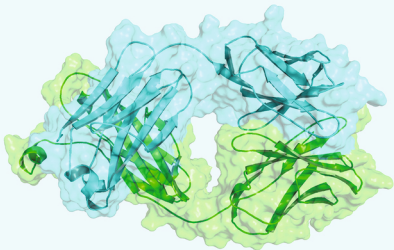


OXFORD

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

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,
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First Edition published in 2018

Impression: 1

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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

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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 measureable 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

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Roman upper case

A	Area	14
$\mathcal{A}$	Constant in the Boltzmann equation	68
A	Helmholtz free energy	385
A	Molar Helmholtz free energy = A/n	385
A	Pre-exponential factor in the Arrhenius equation	456
C	Celsius, unit-of-measure of temperature, °C	44
C_p	Heat capacity at constant pressure	151
C_p	Molar heat capacity at constant pressure = C_p/n	151
C_v	Heat capacity at constant volume	107
C_v	Molar heat capacity at constant volume = C_v/n	108
D°	Bond dissociation energy	187
E	Electrical or electrode potential	603
$\mathcal{E}$	Reversible electrode potential	613
$\mathcal{E}$	Molecular energy	68
E_a	Activation energy	456
E_b	Ebullioscopic constant	575
E_f	Cryoscopic constant	578
F	Faraday constant, $9.6485 \times 10^4 \text{ C mol}^{-1}$	595
F	Force	13
G	Gibbs free energy	374
G	Molar Gibbs free energy = G/n	375
H	Enthalpy	149
H	Molar enthalpy = H/n	149
$\mathcal{H}$	Hartley entropy	346
I	Ionic strength	667
I	Electric current	592
I	Intensity of a measured signal	754
J	Joule, unit-of-measure of work, heat and energy	21
K	Kelvin, unit-of-measure of absolute temperature	44
K_a	Acid dissociation constant	539
K_b	Base dissociation constant	545
K_b	Molality equilibrium constant	521
K_c	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
$\mathfrak{d}$	Inexact differential operator, as in $\mathfrak{d}w$	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, $pK_a = -\log_{10} K_a$), or = $-\log_{10} [X]$ (as, for example, $pH = -\log_{10} [H^+]$)	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
b	Referring to the molality b	515
c	Referring to the molar concentration $[I]$	438
c	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
f	In $\Delta_f H^\circ$ or $\Delta_f G^\circ$, referring to a formation reaction	177
f	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
H	At constant enthalpy	649
i	Referring to a general component i	7
irrev	Referring to an irreversible change	142
isol	Referring to an isolated system	105
max	Maximum value of	236
p	Referring to the partial pressure p	427
P	At constant pressure	114
ph	Referring to a phase change	294
r	In $\Delta_r H$ or $\Delta_r G$, referring to a chemical reaction in general	177
r	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
T	At constant temperature	114
V	At constant volume	106
vap	Referring to vaporisation, liquid $\rightleftharpoons$ vapour	161
x	Referring to the mole fraction x	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
$\ominus$	Specifies standard value, as in ΔH° or ΔG°	177
$\ominus'$	Specifies biochemical standard state value, as in $\Delta G^{\circ'}$	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>i</i>	171
[X]	State X	6
{...}	A finite change in a path function, as $\{ {}_1w_2 \}_X$	26
$\langle \dots \rangle$	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

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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. Its 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.

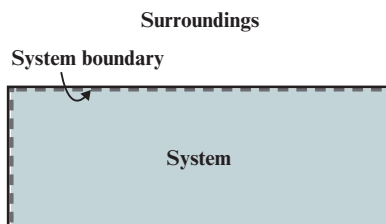


Figure 1.1 A system. This system is a gas within a sealed, rigid, container, with the system boundary being the interior wall (as shown by the somewhat exaggerated dashed line). The gas within the container may be associated with a number of properties, such as its mass M kg, its volume V m³ and its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

$$M = nM$$

in which 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

$$X = nX \quad (1.1a)$$

from which

$$X = \frac{X}{n} \quad (1.1b)$$

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

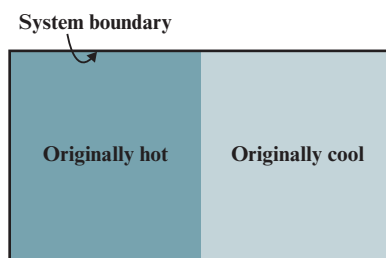


Figure 1.2 A system which is not in equilibrium. This system comprises a hotter block of metal (on the left) in contact with a cooler block of the same mass of the same metal (on the right). Over time, although the mass and volume of this system both remain constant, the temperature at any specific location 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

the state of the system, as expressed by the set of values of that system's state functions, cannot be defined. The assumption made throughout this book is therefore that, unless specifically otherwise stated, measurements of any system refer to equilibrium states of that system, and the corresponding value of any state function, extensive or intensive, is an equilibrium value.

The study of the thermodynamics of equilibrium states, and of changes from one equilibrium state to another, is, unsurprisingly, known as **equilibrium thermodynamics**. During the mid-twentieth century, the concepts of equilibrium thermodynamics were enhanced and enriched to encompass the behaviour of **non-equilibrium states**, and for his pioneering contributions to the development **non-equilibrium thermodynamics**, the Belgian scientist Ilya Prigogine was awarded the 1977 Nobel Prize in Chemistry. Non-equilibrium thermodynamics is a fascinating branch of science, and still very much an active area of research, with applications to a diversity of fields such as biochemistry and even economics, but beyond the scope of this book – for further information, please refer to the titles suggested in the references.

1.9 Changes in state

1.9.1 Identifying changes in state

Consider now the system illustrated in Figure 1.3, which comprises a homogeneous gas within a cylinder fitted with a piston, rather like the cylinder and piston in an internal combustion engine, or a conventional hand-operated pump for inflating the tyres on a bicycle. Let's assume that there is no friction between the piston and the cylinder; let's also assume that the walls of the cylinder are impermeable and that the piston is very close-fitting, so that nothing can get into, or leave, the interior of the cylinder, either through the walls or by leaking past the piston. But unlike the system shown in Figure 1.1, which has a rigid boundary and a fixed volume, the system in Figure 1.3 has a flexible boundary and can change its volume as the piston moves inwards or outwards.

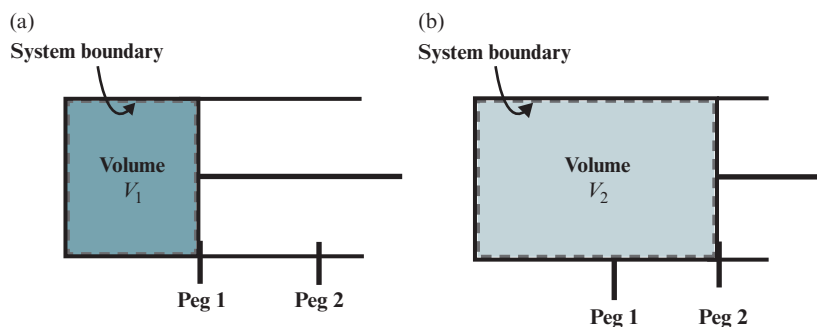


Figure 1.3 A change in state. This system is a gas enclosed in a cylinder fitted with a moveable, frictionless, piston. In (a), the piston is held in place by peg 1, and the volume is V_1 ; in (b), the piston has moved to the right, and is now held in place by peg 2. The volume of the system has increased to V_2 , and there has been a change in state.

Suppose that the piston is held in place by peg 1, as shown in Figure 1.3(a), and that the gas inside the cylinder is in equilibrium. Suppose further that we measure the value of the state function mass to be M_1 and value of the state function volume to be V_1 .

If peg 1 is then taken away, let us suppose, with reference to Figure 1.3(b), that the piston moves a small distance to the right, until it stops at peg 2. Instantaneously after peg 1 is taken away and the piston moves, the gas is turbulent and not in equilibrium, but very soon after the piston has stopped at peg 2, the gas returns to equilibrium. Given our assumptions that the walls of the cylinder are impermeable, and that the piston doesn't allow leaks, the mass of the gas is still M_1 ; but since the gas has expanded, the volume will now be measured as V_2 , which will be larger than the original measurement V_1 . The value of the state function volume V has changed, from which we infer that the system has undergone a change in state.

1.9.2 Measuring changes in state

The measurement of changes in state is central to thermodynamics, which adopts a convention as to how the corresponding change in any state function is represented. So, for example, a change in volume, represented by ΔV , is defined as

$$\Delta V = V_2 - V_1 \quad (1.2a)$$

in which the initial value V_1 is subtracted from the final value V_2 : importantly, the subtraction is *always* that way around

$$\begin{aligned} \text{change in state function} &= \text{value of state function in } \textit{final} \text{ state} \\ &\quad - \text{value of state function in } \textit{initial} \text{ state} \end{aligned}$$

This convention implies that all changes in state functions are signed, algebraic, quantities that convey particular meaning. So, for example, if a gas expands, so that V_2 is greater than V_1 , then $\Delta V = V_2 - V_1$ is a positive number; conversely, if the value of ΔV as associated with any particular change is known to be positive, then we may infer that the volume of the system has expanded. Similarly, if a gas is compressed, so that V_2 is less than V_1 , then $\Delta V = V_2 - V_1$ is a negative number; conversely, if the value of ΔV as associated with any particular change is known to be negative, then we may infer that the volume of the system has contracted.

The symbol Δ is used for macroscopic changes, such as those that are readily measureable. Sometimes, especially in the development of the theory of thermodynamics, it is useful to consider very small, or even infinitesimally small, changes: accordingly, small changes in state functions are conventionally represented using the symbol δ , for example δV , and infinitesimally small changes are represented by the symbol d , for example dV . As with the definition of the macroscopic change ΔV , as expressed by equation (1.2a), both small changes δV and infinitesimal changes dV are defined as (value of state function in final state) – (value of state function in initial state), and are signed algebraic quantities.

Macroscopic changes ΔX for the change in any state function X from state [1] to state [2] can also be represented as the summation of small changes as

$$\Delta X = \sum_{\text{state [1]}}^{\text{state [2]}} \delta X = X_2 - X_1 \quad (1.2b)$$

or as an integral of infinitesimal changes as

$$\Delta X = \int_{\text{state [1]}}^{\text{state [2]}} dX = X_2 - X_1 \quad (1.2c)$$

The fact that expression defined by equation (1.2c) can be integrated directly to give a result of the form $X_2 - X_1$ implies that dX is what is known mathematically as an **exact differential**.

1.9.3 Changes in state can follow many different paths

Suppose that we observe a system in equilibrium, and measure the volume as V_1 . Sometime later, we observe the system again, and measure the volume V_2 , from which we can infer, as we have seen, that the system has undergone a change in state, the change in volume being $\Delta V = V_2 - V_1$. We can verify that a change in state has indeed taken place, but *how* did that change happen? How might we gain some insight as to what took place between the initial state, V_1 , and the final state V_2 ? The answer to these questions is that the measurement of *the change in volume* ΔV **gives no information whatsoever about the change itself**: the observation of the initial state, V_1 , and of the final state V_2 , associated with the calculation of $\Delta V = V_2 - V_1$, tells us *only* about the overall change in state, but nothing about *how* that change took place, nothing about the **path** taken.

This is illustrated in Figure 1.4, which shows a change in state from an initial volume V_1 to a final volume V_2 . This could happen as a single step, as indicated by path 1; alternatively, the

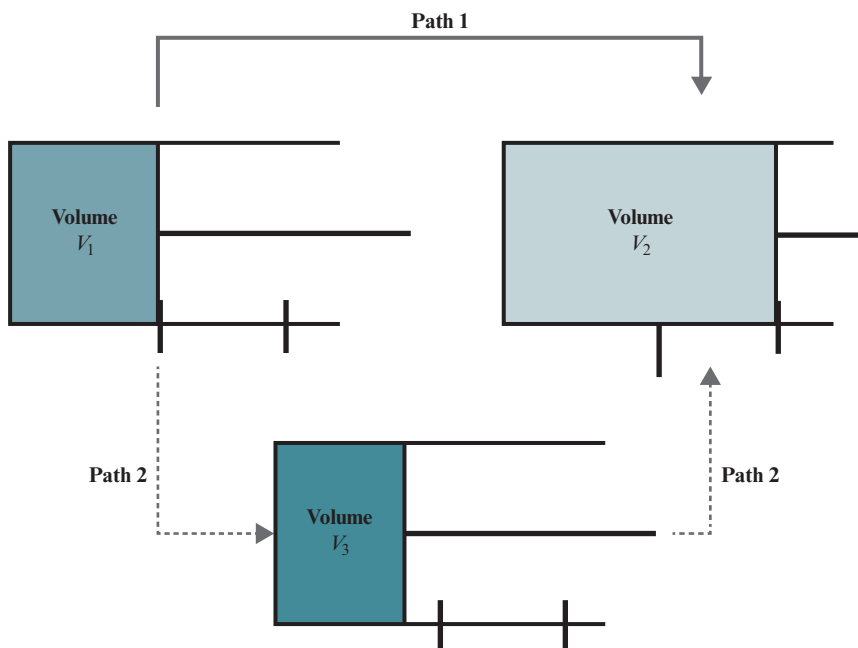


Figure 1.4 A change in a state function is independent of the path of the change. For a change in state from V_1 to V_2 , the change in volume $\Delta V = V_2 - V_1$ is the same, no matter what path is followed.

change could have taken place firstly by compressing the gas to an intermediate equilibrium state with a smaller volume V_3 , followed by an expansion to the final state with volume V_2 , as indicated by path 2. Both paths lead from the same initial state of volume V_1 to the same final state of volume V_2 ; both paths have the same change in volume $\Delta V = V_1 - V_2$. The actual paths taken, however, were different – but measurements of the volume V in the initial and final states can give no information as to whether path 1 was followed, or path 2. Paths 1 and 2, as shown in Figure 1.4, are of course just two possibilities – anything might have happened. The change in volume ΔV , however, is determined solely by values of the volume V in the initial and final states, regardless of what has happened as the change in state took place, and this applies to all state functions: state functions have no ‘memory’ of how the system has evolved – they simply describe the state of the system as it is at the time of measurement.

1.10 The surroundings have state functions too

Most of our attention, quite understandably, is on the system of interest, and on the state functions that describe that system at any time. It’s worth noting, however, that the surroundings are characterised by state functions too – and although the measurement of an extensive function such as volume might be problematic (the surroundings, in principle, extend to the edge of the universe!), no such problems arise with the measurement of intensive functions, such as temperature, since their values are independent of size.

The measurement of the state functions of the surroundings is of especial relevance in connection with a particular type of path. We have already seen that a change in state for a system can take place along any number of paths, and it so happens that one particular type of path is especially important, a path known as a **reversible** path. We’ll explore the properties of reversible paths in more detail later (see pages 117 to 126) – but one feature of a reversible path is relevant here: a reversible path is a path which, when reversed, returns *both* the system *and* the surroundings to their original states, implying that all the state functions, for both the system and the surroundings, are restored to their original values.

1.11 Pressure

1.11.1 Pressure is an intensive state function

With reference to Figure 1.5(a), the piston of the cylinder containing the gas is held in place by peg 1. Suppose that the surroundings of the cylinder are a vacuum. What would we observe if peg 1 is removed?

What would happen is that, as soon as the peg is removed, the piston would move to the right, and probably quite quickly too (the piston is assumed to be frictionless), until the piston is stopped by peg 2, as shown in Figure 1.5(b). Why does the piston move?

The fact that the piston, which was originally at rest (and so has a velocity of zero), starts to move (and so has a non-zero velocity) implies that it accelerates, from which, according to Newton’s Second Law of Motion, we infer that the piston was subject to a **force**. This force must come from the gas within the cylinder, and be a force which is exerted over the internal

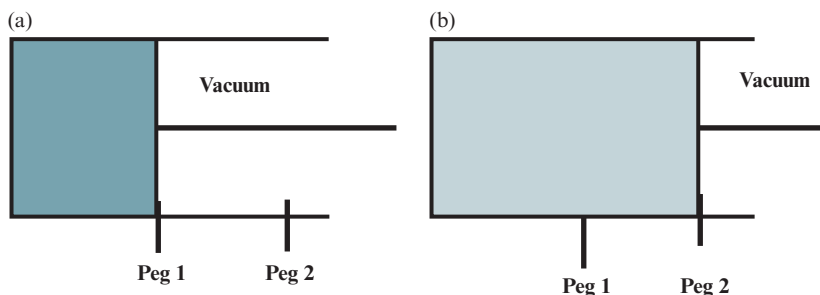


Figure 1.5 Expansion against a vacuum. The piston is initially held in place by peg 1 as in Figure 1.5(a). When peg 1 is removed, the piston moves to the right until stopped by peg 2, as in Figure 1.5(b).

surface of piston. If this force is F N, and if the area of the inner surface of the piston is A m², then we can define the **pressure** P exerted by the gas on the piston as

$$P = \frac{F}{A} \quad \text{Pa}$$

and the force F is given by

$$F = PA \quad \text{N}$$

The pressure P is a property of the system, it can be measured at any point in time, and its value does not depend on the size of the system – all of which imply that pressure P is an intensive state function. The unit of pressure measurement is the Pascal, named after the French mathematician and physicist, Blaise Pascal, with $1 \text{ Pa} = 1 \text{ N m}^{-2}$.

