The background of the book cover features a dynamic, abstract pattern of blue ink swirling and diffusing in water. The ink forms various shapes, from tight, circular bubbles at the top to more fluid, wispy patterns in the center and bottom. The color transitions from a bright, almost white blue at the edges to a deep, saturated blue in the center and along the bottom right edge.

# Physical Chemistry

NINTH EDITION

PETER ATKINS ■ JULIO DE PAULA

*This page intentionally left blank*

## General data and fundamental constants

Quantity	Symbol	Value	Power of ten	Units
Speed of light	$c$	2.997 925 58*	$10^8$	$\text{m s}^{-1}$
Elementary charge	$e$	1.602 176	$10^{-19}$	C
Faraday's constant	$F = N_A e$	9.648 53	$10^4$	$\text{C mol}^{-1}$
Boltzmann's constant	$k$	1.380 65	$10^{-23}$	$\text{J K}^{-1}$
Gas constant	$R = N_A k$	8.314 47		$\text{J K}^{-1} \text{mol}^{-1}$
		8.314 47	$10^{-2}$	$\text{dm}^3 \text{bar K}^{-1} \text{mol}^{-1}$
		8.205 74	$10^{-2}$	$\text{dm}^3 \text{atm K}^{-1} \text{mol}^{-1}$
		6.236 37	10	$\text{dm}^3 \text{Torr K}^{-1} \text{mol}^{-1}$
Planck's constant	$h$	6.626 08	$10^{-34}$	$\text{J s}$
	$\hbar = h/2\pi$	1.054 57	$10^{-34}$	$\text{J s}$
Avogadro's constant	$N_A$	6.022 14	$10^{23}$	$\text{mol}^{-1}$
Atomic mass constant	$m_u$	1.660 54	$10^{-27}$	kg
Mass				
electron	$m_e$	9.109 38	$10^{-31}$	kg
proton	$m_p$	1.672 62	$10^{-27}$	kg
neutron	$m_n$	1.674 93	$10^{-27}$	kg
Vacuum permittivity	$\epsilon_0 = 1/c^2 \mu_0$	8.854 19	$10^{-12}$	$\text{J}^{-1} \text{C}^2 \text{m}^{-1}$
	$4\pi\epsilon_0$	1.112 65	$10^{-10}$	$\text{J}^{-1} \text{C}^2 \text{m}^{-1}$
Vacuum permeability	$\mu_0$	$4\pi$	$10^{-7}$	$\text{J s}^2 \text{C}^{-2} \text{m}^{-1} (= \text{T}^2 \text{J}^{-1} \text{m}^3)$
Magneton				
Bohr	$\mu_B = e\hbar/2m_e$	9.274 01	$10^{-24}$	$\text{J T}^{-1}$
nuclear	$\mu_N = e\hbar/2m_p$	5.050 78	$10^{-27}$	$\text{J T}^{-1}$
<i>g</i> value	$g_e$	2.002 32		
Bohr radius	$a_0 = 4\pi\epsilon_0\hbar^2/m_e e^2$	5.291 77	$10^{-11}$	m
Fine-structure constant	$\alpha = \mu_0 e^2 c / 2h$	7.297 35	$10^{-3}$	
	$\alpha^{-1}$	1.370 36	$10^2$	
Second radiation constant	$c_2 = hc/k$	1.438 78	$10^{-2}$	$\text{m K}$
Stefan–Boltzmann constant	$\sigma = 2\pi^5 k^4 / 15h^3 c^2$	5.670 51	$10^{-8}$	$\text{W m}^{-2} \text{K}^{-4}$
Rydberg constant	$R = m_e e^4 / 8h^3 c \epsilon_0^2$	1.097 37	$10^5$	$\text{cm}^{-1}$
Standard acceleration of free fall	$g$	9.806 65*		$\text{m s}^{-2}$
Gravitational constant	$G$	6.673	$10^{-11}$	$\text{N m}^2 \text{kg}^{-2}$

