in the beginning where the basic thermodynamic concepts are introduced, we find essentially no equations, only simple verbal explanations based on common observations so that the reader will build a clear intuitive understanding of the topic without the all too frequent mathematical barrier. This approach is especially important for readers in the bio field who often do not have the same strong background in mathematical thinking and modelling as those in the hard sciences and engineering. This is not to say that the book has left out all maths, it just comes later when the concepts have been understood. This is a unique pedagogical approach among thermodynamics textbooks, which undoubtedly will facilitate the reader's entry into thermodynamic thinking.

Every chapter starts with a summary of the concepts presented in that chapter, useful both before reading the chapter for giving direction and after reading it for wrapping up the new items into a whole. The exercises at the end of all chapters further emphasise understanding and relations. They are unconventional by not asking the student to calculate a certain quantity, but to explain an observed behaviour, relating different effects, predict a behaviour and find an error in an argument. In other words, they encourage thinking, rather than mechanical calculational skills. The concluding glossary of thermodynamics terms, and the introductory index of symbols, are very useful for the novice when the many new words and symbols become confusing.

I strongly recommend this introductory thermodynamics textbook for its inviting approach, focus on concepts and relationships, comprehensive coverage, and openness toward the biological sciences.

Bjarne Andresen
Niels Bohr Institute, University of Copenhagen

**Oh, you can't pass heat from the cooler to the hotter
You can try it if you like, but you far better notter
'Cause the cold in the cooler will get cooler as a ruler
That's the physical law!**

From *First and Second Law*, by Michael Flanders and Donald Swann, performed in
their musical revue *At the Drop of Another Hat*, 1963

Preface

This book originated as a proposed second edition to *Introductory Chemical Thermodynamics*, published in 1971, with the specific intention of adding material relating to current-day applications of thermodynamics to biology, including topics such as bioenergetics, protein-folding, protein-ligand interactions, and protein aggregation. This has, indeed, been done, but we also took the opportunity to enrich and enhance the discussion of the fundamentals of thermodynamics, the Three Laws, and chemical applications. Accordingly, this book is structured as:

- **Part 1: Fundamentals:** introducing the concepts of work, temperature, heat and energy, state functions and path functions, and some of the mathematical principles that will be used throughout the book.
- **Part 2: The Three Laws:** the core of the book, in which we explore the First Law, internal energy and enthalpy; the Second Law and entropy; and the Third Law and the approach to absolute zero.
- **Part 3: Free energy, spontaneity, and equilibrium:** where we explain the central role of the Gibbs free energy as regards both the spontaneity of change, and also the nature of chemical equilibrium.
- **Part 4: Chemical applications:** covering how the principles discussed so far can be applied to phenomena such as phase equilibria; reactions in solution; acids, bases, and buffer solutions; boiling points and melting points; mixing and osmosis; and electrochemistry.
- **Part 5: Biochemical applications:** where we describe how biological systems capture the free energy within molecules such as glucose, or within light, store it temporarily within molecules such as ATP, and then use that free energy to drive, for example, the synthesis of complex biomolecules; we also explore how proteins fold, and interact with ligands, as well as how proteins self-assemble to form larger-scale structures.

Thermodynamics is notoriously difficult to understand, learn, and use, and so we have taken great care to explain as clearly as possible all the fundamental concepts. As a quantitative branch of science, thermodynamics necessarily uses mathematics to describe how physically measurable phenomena, such as the pressure exerted by a gas, or the concentration of a component within a solution, are related, and how they change as conditions such as the system temperature vary. Much of the required mathematics is explained, and developed, within the text. The only pre-requisites are some knowledge of basic algebra, and of differential and integral calculus (for example, if $y = 3x^2$, then $dy/dx = 6x$, and $\int(1/x) dx = \ln x$).

This book has not been written to support a specific curriculum; rather, it has been written to provide “everything a student needs to know about chemical and biochemical thermodynamics” in the context of passing undergraduate examinations, and providing a solid

platform for more advanced studies. The content of the book is therefore likely to be broader, and in some respects deeper, than the precise requirements for any specific course. We trust, however that it includes all the required content for very many courses. As a consequence, the book will be of value to undergraduate students of chemistry and biochemistry, and related fields, as well as to students of higher-level programmes who seek a source of reference. Also, the exercises associated with each chapter have been designed to stimulate thinking, rather than as practice problems for a specific examination.

Many people have, of course, contributed to our thinking and to the knowledge we are sharing in this book, and we gratefully acknowledge all our own teachers and mentors. In particular, we wish to thank Professor Alan Cooper, of the University of Glasgow, and Professor Bjarne Andresen, of the Niels Bohr Institute at the University of Copenhagen, for their most helpful suggestions and insights. We also thank Harriet Konishi, Shereen Karmali, Megan Betts and Sonke Adlung at OUP, and also Marie Felina Francois, Indumadhi Srinivasan and everyone in the production team, with whom it has been a pleasure to work—and, of course, our wives and children, who have been remarkably patient, supportive, and understanding as we have been (from their totally legitimate standpoint) both distracted and obsessed by the intricacies of reversible changes, electrode potentials, and entropy.

We trust you will enjoy reading this book and will benefit accordingly. If you notice any errors, think any particular topic is poorly explained, or if you have any ideas for making the book clearer or more useful, please do let us know—our email addresses are dennis@silverbulletmachine.com and p.dalby@ucl.ac.uk. Thank you!

Dennis Sherwood
Exton, Rutland

Paul Dalby
University College, London

Contents

Index of symbols	xxi
Index of units-of-measure	xxvii
List of Tables	xxviii

PART 1 FUNDAMENTALS

1 Systems and states 3

SUMMARY	3
1.1 Some very familiar concepts ...	3
1.2 The macroscopic viewpoint	4
1.3 The system, the surroundings, and the system boundary	5
1.4 State functions	5
1.5 Extensive and intensive state functions	6
1.6 The mole number n	7
1.7 The 'ideal' concept	8
1.8 Equilibrium	8
1.9 Changes in state	10
1.10 The surroundings have state functions too	13
1.11 Pressure	13
1.12 The ideal gas	16
1.13 Pressure – a molecular interpretation	17
EXERCISES	18

2 Work and energy 20

SUMMARY	20
2.1 Work – an initial definition	20
2.2 The work done by an expanding gas	21
2.3 Path functions	23
2.4 An important sign convention	26
2.5 Useful work ...	27
2.6 ... and wasted work	28
2.7 Quasistatic paths	28
2.8 Work and Boyle's Law	31
2.9 P, V diagrams	31
2.10 Changes at constant pressure	34