In Figure 1.5 (a), when peg 1 is in place securing the piston, the piston does not move because the force exerted by the gas on the internal surface of the piston is counterbalanced by the force exerted by the peg on the external surface of the piston, so holding the piston in position. When peg 1 is removed, this restraining force is no longer present; furthermore, because the surroundings are a vacuum, and the piston is assumed to be frictionless, there is no longer any opposing force at all, and so the piston moves to the right in Figure 1.5(b), until it is stopped by peg 2.

If, however, the surroundings are not a vacuum, but also gaseous – say the atmosphere – then the surroundings will exert a pressure P_{ex} on the external surface of the piston. If the external surface area of the piston is the same as the internal surface area, A m², then the external force, acting on the piston from right to left in Figure 1.6, is $P_{\text{ex}}A$ N. When peg 1 is removed, and in the absence of any friction, the net force $F_{\text{L} \rightarrow \text{R}}$ acting on the piston, from left to right in Figure 1.6, is therefore given by

$$F_{\text{L} \rightarrow \text{R}} = PA - P_{\text{ex}}A = (P - P_{\text{ex}})A$$

If the internal pressure P and the external pressure P_{ex} are equal, then $(P - P_{\text{ex}}) = 0$, implying that $F_{\text{L} \rightarrow \text{R}} = 0$. There is no net force on the piston, and so the piston does not move.

If, however, the internal pressure P is greater than the external pressure P_{ex}

$$P > P_{\text{ex}}$$

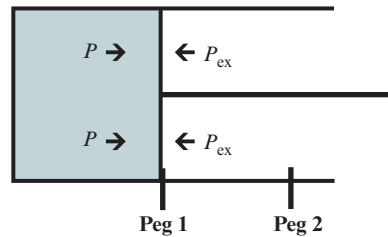


Figure 1.6 Pressure difference. If the pressure P exerted by the gas on the inner surface of the piston is greater than the pressure P_{ex} exerted by the surroundings on the outer surface of the piston, when peg 1 is removed, the piston will move to the right.

then the net force $F_{\text{L} \rightarrow \text{R}}$ is positive, and so the piston will move from left to right in Figure 1.6; but if

$$P < P_{\text{ex}}$$

the net force $F_{\text{L} \rightarrow \text{R}}$ is negative, and so the piston will move from right to left in Figure 1.6. The movement of the piston, and the direction of that movement, therefore depends on the *pressure difference* ($P - P_{\text{ex}}$) between the gas inside the piston and the pressure exerted by the surroundings.

1.11.2 Atmospheric pressure

As just noted, the gases in the earth's atmosphere exert pressure on the earth's surface – and on us too, but we usually don't notice it because the interior of our bodies are at the same pressure. The actual pressure exerted by the atmosphere depends on a number of circumstances, for example, the local weather and the altitude (which is when we do notice things – in an aeroplane, or sometimes in the lift in a high building, we experience our ears 'popping' as the pressure inside our bodies equilibrates with the external pressure), so the term **standard atmospheric pressure**, sometimes (and rather inaccurately) abbreviated to **atmospheric pressure**, or expressed as the unit-of-measure one **atmosphere**, is a reference pressure defined as 101,325 Pa, this being a representative value of the average atmospheric pressure at sea level. Since 101,325 is rather a clumsy number, a numerically simpler, but nearby, unit-of-measure, the **bar**, defined as 10^5 Pa, is commonly used in thermodynamics, especially in applications associated with engineering.

1.11.3 Boyle's Law – an equation-of-state

The study of the atmosphere plays an important part in the early development of thermodynamics, and indeed of modern science, for in the 1660s, a number of scientists were studying how the pressure of a specific quantity of air changed as its volume changed. Some careful experiments were carried out in which a specific mass of air was allowed to come to equilibrium, and measurements made of the air's pressure, say, P_1 , and volume, V_1 . The pressure was then changed to a new value P_2 , and the air once again allowed to come to equilibrium, taking care to ensure that the temperature of the air remained constant throughout. Once the

air had regained equilibrium (which it did quite quickly), the new volume V_2 was recorded. This procedure was repeated several times, so producing a set of pairs of $[P_1, V_2]$, $[P_2, V_2]$, ..., $[P_n, V_n]$, ..., each pair representing the simultaneous values of the two state functions P and V at successive, different, equilibrium states of the system, all of which were at the same temperature. The results were striking: for a given mass of air, the values P_n and V_n were all different, but the product $P_n V_n$ for any pair of simultaneous values turned out to be the same number:

$$PV = \text{a constant, for a fixed mass of air at constant temperature} \quad (1.3)$$

This relationship, now known as **Boyle's Law** (after Robert Boyle, one of the scientists involved), shows that, for a system comprising a fixed mass of air at constant temperature, the simultaneous values of the two state functions, pressure P and volume V , are not independent, but are related to one another by a simple equation. This implies that if the value of either of the state functions P or V is known, the corresponding value of the other can be calculated, so enabling us to predict the behaviour of the system – and the ability to predict with confidence is at the very heart of science. Equations that show how different state functions of a single system are related to one another are known as **equations-of-state**, of which Boyle's Law is our first example.

1.12 The ideal gas

Careful experimentation, using different gases at wide ranges of pressure, demonstrates that Boyle's Law is not universally true – for example, at a temperature of 150 °C and a pressure of 1 atmosphere, water exists as a gas, and for small variations of pressure, Boyle's Law will hold. But as the pressure is increased, and the volume decreases, keeping the temperature constant at 150 °C as required for Boyle's Law, a point is reached at which the behaviour of the gas deviates significantly from that predicted by Boyle's Law, and ultimately – even at 150 °C – a great enough pressure (in fact, not so great – rather less than 5 times normal atmospheric pressure) causes the gas to condense as liquid water, at which point Boyle's Law has no validity at all. In reality, Boyle's Law is an approximation, and an approximation that usually works better for lower pressures (and greater volumes) than higher pressures (and smaller volumes). Various modifications and extensions have been made to Boyle's Law, resulting in more complex equations-of-state for gases that have broader applicability: one, relatively simple, example is the **van der Waals equation**, which can be written as

$$\left(P + \frac{a}{V^2}\right)(V - b) = c \quad (1.4)$$

where, for a given mass of gas at a constant temperature, a , b and c are constants; some rather more complex equations-of-state for real gases are given on page 50, and the considerably more complex equations-of-state for **solids** and **liquids** are best found in texts on condensed matter physics.

To avoid mathematical complexity, it is very helpful to invoke the concept of the **ideal** (or **perfect**) **gas**. Although an ideal gas does not exist in reality, it does provide a very useful 'model' for the development of theory, and so whenever we use the term 'gas' in this book, we are referring to an ideal gas.

Formally, an ideal gas is one whose molecules

- occupy zero volume
- are spherical
- undergo elastic collisions, and
- have no mutual interactions, however far apart or close together.

Most importantly, for an ideal gas, Boyle's Law, equation (1.3), is valid unconditionally, and, as we shall see in this book, this opens the door to the identification of many other important properties of an ideal gas too – properties that give great insight into the behaviour of real systems.

1.13 Pressure – a molecular interpretation

To understand more richly *why* gases exert pressure, we need to consider what is happening at a microscopic, molecular, level. Imagine that the cylinder containing an ideal gas is made of glass, and that the gas has a slight colour. With reference to Figure 1.5, when the piston is held in position towards the left by peg 1, we will see the colour uniformly spread throughout the available space within the cylinder, showing that the gas fills the entire volume. Now think what we would see if peg 1 is removed, and the piston moves to the right to the position defined by peg 2, so allowing the gas to occupy a larger volume. After some initial turbulence, we will see a uniform colour filling the entire, larger, space. From this observation, we can infer that the individual gas molecules are able to move – and move very quickly – over macroscopic, easily observable, distances: if they were not able to move, or if they were able to move only very slowly, the colour would stay 'bunched up' within the volume as defined by the original position of the piston, even after the piston has moved.

The fact that the molecules can move implies that each molecule has a velocity of magnitude v , and, since each molecule also has mass m , each molecule has a corresponding momentum of magnitude mv . So before peg 1 is removed, in accordance with Newton's First Law of Motion, any molecule will be moving with its appropriate velocity in a straight line, until something happens – for example, an elastic collision (by assumption, the molecules of an ideal gas undergo elastic collisions) with another molecule, as a result of which the two colliding molecules move off in different directions, according to the law of conservation of momentum. But instead of colliding with another molecule, a given molecule might undergo an elastic collision with a wall of the cylinder, or the inside surface of the piston. Since the walls of the cylinder are rigid, and the piston is held in position by peg 1, the molecule will bounce back, once again according to the law of conservation of momentum.

Figure 1.7 shows the collision of a molecule of mass m with the inner surface of the piston. The molecule approaches the piston at an angle θ , implying that the component of the velocity parallel to the surface of the piston is $v \sin \theta$ (downwards in Figure 1.7), and that the component perpendicular to the surface of the piston is $v \cos \theta$ (from left to right in Figure 1.7). At the collision, which takes place over a very brief time period $\delta\tau$, the molecule bounces back, but the piston, being held in place by peg 1, and vastly more massive than the molecule, does not

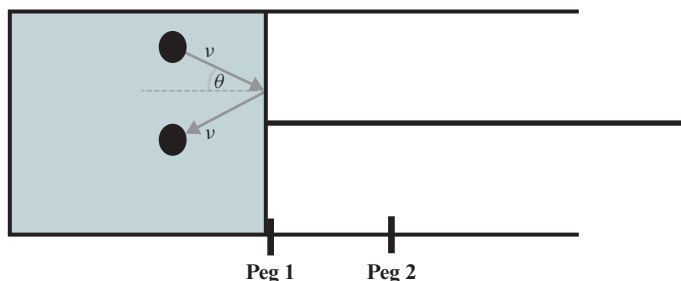


Figure 1.7 Pressure is attributable to molecular collisions. When a molecule of mass m collides with the interior surface of the piston, it undergoes a change in momentum of $-2mv \sin \theta$. This results in a tiny force on the piston. Pressure is the macroscopic effect of all these molecular collisions.

move, nor does the container. If the collision is elastic, so that there is no loss of kinetic energy, then, after the collision, the component of the molecule's velocity parallel to the surface of the piston is unchanged, but the component perpendicular to the surface of the piston becomes $-v \sin \theta$, with the $-$ sign indicating that the molecule is now moving, in Figure 1.7, from right to left. During the collision, the molecule therefore undergoes a change in momentum given by

$$\text{Change in momentum} = \text{New momentum} - \text{Old momentum} = -2mv \sin \theta$$

Now, Newton's Second Law of Motion can be stated as "force equals the rate of change in momentum", implying that, during the collision, the molecule experiences, very briefly, a force of magnitude $-2mv \sin \theta / \delta \tau$, in which the $-$ sign indicates that this force is from right to left in Figure 1.7, so explaining why the molecule bounces back. We now invoke Newton's Third Law of Motion, which tells us that "to every action, there is an equal and opposite reaction". So, if the piston exerts a force of $-2mv \sin \theta / \delta \tau$ on the molecule so causing it to bounce back, then the molecule exerts an equal and opposite force of $+2mv \sin \theta / \delta \tau$ on the piston, the $+$ sign indicating that this force is from left to right in Figure 1.7. Each molecular collision therefore exerts a tiny force on the piston – just like the impact of a tennis ball on a tennis racket. Macroscopically, the huge number of molecular collisions each second results in the total force exerted not only on the piston, but on all the walls of the cylinder too – hence the measurable pressure P .

?

EXERCISES

1. Write down clear, complete, and precise definitions of:

- system
- surroundings
- boundary
- state
- state function
- extensive state function
- intensive state function
- change in state

- path
 - pressure
 - equation-of-state.
2. Classify the following state functions as either extensive or intensive:
- mass
 - molar volume
 - temperature
 - volume
 - pressure
 - surface area
 - density
 - mole number
 - molar concentration (the number of moles of a pure substance, say, sucrose, dissolved in a given volume, say, 1 m^3 , of a solute such as pure water).
3. You are observing a system. How would you determine whether the system is, or is not, in equilibrium?
4. You are observing a system of a given mass of a gas, and make a series of measurements of the system pressure P for a number of equilibrium states:

State	Pressure P , Pa
[1]	1.01325×10^5
[2]	1.00000×10^5
[3]	0.81300×10^5
[4]	2.40000×10^5
[5]	1.25000×10^5
[6]	0.65000×10^5

What is the change ΔP in the system pressure for the following changes in state:

- From state [1] to state [3]?
 - From state [3] to state [1]?
 - From state [4] to state [5]?
 - From state [4] to state [6]?
 - From state [6] to state [5]?
 - From state [6], via state [5], to state [4]?
 - From state [4], via state [2], then state [5], then state [1], to state [3]?
 - From state [3], via state [1], then state [5], then state [2], then state [6], then state [1], then state [4], to state [3]?
5. What are the key characteristics of an ideal gas?
6. A given mass of an ideal gas, within a given volume, exerts a pressure P . If the average molecular velocity doubles, what pressure does the gas now exert? Why? What do you think might cause the average molecular velocity to increase?

2

Work and energy



Summary

Work is a phenomenon observed at the boundary of a system when that system changes state, if and only if something occurs at that boundary (such as the motion of the boundary) which may be interpreted as motion against an external force. An example of work is **P, V work of expansion** – the work a system does when it expands against an external force, for example, the force attributable to atmospheric pressure.

Work takes place only as a system changes state. Work is therefore not a property of the state of a system, and so is not a state function. Rather, the amount of work performed by a system on the surroundings, or by the surroundings on the system, is determined by the **path** taken as the change in state takes place, and so work is an example of a **path function**. This implies that, even if the initial and final states of a system are the same, different amounts of work will be performed according to the path followed between those two states. Mathematically, this path-dependence implies that work cannot be represented by an exact differential, but rather by an **inexact differential**, δw .

A special form of path is a **quasistatic** path, which takes place

- through a sequence of equilibrium states
- in an infinite number of infinitesimal steps
- infinitely slowly

implying that, throughout the change in state, the state functions of the system undergoing the change are well-defined. Quasistatic changes can therefore be represented as a curve on a graph, such as a **P, V diagram**.

A **thermodynamic cycle** is a sequence of steps which return a system back to its original state. For a complete cycle, the change ΔX in any state function X must be zero, hence

$$\oint dX = 0 \quad (2.6)$$

In general, however, for a path function, for example, work w

$$\oint \delta w \neq 0 \quad (2.8)$$

Energy is the capacity to perform work.

2.1 Work – an initial definition

The simplest, and most obvious, example of **work** is the lifting of a mass from the ground. If a mass M kg is on the ground, then gravity is holding it on the surface with a force given by

Mg N, where $g \text{ m sec}^{-2}$ is the acceleration attributable to gravity. To raise the mass, an upwards force, just greater than Mg , is required to overcome the force of gravity, and if the mass is lifted vertically through a distance h m, the work done is defined as

$$\text{Work done} = \text{Force overcome} \times \text{Distance moved in direction of the force} = Mgh \text{ J}$$

where the unit-of-measure is the Joule, J, such that $1 \text{ J} = 1 \text{ N m} = 1 \text{ kg m}^2 \text{ sec}^{-2}$.

2.2 The work done by an expanding gas

2.2.1 An important equation, $\text{work} = P_{\text{ex}} dV$

We now return to the system of the gas in the cylinder, with the piston held in place by a peg. The pressure of the gas is P , and let's assume that the surroundings are the atmosphere, which exerts a pressure P_{ex} . If the atmospheric pressure P_{ex} on the external surface of the piston equals the pressure P of the gas on the internal surface of the piston, and if the internal and external areas A of the piston are equal, then, as we saw on page 14, the forces acting on the piston are also equal. In this case, if the peg holding the piston is removed, the piston stays still.

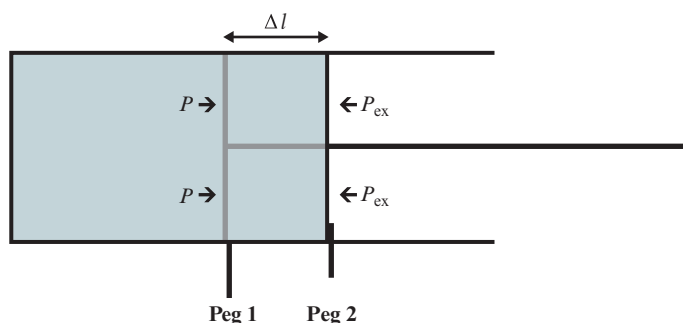


Figure 2.1 Work. If the external pressure P_{ex} on the piston is slightly less than the internal pressure P , when peg 1 is removed, and in the absence of all friction, the piston will move a distance Δl to the right, sweeping out a volume $\Delta V = A\Delta l$, where A is the area of both the interior and exterior faces of the piston. If the external pressure P_{ex} remains constant throughout the change, then the work done by the gas against the surroundings is $P_{\text{ex}}A \Delta l = P_{\text{ex}} \Delta V$.