\*Exact value

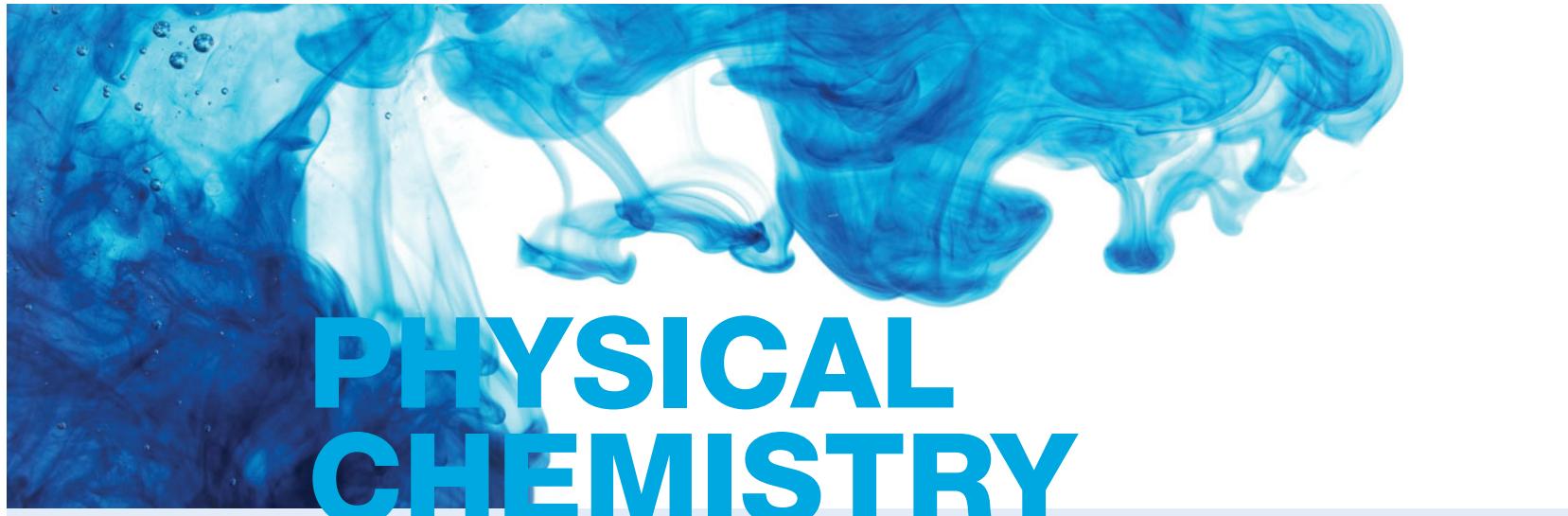
## The Greek alphabet

A, $\alpha$	alpha	H, $\eta$	eta	N, $\nu$	nu	Y, $\upsilon$	upsilon
B, $\beta$	beta	$\Theta, \theta$	theta	$\Xi, \xi$	xi	$\Phi, \phi$	phi
$\Gamma, \gamma$	gamma	I, $\iota$	iota	$\Pi, \pi$	pi	X, $\chi$	chi
$\Delta, \delta$	delta	K, $\kappa$	kappa	P, $\rho$	rho	$\Psi, \psi$	psi
E, $\varepsilon$	epsilon	$\Lambda, \lambda$	lambda	$\Sigma, \sigma$	sigma	$\Omega, \omega$	omega
Z, $\zeta$	zeta	M, $\mu$	mu	T, $\tau$	tau		

*This page intentionally left blank*

# **PHYSICAL CHEMISTRY**

*This page intentionally left blank*



# PHYSICAL CHEMISTRY

---

**Ninth Edition**

**Peter Atkins**

*Fellow of Lincoln College,  
University of Oxford,  
Oxford, UK*

**Julio de Paula**

*Professor of Chemistry,  
Lewis and Clark College,  
Portland, Oregon, USA*



W. H. Freeman and Company  
New York

*Physical Chemistry*, Ninth Edition

© 2010 by Peter Atkins and Julio de Paula

All rights reserved

ISBN: 1-4292-1812-6

ISBN-13: 978-1-429-21812-2

Published in Great Britain by Oxford University Press

This edition has been authorized by Oxford University Press for sale in the  
United States and Canada only and not for export therefrom.

First printing.

W. H. Freeman and Company

41 Madison Avenue

New York, NY 10010

[www.whfreeman.com](http://www.whfreeman.com)

# Preface

---

We have followed our usual tradition in that this new edition of the text is yet another thorough update of the content and its presentation. Our goal is to keep the book flexible to use, accessible to students, broad in scope, and authoritative, without adding bulk. However, it should always be borne in mind that much of the bulk arises from the numerous pedagogical features that we include (such as *Worked examples*, *Checklists of key equations*, and the *Resource section*), not necessarily from density of information.

The text is still divided into three parts, but material has been moved between chapters and the chapters themselves have been reorganized. We continue to respond to the cautious shift in emphasis away from classical thermodynamics by combining several chapters in Part 1 (Equilibrium), bearing in mind that some of the material will already have been covered in earlier courses. For example, material on phase diagrams no longer has its own chapter but is now distributed between Chapters 4 (*Physical transformation of pure substances*) and 5 (*Simple mixtures*). New *Impact* sections highlight the application of principles of thermodynamics to materials science, an area of growing interest to chemists.

In Part 2 (Structure) the chapters have been updated with a discussion of contemporary techniques of materials science—including nanoscience—and spectroscopy. We have also paid more attention to computational chemistry, and have revised the coverage of this topic in Chapter 10.

Part 3 has lost chapters dedicated to kinetics of complex reactions and surface processes, but not the material, which we regard as highly important in a contemporary context. To make the material more readily accessible within the context of courses, descriptions of polymerization, photochemistry, and enzyme- and surface-catalysed reactions are now part of Chapters 21 (*The rates of chemical reactions*) and 22 (*Reaction dynamics*)—already familiar to readers of the text—and a new chapter, Chapter 23, on *Catalysis*.