2.11	Thermodynamic cycles	35
2.12	Energy	40
	EXERCISES	40
<hr/>		
3	Temperature and heat	43
	SUMMARY	43
3.1	Temperature	43
3.2	The ideal gas law	46
3.3	A very important principle	48
3.4	Dalton's law of partial pressures	48
3.5	Some other equations-of-state	50
3.6	Heat	50
3.7	Some more definitions	56
3.8	How to get work from heat	58
3.9	Temperature – a deeper look	67
	EXERCISES	74
<hr/>		
4	Thermodynamics and mathematics	76
	SUMMARY	76
4.1	What this chapter is about	76
4.2	Functions of more than one variable	77
4.3	Partial derivatives	78
4.4	Systems of constant mass	80
4.5	Partial derivatives and state functions	82
4.6	A look ahead ...	84
	EXERCISES	88
<hr/>		
PART 2 THE THREE LAWS		
<hr/>		
5	The First Law of Thermodynamics	93
	SUMMARY	93
5.1	The First Law	94
5.2	A molecular interpretation of internal energy	95
5.3	A reminder of some important sign conventions	96
5.4	Internal energy and temperature	96
5.5	The First Law, state functions, and path functions	99
5.6	The First Law and cycles	101
5.7	The mathematics of U	102
5.8	The First Law in open, closed and isolated systems	104
5.9	The First Law in an isolated system	105
5.10	The First Law in a closed system – the adiabatic change, $dq = 0$	106
5.11	The First Law in a closed system – the isochoric change, $dV = 0$	106
5.12	The heat capacity at constant volume, C_V	107

5.13	The First Law in a closed system – the isothermal change, $dT = 0$, for an ideal gas	114
5.14	The First Law in a closed system – the isobaric change, $dP = 0$	114
5.15	Reversible and irreversible paths	117
5.16	Mixing	126
5.17	Friction	128
5.18	Friction and irreversible paths	134
5.19	Real paths	140
	EXERCISES	144
<hr/>		
6	Enthalpy and thermochemistry	146
	SUMMARY	146
6.1	Man's most important technology	147
6.2	Enthalpy	148
6.3	The mathematics of H	151
6.4	Endothermic and exothermic reactions	153
6.5	Enthalpy, directionality and spontaneity	156
6.6	The difference $\Delta H - \Delta U$	158
6.7	Phase changes	161
6.8	Measuring enthalpy changes – calorimetry	163
6.9	Calculating enthalpy changes – Hess's law	165
6.10	Chemical standards	168
6.11	Standard enthalpies of formation	178
6.12	Ionic enthalpies	184
6.13	Bond energies	185
6.14	The variation of ΔH with temperature	190
6.15	The variation of $\Delta_r H^\circ$ with temperature	198
6.16	Flames and explosions	200
	EXERCISES	206
<hr/>		
7	Ideal gas processes – and two ideal gas case studies too	208
	SUMMARY	208
7.1	What this chapter is about	208
7.2	Ideal gases	209
7.3	Some important assumptions	210
7.4	C_V and C_p for ideal gases	210
7.5	Three formulae that apply to all ideal gas changes	218
7.6	The isochoric path, $dV = 0$	218
7.7	The isobaric path, $dP = 0$	219
7.8	The isothermal path, $dT = 0$	220
7.9	The adiabatic path, $dq = 0$	221
7.10	The key ideal gas equations	229
7.11	Case Study: The Carnot cycle	230
7.12	Case Study: The thermodynamic pendulum	236
	EXERCISES	254

8 Spontaneous changes	258
SUMMARY	258
8.1 A familiar picture	258
8.2 Spontaneity, unidirectionality and irreversibility	260
8.3 Some more examples of spontaneous, unidirectional, and irreversible changes	261
8.4 Spontaneity and causality	263
8.5 The significance of the isolated system	266
EXERCISE	266

9 The Second Law of Thermodynamics	267
SUMMARY	267
9.1 The Second Law	268
9.2 Entropy – a new state function	269
9.3 The Clausius inequality	272
9.4 Real changes	273
9.5 Two examples	275
9.6 The First and Second Laws combined	280
9.7 The mathematics of entropy	282
9.8 Entropy changes for an ideal gas	285
9.9 Entropy changes at constant pressure	290
9.10 Phase changes	291
9.11 The Third Law of Thermodynamics	296
9.12 T, S diagrams	297
EXERCISES	299

10 Clausius, Kelvin, Planck, Carathéodory and Carnot	303
SUMMARY	303
10.1 The Clausius statement of the Second Law	304
10.2 The Kelvin–Planck statement of the Second Law	309
10.3 Heat engines and heat pumps	313
10.4 Irreversibility	315
10.5 A graphical interpretation	317
10.6 The Carathéodory statement	321
10.7 Carnot engines and Carnot pumps	323
10.8 Real engines	328
EXERCISE	331

11 Order, information and time	332
SUMMARY	332
11.1 What this chapter is about	332
11.2 Why do things get muddled?	333
11.3 Order and disorder	333
11.4 Macrostates and microstates	334

11.5	Three important principles	337
11.6	Measuring disorder	337
11.7	What happens when a gas expands into a vacuum	340
11.8	The Boltzmann equation	341
11.9	Maxwell's demon	344
11.10	Entropy and time	347
11.11	Thermoeconomics	347
11.12	Organodynamics	348
	EXERCISES	350

12 The Third Law of Thermodynamics **351**

	SUMMARY	351
12.1	The Third Law	351
12.2	Absolute entropies	352
12.3	Approaching absolute zero	357
	EXERCISES	362

PART 3 FREE ENERGY, SPONTANEITY, AND EQUILIBRIUM

13 Free energy **365**

	SUMMARY	365
13.1	Changes in closed systems	367
13.2	Spontaneous changes in closed systems	369
13.3	Gibbs free energy	374
13.4	The significance of the non-conservative function	375
13.5	Enthalpy- and entropy-driven reactions	377
13.6	The mathematics of G	378
13.7	Helmholtz free energy	385
13.8	The mathematics of A	386
13.9	Maximum available work	386
13.10	How to make non-spontaneous changes happen	390
13.11	Coupled systems ...	391
13.12	... an explanation of frictional heat, and tidying a room ...	393
13.13	... and the maintenance of life	395
13.14	Climate change and global warming – the ‘big picture’	395
13.15	Standard Gibbs free energies	397
13.16	Gibbs free energies at non-standard pressures	399
13.17	The Gibbs free energy of mixtures	401
13.18	The ‘Fourth Law’ of Thermodynamics	408
	EXERCISES	411