But suppose that the external pressure P_{ex} of the atmosphere is a little lower than the internal pressure P of the gas inside the cylinder. When peg 1 is removed, the force exerted by the gas on the piston is greater than the force exerted by the atmosphere, and so, in the absence of all friction, the piston will move to the right, until stopped by peg 2, as shown in Figure 2.1. In so doing, the piston is moving against a force, and through a distance, implying that work is being done by the gas within the cylinder, against the atmosphere outside. If the distance the piston moves is, say, Δl m, then – once again assuming that there is no friction between the piston and the cylinder – the work done by the gas against the surroundings can be quantified as

$$\begin{aligned} \text{Work done by the system on the surroundings} \\ = \text{Force overcome} \times \text{Distance moved in direction of the force} \end{aligned}$$

If the external pressure P_{ex} of the atmosphere is constant throughout the change, as is quite reasonable if the change takes place over a short time, then

$$\text{Work done by the system on the surroundings} = P_{\text{ex}} A \times \Delta l = P_{\text{ex}} \times A \Delta l$$

But $A \Delta l$ is the volume ΔV swept out by the movement of the piston, this being the increase in the volume V of the gas inside the piston, and so

$$\text{Work done by the system on the surroundings} = P_{\text{ex}} \Delta V \quad (2.1)$$

The use of the symbol ΔV for the change of volume suggests that the change in state is finite; exactly the same reasoning can be used for an infinitesimal change, allowing us to express the infinitesimal work done by the system on the surroundings as $P_{\text{ex}} dV$.

These two expressions $P_{\text{ex}} \Delta V$ and $P_{\text{ex}} dV$ for the work done by a system of an expanding gas against the system's surroundings are important, and will be used many times in this book. And there are four aspects of this result which merit particular attention.

2.2.2 Work is done only against an external force

The first is that the work done by the gas inside the cylinder is calculated by reference to the *external* pressure P_{ex} , a state function of the surroundings, not the internal pressure P , a state function of the system, the gas in the cylinder. This is often something of a surprise – but it makes sense in that work is done in *overcoming* a force, and the force that is being overcome in this instance is that attributable to the external pressure P_{ex} , as exerted by the surroundings. Indeed, if the surroundings are a vacuum (or very close to it), then $P_{\text{ex}} = 0$, and so no work is done. As we shall shortly examine in more detail (see page 29), there is a very important circumstance in which P_{ex} is only a very little less than the gas pressure P , in which case $P_{\text{ex}} \approx P$ and so $P_{\text{ex}} \Delta V \approx P \Delta V$, and, for an infinitesimal change, $P_{\text{ex}} dV \approx P dV$. The work done by the system is now expressed in terms only of state functions P and V of the system itself. This is significant, for if we have information on the appropriate equation-of-state (see page 31) specifying how the gas's pressure P , and volume V , are related, we can then compute the actual value of $P \Delta V$, or $P dV$, so enabling us to quantify the amount of work done.

2.2.3 Work done 'by', and work done 'on'

The second important aspect of equation (2.1) is to note that work always involves two 'parties' – 'someone' who *does the work*, and, at the same time, 'someone' *on whom that work is done*. So if I lift a mass from the floor, I do the work, and work is done on the mass. In the case of the gas in the cylinder, if the pressure P of the gas is higher than the pressure P_{ex} of the surroundings, so that the piston moves to the right in Figure 2.1, then, as the gas expands, work is done by the gas on the surroundings; if the pressure P of the gas is less than the pressure P_{ex} of the surroundings, so that the piston moves from right to left in Figure 2.1 so compressing the gas, then work is done on the gas by the surroundings.

2.2.4 Work happens at the system boundary...

The third important aspect of equation (2.1) is rather less obvious, but a moment's thought will verify that work is a phenomenon that can be observed *only at the boundary* of a system, for it is at the boundary that the 'two parties' just referred to – the system and the surroundings – interact. This is helpful, for it tells us where to look if we wish to determine whether work is being done during a change in state, or not: we don't look within the system, we look at the system's boundary.

2.2.5 ...as the system changes state

Furthermore, *work only happens as a system changes state*, as is evident from the presence of the symbol Δ in equation (2.1). This therefore leads to a more sophisticated definition of work as

Work is a phenomenon, identified at the boundary of a system, as that system changes state, if and only if something occurs at that boundary which may be interpreted as motion against an external force.

This definition highlights the two facts that work takes place at the system boundary, and can be identified only during a change in state. In addition, this definition allows for work to be associated with a variety of different contexts. One such context, now very familiar, is when a gas expands, driving the piston of the cylinder against an external pressure at the system boundary – which can indeed “be interpreted as motion against an external force”. This is therefore an instance of work, which, since it concerns changes in the system's pressure P and volume V , is known as *P, V work of expansion*, or, more simply, *P, V work*. But there are other contexts too: the most familiar example is gravitational work done in lifting a mass against the force of a gravitational field; another relates to the motion of an electric charge against an electrical potential difference, this being ‘electrical work’; a third is the work required to stretch a surface, against the force attributable to surface tension (as takes place when a soap bubble expands), known as ‘surface work’; a fourth is the work required to change the orientation of a magnetic dipole against the force attributable to a local magnetic field – ‘magnetic work’; and yet another is the work done to overcome the force of friction, known as ‘frictional work’.

2.3 Path functions

2.3.1 Work is an example of a path function

With reference to Figure 2.2(a), suppose that the piston is originally held in position by peg 1, that the pressure of the gas in the cylinder is P_1 , and that the volume is V_1 . We may therefore represent the initial state of the gas as $[P_1, V_1]$. If the pressure P_{ex} exerted by the surroundings is a little less than the pressure P_1 , then, when peg 1 is removed, and in the absence of all friction, the piston moves to the right, until it is stopped by peg 2, as shown in Figure 2.2(b). The gas inside the cylinder now has a volume V_2 , greater than the original volume V_1 ; the pressure is also likely to have changed too, so let's represent the new pressure as P_2 . The system

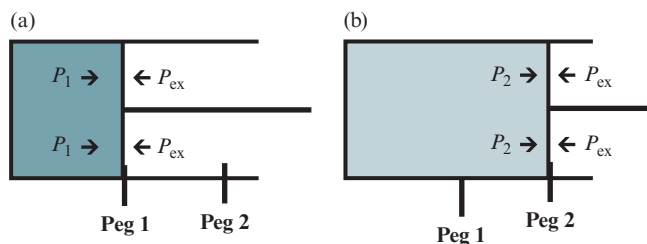


Figure 2.2 A change in state from $[P_1, V_1]$ to $[P_2, V_2]$.

has therefore undergone a change in state from $[P_1, V_1]$ to a different state, which we can represent as $[P_2, V_2]$.

As this change in state took place, the piston moved to the right, from the position defined by peg 1 to that defined by peg 2 in Figure 2.2, and so the system did work against the external pressure P_{ex} of the surroundings, which we can quantify using equation (2.1) as

$$\text{Work done by the system on the surroundings} = P_{ex} \Delta V \quad (2.1)$$

The important words here are “as this change in state took place”, for this emphasises a fundamentally important attribute of work, which we have already noticed: *work happens only as a system changes state*. When the piston stops at peg 2, and the system achieves its final state $[P_2, V_2]$, any work that might have been done has been finished – it no longer exists. Unlike variables such as pressure and volume, which are *properties of states*, work is not a property of a state, but a phenomenon which can occur only when a system *changes* state.

Phenomena which occur as a system changes state are known as **path functions**, of which work is an example. Path functions are fundamentally different from state functions: as we have seen, a *state function describes a specific property of a system at a point in time*, whereas a *path function describes a phenomenon that occurs as a system changes state over time*. The distinction between a state function and a path function is further clarified by imagining what happens when time ‘freezes’. If time is ‘frozen’, the question “What is the volume V of the gas in the cylinder?” has a sensible answer: we can measure that volume as, say, 0.76 m^3 , for the gas has a property called ‘volume’, which we can measure at a specific point in time. In contrast, the question “What is the work of the gas?” is meaningless: the gas does not possess a property called ‘work’, and we can’t measure work at a single point in time. Rather, ‘work’ is a description of a phenomenon which takes place over a period of time, as a system changes from one state to another. So, the sensible question relating to work is not “What is the work of the gas in state 2?”, but rather “What amount of work was done as the system changed from state 1 to state 2?”.

2.3.2 The value of a path function depends on the path taken between two states

An important feature of all path functions is that their value *depends upon the path taken* between any two states. This is different from the behaviour of state functions: as we have seen, the value of any state function, such as volume V or pressure P , is a property of a state

itself, and the values of the changes ΔV and ΔP of the state functions V and P depend only on the values V_1 and P_1 of the initial state in which the system started, and V_2 and P_2 of the final state in which the system ended up. The changes ΔV and ΔP are therefore determined by reference only to the initial state and the final state, and so are independent of how the change in state took place.

Path functions are significantly different: their values are totally dependent on the path, as we shall now demonstrate by reference to the system illustrated in Figure 2.3, the left-hand side of which shows our now-familiar gas in a cylinder, fitted with a frictionless piston, held in place by peg 1.

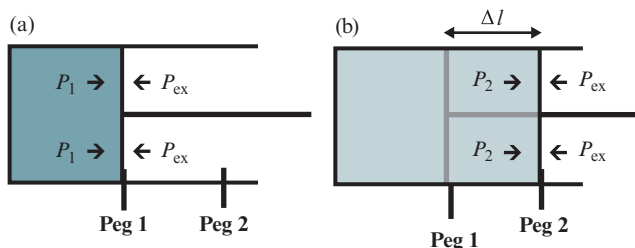


Figure 2.3 Work is a path function. The system is initially in state (a), $[P_1, V_1]$, and, after removal of peg 1, changes to state (b), $[P_2, V_2]$. When the piston moves frictionlessly to the right, from peg 1 to peg 2, the change ΔV in the state function volume depends only on the difference between the final volume V_2 and the initial volume V_1 . The work done by the gas on the surroundings, $P_{ex} \Delta V$, depends on P_{ex} , which can take a wide range of different values, even though the change ΔV in volume is the same in each case. The amount of work done by the gas against the surroundings therefore depends on the way in which the change takes place: work is therefore a path function.

Suppose that, in the state illustrated by Figure 2.3(a), the volume of the gas inside the cylinder is V_1 , and the pressure P_1 . Suppose further that the surroundings are a vacuum, so that the external pressure P_{ex} is zero, or very close to it. When peg 1 is removed, the piston moves frictionlessly to the right in Figure 2.3, and stops at peg 2. In this second state, the volume of the gas inside the cylinder is now V_2 , greater than the original volume V_1 . Since the value V_2 of the state function volume is different as compared to the value V_1 , a change in state has occurred, and we can calculate the change of volume, $\Delta V = V_2 - V_1$.

The work done by the gas during this change in state can be computed using equation (2.1):

$$\text{Work done by gas on the surroundings} = P_{ex} \Delta V \quad (2.1)$$

But, in this case, P_{ex} is zero, so the work done is zero.

Let's do this experiment again, starting with the piston at peg 1, and the volume of gas V_1 and the pressure P_1 , but with an external pressure P_{ex} at some (constant) non-zero value, rather lower than the pressure P_1 of the gas inside the cylinder. When the peg is removed, the higher pressure within the cylinder drives the piston frictionlessly against the external pressure P_{ex} to the right in Figure 2.3, until the piston stops once more at peg 2, with the volume of the gas once again V_2 . The change $\Delta V = V_2 - V_1$ in the volume of the gas is exactly the same as before, but this time, because P_{ex} now has some constant, non-zero, value, the work done by the gas

$$\text{Work done by gas on the surroundings} = P_{ex} \Delta V \quad (2.1)$$

also has a non-zero value, depending on precisely what the values of P_{ex} and ΔV actually are: if P_{ex} is small, then the amount of work done is correspondingly small; if P_{ex} is large (but still less than the pressure inside the cylinder), then the amount of work is larger. We therefore see that the change ΔV in the state function volume is the same in all cases, and depends solely on the values of the state function volume in the initial and final states; the amount of work, however, depends on how the change in state took place, the actual path followed during the change. This demonstrates that work is indeed a path function, and that the amount of work done during any change in state depends on the path taken.

We have already seen that small changes in state functions are represented using the symbols δ or d , as exemplified by δV and dV . In recognition of the different nature of path functions as compared to state functions, small quantities of a path function are represented by the single symbol d – so a small quantity of work is written as $\text{d}w$. The total amount of work done during a change in state from state [1] to state [2] is represented by $\{ {}_1 w_2 \}_X$, where the notation $\{ \dots \}_X$ indicates that the actual value of total work done during any particular change in state depends, as we have seen, on the path X taken. If path X takes place in small steps, we can write

$$\{ {}_1 w_2 \}_X = \sum_{\text{state [1]}}^{\text{state [2]}} \text{d}w \quad (2.2a)$$

and if the path can be considered to be taken in infinitesimal steps, then

$$\{ {}_1 w_2 \}_X = \int_{\text{state [1]}}^{\text{state [2]}} \text{d}w \quad (2.2b)$$

It's important to note that although equation (2.2b), representing the total work done during the change from state [1] to state [2], is written as an integral, this does not imply that the expression can be integrated directly to give a result of the form $w_2 - w_1$, for this would require that w_2 , representing the 'work in state 2', and w_1 , the 'work in state 1', actually exist, and can be subtracted from one another. As we have seen, there is no property w_2 , nor w_1 , so the summation, equation (2.2a), or the integral, equation (2.2b), needs to be determined for each particular circumstance, according to the actual path followed. The fact that the expression (2.2b) cannot be integrated directly implies that $\text{d}w$, an infinitesimal change of a path function, is what mathematicians call an **inexact differential** – in contrast to the exact differential dX , representing an infinitesimal change of the state function X that we met in equation (1.2c).

2.4 An important sign convention

As we have seen (see page 11), changes in state functions, whether large, as symbolised by ΔV , small (δV), or infinitesimal (dV), are signed quantities, so that a positive value implies (in this case) that the volume of the system has increased, and a negative value, that the volume has decreased. Work too is a signed quantity, and the sign also has significance. Reference to equation (2.1) will show that if the gas expands, ΔV is positive. Since the force against which work is done is always positive, then the product $P_{\text{ex}} \Delta V$ is positive. The work done **by** the

system on the surroundings is therefore a positive number. In contrast, if work is done by the surroundings **on** the system, the gas is compressed and so ΔV is negative, implying that the work done on the gas is a negative number. This is an important sign convention, which we can summarise as

- Work done **by** a system is represented by a **positive** number.
- Work done **on** a system is represented by a **negative** number.

2.5 Useful work ...

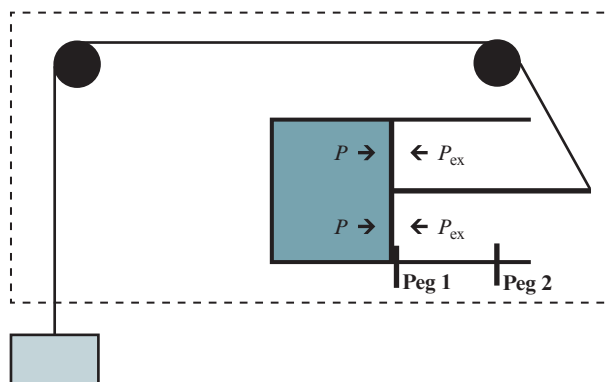


Figure 2.4 Two types of work. If $P > P_{\text{ex}}$, then as the piston moves to the right, the system does two types of work: P, V work of expansion $P_{\text{ex}} \Delta V$ against the atmosphere, and also gravitational work $Mg\Delta h$ as required to lift the mass.

In Figure 2.4, the system of the now-familiar gas within a cylinder fitted with a frictionless piston is connected to a mass M . Let us now suppose that peg 1 is removed, and the piston moves to the right. In so doing, the system of the gas in the cylinder necessarily does P, V work of expansion against the external pressure P_{ex} , and, in addition, causes the mass M to be raised by a distance Δh . The total work done by the system of the gas inside the cylinder is therefore the sum of the P, V work of expansion $P_{\text{ex}} \Delta V$, plus the work $Mg\Delta h$ done in lifting the mass

$$\text{Total work done by system} = P_{\text{ex}} \Delta V + Mg\Delta h$$

If the purpose of the system is to lift the mass, then we see that the total work done by the system is not all available – some work, $P_{\text{ex}} \Delta V$, has to be done to ‘push the atmosphere out of the way’ as the piston moves to the right. The **useful work**, or **available work**, that a system can perform is therefore defined as the difference between the total work done by the system, and any P, V work of expansion against the atmosphere that cannot otherwise be harnessed:

$$\text{Useful work} = \text{Total work} - P, V \text{ work of expansion that cannot otherwise be used}$$

Many chemical reactions, especially those which involve gases, are necessarily accompanied by P, V work of expansion against the atmosphere, and so the distinction between total work and useful work has considerable significance, as will be discussed further on pages 386 to 390.