We have discarded the Appendices of earlier editions. Material on mathematics covered in the appendices is now dispersed through the text in the form of *Mathematical background* sections, which review and expand knowledge of mathematical techniques where they are needed in the text. The review of introductory chemistry and physics, done in earlier editions in appendices, will now be found in a new *Fundamentals* chapter that opens the text, and particular points are developed as *Brief comments* or as part of *Further information* sections throughout the text. By liberating these topics from their appendices and relaxing the style of presentation we believe they are more likely to be used and read.

The vigorous discussion in the physical chemistry community about the choice of a ‘quantum first’ or a ‘thermodynamics first’ approach continues. In response we have paid particular attention to making the organization flexible. The strategic aim of this revision is to make it possible to work through the text in a variety of orders and at the end of this Preface we once again include two suggested paths through the text. For those who require a more thorough-going ‘quantum first’ approach we draw attention to our *Quanta, matter, and change* (with Ron Friedman) which covers similar material to this text in a similar style but, because of the different approach, adopts a different philosophy.

The concern expressed in previous editions about the level of mathematical ability has not evaporated, of course, and we have developed further our strategies for

showing the absolute centrality of mathematics to physical chemistry and to make it accessible. In addition to associating *Mathematical background* sections with appropriate chapters, we continue to give more help with the development of equations, motivate them, justify them, and comment on the steps. We have kept in mind the struggling student, and have tried to provide help at every turn.

We are, of course, alert to the developments in electronic resources and have made a special effort in this edition to encourage the use of the resources on our website (at [www.whfreeman.com/pchem](http://www.whfreeman.com/pchem)). In particular, we think it important to encourage students to use the *Living graphs* on the website (and their considerable extension in the electronic book and *Explorations CD*). To do so, wherever we call out a *Living graph* (by an icon attached to a graph in the text), we include an *interActivity* in the figure legend, suggesting how to explore the consequences of changing parameters.

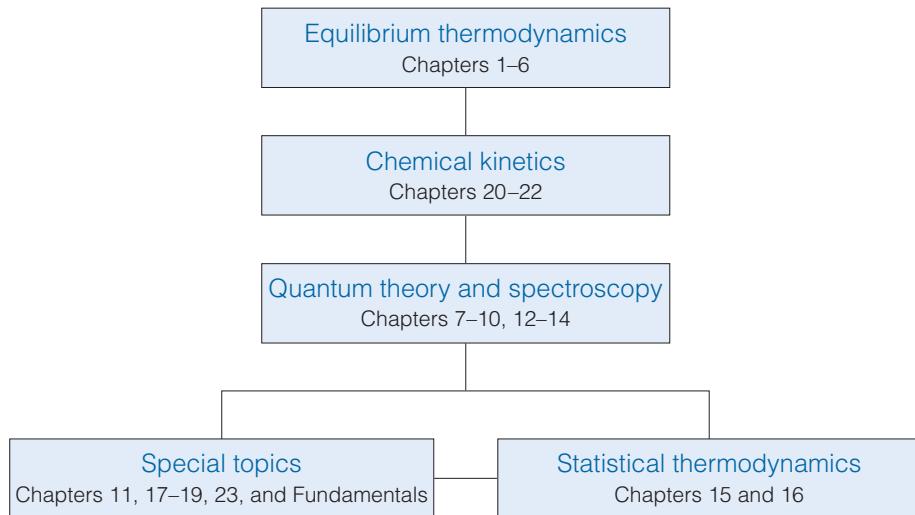
Many other revisions have been designed to make the text more efficient and helpful and the subject more enjoyable. For instance, we have redrawn nearly every one of the 1000 pieces of art in a consistent style. The *Checklists of key equations* at the end of each chapter are a useful distillation of the most important equations from the large number that necessarily appear in the exposition. Another innovation is the collection of *Road maps* in the *Resource section*, which suggest how to select an appropriate expression and trace it back to its roots.

Overall, we have taken this opportunity to refresh the text thoroughly, to integrate applications, to encourage the use of electronic resources, and to make the text even more flexible and up-to-date.