14 Chemical equilibrium and chemical kinetics **413**

	SUMMARY	413
14.1	Chemical reactions	415
14.2	How $G_{\text{sys}}(\tau)$ varies over time	417

14.3	Chemical equilibrium	423
14.4	The pressure thermodynamic equilibrium constant K_p ...	428
14.5	... and the meaning of $\Delta_r G_p^\circ$	430
14.6	Non-equilibrium systems	432
14.7	Another equilibrium constant, K_x ...	436
14.8	... and a third equilibrium constant, K_c	437
14.9	Two worked examples – methane and ammonia	439
14.10	How the equilibrium constant varies with temperature	444
14.11	Le Chatelier's principle	448
14.12	Thermodynamics meets kinetics	449
14.13	The Arrhenius equation	455
14.14	The overall effect of temperature on chemical reactions	459
14.15	A final thought	460
	EXERCISES	461

PART 4 CHEMICAL APPLICATIONS

15 Phase equilibria 467

	SUMMARY	467
15.1	Vapour pressure	467
15.2	Vapour pressure and external pressure	470
15.3	The Gibbs free energy of phase changes	471
15.4	Melting and boiling	472
15.5	Changing the external pressure P_{ex}	478
15.6	The Clapeyron and Clausius–Clapeyron equations	481
15.7	Phase changes, ideal gases and real gases	485
15.8	The mathematics of G_s , G_l and G_g	497
	EXERCISES	500

16 Reactions in solution 502

	SUMMARY	502
16.1	The ideal solution	503
16.2	The Gibbs free energy of an ideal solution	511
16.3	Equilibria of reactions in solution	517
16.4	Dilute solutions, molalities and molar concentrations	520
16.5	Multi-state equilibria and chemical activity	522
16.6	Coupled reactions in solution	526
	EXERCISES	530

17 Acids, bases and buffer solutions 534

	SUMMARY	534
17.1	Dissociation	535
17.2	The ionisation of pure water, pH and pOH	536
17.3	Acids	538

17.4	Bases	545
17.5	The Henderson-Hasselbalch approximation	548
17.6	Buffer solutions	549
17.7	Why buffer solutions maintain constant pH	552
17.8	How approximate is the Henderson-Hasselbalch approximation?	553
17.9	Buffer capacity	554
17.10	Other reactions involving hydrogen ions	561
17.11	The mass action effect	566
17.12	Water as a reagent	567
	EXERCISES	569
<hr/>		
18	Boiling points and melting points	571
	SUMMARY	571
18.1	Non-volatile solutes	571
18.2	Elevation of the boiling point	572
18.3	Depression of the freezing point	575
	EXERCISE	579
<hr/>		
19	Mixing and osmosis	580
	SUMMARY	580
19.1	Mixing	580
19.2	Osmosis	582
19.3	Osmotic pressure	583
19.4	Reverse osmosis	588
19.5	A note on hydrostatic pressure	588
	EXERCISES	590
<hr/>		
20	Electrochemistry	591
	SUMMARY	591
20.1	Work and electricity	592
20.2	Electrical work and Gibbs free energy	594
20.3	Half-cells	596
20.4	The electrochemical cell	599
20.5	Anodes and cathodes ...	600
20.6	... and the flow of ions and electrons	601
20.7	The chemistry of the Daniell Cell	602
20.8	Currents, voltages and electrode potentials	603
20.9	A different type of Daniell cell	604
20.10	Different types of electrode	605
20.11	Different types of electrochemical cell	607
20.12	The electromotive force	612
20.13	Oxidising agents and reducing agents	619
20.14	The thermodynamics of electrochemical cells	621

20.15	The Nernst equation	624
20.16	Redox reactions	628
	EXERCISES	631
<hr/>		
21	Mathematical round up	633
	SUMMARY	633
21.1	The fundamental functions	634
21.2	Pure substances	635
21.3	Heat capacities	636
21.4	The Maxwell relations	637
21.5	The chain rule	640
21.6	The thermodynamic equations-of-state	641
21.7	The difference $C_p - C_V$	645
21.8	The Joule–Thomson coefficient	648
21.9	The compressibility factor	652
	EXERCISES	654
<hr/>		
22	From ideal to real	655
	SUMMARY	655
22.1	Real gases and fugacity	656
22.2	Real solutions and activity	659
22.3	A final thought	668
	EXERCISES	668
<hr/>		
PART 5 BIOCHEMICAL APPLICATIONS		
<hr/>		
23	The biochemical standard state	673
	SUMMARY	673
23.1	Thermodynamics and biochemistry	674
23.2	A note on standards	675
23.3	The biochemical standard state	676
23.4	Why this is important	678
23.5	The implications of the biochemical standard state	679
23.6	Transformed equations	681
23.7	$G(H^+)$ and $G'(H^+)$, and $\Delta_f G^*(H^+)$ and $\Delta_f G'^*(H^+)$	683
23.8	$\mathcal{E}^*(H^+, H_2)$ and $\mathcal{E}'^*(H^+, H_2)$	686
23.9	$\Delta_f G'^*(H_2)$	689
23.10	Transformed standard molar Gibbs free energies of formation $\Delta_f G'^*$	691
23.11	$\Delta_r G^*$ and $\Delta_r G'^*$	694
23.12	K_r and K_r'	696
23.13	G_{sys} and G_{sys}' for an unbuffered reaction	697
23.14	G_{sys} and G_{sys}' for a buffered reaction	704

23.15	Water as a biochemical reagent	707
23.16	The rules for converting into the biochemical standard	708
	EXERCISES	708
<hr/>		
24	The bioenergetics of living cells	711
	SUMMARY	711
24.1	Creating order without breaking the Second Law: open systems	711
24.2	Metabolic pathways, mass action and pseudo-equilibria	712
24.3	Life's primary 'energy currency' – ATP	712
24.4	NADH is an energy currency too	715
24.5	Glycolysis – substrate-level phosphorylation of ADP	716
24.6	The metabolism of pyruvate	719
24.7	The TCA cycle	720
24.8	Oxidative phosphorylation, and the chemi-osmotic potential	723
24.9	The efficiency of glucose metabolism	735
24.10	Photosynthesis	737
	EXERCISES	745
<hr/>		
25	Macromolecular conformations and interactions	747
	SUMMARY	747
25.1	Protein structure	747
25.2	The thermodynamics of protein folding	748
25.3	Protein-ligand interactions	763
25.4	Protein folding kinetics	769
	EXERCISES	779
<hr/>		
26	Thermodynamics today – and tomorrow	780
	SUMMARY	780
26.1	Self-assembly of large complexes	780
26.2	Non-ideal gases and the formation of liquids	781
26.3	Kinetics of nucleated molecular polymerisation	782
26.4	Molecular mechanisms in protein aggregation	786
26.5	The end-point of protein aggregation	787
26.6	The thermodynamics of self-assembly for systems with defined final structures	787
26.7	Towards the design of self-assembling systems	791
	EXERCISES	793
	Glossary	795
	Bibliography	844
	Index	847