2.6 ...and wasted work

All the examples we have studied so far have related to the expansion of a gas within a frictionless cylinder. Let's now examine what happens when friction is present between the rim of the piston and the internal surface of the cylinder.

Friction is of two types – **static friction**, and **dynamic friction**. Static friction is what makes surfaces 'sticky', so that they do not easily slide over one another, and it is thanks to static friction that we can (usually) lean a ladder against a wall, and climb the ladder without fearing that it might slip backwards (but, for safety, it's always advisable for someone to be holding the ladder to make sure!). Dynamic friction (sometimes known as kinetic friction) arises when two surfaces are moving against one another, as happens, for example, when a saw moves against wood, or a drill bites into metal, or – as is relevant here – when the rim of the piston scrapes along the inside of the cylinder as it moves.

Both types of friction apply to our system of a gas at pressure P_{ex} inside a cylinder fitted with a piston. If the external pressure P_{ex} equals the internal pressure P , then the forces on each side of the piston are equal, and the piston does not move. If the external pressure P_{ex} is reduced, in the absence of friction, the pressure difference $P - P_{\text{ex}}$ will cause the piston to move outwards, but in the presence of static friction, a small pressure difference will not cause the piston to move, for the force exerted by the static friction acts like a peg, resisting the movement of the piston. If the external pressure P_{ex} is progressively reduced, the pressure difference $P - P_{\text{ex}}$ increases, until a point is reached such that the force exerted by the pressure difference is large enough to overcome the static friction, and the piston jerks outwards.

Thereafter, the piston slides against the internal surface of the cylinder, against the force exerted by dynamic friction, which acts to oppose the motion. And in so doing, the gas inside the cylinder is doing **frictional work** against the dynamic friction, as well as P, V work of expansion against the external pressure, and perhaps gravitational work in lifting a weight too. Eventually the piston will come to rest, and the total work done by the system can be expressed as

$$\begin{aligned} \text{Total work done by system} &= P, V \text{ work of expansion} \\ &+ \text{work done against dynamic friction} \\ &+ \text{work done in lifting a weight} \end{aligned}$$

Once again, if the purpose of our system is to lift a weight, or to do useful work of any sort (such as power a machine, or drive an engine), then not only is the P, V work of expansion not available, but the work done against dynamic friction is wasted too. And wasted in a very particular way: as we shall see in the next chapter, frictional work is inevitably lost as heat – which is why saws get hot as they cut through wood, and drills get hot as they bore through metal. This also explains why so many of the examples used in this book refer to frictionless systems, so ensuring that this waste is not present.

2.7 Quasistatic paths

Let's do the experiment illustrated in Figure 2.3 once more, with exactly the same initial state: the volume of the gas is V_1 , the pressure P_1 , and the piston is held in place by a peg. The

difference in this experiment is that the initial external pressure – let's represent this as $P_{\text{ex},1}$ – is now exactly equal to the internal gas pressure P_1 . Since the pressures on both sides of the piston are the same, the force acting on the inside of the piston from the gas within the cylinder is exactly balanced by the force acting on the outside of the piston by the gas in the surroundings. If the peg is removed, the piston will stay absolutely still.

Suppose now that the external pressure is reduced by an infinitesimally small amount, dP_{ex} , to a new, slightly lower, external pressure $P_{\text{ex},2} = P_{\text{ex},1} - dP_{\text{ex}}$. The internal pressure on the piston, P_1 is now infinitesimally greater than the external pressure, and so, in the absence of all friction, the piston will move against the external pressure $P_{\text{ex},2}$. The volume of the gas will therefore change from its initial volume V_1 to an infinitesimally larger volume $V_2 = V_1 + dV_1$; simultaneously, since in general the pressure of a gas drops as the volume increases, the pressure will change from its initial value P_1 to a new, infinitesimally lower, value $P_2 = P_1 - dP_1$. When the new gas pressure P_2 equals the external pressure $P_{\text{ex},2}$, the piston will stop moving, and the system will return to equilibrium. Overall, the gas has changed from its original state $[P_1, V_1]$ to a final state $[P_2, V_2]$, and the surroundings have changed from pressure $P_{\text{ex},1}$ to $P_{\text{ex},2}$.

As the gas inside the cylinder expands, the gas does P, V work of expansion against the surroundings. Assuming as usual that the piston, and the system as a whole, are perfectly frictionless, then that the only work done by the gas within the system is P, V work of expansion against the surroundings, given by

$$\begin{aligned} \text{Work done by system during change from } [P_1, V_1] \text{ to } [P_2, V_2] &= P_{\text{ex},2} dV_1 \\ &= (P_{\text{ex},1} - dP_{\text{ex}}) dV_1 = P_{\text{ex},1} dV_1 - dP_{\text{ex}} dV_1 \end{aligned}$$

Now, the changes dP_{ex} and dV_1 are both very small, in which case the product $dP_{\text{ex}} dV_1$ is very small indeed, and certainly much smaller than the product $P_{\text{ex},1} dV_1$. Hence we may write

$$\text{Work done by system during change from } [P_1, V_1] \text{ to } [P_2, V_2] = P_{\text{ex},1} dV_1$$

But we also know that the initial external pressure $P_{\text{ex},1}$ was equal to the initial internal pressure P_1 , hence

$$\text{Work done by system during change from } [P_1, V_1] \text{ to } [P_2, V_2] = P_1 dV_1$$

The significance of this equation for the work done by the system is that it is expressed in terms *only of variables relating to the system* – P_1 , the initial pressure of the system, and dV_1 , the change of volume of the system. This is in contrast to the equation (2.1), which expressed the work done by the system in terms of one variable relating to the system, dV , and a second relating not to the system, but to the surroundings, P_{ex} .

Let's consider now what happens when the external pressure is reduced by another very small amount dP_{ex} from $P_{\text{ex},2}$ to $P_{\text{ex},3} = P_{\text{ex},2} - dP_{\text{ex}}$. The pressure P_2 of the gas in the cylinder is once again infinitesimally higher than the pressure in the surroundings, and so the piston will once more move frictionlessly and infinitesimally to the right. The system of the gas in the cylinder changes state from $[P_2, V_2]$ to $[P_3, V_3]$, such that $V_3 = V_2 + dV_2$ and $P_3 = P_2 - dP_2$. As before, during this change, the gas in the cylinder does work against the surroundings equal to $P_{\text{ex},2} dV_2$, and we can use exactly the same reasoning as before to show that

$$\text{Work done by system during change from } [P_2, V_2] \text{ to } [P_3, V_3] = P_2 dV_2$$

This implies that the total work done by the gas in changing state from $[P_1, V_1]$ to $[P_3, V_3]$ via $[P_2, V_2]$ is given by

$$\text{Work done by system during change from } [P_1, V_1] \text{ to } [P_3, V_3] = P_1 dV_1 + P_2 dV_2$$

You can see the pattern: if we were to reduce the pressure in the surroundings in a sequence of infinitesimally small steps, each of dP_{ex} , then

$$\text{Work done by system during change from } [P_1, V_1] \text{ to } [P_n, V_n] = \sum_1^{n-1} P_n dV_n$$

Since the volume changes dV are so small as to be infinitesimal, then the total work done by the gas as it expands from its initial volume V_1 to its final volume V_n can be expressed as an integral:

$$\text{Work done by system during change from } [P_1, V_1] \text{ to } [P_n, V_n] = \int_{V_1}^{V_n} P dV \quad (2.3)$$

Equation (2.3) allows us to express the total work done by the system for a finite change between any two states in terms of state functions of the system alone. The derivation of equation (2.3), however, rests on three key assumptions about the nature of the change: specifically, that the change took place along a particular path

- through a sequence of equilibrium states
- in an infinite number of infinitesimal steps
- infinitely slowly.

The significance of the first condition – the sequence of equilibrium states – ensures that the state functions P and V are well-defined throughout the change, and the second condition – the infinitesimal steps – allowed us to replace the external pressure P_{ex} by the internal pressure P . The third condition is a corollary of the first two; in principle, this third assumption can be relaxed to a condition which is that the change takes place sufficiently slowly to allow the first two conditions to apply. Any path which obeys these three conditions is known as a **quasistatic path**, and a change in state which takes place along a quasistatic path is known as a **quasistatic change**.

The quasistatic path discussed here has been in the context of an infinitesimal pressure difference across the system boundary, resulting in the performance of P, V work, either by the system on the surroundings, or by the surroundings on the system. In fact, the concept of the quasistatic path applies in other contexts too, of which two are of particular relevance. The first is the flow of heat: a quasistatic flow of heat is one which takes place infinitely slowly through an infinite number of steps such that

- the temperature difference driving the flow of heat is infinitely small, and
- the two systems between which the heat is flowing are in equilibrium throughout.

This implies that any heat flow down a finite temperature gradient is necessarily non-quasistatic – which applies to all real heat flows.

Similarly, a quasistatic chemical reaction takes place infinitely slowly through a sequence of states of chemical equilibrium – which is, once again, a theoretical concept rather than a reality.

2.8 Work and Boyle's Law

Equation (2.3) for the work done by an expanding gas, and the concept of the quasistatic change on which equation (2.3) rests, are important, in that it expresses the P, V work of expansion of a frictionless system in terms of *state functions of the system alone*. And if we know the relevant equation-of-state, such as Boyle's Law, equation (1.3)

$$PV = c \quad (1.3)$$

where c is a constant for a given mass of gas at a given temperature, then we can compute what the work done during any change in state actually is. So, combining equations (2.3) and (1.3), we have

Work done by system during change from $[P_1, V_1]$ to $[P_2, V_2]$

$$= \int_{V_1}^{V_2} P \, dV = \int_{V_1}^{V_2} \frac{c}{V} \, dV = c \ln \left(\frac{V_2}{V_1} \right) \quad (2.4)$$

This result, equation (2.4), is a special case, valid only if two conditions are simultaneously fulfilled: firstly, that the change in state from $[P_1, V_1]$ to $[P_2, V_2]$ is quasistatic, and, secondly, that Boyle's Law is valid throughout. It does, however, illustrate an important general point: because equation (2.3) is expressed only in terms of variables relating to the system, then, if an appropriate equation-of-state for that system is known (as it often is), then equation (2.3) may be used to compute, and therefore predict, how much work a system can do. It's important, though, to re-emphasise that equation (2.3) is based on the assumption that the change is quasistatic, taking place through a very large (mathematically, infinite) number of very small (infinitesimal) frictionless steps. In reality, such a change is impossible, but theoretically, it provides a very useful way to compute quantities mathematically.

2.9 P, V diagrams

2.9.1 A graphical representation of a frictionless quasistatic change in state ...

As we have now seen, many of the changes in state of a gas in a cylinder are associated with changes in the system's pressure P and volume V . A very useful way of representing these changes is by plotting the simultaneous values of these state functions on a graph, the vertical axis of which represents the system pressure P , and the horizontal axis, the system volume V . Reasonably enough, such a representation is known as a **P, V diagram**. As an example, Figure 2.5 shows a P, V diagram representing a change in state, in which the gas shown in

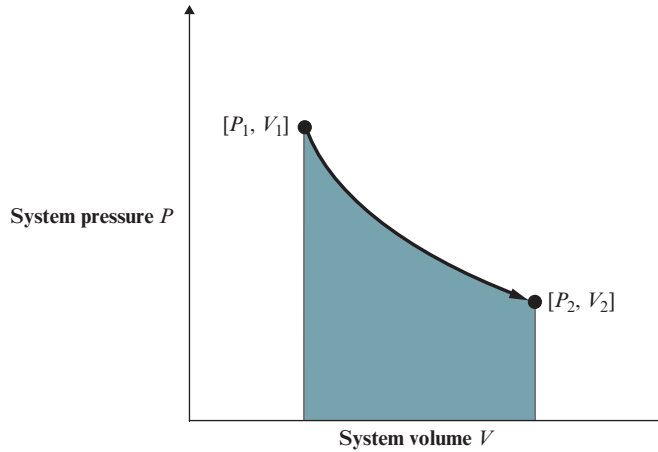


Figure 2.5 A P, V diagram for a frictionless quasistatic change in state. The system undergoes a frictionless quasistatic change in state from $[P_1, V_1]$ to $[P_2, V_2]$, as indicated by the direction of the arrow, under conditions in which Boyle's Law is valid. The work done by the system on the surroundings is represented by the shaded area. Note that, in P, V diagrams, it is conventional to define states as, for example, $[P_1, V_1]$, even though pressure is the vertical (y) axis, and volume the horizontal (x) axis.

Figure 2.3 expands quasistatically, and in the absence of all friction, from an initial equilibrium state $[P_1, V_1]$, to a final, different, equilibrium state $[P_2, V_2]$, under conditions of constant temperature so that Boyle's Law, $PV = c$, equation (1.2), holds.

Since the change in state is assumed to be quasistatic, the change takes place through an infinite succession of intermediate equilibrium states. Each of these has its own, well-defined, values of pressure and volume, and so each can be represented by a specific point on the P, V diagram. A quasistatic change, starting at state $[P_1, V_1]$ and ending in state $[P_2, V_2]$, can therefore be represented on a P, V diagram by a solid line, as shown in Figure 2.5, such that each point on the line represents the corresponding intermediate equilibrium state, and with the direction of the change being shown by the arrow.

In the total absence of friction, all the work done by the system is P, V work of expansion against the surroundings, as given by equation (2.3)

$$\text{Work done by system during change from } [P_1, V_1] \text{ to } [P_2, V_2] = \int_{V_1}^{V_2} P \, dV \quad (2.3)$$

Since Boyle's Law is assumed to be valid for this particular change, equation (2.3) becomes

$$\text{Work done by system during change from } [P_1, V_1] \text{ to } [P_2, V_2] = c \int_{V_1}^{V_2} \frac{dV}{V} = c \ln \left(\frac{V_2}{V_1} \right) \quad (2.4)$$

The work done is represented by the shaded area between the graph of the change in state and the horizontal axis, as shown in Figure 2.5.

2.9.2 ... and of a non-quasistatic change

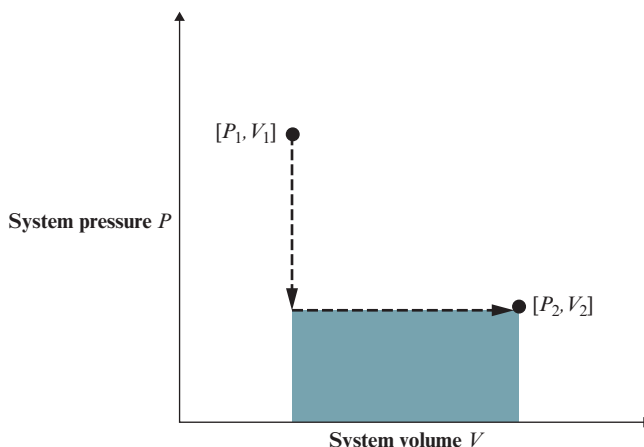


Figure 2.6 A P, V diagram for a frictionless non-quasistatic change in state. The external pressure P_{ex} on the cylinder is abruptly reduced to P_2 , and the gas in the cylinder expands non-quasistatically at constant pressure P_2 to its final equilibrium state $[P_2, V_2]$. During the change in state, the system is not in equilibrium, and so it is not possible to define ‘the’ pressure and ‘the’ volume of the system at any intermediate state. The path of the change in state is therefore represented by a dashed line, which indicates a plausible path, consistent with the known fact that the work done by the gas during the change is certainly $P_2 \Delta V$, as shown by the shaded area.

Figure 2.6 shows another change in state from $[P_1, V_1]$ to $[P_2, V_2]$, but by a different path: in this case, the gas expands against a constant external pressure $P_{\text{ex}} = P_2$, as would happen, for example, if P_{ex} in Figure 2.3(a) and 2.3(b) were equal to P_2 , and peg 1 is removed.

In this case, there is a substantial difference between the initial pressure P_1 and the external pressure P_2 , so that, when the peg is removed, and in the absence of friction, the piston moves to the right very quickly. This creates initial turbulence within the system, and although the system started in an equilibrium state $[P_1, V_1]$, and ended at another equilibrium state $[P_2, V_2]$, during the change, the system is not in equilibrium. The change in state therefore does not take place through an infinitesimal sequence of equilibrium states, and so is a non-quasistatic change.

During the change, the pressure within the system will have different values at different points within the system; likewise, the volume of the system is uncertain since the molecules are not distributed evenly. As a consequence, it is not possible to specify ‘the’ pressure or ‘the’ volume at any intermediate state, implying that we cannot plot the path between $[P_1, V_1]$ and $[P_2, V_2]$ with any certainty. But we do know, from equation (2.1), that in the absence of friction, the work done by the gas against the surroundings is given by $P_{\text{ex}} \Delta V = P_2 \Delta V$ since P_{ex} is equal to P_2 . Now $P_2 \Delta V$ is the shaded area in Figure 2.6, and so we can represent the frictionless non-quasistatic change from $[P_1, V_1]$ to $[P_2, V_2]$ by the dashed line as shown. The use of a dashed line, rather than a solid line, indicates that the values of the pressure and volume of the gas whilst the change is taking place are indeterminate, but the general shape is meaningful. Certainly, the area under the horizontal dashed line gives the right answer for the work done by the system, and the piston does move against a constant external pressure $P_{\text{ex}} = P_2$, so

the horizontal dashed line is plausible. But whereas the solid line in Figure 2.5, indicating a quasistatic path, is ‘the truth’, the dashed line in Figure 2.6, indicating a non-quasistatic path, is just a representation.