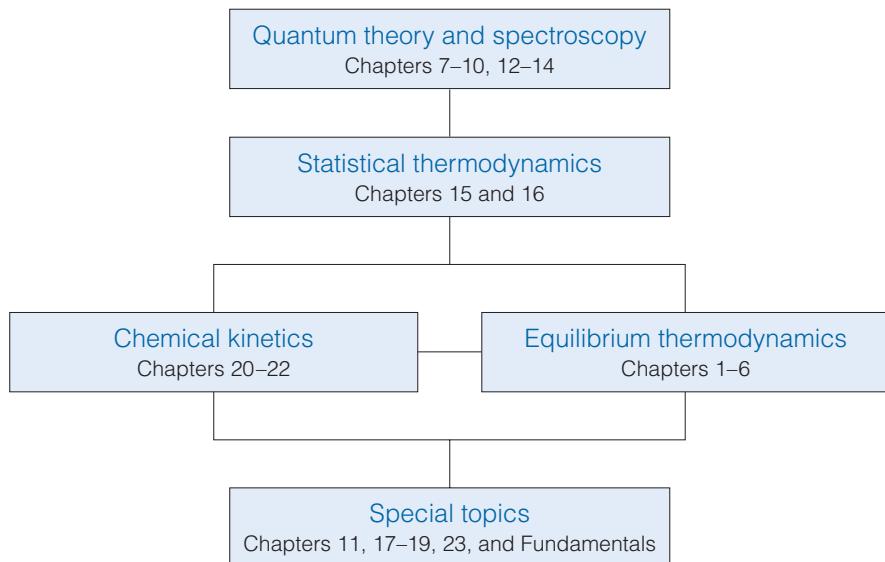
*Oxford  
Portland*

P.W.A.  
J.de P.

### Traditional approach



### Molecular approach



This text is available as a customizable ebook. This text can also be purchased in two volumes. For more information on these options please see pages xv and xvi.

# About the book

There are numerous features in this edition that are designed to make learning physical chemistry more effective and more enjoyable. One of the problems that make the subject daunting is the sheer amount of information: we have introduced several devices for organizing the material: see *Organizing the information*. We appreciate that mathematics is often troublesome, and therefore have taken care to give help with this enormously important aspect of physical chemistry: see *Mathematics support*. Problem solving—especially, ‘where do I start?’—is often a challenge, and we have done our best to help overcome this first hurdle: see *Problem solving*. Finally, the web is an extraordinary resource, but it is necessary to know where to start, or where to go for a particular piece of information; we have tried to indicate the right direction: see *About the Book Companion Site*. The following paragraphs explain the features in more detail.

## Organizing the information

### Key points

The *Key points* act as a summary of the main take-home message(s) of the section that follows. They alert you to the principal ideas being introduced.

#### 1.1 The states of gases

**Key points** Each substance is described by an equation of state. (a) Pressure, force divided by area, provides a criterion of mechanical equilibrium for systems free to change their volume. (b) Pressure is measured with a barometer. (c) Through the Zeroth Law of thermodynamics, temperature provides a criterion of thermal equilibrium.

The physical state of a sample of a substance, its physical condition, is defined by its physical properties. Two samples of a substance that have the same physical proper-

### Equation and concept tags

The most significant equations and concepts—which we urge you to make a particular effort to remember—are flagged with an annotation, as shown here.

mental fact that each substance is described by an **equation of state**, an equation that interrelates these four variables.

The general form of an equation of state is

$$p = f(T, V, n)$$

General form of  
an equation of state (1.1)

### Justifications

On first reading it might be sufficient simply to appreciate the ‘bottom line’ rather than work through detailed development of a mathematical expression. However, mathematical development is an intrinsic part of physical chemistry, and to achieve full understanding it is important to see how a particular expression is obtained. The *Justifications* let you adjust the level of detail that you require to your current needs, and make it easier to review material.

These relations are called the Margules equations.

#### Justification 5.5 The Margules equations

The Gibbs energy of mixing to form a nonideal solution is

$$\Delta_{\text{mix}}G = nRT\{x_A \ln x_A + x_B \ln x_B\}$$

This relation follows from the derivation of eqn 5.16 with activities in place of mole fractions. If each activity is replaced by  $\gamma x$ , this expression becomes

$$\Delta_{\text{mix}}G = nRT\{x_A \ln x_A + x_B \ln x_B + x_A \ln \gamma_A + x_B \ln \gamma_B\}$$

Now we introduce the two expressions in eqn 5.64, and use  $x_A + x_B = 1$ , which gives

$$\begin{aligned} \Delta_{\text{mix}}G &= nRT\{x_A \ln x_A + x_B \ln x_B + \xi x_A x_B^2 + \xi x_B x_A^2\} \\ &= nRT\{x_A \ln x_A + x_B \ln x_B + \xi x_A x_B (x_A + x_B)\} \\ &= nRT\{x_A \ln x_A + x_B \ln x_B + \xi x_A x_B\} \end{aligned}$$

as required by eqn 5.29. Note, moreover, that the activity coefficients behave correctly for dilute solutions:  $\gamma_A \rightarrow 1$  as  $x_B \rightarrow 0$  and  $\gamma_B \rightarrow 1$  as  $x_A \rightarrow 0$ .

At this point we can use the Margules equations to write the activity of A as

## Checklists of key equations

We have summarized the most important equations introduced in each chapter as a checklist. Where appropriate, we describe the conditions under which an equation applies.