Index of symbols

Roman upper case

<i>A</i>	Area	14
<i>A</i>	Constant in the Boltzmann equation	68
<i>A</i>	Helmholtz free energy	385
<i>A</i>	Molar Helmholtz free energy = A/n	385
<i>A</i>	Pre-exponential factor in the Arrhenius equation	456
<i>C</i>	Celsius, unit-of-measure of temperature, °C	44
<i>C_p</i>	Heat capacity at constant pressure	151
<i>C_p</i>	Molar heat capacity at constant pressure = C_p/n	151
<i>C_v</i>	Heat capacity at constant volume	107
<i>C_v</i>	Molar heat capacity at constant volume = C_v/n	108
<i>D^o</i>	Bond dissociation energy	187
<i>E</i>	Electrical or electrode potential	603
<i>E</i>	Reversible electrode potential	613
<i>E</i>	Molecular energy	68
<i>E_a</i>	Activation energy	456
<i>E_b</i>	Ebullioscopic constant	575
<i>E_f</i>	Cryoscopic constant	578
<i>F</i>	Faraday constant, $9.6485 \times 10^4 \text{ C mol}^{-1}$	595
<i>F</i>	Force	13
<i>G</i>	Gibbs free energy	374
<i>G</i>	Molar Gibbs free energy = G/n	375
<i>H</i>	Enthalpy	149
<i>H</i>	Molar enthalpy = H/n	149
<i>H</i>	Hartley entropy	346
<i>I</i>	Ionic strength	667
<i>I</i>	Electric current	592
<i>I</i>	Intensity of a measured signal	754
<i>J</i>	Joule, unit-of-measure of work, heat and energy	21
<i>K</i>	Kelvin, unit-of-measure of absolute temperature	44
<i>K_a</i>	Acid dissociation constant	539
<i>K_b</i>	Base dissociation constant	545
<i>K_b</i>	Molality equilibrium constant	521
<i>K_c</i>	Concentration equilibrium constant	438

K_d	General dissociation constant	535
K_p	Pressure equilibrium constant	427
K_r	Activity, or generalised, equilibrium constant	523
K_{unf}	Equilibrium constant of protein unfolding	751
K_w	Ionic product of water = 10^{-14}	536
K_x	Mole fraction equilibrium constant	437
M	Mass	6
\mathbf{M}	Molar mass = M/n , the molecular weight in kg mol^{-1}	7
M	Molarity	171
\mathcal{M}	Message transmission multiplicity	346
N	Newton, unit-of-measure of force	14
N_A	Avogadro constant, $6.022 \times 10^{23} \text{ mol}^{-1}$	7
\mathcal{P}	Mathematical probability	339
P	Pressure	14
Pa	Pascal = 1 N m^{-2} , unit-of-measure of pressure	14
Q	Quantity of electric charge	595
R	Ideal gas constant, $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$	47
R	Electrical resistance	592
S	Entropy	269
\mathbf{S}	Molar entropy = S/n	269
T	Thermodynamic temperature, as measured in K	44
\mathcal{T}	Time	251
\mathcal{T}	Thermodynamic temperature, as measured in K	354
U	Internal energy	94
\mathbf{U}	Molar internal energy = U/n	94
V	Volume	6
\mathbf{V}	Molar volume = V/n	48
V	Volt, unit-of-measure of electrical potential	593
W	Macrostate multiplicity, or thermodynamic probability	337
X	Arbitrary state function	7
Z	Compressibility factor	652

Roman lower case

a	Chemical activity	523
a	Van der Waals parameter	486
\bar{a}	Average effective ionic diameter	668
aq	In aqueous solution	184
b	Molality	171
b	Van der Waals parameter	487
c	velocity of light	738
d	Exact differential operator, as in dV	11
đ	Inexact differential operator, as in $\text{đ}w$	26

dm	Decimetre = 10^{-1} m, unit-of-measure of length	170
e	Base of natural logarithms, 2.71828...	68
e^{-}	Electron	596
f	Arbitrary path function	230
f	Frequency of simple harmonic motion	237
f	Fugacity	657
g	Acceleration due to gravity = 9.81 m sec^{-2}	21
g	Gas phase	154
h	Planck's constant, $6.6261 \times 10^{-34} \text{ J sec}^{-1}$	738
h	Height	21
k	Arbitrary constant	238
k	Reaction rate constant	452
k_B	Boltzmann's constant, $1.381 \times 10^{-23} \text{ J K}^{-1}$	70
$k_{H,i}$	Henry's law constant for component i	510
kg	Kilogram, unit-of-measure of mass	6
kJ	Kilojoule = 10^3 J, unit-of-measure of work, heat and energy	154
l	Liquid phase	155
l	Litre = $1 \text{ dm}^3 = 10^{-3} \text{ m}^3$, unit-of-measure of volume	170
m	Mass	17
m	Metre, unit-of-measure of distance	21
mol	Mole, unit-of-measure of quantity	7
n	Mole number	7
n_e	Number of electrons	595
n^*	Critical number of monomers for nucleation	782
nm	Nanometre = 10^{-9} m, unit-of-measure of length	724
ox, red	Referring to a redox reaction	619
p	Partial pressure	49
p	Proton motive force, as in Δp	732
pX	= $-\log_{10} X$ (as, for example, $\text{p}K_a = -\log_{10}K_a$), or = $-\log_{10}[X]$ (as, for example, $\text{pH} = -\log_{10}[\text{H}^+]$)	539 537
q	Heat	56
s	Solid phase	154
sec	Second, unit-of-measure of time	21
t	Temperature as measured in $^{\circ}\text{C}$	6
v	Rate of reaction	450
w	Work	26
x	Arbitrary variable	77
x	Linear distance	133
x	Mole fraction	170
y	Arbitrary variable	77
z	Arbitrary variable	88
z	Charge number	667

Greek upper case

Γ	Mass action ratio	432
Δ	Difference operator	11
$\Delta_r G$	Reaction Gibbs free energy, = $dG_{\text{sys}}(\xi)/d\xi$	432
Λ	= $K_c / [\text{H}^+]_{\text{eq}}^h$	563
Π	Osmotic pressure	587
Σ	Summation operator	11
Φ	Phi-value, alternative to ϕ_F	777
Ψ	Membrane potential, as in $\Delta\Psi$	731
Ω	Macrostate multiplicity, or thermodynamic probability	337
Ω	Ohm, unit-of-measure of electrical resistance	592