2.10 Changes at constant pressure

Figure 2.6 describes a non-quasistatic expansion of a gas against a constant external pressure P_{ex} . As a moment’s thought will verify, there are very many real events that take place under conditions of constant external pressure, especially when that pressure is exerted by the atmosphere. So, for example, many chemical reactions take place in vessels open to the atmosphere; most industrial processes – and many engines – operate in the atmosphere; and the same applies to many living processes too, whether under the pressure of the atmosphere, or the local pressure at a given depth in sea. And although the local atmospheric pressure can vary, for example, with the weather and the altitude, and the pressure in the oceans varies with depth, over the time taken for many of these processes to take place – typically fractions of seconds, seconds and minutes – the local pressure is constant. Changes at constant pressure are therefore very common, and important, and will feature strongly in this book.

But there is a subtlety here, a subtlety best explored by re-examining the interaction between a system and its surroundings when a gas expands from an initial state $[P_1, V_1]$ to a final state $[P_2, V_2]$. So, consider Figure 2.7, which represents both the system of interest and the surroundings, which together constitute the universe.

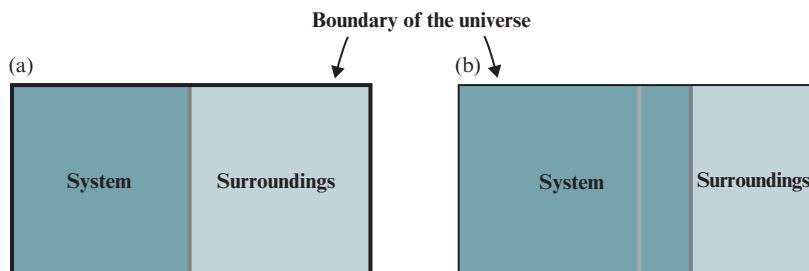


Figure 2.7 Can a system expand at constant pressure? As the gas in the system expands, from the state shown in Figure 2.7(a) to that shown in Figure 2.7(b), the volume of the gas in the system increases, and the pressure of the gas decreases. Simultaneously, the gas in the surroundings is compressed, and its pressure must correspondingly increase. Does this imply that it is impossible for a system to expand at constant pressure?

As the gas in the system expands against the surroundings, the volume of the system increases, and the pressure of the system falls. But, as implied by Figure 2.7, an *increase* in the volume of the system results in a corresponding *decrease* in the volume of the surroundings. The gas in the surroundings is therefore being compressed, and so we would expect the pressure of the gas in the surroundings to increase. That presents a puzzle: how is it possible for the gas in the cylinder to expand against a *constant* pressure? Surely, as the gas in the surroundings – the atmosphere – becomes compressed, the pressure in the atmosphere must increase, so it seems to be impossible for the gas in the cylinder to expand against a constant pressure. Is

the concept of a change at constant pressure just theoretical (like the concept of the quasistatic change), or are changes at constant pressure real?

If the situation were indeed as illustrated in Figure 2.7, this would all be true: the pressure of the surroundings would increase as the system expands. Figure 2.7, however, is misleading, for two reasons: firstly, for ease of drawing, the volumes of the system and the surroundings have been depicted as about the same; secondly, the heavy line representing the ‘boundary of the universe’ is shown as a solid line, suggesting that it is rigid.

When we think more deeply about Figure 2.7, we realise that, in reality, the volume V_{ex} of the surroundings – the rest of the universe – is vastly, vastly, greater than the volume V of the system: V_{ex} is an unimaginably large number. When the piston moves to the right in Figure 2.7, the change of the volume of the system is ΔV , implying that the change of the volume of the surroundings is $-\Delta V$ (with the $-$ sign indicating a decrease in volume as expected). The volume of the surroundings after the change is therefore $V_{\text{ex}} - \Delta V$, which, as expected is less than the original volume V_{ex} . But not by much: because the volume V_{ex} of the surroundings is such a huge number, $V_{\text{ex}} - \Delta V \approx V_{\text{ex}}$. In practice, the volume of the surroundings remains unchanged, despite the expansion of the gas in the system, and so the pressure of the surroundings stays constant.

Furthermore, if the boundary of the universe is not rigid – and we have no reason to believe that it is – then the volume of the atmosphere is not constrained, implying that the atmosphere can increase its volume as much as it ‘likes’, without any change of pressure.

Both explanations are valid, and both have the same conclusion: events that happen within systems open to the atmosphere, or within the vastness of the ocean, take place at constant pressure. The puzzle is resolved: changes at constant pressure are not theoretical concepts; on the contrary, changes at constant pressure are both possible and real.

2.11 Thermodynamic cycles

2.11.1 From here to there – and back again

Let’s now take matters further, and consider what happens when the gas in the cylinder starts in the equilibrium state $[P_1, V_1]$, and follows the frictionless non-quasistatic path illustrated in the P, V diagram shown in Figure 2.6, expanding at constant pressure P_2 , to the equilibrium state $[P_2, V_2]$. During this change, as is now familiar, work is done by the gas on the surroundings, equal to $P_2 \Delta V$. Having established an equilibrium state $[P_2, V_2]$, suppose now that the gas in the cylinder undergoes a frictionless *quasistatic* compression, reducing the volume and increasing the pressure. If the conditions are such that the temperature of the system is constant and Boyle’s Law is valid, then the system will retrace the quasistatic path illustrated in the P, V diagram shown in Figure 2.5, and return to state $[P_1, V_1]$. During this frictionless quasistatic change, the work done by the gas is given by equation (2.4), but with the limits of the integration switched, since the change in state in this case is from $[P_2, V_2]$ to $[P_1, V_1]$:

$$\text{Work done by system during change from } [P_2, V_2] \text{ to } [P_1, V_1] = c \int_{V_2}^{V_1} \frac{dV}{V} = c \ln \left(\frac{V_1}{V_2} \right) \quad (2.4)$$

Since V_1 is less than V_2 , the ratio V_1/V_2 is less than one, and so we may write

$$\text{Work done by system during change from } [P_2, V_2] \text{ to } [P_1, V_1] = -c \ln \left(\frac{V_2}{V_1} \right) \quad (2.5)$$

In this expression, V_2/V_1 is greater than one, implying that $\ln(V_2/V_1)$ is positive. Since the constant c is also positive, then the product $c \ln(V_2/V_1)$ is positive, and so $-c \ln(V_2/V_1)$ is necessarily negative. This therefore indicates that, during the change in state from $[P_2, V_2]$ to $[P_1, V_1]$, work is done *on* the gas by the surroundings (see page 27), as makes sense since this is a compression.

These changes are all illustrated in Figure 2.8.

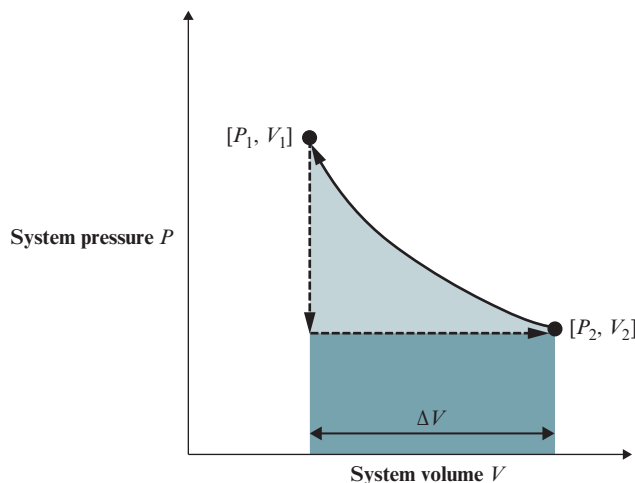


Figure 2.8 A P, V diagram for a thermodynamic cycle. The system is initially in the equilibrium state $[P_1, V_1]$, and then follows the frictionless non-quasistatic path (represented by the dashed line), at constant pressure P_2 , to the equilibrium state $[P_2, V_2]$. During this change, the system does work $P_2 \Delta V$ on the surroundings, as shown by the dark-blue rectangular area. The system is then compressed along the frictionless quasistatic path (shown by the solid line), returning to the equilibrium state $[P_1, V_1]$, so completing the thermodynamic cycle. During this change, the surroundings do work $c \ln(V_2/V_1)$ on the system, represented by the total area under the curve, comprising both the light-blue and dark-blue areas. For the entire cycle, there is no change to either the state function P , or the state function V , and so $\oint dP = \oint dV = 0$. But as can be seen from the diagram, more work is done on the system in the change from $[P_2, V_2]$ to $[P_1, V_1]$ than was done by the system in the change from $[P_1, V_1]$ to $[P_2, V_2]$, and so $\oint dw \neq 0$, as represented by the near-triangular area in the middle of the diagram.

Any process in which a thermodynamic system starts in a particular equilibrium state, then undergoes one or more changes in state, and finally returns to the original equilibrium state – of which Figure 2.8 is an example – is known as a **thermodynamic cycle**. As we shall see during this book, thermodynamic cycles are of considerable significance: all engines – for example, steam engines, internal combustion engines, and jet engines – operate in cycles, and cycles feature in many important biological processes, such as the tricarboxylic acid cycle (sometimes known as the Krebs cycle) associated with the metabolism of sugars, and the light-dependent Calvin cycle (or Calvin–Benson–Bassham cycle, to give credit to Melvin Calvin’s co-researchers at the University of California, Berkeley), central to plant photosynthesis.

Of particular relevance here are two insights: the first concerning the behaviour of state functions throughout a complete thermodynamic cycle; the second, concerning the behaviour of path functions.

2.11.2 Thermodynamic cycles and state functions

Let's firstly consider what happens to the state function V throughout the cycle. The system starts in an equilibrium state of volume V_1 , and changes to a different equilibrium state of volume V_2 . Accordingly, the volume change $\Delta V_{1 \rightarrow 2}$ is given by

$$\Delta V_{1 \rightarrow 2} = V_2 - V_1$$

If the change takes place through a sequence of infinitesimal steps, this can also be written as

$$\Delta V_{1 \rightarrow 2} = V_2 - V_1 = \int_{V_1}^{V_2} dV$$

Similarly, for the change from $[P_2, V_2]$ back to $[P_1, V_1]$, we may write

$$\Delta V_{2 \rightarrow 1} = V_1 - V_2 = \int_{V_2}^{V_1} dV$$

The total change of volume $\Delta V_{1 \rightarrow 2 \rightarrow 1}$, from $[P_1, V_1]$ to $[P_2, V_2]$ and back to $[P_1, V_1]$ is therefore

$$\Delta V_{1 \rightarrow 2 \rightarrow 1} = \Delta V_{1 \rightarrow 2} + \Delta V_{2 \rightarrow 1} = V_2 - V_1 + V_1 - V_2 = 0 = \int_{V_1}^{V_2} dV + \int_{V_2}^{V_1} dV$$

The total change of volume for the entire cycle is therefore zero – which is entirely as expected: volume is a state function, and we know that the value of the change in any state function is the value of that state function in the final state minus the value in the initial state. Since, for a cycle, the volume of the final state necessarily equals that of the initial state, then the change of volume for the entire cycle must be zero.

Let's, however, look more closely at the integral expression of this:

$$\Delta V_{1 \rightarrow 2 \rightarrow 1} = 0 = \int_{V_1}^{V_2} dV + \int_{V_2}^{V_1} dV$$

Now the sum of those two integrals, the first from V_1 to V_2 , and the second from V_2 to V_1 , represents an integral over the entire cycle from V_1 to V_2 and back to V_1 again, and can be represented as a cyclic integral $\oint$

$$\int_{V_1}^{V_2} dV + \int_{V_2}^{V_1} dV = \oint dV = 0$$

This shows that, for the state function volume, the cyclic integral, around any thermodynamic cycle, will be zero. This is an important general result which holds for all state functions: if a function X is a state function, then, for any thermodynamic cycle

$$\oint dX = 0 \quad (2.6)$$

Conversely, if it can be demonstrated for a function X that $\oint dX = 0$, then this proves that the function X is a state function, and dX is then said to be an **exact differential**.

2.11.3 Thermodynamic cycles and path functions

Let's now consider the work done during the cycle. During the frictionless non-quasistatic change from $[P_1, V_1]$ to $[P_2, V_2]$, all the work done by the system is P, V work of expansion against the surroundings, given by

Work done by system on surroundings in change from state 1 to state 2 = $P_2 \Delta V$

as represented by the dark-blue shaded area in Figure 2.8.

We have also just shown that the work done by the gas on the surroundings during the quasistatic change from $[P_2, V_2]$ back to $[P_1, V_1]$ is given by

$$\text{Work done by system on surroundings in change from state 2 to state 1} = -c \ln \left(\frac{V_2}{V_1} \right) \quad (2.5)$$

where the negative sign indicates that work is in fact done on the system by the surroundings during this compression. This is represented in Figure 2.8 by the total area under the solid line between $[P_2, V_2]$ and $[P_1, V_1]$, as represented by the combination of the dark-blue, and light-blue, areas.

The total work done by the system on the surroundings for the entire thermodynamic cycle can be determined by adding these together:

$$\begin{aligned} \text{Total work done by gas during the cycle} &= P_2 \Delta V - c \ln \left(\frac{V_2}{V_1} \right) \\ &= P_2(V_2 - V_1) - c \ln \left(\frac{V_2}{V_1} \right) \end{aligned} \quad (2.7)$$

The number represented by the value of equation (2.7) is determined by the volumes V_1 and V_2 , the final pressure P_2 , and the appropriate Boyle's Law constant c . If it so happens that $V_1 = V_2$, then this number is zero - but if $V_1 \neq V_2$, then Boyle's Law tells us that $P_1 \neq P_2$ as well, implying that no change has taken place. If, however, a change *has* taken place, V_1 and V_2 will be different, and the numerical result of equation (2.7) will depend on the specific circumstances. But whatever the specific circumstances, it is invariably true is that this number will *not* be zero. Indeed, as reference to the particular thermodynamic cycle represented by the P, V diagram shown in Figure 2.8 makes quite clear, in this case, the result of equation (2.7) is a negative number, for the work $P_2 \Delta V$ done by the system on the surroundings in the expansion from $[P_1, V_1]$ to $[P_2, V_2]$, as represented by the dark blue shaded area in Figure 2.8, is clearly less than the work $c \ln(V_2/V_1)$ done on the system by the surroundings during the compression, as represented by the total area between the curved line and the horizontal axis in Figure 2.8. This diagram therefore vividly illustrates that more work is required to compress

the gas quasistatically from $[P_2, V_2]$ back to $[P_1, V_1]$ than was done by the gas in expanding non-quasistatically from $[P_1, V_1]$ to $[P_2, V_2]$ – the net difference being represented by the nearly triangular figure in the centre of Figure 2.8.

If the amount of work done by the gas on the surroundings during any infinitesimal change is represented as δw , then the total amount of work done by the gas on the surroundings during any thermodynamic cycle may be expressed as a cyclic integral, the value of which must, in general, be some non-zero number:

$$\oint \delta w \neq 0 \quad (2.8)$$

There is only one, very special, case in which the value of this cyclic integral is zero, and that is – with reference to Figure 2.8 – when the path from state $[P_2, V_2]$ back to state $[P_1, V_1]$ traces exactly the same frictionless quasistatic path as the original frictionless quasistatic path from state $[P_1, V_1]$ to state $[P_2, V_2]$, but in the reverse direction. This implies that the two paths, as shown on the diagram, would be identical, and so the area of the near-triangular area in the centre would shrink to zero.

Other than this particular case, the inequality of expression (2.8) is in general true: the total work done by a system through a generalised thermodynamic cycle will be some, non-zero, number. We can't predict, in general, what this number might be, for its value depends on the specific circumstances. Furthermore, the value might be a negative number, as in the particular case we have examined as illustrated in Figure 2.8; it could, however, also be a positive number, as indeed happens if the thermodynamic cycle shown on Figure 2.8 were to be carried out in the other direction, with a quasistatic *expansion* from $[P_1, V_1]$ to $[P_2, V_2]$ happening first, and then followed by a non-quasistatic compression at constant pressure P_2 . What's important about equation (2.8) is not the specific value in any particular circumstances, but the fact that the result is, in general, some number other than zero.

We know that work is a path function, and Figure 2.8 demonstrates diagrammatically that the amount of work done by a system as it changes state does indeed depend on the path taken. Mathematically, this is represented by equation (2.8), which applies to all path functions, and, as we noted earlier (see page 26), δw is known as an **inexact differential** – hence the symbol δ , to distinguish between an inexact differential δ and an exact differential d . If we are dealing with any path function, then we can predict that the cyclic integral of that function around any thermodynamic cycle will be some number other than zero; likewise, if we can verify that the cyclic integral of any function around any thermodynamic cycle is non-zero, then we may infer that the function in question is a path function.