Checklist of key equations		
Property	Equation	Comment
Chemical potential	$\mu_i = (\partial G/\partial n_i)_{T, p, c}$	
Fundamental equation of chemica thermodynamics	$dG = VdT - SdT + \mu_1 dn_1 + \mu_2 dn_2 + \dots$	
Gibbs-Duhem equation	$\sum_i n_i d\mu_i = 0$	
Chemical potential of a gas	$\mu = \mu^\circ + RT \ln(p/p^\circ)$	Perfect gas
Thermodynamic properties of mixing	$\Delta_{mix}G = -RT(x_A \ln x_A + x_B \ln x_B)$ $\Delta_{mix}S = -R(x_A \ln x_A + x_B \ln x_B)$ $\Delta_{mix}H = H_A + H_B$	Perfect gases and ideal solutions
Raoult's law	$P_A = x_A P_A^\circ$	True for ideal solutions; limiting law as $x_A \rightarrow 1$
Henry's law	$P_B = x_B K_B$	True for ideal-dilute solutions; limiting law as $x_B \rightarrow 0$
van't Hoff equation	$T = [B]/RT$	Valid as $ B  \rightarrow 0$
Activity of a solvent	$a_A = P_A/P_A^\circ$	$a_A \rightarrow x_A$ as $x_A \rightarrow 1$
Chemical potential	$\mu_i = \mu_i^\circ + RT \ln a_i$	General form for a species $j$
Conversion to biological standard state	$\theta^B(H^+) = \theta^B(H^+) - 7kT \ln 10$	
Mean activity coefficient	$\gamma_i = (\gamma_i^\circ)^{1/(1-q)}$	
Ionic strength	$I = \frac{1}{2} \sum_i z_i^2 (b_i/b^\circ)$	Definition
Debye-Hückel limiting law	$\log Y_{i+} = -I - z_i A  F ^{1/2}$	Valid as $I \rightarrow 0$
Margules equation	$\ln Y_i = \frac{1}{z_i^2} I$	Model of regular solution
Lever rule	$n_A/n_B = n_A^\circ/n_B^\circ$	

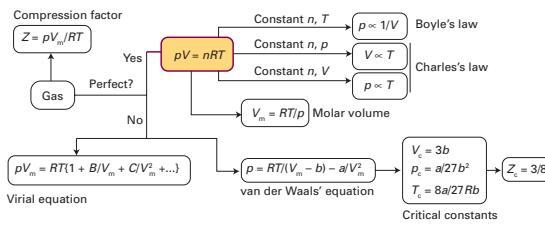
## Road maps

In many cases it is helpful to see the relations between equations. The suite of ‘Road maps’ summarizing these relations are found in the *Resource section* at the end of the text.

## Part 1 Road maps

## Gas laws (Chapter 1)

## Gas laws (Chapter 1)



The First Law (Chapter 2)

## Impact sections

Where appropriate, we have separated the principles from their applications: the principles are constant and straightforward; the applications come and go as the subject progresses. The *Impact* sections show how the principles developed in the chapter are currently being applied in a variety of modern contexts.

IMPACT ON NANOSCIENCE

## I8.1 Quantum dots

Nanoscience is the study of atomic and molecular assemblies with dimensions ranging from 1 nm to about 100 nm and nanotechnology is concerned with the incorporation of such assemblies into devices. The future economic impact of nanotechnology could be very significant. For example, increased demand for very small digital electronic devices has driven the design of ever smaller and more powerful microprocessors. However, there is an upper limit on the density of electronic circuits that can be incorporated into silicon-based chips with current fabrication technologies. As the ability to process data increases with the number of components in a chip, it follows that soon chips and the devices that use them will have to become bigger if processing

## Notes on good practice

Science is a precise activity and its language should be used accurately. We have used this feature to help encourage the use of the language and procedures of science in conformity to international practice (as specified by IUPAC, the International Union of Pure and Applied Chemistry) and to help avoid common mistakes.

**Answer** The number of photons is

$$N = \frac{E}{hv} = \frac{P\Delta t}{h c(\lambda)} = \frac{\lambda P\Delta t}{hc}$$

Substitution of the data gives

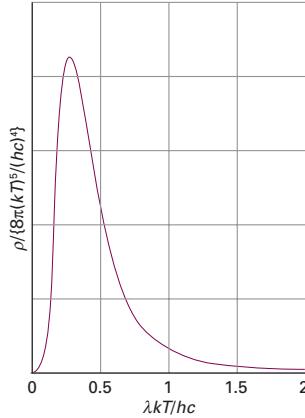
$$N = \frac{(5.60 \times 10^{-7} \text{ m}) \times (100 \text{ J s}^{-1}) \times (1.0 \text{ s})}{(6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^8 \text{ m s}^{-1})} = 2.8 \times 10^{20}$$

Note that it would take the lamp nearly 40 min to produce 1 mol of these photons.