Greek lower case

α	Parameter in phi-value analysis	776
α_V	Volumetric expansion coefficient	89
β	= $1/k_B T$	70
β	Buffer capacity	555
β	Parameter in phi-value analysis	776
γ	Activity coefficient	661
γ	Ratio C_p/C_V	224
γ	Parameter in phi-value analysis	776
δ	Infinitesimal increment	11
∂	Partial derivative operator	79
ϵ	Mean bond energy	187
η	Efficiency	234
κ	Transmission coefficient	771
κ_T	Isothermal compressibility	89
λ	Wavelength of electromagnetic radiation	738
μ	Chemical potential	404
μ_{JT}	Joule-Thomson coefficient	650
ν	Frequency of electromagnetic radiation	738
ξ	Extent-of-reaction	417
π	Circumference/diameter ratio of a circle = 3.1416...	667
ρ	Density	7
τ	Time	133
φ	Frictional force parameter	133
ϕ	Fugacity coefficient	657
ϕ_F	Phi-value	771
ω	Frequency of simple harmonic motion = $2\pi f$	237

Subscripts

adi	Referring to an adiabatic change	106
an	Referring to the anode of an electrochemical cell	603
<i>b</i>	Referring to the molality <i>b</i>	515
<i>c</i>	Referring to the molar concentration [I]	438
<i>c</i>	In $\Delta_c H$, referring to a combustion reaction	177
C	Referring to a cold reservoir	230
cat	Referring to the cathode of an electrochemical cell	603
cell	Referring to an electrochemical cell	613
crit	Referring to the critical state of a real gas	480
D	Referring to a dissolved solute	503
eq	Referring to an equilibrium state	422
ex	External to the system	21
<i>f</i>	In $\Delta_f H^\circ$ or $\Delta_f G^\circ$, referring to a formation reaction	177
<i>f</i>	Referring to a forward reaction	450
fric	Referring to friction	130
fus	Referring to fusion, solid \rightleftharpoons liquid	161
H	Referring to a hot reservoir	230
<i>H</i>	At constant enthalpy	649
<i>i</i>	Referring to a general component <i>i</i>	7
irrev	Referring to an irreversible change	142
isol	Referring to an isolated system	105
max	Maximum value of	236
<i>p</i>	Referring to the partial pressure <i>p</i>	427
<i>P</i>	At constant pressure	114
ph	Referring to a phase change	294
<i>r</i>	In $\Delta_r H$ or $\Delta_r G$, referring to a chemical reaction in general	177
<i>r</i>	Referring to a reverse reaction	450
rev	Referring to a reversible change	142
S	Referring to a solvent	503
sub	Referring to sublimation, solid \rightleftharpoons vapour	161
sur	Referring to the surroundings	117
sys	Referring to the system	117
<i>T</i>	At constant temperature	114
<i>V</i>	At constant volume	106
vap	Referring to vaporisation, liquid \rightleftharpoons vapour	161
<i>x</i>	Referring to the mole fraction <i>x</i>	437
\pm	Relating to a cation-anion pair	666

Superscripts

E	Referring to a heat engine	325
P	Referring to a heat pump	325
+	Relating to cations	504
–	Relating to anions	504
⊖	Specifies standard value, as in ΔH^\ominus or ΔG^\ominus	177
⊖'	Specifies biochemical standard state value, as in $\Delta G^{\ominus'}$	677
/	Referring to the biochemical standard	677
*	Referring to the pure material	505
°	Degree Celsius, as °C, measurement of temperature	44

Other symbols

[I]	Molar concentration of component i	171
[X]	State X	6
{...}	A finite change in a path function, as $\{w_1 w_2\}_X$	26
⟨...⟩	Average, as in $\langle \mathcal{E} \rangle$	68
...	Absolute, and therefore necessarily positive, magnitude	307
⋯	Intermolecular interaction or force	507
‡	Referring to the activated state or complex	457
$\int_{X_1}^{X_2} \dots dX$	Integral, usually evaluated between two limits, for example, from an initial value X_1 to a final value X_2	12
$\oint df$	Cyclic integral, necessarily evaluated around a closed path	37

Index of units-of-measure

amp	unit-of-measure of electric current	592
bar	Bar, unit-of-measure of pressure = 10^5 Pa	170
C	Coulomb, unit-of-measure of electric charge	595
°C	Centigrade degree, unit-of-measure of temperature	44
dm	Decimetre, unit-of-measure of length = 10^{-1} m	170
J	Joule, unit-of-measure of energy and work = 1 N m	170
K	Kelvin, unit-of-measure of absolute temperature	44
kg	Kilogram, unit-of-measure of mass	170
kJ	Kilojoule, unit-of-measure of energy and work = 10^3 J	154
l	Litre, unit-of-measure of volume = 10^{-6} m ³ = 10^{-3} dm ³	170
m	Metre, unit-of-measure of length	6
mol	Mole, unit-of-measure of amount of substance = 6.022×10^{23} particles	7
N	Newton, unit-of-measure of force = 1 kg m sec ⁻²	14
nm	Nanometre, unit-of-measure of length = 10^{-9} m	724
Pa	Pascal, unit-of-measure of pressure = 1 N m ⁻²	170
sec	Second, unit-of-measure of time	21
V	Volt, unit-of-measure of electrical potential	593
Ω	Ohm, unit of measure of electrical resistance	592