Equations (2.6) and (2.8) are therefore the fundamental mathematical definitions of state functions and path functions respectively.

2.11.4 An important link between path functions and state functions

Finally in this section, we note an important link between path functions and state functions, as exemplified by the now-familiar equation for the work δw done by a gas at pressure P , expanding quasistatically by a volume dV :

$$\delta w = P dV \quad (2.9)$$

This equation links a path function, δw , to the product of two state functions, expressed in the form an [intensive state function, pressure] $\times$ change of an [extensive state function, volume]. As we shall see in due course, this is an example of a generic relationship of the form

$$\delta(\text{path function}) = (\text{intensive state function}) \times d(\text{extensive state function})$$

2.12 Energy

As we have examined now in some detail, when a gas in a cylinder expands against the pressure P_{ex} of the surroundings, the gas inside the cylinder does work, quantified as $P_{\text{ex}} \Delta V$, on the surroundings. If the piston were linked to other appropriate mechanisms, this work could be harnessed, for example, to lift a weight, or to drive an engine – for all steam, petrol and diesel engines operate by the expansion of gases in cylinders against external pressure.

Before, however, the system does any work – before the piston actually moves – the gas in the cylinder must have possessed the *potential to do work*: it's as if the gas in the cylinder has some sort of hidden property, a property which, once released, can do useful things like work. So let's give this hidden property, this potential to do work, a name – **energy**. Given that work is a manifestation of energy, and that energy is 'work-in-waiting', energy and work have the same unit of measurement, the Joule, J.

Energy is the central concept in this book, and indeed is the central concept in much of science too. We'll gain a much richer understanding of energy as the book evolves, but this is a good place to start – the realisation that if a system is capable of performing work, then, before that work is performed, the potential to perform that work is a property of the original system. And if energy is a property of a system, then maybe there is a state function associated with it. Indeed there is – as we shall see in Chapter 5.

?

EXERCISES

1. In thermodynamics, what, precisely, is meant by the term 'work'? What is meant by 'work done on a system'? And by 'work done by a system'? What is ' P, V work'? Identify at least three examples of work, other than P, V work.
2. What is a 'path function'? How does a path function differ from a state function?
3. What are the characteristics of a 'quasistatic' path? Why are quasistatic paths important?
4. A system comprises a fixed mass of gas is contained within a cylinder, fitted with a frictionless piston, such that the system is in equilibrium with a volume of 0.5 m^3 , and at a pressure of $1 \text{ bar} = 1 \times 10^5 \text{ Pa}$. Calculate the P, V work of expansion done by, or P, V work of compression done on, the system, under the following circumstances, all of which take place at constant temperature:
 - The volume of the system increases to 0.75 m^3 quasistatically.
 - The volume of the system increases to 0.75 m^3 against a constant external pressure of $0.8 \times 10^5 \text{ Pa}$.
 - The volume of the system increases to 0.75 m^3 against a vacuum.
 - The volume of the system decreases to 0.3 m^3 quasistatically.

- The volume of the system firstly increases to 0.75 m^3 against a vacuum, and then decreases to 0.3 m^3 quasistatically.
- The volume of the system firstly increases to 0.75 m^3 quasistatically, and then decreases to 0.3 m^3 quasistatically.

Calculate the final pressure of the system in each case, and illustrate each of your answers using a P, V diagram.

5. For the system described in question 4, suppose that the external pressure is initially $1 \times 10^5 \text{ Pa}$. If the external pressure is increased quasistatically to $2 \times 10^5 \text{ Pa}$, what is the final equilibrium pressure of the system if the temperature of the system is maintained constant? What is the corresponding final volume? How much work is done on the system by the surroundings for the change from the system's initial state to the system's final state? How would you represent this change on a P, V diagram?
6. In a P, V diagram, why must all real changes be represented by a dashed line, rather than a solid line?
7. For a change from any state [1] to any state [2], the work performed may be expressed as the integral of the infinitesimal amounts of work δw

$$\text{Total work done in change from state [1] to state [2]} = \int_{\text{state [1]}}^{\text{state [2]}} \delta w$$

How would you explain that, although this integral is valid and meaningful, the statement

$$\int_{\text{state [1]}}^{\text{state [2]}} \delta w = w(\text{state [2]}) - w(\text{state [1]})$$

is not only wrong, but meaningless? And if this is indeed wrong and meaningless, how,

if at all, can the integral $\int_{\text{state [1]}}^{\text{state [2]}} \delta w$ be evaluated?

8. Rather harder: As in question 5, the external pressure is initially $1 \times 10^5 \text{ Pa}$, but now this is increased instantaneously to $2 \times 10^5 \text{ Pa}$. Suppose that the system's final equilibrium state is that same as the final state of question 5. Assuming that the change of state takes place at constant temperature, is the change in state of the system quasistatic? How might you represent this change in state on a P, V diagram? How might you estimate the work done on the system by the surroundings? How does this answer compare to the answer to question 5?
9. What are 'static' friction and 'dynamic' friction? In questions 4, 5 and 6, one of the assumptions we made was that the piston was frictionless. Suppose now that the surfaces between the piston and the interior of the cylinder are subject to both these types of friction. The initial state of the system is a volume of 0.5 m^3 , and a pressure of $1 \text{ bar} = 1 \times 10^5 \text{ Pa}$, and the external pressure is also $1 \text{ bar} = 1 \times 10^5 \text{ Pa}$. The external pressure now reduces by an infinitesimal amount – which, in the absence of friction, would cause the piston to move against the (now infinitesimally smaller) external pressure, as

described on page 29. But what happens in the presence of both static and dynamic friction? Describe what you would observe as the external pressure is progressively reduced until the piston has moved such that the final volume of the system is 0.75 m^3 . What is the final pressure of the system? Represent the path actually followed, in the presence of friction, on a P, V diagram. What is the P, V work of expansion done by the system on the surroundings? How does this quantity of work compare to the quantity of work that would have been performed in the absence of friction?

3

Temperature and heat



Summary

Temperature is an intensive state function, and a measure of the average energy of the molecules with the system.

Heat is the transfer of energy between two systems at different temperatures. Like work, heat q is a path function, and an infinitesimal flow of heat is represented as an inexact differential δq .

The **Zeroth Law of Thermodynamics** states that

If two systems are each in thermal equilibrium with a third system, then they will be in thermal equilibrium with each other. Each of the three systems may be associated with an intensive state function, temperature, which, in this case, will take the same value for each system.

An **ideal gas** is one that obeys the **equation-of-state**

$$PV = nRT \quad (3.3)$$

An **isolated** system is surrounded by a boundary which prevents both the flow of matter, and also the flow of energy in the form of heat and work.

A **closed** system is surrounded by a boundary which prevents the flow of matter, but allows the exchange of energy, in the form of both heat and work, between the system and the surroundings.

An **open** system is surrounded by a boundary which allows the exchange of matter, and also the exchange of energy, in the form of both heat and work, between the system and the surroundings.

The average molecular energy $\langle \mathcal{E} \rangle$ of an ideal monatomic gas is proportional to the temperature T as

$$\langle \mathcal{E} \rangle = \frac{3}{2} k_B T \quad (3.19)$$

where k_B is Boltzmann's constant. Although equation (3.19) is valid only for an ideal monatomic gas, the interpretation of the temperature T as a measure of a system's average molecular energy is of more general applicability.

3.1 Temperature

3.1.1 Temperature is an intensive state function

Another state function of any system is its temperature, which determines how hot, or cold, the system is. Since the temperature of a system does not depend on the system's size or extent,

temperature is an intensive state function. And to measure temperature, we need a suitable scale of measurement, and an appropriate instrument.

3.1.2 Temperature scales

Over the years, several scales of measurement have been devised, of which four in particular have been widely accepted. The **Fahrenheit** scale is named after Daniel Fahrenheit, a German physicist, who, in 1724, took the freezing point of pure water as '32' on his scale, and the boiling point as '212', dividing the interval between these two points into 180 equally-spaced 'degrees', designated °F. Twenty years later, the Swedish astronomer Anders Celsius defined the zero of the **Celsius** (alternatively, and now less commonly, **Centigrade**) scale as the freezing point of pure water, and the boiling point as 100, with 100 intermediate degrees, °C. Temperatures measured in °C are conventionally represented by the symbol t .

A third scale, the **thermodynamic scale**, is of especial significance to scientists in general, and this book in particular. The unit of measurement of the thermodynamic scale is the kelvin, K, (without the ° symbol), named in honour of William Thomson, Lord Kelvin, one of the greatest scientists of the nineteenth century, and whose name will appear many times in this book. As we have just seen, the Fahrenheit and Celsius scales both took two reference points – freezing water and boiling water – and then determined the size of the unit of measurement by dividing the interval between these two reference points into 180 or 100 equally-spaced degrees. The thermodynamic scale is derived rather differently: the size of the unit of measurement, one K, is defined to be the same as one °C, and so only one reference point is needed, this being a somewhat less familiar property of water known as the **triple point** – the state in which ice, (liquid) water and water vapour are mutually in thermodynamic equilibrium. The triple point of water is a very special state, for it can exist only at a single, specific combination of temperature and pressure – if the pressure is maintained, then at higher temperatures, the ice is unstable and melts, with liquid water being in thermodynamic equilibrium with water vapour until the water boils; and at lower temperatures, liquid water freezes. The thermodynamic scale of temperature uses the triple point of water as its reference point, defining – for reasons that will be explained later in this book (see page 480) – the corresponding temperature as 273.16 K, with the freezing point of water being very close by, 273.15 K. Temperatures measured in kelvin are conventionally represented by the symbol T , where the use of upper case distinguishes the use of the Kelvin scale from the use of the Celsius scale, which, as we have seen, is represented by the lower case symbol t . Zero on the thermodynamic scale, equivalent to -273.15°C , is known as **absolute zero**: as we shall see in Chapter 12, this extremely low temperature can be approached, but never actually reached.

The fourth scale, known as the **ideal gas scale** and, like the thermodynamic scale, defines its unit-of-measure as the kelvin K, equal to 1°C . Whereas the thermodynamic scale uses the triple point of water as its reference point, the ideal gas scale takes its reference, and zero, point to be absolute zero, -273.15°C .

3.1.3 Temperature measurement

To measure the temperature of a system of interest, an appropriate instrument – a thermometer – is usually placed in contact with the system, and, a very short time later, we take a reading from the thermometer's scale. A moment's thought shows that the temperature we actually measure is the *temperature of the thermometer*, rather than the temperature of the system, and we then assume that the thermometer's temperature is also the temperature of the system. We never think about, or even recognise, this assumption, so let's take a moment here to examine it, and to understand the underlying science.

All temperature measurement is based on a very familiar phenomenon: when a colder system is in contact with a hotter one, the colder one becomes hotter, and the hotter one colder, until both systems achieve the same, stable, temperature, indicating that the two systems are now in thermal equilibrium. The final, equilibrium, temperature is somewhere between the two original temperatures, depending on the masses, and materials, of the two systems: if the materials are the same, and the two masses equal, then the final equilibrium temperature is half-way between the two original temperatures; if the materials are the same, and one mass is rather greater than the other, then the final temperature is towards the original temperature of the greater mass; and if the mass of one of the two systems is negligible compared to the mass of the other, then the final equilibrium temperature is sensibly equal to the original temperature of the greater mass. The implication for this as regards the measurement of temperature is that any instrument used for that measurement – a thermometer – must be very small and light compared to the system whose temperature is to be measured, so that, when the thermometer is in contact with that system, the final equilibrium temperature of the thermometer is as closely as possible equal to the original temperature of the system.

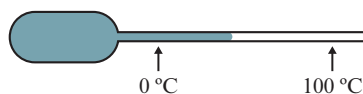


Figure 3.1 A representation of a mercury-in-glass thermometer. As the temperature of the mercury changes, the volume the mercury occupies also changes. Since the volume of the bulb on the left is fixed, this change in volume can be seen as a change in the length of the column of mercury within the sealed capillary tube. The void space in the capillary tube is a vacuum, so ensuring that the mercury can expand or contract freely, without being subject to an external pressure.

To enable the temperature of a thermometer to be measured easily, the thermometer needs to make use of a property that changes with temperature. A good example of this is the (nowadays somewhat old-fashioned!) mercury-in-glass thermometer, depicted in Figure 3.1, which comprises a reservoir of mercury, attached to a very narrow, sealed, capillary tube, the void space of which is a vacuum. Over a wide range of every-day temperatures, mercury is a liquid – a liquid whose volume changes with temperature, such that the higher the temperature, the greater the volume. When the bulb of the thermometer is placed in contact with the system whose temperature is to be measured, the mercury will contract or expand. Since the volume of the bulb is fixed, this contraction or expansion takes place within the capillary

tube. Because the diameter of the capillary tube is very small, any changes in the volume of the mercury correspond to easily observable changes in the length of the mercury within the capillary. When the thermometer is placed in a mixture of ice and water, under normal atmospheric pressure, the position of the mercury in the capillary can be marked as 0°C , and when the bulb is placed into gently boiling water, also under normal atmospheric pressure, the (now different) position of the mercury can be marked as 100°C . The interval between these two marks can then be divided into 100 equal divisions, allowing the temperature of any other body (within these ranges), as measured on the Celsius scale, to be determined with ease.

All other types of thermometer work on the same principle, but using other properties which are sensitive to temperature, such as the resistance of an electrical circuit or the colour of a liquid crystal, and many modern thermometers have a digital readout.

3.2 The ideal gas law

As we saw on page 16, Boyle's Law

$$PV = \text{constant} \quad (1.3)$$

describes the relationship between the pressure P and volume V of a fixed mass of an ideal gas, undergoing changes in state at constant temperature. What, though, happens when the temperature changes? Around 1700, the French scientist Guillaume Amontons demonstrated that, at constant volume, the pressure of a given mass of air increases linearly with temperature; rather later – in the 1780s – another French scientist, Jacques Charles, also showed that, at constant pressure, the volume of a given mass of air increases linearly with temperature. These results are valid at temperatures easily accessible in a laboratory, but – as we saw with Boyle's Law – for real gases, these simple relationships break down as the conditions become more extreme. If, however, we consider the hypothetical ideal gas, then we can assert that these linear relationships apply at all temperatures, illustrated graphically in Figure 3.2, in which the horizontal temperature axes are defined using the Celsius scale.

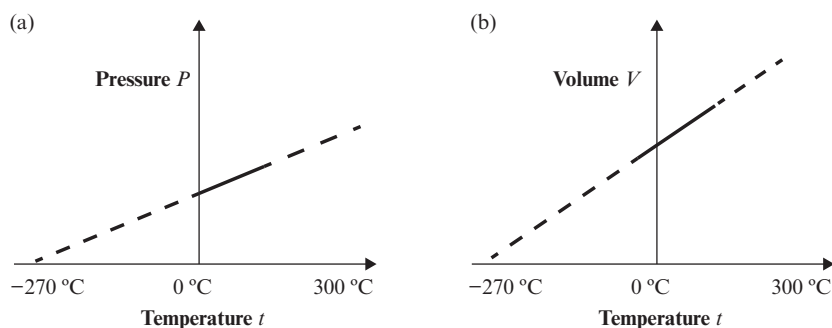


Figure 3.2 The ideal gas law. Graph (a) shows the linear relationship between the pressure P and temperature t of a given mass of an ideal gas at constant volume, and graph (b) shows the linear relationship between the volume V and temperature t of a given mass of ideal gas at constant pressure. If the temperature is measured on the Celsius scale, although the two lines have different slopes, they both intercept the temperature axis at the same point, close to -270°C .

Experimentally, measurements are usually made at temperatures which are readily attained in a laboratory, say from a few degrees below 0 °C, to temperatures around 100 °C, as indicated by the solid line segments in Figure 3.2. Although the slopes of the volume-temperature and pressure-temperature graphs are different, when extrapolated, they both intercept the temperature axis at the same point, close to –270 °C. One interpretation of this is that, as the temperature approaches –270 °C, the volume of the gas approaches zero, as does its pressure. Since it is difficult to imagine a gas with a volume, or pressure, less than zero, the temperature close to –270 °C – now recognised as –273.15 °C – was designated as **absolute zero**, the lowest possible temperature.

Mathematically, we can represent these two linear relationships as

$$P = c_1(t + 273.15) \quad \text{for a given mass of gas at constant volume}$$

and

$$V = c_2(t + 273.15) \quad \text{for a given mass of gas at constant pressure}$$

In these equations, c_1 and c_2 are appropriate constants, and, in accordance with the extrapolation of experimental data, when $t = -273.15$ °C, both $P = 0$ and $V = 0$.