**Self-test 7.1** How many photons does a monochromatic (single frequency) infrared rangefinder of power 1 mW and wavelength 1000 nm emit in 0.1 s?  $[5 \times 10^{14}]$

# interActivities

You will find that many of the graphs in the text have an interActivity attached: this is a suggestion about how you can explore the consequences of changing various parameters or of carrying out a more elaborate investigation related to the material in the illustration. In many cases, the activities can be completed by using the online resources of the book's website.



**Fig. 7.7** The Planck distribution (eqn 7.8) accounts very well for the experimentally determined distribution of black-body radiation. Planck's quantization hypothesis essentially quenches the contributions of high frequency, short wavelength oscillators. The distribution coincides with the Rayleigh–Jeans distribution at long wavelengths.

-Louis Dulong and Alexis-  
 $\rangle_V$  (Section 2.4), of a num-  
 that slender experimental  
 l monatomic solids are the

ssical physics in much the same way as the theory of relativity did for electromagnetism. If classical physics is correct, then it must be true that the mean energy of each particle is  $T$  for each direction of displacement, and that the average energy of each particle is  $T$ , where  $T$  is the distribution of this motion to be expected.

 **interActivity** Plot the Planck distribution at several temperatures and confirm that eqn 7.8 predicts the behaviour summarized by Fig. 7.3.

## Further information

In some cases, we have judged that a derivation is too long, too detailed, or too different in level for it to be included in the text. In these cases, the derivations will be found less obtrusively at the end of the chapter.

**Further information**

**Further information 7.1 Classical mechanics**

Classical mechanics describes the behaviour of objects in terms of two equations. One expresses the fact that the total energy is constant in the absence of external forces; the other expresses the response of particles to the forces acting on them.

**(a) The trajectory in terms of the energy**

The velocity,  $v$ , of a particle is the rate of change of its position:

$$v = \frac{dr}{dt} \quad (7.44)$$

Definition of velocity

The velocity is a vector, with both direction and magnitude. (Vectors are discussed in *Mathematical background 5*.) The magnitude of the velocity is the speed,  $v$ . The linear momentum,  $p$ , of a particle of mass  $m$  is related to its velocity,  $v$ , by

$$p = mv \quad (7.45)$$

Definition of linear momentum

Like the velocity vector, the linear momentum vector points in the direction of travel of the particle (Fig. 7.31). In terms of the linear

**Fig. 7.31** The linear momentum of a particle is a vector property and points in the direction of motion.

momentum, the total energy—the sum of the kinetic and potential energy—of a particle is

$$E = E_k + V(x) = \frac{p^2}{2m} + V(x) \quad (7.46)$$

## Resource section

Long tables of data are helpful for assembling and solving exercises and problems, but can break up the flow of the text. The *Resource section* at the end of the text consists of the *Road maps*, a *Data section* with a lot of useful numerical information, and *Character tables*. Short extracts of the tables in the text itself give an idea of the typical values of the physical quantities being discussed.

van der Waals equation of state	<b>Table 1.6*</b> van der Waals coefficients
(1.21a)	$a/(\text{atm dm}^6 \text{ mol}^{-2})$ $b/(10^{-2} \text{ dm}^3 \text{ mol}^{-1})$
equation is often written in	Ar    1.337    3.20 CO <sub>2</sub> 3.610    4.29 He    0.0341    2.38 Xe    4.137    5.16
(1.21b)	* More values are given in the <i>Data section</i> .

## Mathematics support

### A brief comment

A topic often needs to draw on a mathematical procedure or a concept of physics; a brief comment is a quick reminder of the procedure or concept.

### in magnetic fields

fields, which remove the degeneracy of the quantized

moment  $\mu$  in a magnetic field  $\mathcal{B}$  is equal to the

$$(14.1)$$

induction and is measured in tesla, T; 1 T =  $10^4$  G. It is also occasionally used: 1 T =  $10^4$  G.

### A brief comment

Scalar products (or ‘dot products’) are explained in *Mathematical background 5* following Chapter 9.

## Mathematical background

It is often the case that you need a more full-bodied account of a mathematical concept, either because it is important to understand the procedure more fully or because you need to use a series of tools to develop an equation. The *Mathematical background* sections are located between some chapters, primarily where they are first needed, and include many illustrations of how each concept is used.

### MATHEMATICAL BACKGROUND 5

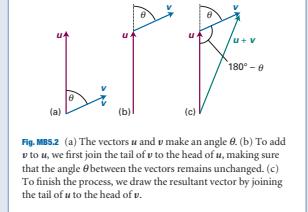
#### Vectors

A vector quantity has both magnitude and direction. The vector shown in Fig. MBS.1 has components on the x, y, and z axes with magnitudes  $v_x$ ,  $v_y$ , and  $v_z$ , respectively. The vector may be represented as

$$\mathbf{v} = v_x \mathbf{i} + v_y \mathbf{j} + v_z \mathbf{k} \quad (\text{MBS.1})$$

where  $\mathbf{i}$ ,  $\mathbf{j}$ , and  $\mathbf{k}$  are unit vectors, vectors of magnitude 1, pointing along the positive directions on the x-, y-, and z-axes. The magnitude of the vector is denoted  $v$  or  $|\mathbf{v}|$  and is given by

$$v = (v_x^2 + v_y^2 + v_z^2)^{1/2} \quad (\text{MBS.2})$$



## Problem solving

### A brief illustration

A brief illustration is a short example of how to use an equation that has just been introduced in the text. In particular, we show how to use data and how to manipulate units correctly.