List of Tables

5.1	Values of the molar heat capacity at constant volume, C_V , for selected gases	109
5.2	Thermodynamic data corresponding to the changes depicted in Figure 5.4	119
5.3	Thermodynamic data corresponding to the changes depicted in Figure 5.6	124
5.4	Key thermodynamic variables for the system and the surroundings corresponding to the quasistatic, adiabatic, cyclic change depicted in Figure 5.8 in which friction is present	137
6.1	Values of C_p for selected materials, at 1 bar and 298.15 K	152
6.2	Values of C_p for water, at 1 bar and a variety of temperatures	152
6.3	Some values of $\Delta_{\text{fus}}H$ and $\Delta_{\text{vap}}H$ for phase changes for some selected materials at the stated temperatures	162
6.4	IUPAC standard states	172
6.5	Common reaction categories	177
6.6	Some standard enthalpies of formation $\Delta_f H^\ominus$	180
6.7	Standard enthalpies of formation $\Delta_f H^\ominus$ for some selected aqueous ions at a temperature of 298.15 K = 25 °C	185
6.8	Bond dissociation energies D^\ominus for some selected bonds, as shown by the – symbol, at 1 bar and 298.15 K	188
6.9	Mean bond energies ϵ (X–Y) for some selected bonds	189
6.10	The temperature variation of $C_p = a + bT + cT^2 + dT^3 + eT^4$ for some selected gases	195
6.11	The Shomate temperature variation of $C_p = A + BT + CT^2 + DT^3 + E/T^2$ for some selected gases	196
7.1	Molar heat capacities of selected elements and compounds	217
7.2	Summary of ideal gas processes	229
9.1	Some thermodynamic data for phase changes	293
11.1	The number of microstates corresponding to a given macrostate for a system of 10 molecules, as illustrated in Figure 11.1, and the associated probabilities	339
12.1	Some standard molar entropies S^\ominus	356
13.1	Some standard molar Gibbs free energies of formation $\Delta_f G^\ominus$	398
14.1	Parameters used for the computation of $G_{\text{sys}}(\xi)$	424

15.1	Van der Waals parameters a and b for selected gases	488
17.1	Values of pK_a for some selected acids in aqueous solution at 298 K	540
17.2	Values of pK_b for some selected bases in aqueous solution at 298 K	546
17.3	Some materials suitable for buffer solutions at 298.15 K and 1 bar pressure	554
18.1	Some values of the ebullioscopic constant E_b at 1 atm	575
18.2	Some values of the cryoscopic constant E_f at 1 atm	578
20.1	(Near) standard reversible electrode potentials	616
20.2	(Near) standard reversible redox potentials E^\ominus of aqueous ions	617
23.1	Some standard transformed reversible redox potentials $E^{\ominus'}$ for selected biochemical redox reactions in aqueous solution, in accordance with the biochemical standard	688
23.2	Some values of standard molar Gibbs free energy of formation as measured in accordance with conventional standards, $\Delta_f G^\ominus$, and the biochemical standard, $\Delta_f G^{\ominus'}$, for selected molecules at 298.15 K, and an ionic strength of zero	693
24.1	Overall free energy changes for the complete metabolism of glucose in mitochondria, including the capture of free energy by ATP	737

PART 1

Fundamentals

1

Systems and states



Summary

Thermodynamics is the macroscopic study of **heat, work** and **energy**.

The domain of the universe selected for study comprises the **system**, and the rest of the universe constitutes the **surroundings**. The system and the surroundings are separated by the system **boundary**.

At any time, any system has a number of properties, known as **state functions**, which can be measured, and serve to define the state of the system at any time. **Extensive state functions**, such as mass, depend on the extent of the system; **intensive state functions**, such as temperature, are independent of the extent of the system. All extensive state functions per unit mass are intensive state functions.

Thermodynamic equilibrium is a state in which all state functions are constant over time, and for which all intensive state functions have the same values at all locations within the system.

If measurements are taken on an equilibrium system at different times, and if the value of at least one state function X has changed from an initial value X_1 to a value X_2 , then the system has undergone a **change in state**. The corresponding change ΔX in the state function X is defined as

$$\Delta X = X_2 - X_1 \quad (1.2a)$$

in which the initial value X_1 is subtracted from the final value X_2 . Mathematically, all state functions are defined by an **exact differential** dX .

A consequence of equation (1.2a) is that the change ΔX in any state function X depends only on the values X_1 and X_2 of X in the initial and final states, and is independent of the path followed during the change in state. The value of ΔX therefore contains no information of how a particular change in state took place.

An **ideal system** – of which an **ideal gas** is one example – is a system in which, fundamentally, there are no intermolecular interactions. Any macroscopic properties, such as the thermodynamic state functions, are linear additions of the state functions of smaller sub-systems, and, ultimately, of the microscopic properties of the molecules themselves. In real systems, molecules do interact, and so ideal systems are a theoretical abstraction. They are, however, much simpler to describe and analyse, and so the study of ideal systems provides a very useful model, which can then be used as a basis of the study of more complex, real, systems.

1.1 Some very familiar concepts ...

We all know that iced water feels cold, that freshly made tea or coffee feels hot, and that many of the meals we eat are warm – not as cold as the iced water, not as hot as the tea,

but somewhere in-between. From a very early age, we learn that the degree of ‘coldness’ or ‘hotness’ we experience is associated with a concept we call ‘temperature’ – things that feel hot have a high temperature, things that feel cold have a low temperature.

We also know that flames are very hot indeed, far too hot for us to feel directly with our hands. And when we put a saucepan containing cold water in contact with a hot flame – as we do when we’re cooking – we know that the water in the saucepan gets steadily warmer: the proximity of the hot flame to the cold water heats the water up.

Putting something hot next to something cold is not the only way things can get warmer: another way is by working. Once again, we all know that when we work hard – for example, by vigorous physical exercise such as running hard, digging a hole, or carrying heavy weights – we quickly become very warm, just as warm as we would by sitting quietly by a log fire. And after we’ve worked hard for a while, we become tired, and we feel we’ve lost energy, as if the energy that was in our body earlier in the day has been used up because of the work we have done. So we rest, perhaps have something to eat, and after a while, we feel we have more energy, and can then do some more work.

This is very familiar to all of us – words such as cold, hot, temperature, heat, work and energy are part of our natural every-day language. They are also the fundamental concepts underpinning the science of **thermodynamics**, and to explore that science – as we will do in this book – we need to enrich our understanding of what words such as ‘temperature’, ‘heat’, ‘work’ and ‘energy’ actually mean, moving beyond subjective feelings such as ‘hotness’ and ‘coldness’ to well-formulated scientific definitions. So, our purpose in the first three chapters is to do just that, and to offer some deeper insights into these familiar every-day phenomena.

1.2 The macroscopic viewpoint

Thermodynamics is a very practical branch of science. It’s development, during the nineteenth century, was closely associated with the need to gain a better understanding of steam engines, addressing questions such as:

- How much work can a steam engine actually do?
- How might we design better engines – engines that can perform more work for the same amount of coal or wood used as fuel?
- Is there a maximum amount of work a steam engine might do for a given amount of coal or wood? In which case, what might this optimal design be?

Given the importance of steam engines at that time – engines that provided mechanical power to factories, motive power to railways, as well as releasing ships from their reliance on the wind – this is practical stuff indeed.