If, however, we define a new variable T such that

$$T = t + 273.15$$

then we can write two rather simpler relationships

$$P = c_1 T \quad \text{for a given mass of gas at constant volume} \quad (3.1)$$

$$V = c_2 T \quad \text{for a given mass of gas at constant pressure} \quad (3.2)$$

so that when $T = 0$, both $P = 0$ and $V = 0$. The variable T defines a new temperature scale, the ideal gas scale, whose zero is at absolute zero, –273.15 °C, and whose unit of measurement is of the same size as one °C. The ideal gas scale is identical to the thermodynamic scale, subject to the slight (but important) difference in the definition of each scale's reference point – the reference point of the ideal gas scale is (the in practice unattainable) absolute zero, whereas the reference point of the thermodynamic scale is the well-defined, and directly observable, triple point of water. As we noted earlier (see page 44), given the equivalence between the ideal gas scale and the thermodynamic scale, both use the same unit of measurement, the kelvin K.

Equations (3.1) and (3.2) can be combined with Boyle's Law

$$PV = c_3 \quad \text{for a given mass of gas at constant temperature} \quad (1.3)$$

into a single equation, first identified by the French scientist Émile Clapeyron in 1834,

$$PV = nRT \quad (3.3)$$

In which n represents the number of moles of gas (and hence the amount, and – given the appropriate molecular weight – the mass, of gas), and R is a constant, known as the **ideal gas constant**, **universal gas constant**, or **gas constant**, and whose value is $8.314462 \text{ J K}^{-1} \text{ mol}^{-1}$.

Equation (3.3) is known as the **ideal gas law**, and represents a more complete equation-of-state for an ideal gas than Boyle's Law, and the two associated laws, equations (3.1) and (3.2).

3.3 A very important principle

If we define the **molar volume** $V = V/n$, then the ideal gas law becomes

$$PV = RT \quad (3.4)$$

Whereas V and n are both extensive state functions, the ratio $V/n = V$ is an intensive state function, implying that – since R is a constant – the equation-of-state (3.4) is expressed in terms only of intensive state functions. Furthermore, if any two of the variables P , V or T are known, then equation (3.4) allows us to compute the third, unknown, variable. This implies that an ideal gas, as described by the equation-of-state (3.4), has two, and only two, independent state functions.

This is in fact a special case of a very important general principle:

In the absence of gravitation, motion, electric, magnetic and surface effects, a fixed mass of a pure substance has two, and only two, independent state functions.

From the standpoint of most of chemical and biochemical thermodynamics, the exclusion of gravitation and the rest is not a problem – and if any of these effects (such as an electric effect, as is relevant to electrochemistry) do apply in a particular instance, the principle can be modified accordingly.

This principle is therefore of very broad applicability, and it is important because it tells us that the state of a given, constant, mass of any pure substance can be defined by reference to two, and only two, state functions. If any two state functions are known, all other state functions can be calculated, once we know the appropriate mathematical relationships, of which the ideal gas law, equation (3.4) is one example. And if we need to calculate the value of any of the extensive state functions, then we can do this once we know n , the number of moles present in the system of interest.

We shall refer to this principle many times in this book, for it is the starting point for gaining an understanding of many thermodynamic systems.

3.4 Dalton's law of partial pressures

The ideal gas law, as written in the form

$$PV = nRT \quad (3.3)$$

applies to n mol of a pure substance. Furthermore, two of the assumptions underpinning the definition of an ideal gas are that

- the molecules of an ideal gas occupy no volume, and
- there are no intermolecular interactions.

A consequence of the first assumption is that the total volume V of the system is available to every individual molecule – no space is denied as a result of being ‘full of something else’. The

second assumption implies that no individual molecule is influenced in any way by any other molecules that are present – the behaviour of each molecule is independent of all the others.

Suppose, then, that a vessel of interior volume V contains molecules of two different ideal gases: say, n_A mol of an ideal gas A and n_B mol of an ideal gas B, giving a total $n = n_A + n_B$ mols for the whole system. Each molecule of ideal gas A has access to the entire volume V , and, at a given temperature T , moves around that volume at random, occasionally impacting the walls of the vessel, and exerting pressure, as described on page 17. If we represent the total pressure exerted by the n_A molecules of ideal gas A as p_A , then equation (3.3) must apply, and we may write

$$p_A V = n_A RT$$

Similarly, the molecules of ideal gas B are also exerting a pressure p_B such that

$$p_B V = n_B RT$$

The total pressure P exerted on the inside of the vessel is attributable to all molecular impacts, and so

$$P = p_A + p_B$$

Multiplying by V , we have

$$PV = p_A V + p_B V = n_A RT + n_B RT = (n_A + n_B) RT$$

Since the total number n of molecules, of both types, is $(n_A + n_B)$, we therefore return to the familiar ideal gas law

$$PV = nRT \tag{3.3}$$

where, for a mixture of n_A mol of an ideal gas A and n_B mol of an ideal gas B,

$$n = n_A + n_B$$

and

$$P = p_A + p_B$$

The two pressures, p_A and p_B , are each known as the **partial pressure** of the appropriate component. Physically, each represents the pressure that each gas would exert, independently, if it were to occupy the whole volume V alone, as is consistent with the assumption of the ideal gas. For a mixture of more than two ideal gases, the total pressure P of the system is the sum of the individual partial pressures p_i for each component

$$P = \sum_i p_i \tag{3.5}$$

This result is known as **Dalton's law of partial pressures**, and, as we shall see (particularly in Chapter 14), it plays a central role in understanding gas phase chemical reactions, which are inherently gaseous mixtures in which the quantities of the various components – and hence their partial pressures – change as the reaction progresses.

Dalton's law represents a special case of the linear additivity of state functions – applied, in this case, to the intensive state functions, the partial pressures of the components A and B. As we saw on page 8, linear additivity is a characteristic of ideal substances, as is consistent with the assumption that both A and B are ideal gases, and that the ideal gas law applies.

3.5 Some other equations-of-state

The ideal gas law, equation (3.3)

$$PV = nRT \quad (3.3)$$

is just one example of an equation-of-state. For solids and liquids, the determination of valid equations-of-state is a challenging problem in condensed matter physics; for **real gases**, the ideal gas equation can be modified to relax the ideal assumptions noted on page 17 that the molecules occupy no volume, and that there are no intermolecular interactions, as, for example, expressed by the **van der Waals equation**

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \quad (3.6)$$

Berthelot's equation

$$\left(P + \frac{an^2}{TV^2}\right)(V - nb) = nRT \quad (3.7)$$

and

Dieterici's equation

$$P(V - nb) = nRT \exp\left(-\frac{na}{RTV}\right) \quad (3.8)$$

In all of these equations, a is a constant related to the strength of intermolecular forces (which tend to bind neighbouring molecules together), and b represents the actual volume occupied by 1 mole of molecules (which acts to reduce the volume available for the gas to occupy).

From a pragmatic standpoint, the **virial equation-of-state**

$$PV = nRT \left(1 + B\frac{n}{V} + C\frac{n^2}{V^2} + D\frac{n^3}{V^3} + \dots\right) \quad (3.9)$$

in which $B, C, D \dots$ are known as the second, third, fourth ... **virial coefficients**, is very useful: the parameters $B, C, D \dots$ are not directly related to physical quantities such as the volume actually occupied by the molecules – rather, they are determined empirically from experimental data for any given real gas. The virial equation-of-state therefore makes no fundamental physical assumptions that may, or may not, apply in any specific circumstances, but is rooted in experimental reality.

3.6 Heat

3.6.1 What happens when hot things cool down, and cold things warm up?

When a hot block of metal at, say, 80 °C is in contact with a colder block of the same metal at, say, 20 °C, we observe that the originally hot block cools down, and the originally colder block heats up, until both blocks achieve the same temperature somewhere between 80 °C and 20 °C. That's a very common-place observation - but what is actually happening?

It's very tempting to explain this observation in terms of the transfer of some 'substance X' from one system to another. If we imagine that the presence of this 'substance X' confers

‘hotness’, with hotter bodies having more of ‘substance X’ than colder ones, then when the two blocks of metal are in contact, it seems as if the originally hotter block loses some ‘substance X’, so becoming cooler, whilst, at the same time, the originally colder block gains some ‘substance X’, so becoming hotter.

And it’s even more tempting to imagine that the amount of ‘substance X’ lost by the originally hotter system is equal to the amount gained by the originally colder system, so that the total quantity of ‘substance X’ remains the same. This would imply some sort of ‘law of conservation’, in which the total quantity of ‘substance X’ is constant, but with this total quantity being distributed around different systems in different ways. Let’s, for the moment, call ‘substance X’ heat.

So far, so good, and the ‘law of the conservation of heat’ satisfactorily explains what happens in many situations in which hotter systems are in contact with colder ones. But there was another, very familiar, phenomenon where it was a lot harder to understand how a ‘law of the conservation of heat’ might actually work.

3.6.2 The experiments of Rumford and Joule

That other phenomenon is the way in which a colder system can become hotter, not by contact with something hotter, but as a result of work. We all experience this personally, as we become progressively warmer as we work progressively harder; and we’ve all noticed a very similar effect whenever our work involves friction – for example, when cutting wood with a saw, our experience is that both the saw *and* the wood become hot. And we become hot too, as a result of all that hard work! This is a real puzzle: how is it possible for three originally cold systems – the saw, the wood and me – all to become hot together, without any of these three systems being in direct contact with something hotter to start with? And the more work we do, the hotter everything becomes, as if the work is somehow creating heat from absolutely nothing. This poses a fundamental problem for a ‘law of the conservation of heat’: by definition, a ‘conservation’ law rules out the possibility that heat can be ‘created’, apparently out of nothing – but this is precisely what appears to be happening with work.

The fact that work can make things hotter has been known since ancient times, but was first explored methodically by one of the more colourful figures in the history of science – Benjamin Thompson, Count Rumford (no relation to William Thomson, Lord Kelvin, despite the similarity in names and their noble titles!). Born in 1753 in a small village in the then-English colony of Massachusetts, Rumford came to London in 1781, spent many years in Bavaria, and died in 1814 in Paris. Whilst involved with the reorganisation of the Bavarian army, he became interested in the manufacture of cannon. The barrel of a cannon is a cylinder of metal, with a deep ‘hole’ in it – the ‘hole’ through which the cannon ball will be fired. In Rumford’s day, the barrel was typically made from solid bronze, and the ‘hole’ was then drilled out. Rumford noticed that as the drilling took place, the bronze became progressively hotter, without limit: the more drilling that was done, the hotter the metal became – observations which he published in 1798. Rumford realised that the rise in temperature was attributable to the friction between the drill and the bronze, friction directly associated with the work being done to drive the drill through the metal.

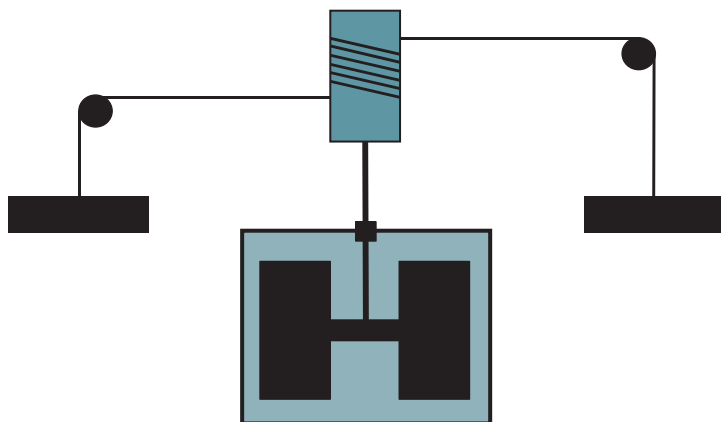


Figure 3.3 A schematic representation of Joule's apparatus. As the masses to the left and right fall, the paddle rotates within some water. The temperature of the water is observed to rise.

Rumford's findings were refined by James Joule, a somewhat less exotic figure, but a great scientist nonetheless. In his laboratories in Manchester, England, Joule carried out a series of meticulous experiments during the early 1840s to investigate the relationship between work and heat. His most ingenious apparatus, illustrated in Figure 3.3, was a mechanism in which two falling masses, each of mass M kg, caused a paddle, immersed in water, to rotate. As the masses fall a distance h m, they do work equal to $2Mgh$ J; this work is harnessed to drive the paddle; and, as the paddle rotates against the water, the internal friction causes the temperature of the water to rise – just like the result of the friction between Rumford's drill and the bronze. Joule's studies, reported in 1845, determined that 4410 J of work (the unit of work is named in his honour) consistently raise the temperature of 1 kg of water by 1°C , so quantifying what became known as the **mechanical equivalent of heat**. In 1850, Joule published a refined estimate of 4159 J – very close to the currently accepted value of 4186 J.

3.6.3 A modification of Joule's experiment

Let's now make an imaginary modification to Joule's experiment – instead of using falling masses to rotate the paddle, let's connect the shaft of the paddle to the piston of a cylinder, so that as the piston moves to the right in Figure 3.4, the paddle rotates.

The piston is held in place by the now-familiar peg 1. When this peg is removed, and if the gas pressure P inside the cylinder is greater than the external pressure P_{ex} , the piston moves to the right, so causing the paddle to rotate. And in expanding, the gas is doing work, some of which (as we saw on page 27) is required to 'push back the atmosphere,' and some used to rotate the paddle. Now the paddle, and the surrounding water, do not 'know' that the paddle is being rotated by the expansion of a gas rather than by the falling of a mass – as far as the water is concerned, the paddle is rotating and the water is getting hotter. And if there happens to be 1 kg of water, then it will take 4186 J of work to raise the temperature by 1°C , regardless of whether the work is performed by a falling mass, or by the expansion of a gas in a cylinder.

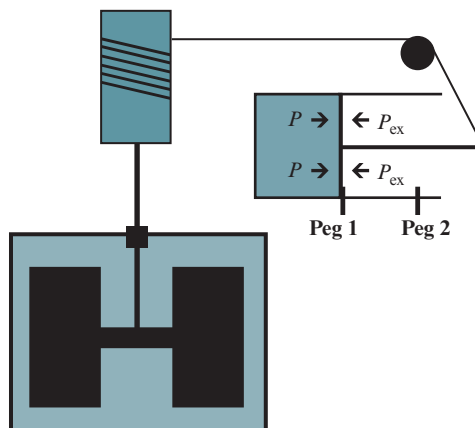


Figure 3.4 An alternative version of Joule's experiment. In this experiment, the pressure P inside the cylinder is greater than the external pressure P_{ex} . If peg 1 is removed, the piston moves to the right, the paddle rotates, and the temperature of the water rises – just as happens when the rotation of the paddle is caused by the falling of a mass.

The heating of the water is attributable to the work done by the expansion of the gas, but, as we saw on page 40, the work performed by the expansion of the gas is itself attributable to the energy of the gas in the cylinder before the peg was removed. In this experiment, the energy originally in the gas has been transformed firstly into work, and then into heat – indeed, if much of the mechanics of the apparatus were contained within a ‘black box’, we would not observe the intermediate stages, and we would infer that the energy of the gas is directly causing the temperature of the water to rise. This therefore implies that *energy is not only the capacity to perform work: it's also the capacity to transfer heat*.

3.6.4 The conservation of energy

Joule's experiment confirmed the ‘mechanical equivalent of heat’, the fact that it is possible to transform a given amount of work into a corresponding amount of heat. But our extension of Joule's experiment illustrates that the ‘mechanical equivalent of heat’ is, more fundamentally, an ‘energetic equivalent of heat’: since energy is the capacity to perform work as well as the capacity to transfer heat, then energy, work and heat are all, fundamentally, the same.

This insight resolves the paradox of the ‘law of the conservation of heat’: it isn't heat that is being conserved – it's energy. So, when a hotter system is placed in contact with the colder system, energy is transferred from the hotter system to the colder system, so that the hotter system cools down, and the colder system warms up, until both systems achieve the same temperature. The *process of energy transfer* from the hotter system to the colder one is what we call **heat**, and whilst this process is taking place, the energy lost by the hotter system equals that gained by the colder system, and so energy is conserved.

In Count Rumford's experiments on drilling bronze cannon, the heat produced during the process of drilling isn't ‘created from nothing’ – it's the transfer of energy resulting from the work needed to operate the drill. So, once again, energy is conserved.

We'll take a more extensive look at the relationships between energy, work and heat, and also at the corresponding conservation law, in the next chapter: for the moment, we'll look at some further aspects of heat and temperature.

3.6.5 Units of measurement for heat

Since energy, as well as being 'work-in-waiting', is also 'heat-in-waiting', then the unit of measurement for heat is most sensibly the same as the unit of measurement used for both energy and work, namely the Joule, J. Historically, however, heat was being studied for a long time before it was realised that heat is in fact a manifestation of energy. These studies required a unit of measurement, and so the 'calorie' was defined as 'the amount of heat required to raise the temperature of 1 gram of pure water by 1 °C (specifically, from 14.5 °C to 15.5 °C) at a pressure of 1 atmosphere'. An associated unit, the 'Calorie' (with an upper case C) or 'kilocalorie', has a similar definition, but as applied to 1 kilogram of pure water. When Joule's experiment established that $4159 \text{ J} = 1 \text{ Calorie}$, the use of the calorie, and Calorie, as units of measurement for heat became redundant, for any measurement in calories (or Calories) can be converted into a measurement in J using the conversion factor $1 \text{ Calorie} = 4159 \text{ J}$. As it happened, however, the calorie, and Calorie, remained in use for many years as the units of measurement for heat, long after Joule's experiment, and continue to be used to this day in connection with, for example, the specification of the energy content of many foods, as shown on the labels on food packaging. Scientifically, however, the SI unit for work, energy and heat is the Joule, J.