#### • A brief illustration

The unpaired electron in the ground state of an alkali metal atom has  $l = 0$ , so  $j = \frac{1}{2}$ . Because the orbital angular momentum is zero in this state, the spin-orbit coupling energy is zero (as is confirmed by setting  $j = s$  and  $l = 0$  in eqn 9.42). When the electron is excited to an orbital with  $l = 1$ , it has orbital angular momentum and can give rise to a magnetic field that interacts with its spin. In this configuration the electron can have  $j = \frac{3}{2}$  or  $j = \frac{1}{2}$ , and the energies of these levels are

$$E_{3/2} = \frac{1}{2} hc\bar{A} [\frac{3}{2} \times \frac{5}{2} - 1 \times 2 - \frac{1}{2} \times \frac{3}{2}] = \frac{1}{2} hc\bar{A}$$

$$E_{1/2} = \frac{1}{2} hc\bar{A} [\frac{1}{2} \times \frac{3}{2} - 1 \times 2 - \frac{1}{2} \times \frac{3}{2}] = -hc\bar{A}$$

The corresponding energies are shown in Fig. 9.30. Note that the baricentre (the ‘centre of gravity’) of the levels is unchanged, because there are four states of energy  $\frac{1}{2}hc\bar{A}$  and two of energy  $-hc\bar{A}$ . •

## Examples

We present many worked examples throughout the text to show how concepts are used, sometimes in combination with material from elsewhere in the text. Each worked example has a *Method* section suggesting an approach as well as a fully worked out answer.

### Example 9.2 Calculating the mean radius of an orbital

Use hydrogenic orbitals to calculate the mean radius of a 1s orbital.

**Method** The mean radius is the expectation value

$$\langle r \rangle = \int \psi^* r \psi d\tau = \int r |\psi|^2 d\tau$$

We therefore need to evaluate the integral using the wavefunctions given in Table 9.1 and  $d\tau = r^2 dr \sin \theta d\theta d\phi$ . The angular parts of the wavefunction (Table 8.2) are normalized in the sense that

$$\int_0^\pi \int_0^{2\pi} |Y_{l,m_l}|^2 \sin \theta d\theta d\phi = 1$$

The integral over  $r$  required is given in Example 7.4.

**Answer** With the wavefunction written in the form  $\psi = RY$ , the integration is

$$\langle r \rangle = \int_0^\infty \int_0^\pi \int_0^{2\pi} r R_{n,l}^2 |Y_{l,m_l}|^2 r^2 dr \sin \theta d\theta d\phi = \int_0^\infty r^3 R_{n,l}^2 dr$$

For a 1s orbital

$$R_{1,0} = 2 \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0}$$

Hence

$$\langle r \rangle = \frac{4Z^3}{a_0^3} \int_0^\infty r^3 e^{-2Zr/a_0} dr = \frac{3a_0}{2Z}$$

## Self-tests

Each *Example* has a *Self-test* with the answer provided as a check that the procedure has been mastered. There are also a number of free-standing *Self-tests* that are located where we thought it a good idea to provide a question to check your understanding. Think of *Self-tests* as in-chapter exercises designed to help you monitor your progress.

**Self-test 9.4** Evaluate the mean radius of a 3s orbital by integration. [ $27a_0/2Z$ ]

## Discussion questions

The end-of-chapter material starts with a short set of questions that are intended to encourage reflection on the material and to view it in a broader context than is obtained by solving numerical problems.

### Discussion questions

- 9.1** Discuss the origin of the series of lines in the emission spectra of hydrogen. What region of the electromagnetic spectrum is associated with each of the series shown in Fig. 9.1?
- 9.2** Describe the separation of variables procedure as it is applied to simplify the description of a hydrogen atom free to move through space.
- 9.3** List and describe the significance of the quantum numbers needed to specify the internal state of a hydrogenic atom.
- 9.4** Specify and account for the selection rules for transitions in hydrogenic atoms.
- 9.5** Explain the significance of (a) a boundary surface and (b) the radial distribution function for hydrogenic orbitals.
- 9.6** Outline the electron configurations of many-electron atoms in terms of their location in the periodic table.
- 9.7** Describe and account for the variation of first ionization energies along Period 2 of the periodic table. Would you expect the same variation in Period 3?
- 9.8** Describe the orbital approximation for the wavefunction of a many-electron atom. What are the limitations of the approximation?
- 9.9** Explain the origin of spin-orbit coupling and how it affects the appearance of a spectrum.
- 9.10** Describe the physical origins of linewidths in absorption and emission spectra. Do you expect the same contributions for species in condensed and gas phases?