As a consequence, thermodynamics is concerned with quantities that are readily measurable in real circumstances – quantities such as the mass of an engine, the volume of a boiler, the temperature of the steam in a turbine. These quantities all at a ‘human scale’, they are all **macroscopic**. Macroscopic quantities may be contrasted with **microscopic** quantities, where in this context, the term ‘microscopic’ does not relate to what you might observe in the optical instrument known as a microscope; rather, it refers to phenomena associated with the

atomic and molecular structures of, for example, the engine, the boiler or the steam. We now know, without any doubt, that atoms and molecules exist, and we now have a deep understanding of their behaviour. But when thermodynamics was developed, the concepts of atoms and molecules were theoretical, and very much under exploration – there was at that time no direct evidence that these invisible particles actually existed, and there were no measurements of their properties.

One of the strengths of thermodynamics is that the intellectual framework, and very many of its practical applications, are rooted firmly in the macroscopic, directly observable, world. As a consequence, thermodynamics does not rely on any assumptions or knowledge of microscopic entities such as atoms and molecules. That said, now that we have some very powerful theories of atomic and molecular behaviour, it is often both possible, and helpful, to interpret the macroscopically observed behaviour of real systems, as expressed and understood by thermodynamics, in terms of the aggregate microscopic behaviour of large numbers of atoms and molecules – that's the realm of the branch of science known as **statistical mechanics**, which forms a bridge between the microscopic world of the atom and molecule, and the macroscopic world of the readily observable.

Accordingly, much of this book will deal with the macroscopic, observable world – but on occasion, especially when the interpretation of macroscopic behaviour is made more insightful by reference to what is happening at an atomic or molecular level, we'll take a microscopic view too.

1.3 The system, the surroundings, and the system boundary

Our universe is huge and complex, and however much we may wish to understand the universe as a whole, we often choose to examine only a small portion of it, and seek to understand that. The areas of study that different people might select can be very diverse in scope, and of very different scales: so, for example, a sociologist might seek to understand the social interactions in a city; an astrophysicist, a star; a biochemist, the structure of a protein. We use the term **system** to define the domain of interest in any specific circumstance, so, for the sociologist, the relevant system will be a chosen city; for the astrophysicist, a particular star; for the biochemist, a specific protein. Everything outside the defined system constitutes the **surroundings**, and the system and the surroundings collectively make up the **universe**. Given the distinction between the system of interest and the surroundings, we use the term **system boundary** to refer to the system's outer perimeter, defining precisely where the system meets the surroundings: everything within the system boundary comprises the system, everything beyond it, the surroundings. The system boundary may be rigid if the system is of fixed size and shape, but this is not a necessary condition – many systems of interest can change their size or shape, changing the boundary accordingly.

1.4 State functions

That said, our study of thermodynamics will start with a system that does have a rigid boundary – a system comprised of a homogeneous **gas**, within a sealed container, the walls

of which are assumed to be rigid (for example, steel), rather than flexible (for example, a rubber, inflatable, balloon). The interior surface of the container wall forms the system boundary, as shown in Figure 1.1, with the container itself being in the surroundings.

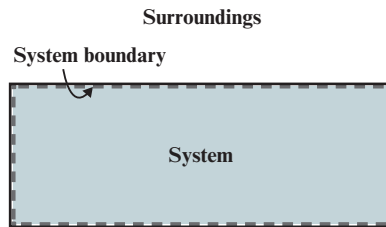


Figure 1.1 A system. This system is a gas within a sealed, rigid, container, with the system boundary being the interior wall (as shown by the somewhat exaggerated dashed line). The gas within the container may be associated with a number of properties, such as its mass M kg, its volume V m³ and its temperature t °C.

At any time, any system will be associated with a number of relevant properties. So, for example, the system of a homogeneous gas within a container will have a mass M kg (that's the mass of just the gas, not including the mass of the container that holds the gas), the gas will occupy a volume V m³, and the gas will have a temperature t °C. Properties of a system that can be measured at any single point in time – of which mass, volume and temperature are three examples – are known as **state functions**. The simultaneous values of all the state functions relevant to any particular system collectively define the **state** of the system at the time of measurement, and a state may be represented by specifying the appropriate state function values within square brackets as $[M, V, t, \dots]$.

1.5 Extensive and intensive state functions

All state functions may be classified as either **extensive** or **intensive**, according to whether or not a measurement of that state function depends on the size and scale of the system.

So, for example, a system's volume clearly depends on how big the system is, and if an imaginary partition is drawn half-way across a system of volume V , this would result in two sub-systems, each of volume $V/2$. Volume is therefore classified as an extensive function, as is mass M , and to determine the value of any extensive state function, we need to make a measurement on the system as a whole.

In contrast, an intensive state function does not require a measurement to be taken on the system as a whole: rather, a meaningful measurement can be taken at any location within a system. One example of an intensive state function is temperature; another is density = mass/volume, where we see that the intensive state function, density, is the ratio of two extensive functions, mass and volume.

In general, extensive state functions are additive, whereas many intensive state functions are not. To illustrate this, consider two systems: the first a solid of a given material of mass M_1 kg, volume V_1 m³, density $\rho_1 = M_1/V_1$ kg/m³ and temperature t °C; and the second, a solid of a different material of mass M_2 kg, volume V_2 m³, density $\rho_2 = M_2/V_2$ kg/m³ and at the

same temperature t °C. If the two systems are combined, then, according to the Law of the Conservation of Mass, the mass of the resulting system is $M_1 + M_2$ kg, and we would expect the volume to be $V_1 + V_2$ m³. The density of the combined system, however, is $(M_1 + M_2)/(V_1 + V_2)$ kg/m³, which is not in general equal to the sum $\rho_1 + \rho_2 = M_1/V_1 + M_2/V_2$; furthermore, given that both systems were at the same temperature t °C, the temperature of the combined system is also t °C, and not the sum of the temperatures $2t$ °C. Extensive functions are therefore additive, but many intensive functions are not.

1.6 The mole number n

An extensive state function that will feature strongly throughout this book is the **mole number** n , which specifies the number of **moles** of material within any given system. By definition, 1 mol of material comprises a fixed number of particles, which may be atoms, molecules or ions, depending on the nature of the system in question. The “fixed number” is defined by the **Avogadro constant** $N_A = 6.022141$ particles mol⁻¹. The mole number n defines how much material is within any given system, so for example, the total mass M_i of a system of n_i mol of any pure substance i is given by $M_i = n_i m_i$, where m_i is the mass of a single particle, this being an atom, molecule or ion as appropriate.

As we have just seen, the value of any extensive function for any system depends on the extent of that system, where ‘extent’ is determined by how much material is contained within the system. For a system comprised of a single pure substance i , all extensive functions therefore depend linearly on the mole number n_i . Accordingly, the mass M of any system is related to the mole number n as

$$M = n \mathbf{M}$$

in which \mathbf{M} , the **molar mass**, is the mass M of a system comprising precisely 1 mol of material, where, as before, the ‘material’ refers to the particles from which the system is composed, these being atoms, molecules or ions as appropriate.