3.6.6 Thermal contact

If heat can flow from one system to another, then those systems are said to be in **thermal contact**. Thermal contact can be the result of physical proximity, as when something hot is in direct contact with something cold, in which case we speak of the **conduction** of heat (for heat flow within, or between, solids), or the **convection** of heat (for heat flow within, or between, fluids). Heat flow can also take place across distances – for example, the heat flow from the sun to the earth – in which case we speak of **radiation**.

3.6.7 Heat isn't a substance, it's a description of a process

Very importantly, we now appreciate that heat isn't some form of *substance*; rather, it's the name we give to the *process* in which energy is transferred either

- between two systems in thermal contact, one hotter and one colder, so that the hotter system becomes cooler, and the colder system hotter, or
- as the result of work being done on a system, causing that system to become hotter.

Taking the case of the transfer of energy from a hotter system to a colder system, we also know that hotter systems are associated with higher temperatures, and colder systems with lower temperatures. A temperature difference between two systems is known as a **temperature gradient**, so another way of defining heat is the process of energy flow down a temperature gradient.

3.6.8 The 'Zeroth' Law of Thermodynamics

The definition of heat as the process of energy flow down a temperature gradient has two, rather hidden, implications. The first is that if there is no temperature gradient between two systems – that is, if the two systems have the same temperature – then there is no transfer of energy, and no flow of heat, this being the situation which we have already defined (see page 9) as thermal equilibrium. Looked at the other way around, if two systems are in thermal contact and there is no flow heat, then we can infer that they are at the same temperature. This leads to what is sometimes called the **'Zeroth' Law of Thermodynamics**:

If two systems are each in thermal equilibrium with a third system, then they will be in thermal equilibrium with each other. Each of the three systems may be associated with an intensive state function, temperature, which, in this case, will take the same value for each system.

This statement highlights an empirical observation – thermal equilibrium, and the corresponding absence of heat flow – and introduces an associated thermodynamic state function, in this case, temperature. We all experience situations in which we detect heat flows between systems, and we also experience systems which are not associated with the flow of heat: these are every-day empirical observations. The Zeroth Law then tells us that if each system can be associated with an intensive state function, temperature, then if the temperatures of two systems are the same, there will be no heat flow, but if the temperatures of the two systems are different, then heat flow between them. Conversely, if we detect no heat flow between two systems in thermal contact, then they are at the same temperature; if we do detect a flow of heat, then they are at different temperatures. As we shall see for the First and Second Laws of Thermodynamics (see pages 94 and 268, respectively), these too can be expressed in terms of an empirical observation, and the introduction of an associated state function.

3.6.9 Heat flow is unidirectional

The second implication of the fact that a temperature gradient between two systems in thermal contact causes a flow of energy so that the originally hotter system becomes colder, and the originally colder system becomes hotter, is that this statement implicitly contains a statement of directionality – the energy flow is *down* the temperature gradient, from the higher temperature system to the lower, not *up* it. This 'unidirectionality' has very considerable significance, as we shall see in Chapter 8.

3.6.10 Heat is a path function

We now appreciate that a system does not 'have' heat; rather, heat is the name we give to the process in which heat is transferred between two systems, in thermal contact and originally at different temperatures, until such time as the temperature across both systems becomes uniform, and the flow of heat stops. Heat is therefore not a property of a state, but rather a phenomenon that can be measured only as a system changes state – just as we saw on pages

24 in relation to work. Heat, like work, is therefore a **path function**, and the amount of heat transferred during any change of state will depend on the path taken. Accordingly, a small quantity of heat is represented as δq and, like δw , δq is signed, according to whether the system gains or loses heat during the corresponding change of state:

- Heat **gained by** a system is represented by a **positive** number.
- Heat **lost from** a system is represented by a **negative** number.

For any finite change of state from state [1] to state [2], the total amount of heat $\{q_2\}_X$ gained by, or lost from, the system can be determined by summation or integration as

$$\{q_2\}_X = \sum_{\text{state [1]}}^{\text{state [2]}} \delta q = \int_{\text{state [1]}}^{\text{state [2]}} \delta q \quad (3.10)$$

where the notation $\{ \dots \}_X$ indicates that the specific value of $\{q_2\}_X$ for a particular change in state depends on the path X taken.

Also, since heat is a path function, this implies that, for any thermodynamic cycle

$$\oint \delta q \neq 0 \quad (3.11)$$

As with work, the net amount of heat gained by, or lost from, a system during a thermodynamic cycle can be evaluated only by reference to the specific path followed, some elements of which will be associated with the gain of heat, some with the loss. Overall, however, for a complete thermodynamic cycle, the result will be either a positive (net heat gained) or a negative (net heat lost) number; it will not be zero.

One further thought in relation to heat as a path function: as we saw earlier (see page 39), the path function work, δw , is linked to the two state functions pressure P and volume V by the equation

$$\delta w = P dV$$

which we expressed in a more generic form

$$\delta(\text{path function}) = (\text{intensive state function}) \times d(\text{extensive state function})$$

We now know that heat, δq , is a path function, and very much associated with the intensive state function temperature T . So that triggers a hunch that

$$\delta q = T d(\text{an extensive state function})$$

What that extensive state function might be is not so obvious, and, as we shall see in Chapter 9, one of the great triumphs of thermodynamics was the discovery of what that state function actually is.

3.7 Some more definitions

Now we have a deeper understanding of heat, there are a few more technical terms that we need to define, which we do here.

3.7.1 Isolated, closed and open systems

We have already seen that a system is that part of the universe selected for study, and that any system is separated from the surroundings by the system boundary. Within this broad definition of ‘system’, it is useful to distinguish three categories:

- An **isolated system** is one whose boundary prevents the exchange of both matter and energy with the surroundings.
- A **closed system** is one whose boundary prevents the exchange of matter with the surroundings, but allows the transfer of energy, for example, as work or heat.
- An **open system** is one whose boundary allows the transfer of both matter and energy with the surroundings.

Living things are open systems in that all living things exchange matter with their surroundings (for example, by eating and breathing), as well as energy (photosynthesis in green plants, for example, uses light energy to transform carbon dioxide and water into glucose and oxygen).

The now-familiar system of a gas in a cylinder with a moveable piston is an example of a closed system – the walls of the cylinder and the seal around the piston stop any of the internal gas from leaking out, as well as stopping any matter in the surroundings from getting in, so preventing the exchange of matter, whilst the moveable piston allows the system to perform work on the surroundings (if the piston moves outwards), and also the surroundings to perform work on the system (if the piston moves inwards). Furthermore, if the walls of the cylinder are made of a material which can conduct heat – for example, metal – then heat too can be exchanged with the surroundings.

An example of an isolated system is a gas within a sealed container, the walls of which are fixed, and made of a material that provides perfect thermal insulation. The fact that the container is sealed stops any matter from getting in or out; the rigid walls can’t move, and so no work can be done either by the system or on it; and the thermal insulation prevents any exchange of heat. In practice, however, there are no truly perfect thermal insulators, so any real system (with one exception, to be noted very shortly) is only an approximation to a theoretical isolated system: the exception is the universe as a whole, for we are free to position the boundary as far into deep space as we like ...

3.7.2 Isothermal and adiabatic changes in state

Systems can change their state in many different ways, but two types of change of state are particularly important:

- An **isothermal** change of state is one in which the temperature of the system is maintained constant throughout the change, and an **isotherm** is a plot on a diagram, such as a P, V diagram, that defines an isothermal path.
- An **adiabatic** change of state is one in which there is no exchange of heat between the system and the surroundings, and an **adiabat** is a plot on a diagram, such as a P, V diagram, that defines an adiabatic path.

An isothermal change usually requires the flow of heat into, or out of, the system, and so can take place within an open or a closed system, but not within an isolated one; changes within

an isolated system are necessarily adiabatic. A closed system can undergo an adiabatic change if its boundaries allow work to be done by, or on, the system, but block the transfer of heat; an open system can in principle undergo an adiabatic change under specific circumstances in which heat is not exchanged with the surroundings, even though heat exchange is in principle possible – but this is very rare.

3.7.3 Isobaric and isochoric changes in state

The terms isothermal and adiabatic are used frequently; here are two other terms which, though used rather less frequently, are also worth noting:

- An **isobaric** change of state is one in which the pressure of the system is maintained constant throughout the change, and an **isobar** is a plot on a diagram, such as a P, V diagram, that defines an isobaric path. On a P, V diagram, an isobar is necessarily horizontal.
- An **isochoric** change of state is one in which the volume of the system is maintained constant throughout the change, and an **isochore** is a plot on a diagram, such as a P, V diagram, that defines an isochoric path. On a P, V diagram, an isochore is necessarily vertical.

3.8 How to get work from heat

3.8.1 The steam engine

Around the time that Count Rumford was in Bavaria studying how work is converted into heat during the drilling of bronze cannon, some 2,000 km away to the north-west, the brilliant Scottish engineer James Watt, working firstly in Scotland and then in England, was doing the very opposite – perfecting his machine that converted heat into work, a machine known as a steam engine. Steam engines played a very important role in the development of thermodynamics, for they are devices that transform the heat produced from burning a fuel such as wood or coal, and later oil, into useful work that can be harnessed to drive a locomotive or industrial machinery, as achieved by exploiting the P, V work done by the expansion of a gas, steam. The invention, and development, of a reliable steam engine was of enormous significance: up to that time, the only sources of work were animals and human beings (which need to be fed, and get tired), windmills (which rely on the wind), water-mills (which require a steady flow of water, and need to be sited accordingly), and – to a very much more limited extent – falling weights (as used to power clocks). Steam engines are much more reliable, and can be sited anywhere – all they need is a supply of fuel to burn, and water to boil.

Watt's steam engines were sophisticated machines, and – as with all great inventions – built on a succession of earlier endeavours, such as the engines designed and constructed by Thomas Newcomen (who, with John Cawley, was awarded a patent in 1705), Thomas Savery (around 1698), Denis Papin (1688), the Marquis of Worcester (1663), and Giovanni Branca (1629) – indeed the earliest documented record of heat producing work, of the very first steam engine, is the 'aeolipile', described by Heron (sometimes known as Hero) of Alexandria some 2,000 years ago, as illustrated schematically in Figure 3.5.

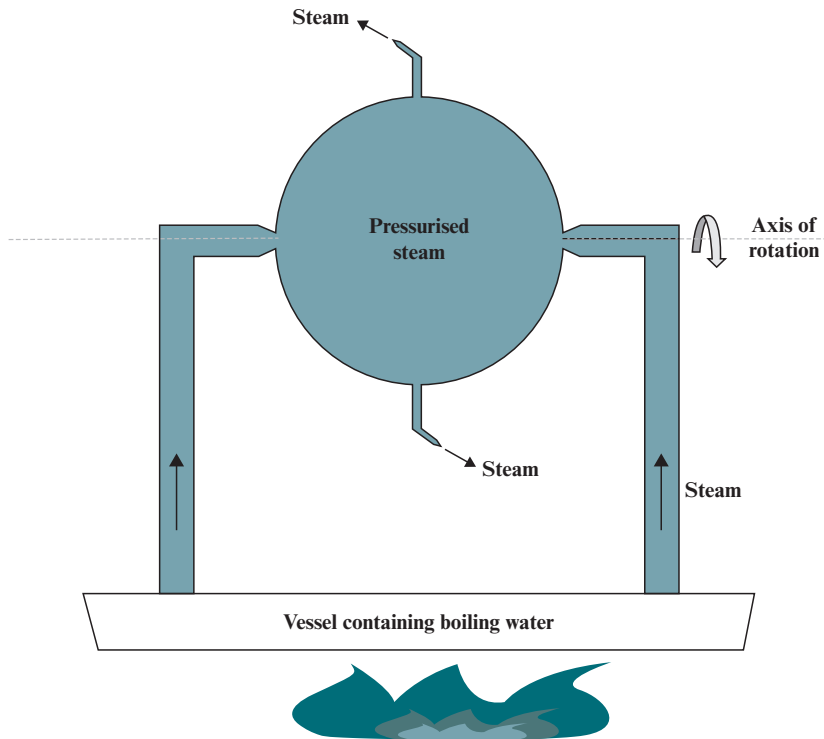


Figure 3.5 Heron's aeolipile. Steam from boiling water passes into a hollow sphere, which can rotate about a horizontal axis. The steam can escape only through two narrow L-shaped pipes, each ending in a narrow outlet: in this diagram, the lower outlet is projecting perpendicularly out of the paper towards the reader, and the upper outlet is projecting out of the paper away from the reader. As the pressurised steam escapes through the outlets, the sphere rotates in the opposite direction. The rotation of the sphere, driven by the P, V work done by the expanding steam, could, in principle, be harnessed to lift a weight.

3.8.2 How to harness the P, V work of an expanding gas

One feature of Heron's aeolipile is that the steam emitted from the outlets expands freely against the atmosphere. In Watt's steam engine, in contrast, the steam is kept enclosed within a cylinder, and expands against a moveable piston. In this section, we will build on our discussion in Chapter 2 to explore in more detail how a heated, expanding, gas can be used to perform useful work.

As we saw in Chapter 2, in principle, the conversion of heat into work, using a gas expanding against a piston, is very simple. If the piston in Figure 3.6 is initially held fixed, the volume V of the system is held constant. On heating the gas – say, air – its temperature T increases, and, assuming that the ideal gas law $PV = nRT$ is reasonably valid, since the volume V is constant, the pressure P will increase accordingly. When the pressure P has reached a given level above atmospheric pressure, peg 1 can be removed, so that the piston moves against the atmosphere. The expansion of the air therefore does P, V work as we discussed on page 27, 'pushing the atmosphere out of the way', and doing other 'useful work' too – if the piston is

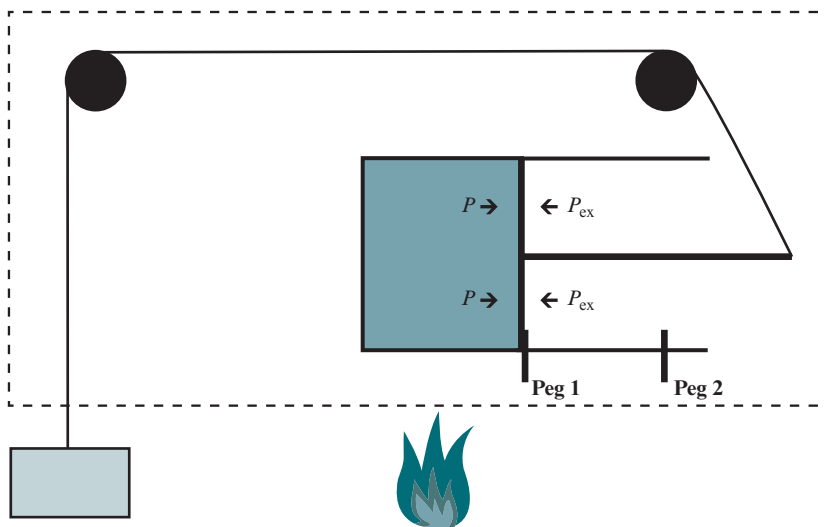


Figure 3.6 Producing work from heat. When the air inside the piston is heated, its pressure P increases. On removing peg 1, the piston then expands against the external atmospheric pressure P_{ex} until it stops at peg 2. As the piston moves to the right, the mass is raised. The device inside the dashed line acts as a machine that converts the heat from the flame into the work required to lift the mass.

suitably connected mechanically to another device, then the motion of the piston during this ‘power stroke’ can be used to lift a weight, or rotate, say, a mill-wheel. Overall, this device converts heat into work.

There is, however, a very practical problem: the work that this device performs takes place only as the piston moves to the right, and stops when the piston has reached the position defined by peg 2. This could happen quite quickly, and so any work that is performed will be finished within a very short time. It may be that this time is long enough to raise the weight to the required position, but this might just be a fortunate co-incidence – what we seek is a device that can perform work as long as we wish it to, rather than one that can only perform work in a short burst.

One way of increasing the time over which work is performed is to use a longer cylinder, so that the distance between peg 1 and peg 2 is significantly greater. But in practice, how long can a cylinder be? And even if it were possible to use a longer cylinder, another problem will soon arise. As the piston moves against the atmosphere, the volume within the cylinder increases, and so the pressure of the air inside the cylinder drops. Eventually, the pressure of the air inside the cylinder will fall to that of the atmosphere, and so the piston will stop, even if it hasn’t yet reached peg 2. This problem, too, can be avoided, in two different ways. The first is to heat the air to a very high pressure, before releasing peg 1, so that the piston will move through a longer distance before the internal and external pressures equilibrate. And the second is to keep the temperature of the air inside the cylinder high, so that the pressure drop attributable to the volume increase is compensated by the higher temperature – which is all about manipulating $PV = nRT$ so that the internal pressure P remains higher than the external atmospheric pressure P_{ex} even as the volume V increases. Both these ‘solutions’ require a lot of heat