Our example so far has referred only to the mass M ; in fact, for any system of n mol, any extensive state function X is related to its molar equivalent by an equation of the form

$$X = n \mathbf{X} \tag{1.1a}$$

from which

$$\mathbf{X} = \frac{X}{n} \tag{1.1b}$$

Equations (1.1a) and (1.1b) have a particularly important implication. Since any molar state extensive function \mathbf{X} is defined for a specific, fixed, quantity of material, 1 mol, then the value of any molar extensive function \mathbf{X} cannot depend on the extent of the corresponding system – that extent is totally defined as 1 mol. Any molar extensive state function \mathbf{X} is therefore itself an *intensive* state function. It is therefore always possible to convert any extensive state function X into its intensive counterpart \mathbf{X} by dividing X by the appropriate mole number n .

1.7 The 'ideal' concept

In the previous paragraphs, we used our words carefully: so, for example, we said “in general, state functions are directly additive ...”, “according to the Law of the Conservation of Mass ...” and “we would expect the volume to be $V_1 + V_2$ m³”. These words might appear to be superfluous: of course adding a mass M_1 kg to a mass M_2 kg results in a combined mass of $(M_1 + M_2)$ kg; of course adding a volume V_1 m³ to a volume V_2 m³ results in a system of volume $(V_1 + V_2)$ m³. Both of these statements are often true, but not always. So, for example, at room temperature, if 1 m³ of pure ethanol C₂H₅OH is added to 1 m³ of pure water, the resulting volume is not 2 m³ – rather, it is about 1.92 m³. And if two masses of 0.75 kg of uranium-235 are added, the result is not a mass of 1.50 kg – it is a nuclear explosion.

Being able to add the values of extensive state functions is very useful, and so two substances are said to be **ideal** if the value of any extensive state function – such as the mass or the volume – of any mixture of those two substances is the sum of the appropriate values of the corresponding state functions of each substance in its pure state. This concept also applies to a pure substance too, for a system comprising any given mass M kg of a pure substance is, in principle, a mixture of two half-systems, each of mass $M/2$ kg. All extensive state functions of ideal substances are therefore linear with the quantity of matter, usually measured in terms of the mole number, the number of moles of material present, as represented by the symbol n .

As will be seen throughout this book, ideal behaviour is much easier to analyse, and to represent mathematically, than real behaviour. And although ideal behaviour is fundamentally a theoretical abstraction, the behaviour of many real systems approximates to the ideal closely enough for ideal analysis to have real practical value. Also, the theoretical foundations of ideal behaviour act as a very sound basis for adding the additional complexities required for a better understanding of real behaviour. We will identify some further properties of ideal systems elsewhere (see, for example, page 17); in general, throughout this book, unless explicitly stated otherwise, all systems will be assumed to be ideal, and associated with linearly additive extensive state functions.

1.8 Equilibrium

Suppose we observe a system over a time interval, and measure all the system's state functions continuously. If all the state functions maintain the same values throughout that time, then the system is stable and unchanging – it is in **equilibrium**. Then, as time continues, if the value of even just one state function changes, the system is said to have undergone a **change in state**. Once again, that's all obvious – but there is a subtlety: we haven't specified how long that 'time interval' is. If the time interval is long – say, hours, days or years – and the values of all the state functions maintain the same values, then words such as 'stable', 'unchanging' and 'equilibrium' all make sense. But if the time interval is very short – say, nanoseconds – then we would expect many systems to be 'stable' over this very short timescale, but not over a somewhat longer timescale, say, a few milliseconds or seconds. This implies that, if the time interval over which measurements are made is short enough, *all* systems will be identified as stable, unchanging, in equilibrium – at which point, these concepts become unhelpful.

To avoid this problem, this book will make the assumption that the time interval over which any system is being observed is ‘long’ – that means seconds at the very minimum, and often in principle hours and days – rather than ‘short’ (picoseconds, nanoseconds, milliseconds).

A special, and limited, case of equilibrium is **thermal equilibrium**, as happens when two systems, or different component parts within a single system, are at the same temperature. **Thermodynamic equilibrium** is a broader concept, requiring all thermodynamic state functions to be in equilibrium. It is therefore possible for a given system to be in thermal equilibrium, but not in thermodynamic equilibrium – as, for example, happens when a gas expands, so changing its volume, but keeping its temperature constant.

A further feature of an equilibrium state is that, at any time, the values of all intensive state functions are the same at all locations within the system, whereas in a non-equilibrium system, it’s likely that at least one intensive state function will have different values at different locations. As an example, consider a system composed of a block of metal at a higher temperature, placed in direct physical contact with a block of an equal mass of the same metal at a lower temperature, as shown in Figure 1.2.

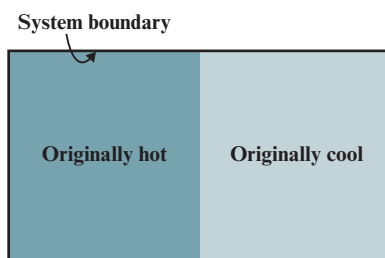


Figure 1.2 A system which is not in equilibrium. This system comprises a hotter block of metal (on the left) in contact with a cooler block of the same mass of the same metal (on the right). Over time, although the mass and volume of this system both remain constant, the temperature at any specific location in the system will change as the originally hotter block becomes cooler, and the originally cooler block becomes hotter. Furthermore, at any one time, the temperature will be different at different locations. Ultimately, both blocks will assume the same temperature, and that temperature will be uniform throughout the system: the system will then be in equilibrium.

An observer of this system would notice that, as time passes, the hotter block becomes cooler, and the cooler one hotter. Although the mass of the system remains constant, as does the volume (assuming that any thermal expansion or compression is negligible), the temperature at any single location within the system changes over time; furthermore, at any one time, the temperature will be different at different locations within the system. These observations verify that the system is not in equilibrium. Ultimately, the system arrives at a state in which, at any location, the temperature no longer changes over time; furthermore, throughout the system, the temperature has the same value. Thermal, and thermodynamic, equilibrium have now been achieved.

Equilibrium is an important concept since it underpins measurement: if a system is not in equilibrium, then the values of at least one state function will be changing over time; furthermore, at any one time, it is also likely that at least one intensive state function will have different values in different locations within the system. Under these conditions, it is impossible to make statements of the form “the value of [this] state function is [this number]”, and so