## Exercises and Problems

The core of testing understanding is the collection of end-of-chapter *Exercises* and *Problems*. The *Exercises* are straightforward numerical tests that give practice with manipulating numerical data. The *Problems* are more searching. They are divided into ‘numerical’, where the emphasis is on the manipulation of data, and ‘theoretical’, where the emphasis is on the manipulation of equations before (in some cases) using numerical data. At the end of the *Problems* are collections of problems that focus on practical applications of various kinds, including the material covered in the *Impact* sections.

### Exercises

- 9.1(a)** Determine the shortest and longest wavelength lines in the Lyman series.
- 9.1(b)** The Pfund series has  $n_f = 5$ . Determine the shortest and longest wavelength lines in the Pfund series.
- 9.2(a)** Compute the wavelength, frequency, and wavenumber of the  $n = 2 \rightarrow n = 1$  transition in  $\text{He}^+$ .
- 9.2(b)** Compute the wavelength, frequency, and wavenumber of the  $n = 5 \rightarrow n = 4$  transition in  $\text{Li}^+$ .
- 9.3(a)** When ultraviolet radiation of wavelength 58.4 nm from a helium lamp is directed onto a sample of krypton, electrons are ejected with a speed of  $1.59 \text{ Mm s}^{-1}$ . Calculate the ionization energy of krypton.
- 9.3(b)** When ultraviolet radiation of wavelength 58.4 nm from a helium lamp is directed onto a sample of xenon, electrons are ejected with a speed of  $1.79 \text{ Mm s}^{-1}$ . Calculate the ionization energy of xenon.
- 9.12(a)** What is the orbital angular momentum of an electron in the orbitals (a) 1s, (b) 3s, (c) 3d? Give the numbers of angular and radial nodes in each case.
- 9.12(b)** What is the orbital angular momentum of an electron in the orbitals (a) 4d, (b) 2p, (c) 3p? Give the numbers of angular and radial nodes in each case.
- 9.13(a)** Locate the angular nodes and nodal planes of each of the 2p orbitals of a hydrogenic atom of atomic number Z. To locate the angular nodes, give the angle that the plane makes with the z-axis.
- 9.13(b)** Locate the angular nodes and nodal planes of each of the 3d orbitals of a hydrogenic atom of atomic number Z. To locate the angular nodes, give the angle that the plane makes with the z-axis.
- 9.14(a)** Which of the following transitions are allowed in the normal electronic emission spectrum of an atom: (a)  $2s \rightarrow 1s$ , (b)  $2p \rightarrow 1s$ , (c)  $3d \rightarrow 2p$ ?
- 9.14(b)** Which of the following transitions are allowed in the normal electronic

### Problems\*

#### Numerical problems

- 9.1** The Humphreys series is a group of lines in the spectrum of atomic hydrogen. It begins at 12 368 nm and has been traced to 328.14 nm. What are the transitions involved? What are the wavelengths of the intermediate transitions?
- 9.2** A series of lines in the spectrum of atomic hydrogen lies at 656.46 nm, 488.27 nm, 434.17 nm, and 410.29 nm. What is the wavelength of the next line in the series? What is the ionization energy of the atom when it is in the lower state of the transitions?
- 9.3** The  $\text{Li}^{1+}$  ion is hydrogenic and has a Lyman series at  $740.747 \text{ cm}^{-1}$ ,  $871.924 \text{ cm}^{-1}$ ,  $925.933 \text{ cm}^{-1}$ , and beyond. Show that the energy levels are in the series? What is the ionization energy of the atom when it is in the lower state of the transitions?
- 9.4** The  $\text{Li}^{1+}$  ion is hydrogenic and has a Lyman series at  $740.747 \text{ cm}^{-1}$ ,  $871.924 \text{ cm}^{-1}$ ,  $925.933 \text{ cm}^{-1}$ , and beyond. Show that the energy levels are in the series? What is the ionization energy of the atom when it is in the lower state of the transitions?
- 9.5** The  $\text{Li}^{1+}$  ion is hydrogenic and has a Lyman series at  $740.747 \text{ cm}^{-1}$ ,  $871.924 \text{ cm}^{-1}$ ,  $925.933 \text{ cm}^{-1}$ , and beyond. Show that the energy levels are in the series? What is the ionization energy of the atom when it is in the lower state of the transitions?
- 9.6** The Zeeman effect is the modification of an atomic spectrum by the application of a static magnetic field. It arises from the interaction between applied magnetic fields and the magnetic moments due to orbital and spin angular momenta (recall the evidence provided for electron spin by the Stern-Gerlach experiment, Section 8.8). To gain some appreciation for the so-called *normal Zeeman effect*, which is observed in transitions involving singlet states, consider a  $\text{e}^-$  electron, with  $l = 1$  and  $m_l = 0, \pm 1$ . In the absence of a magnetic field, these three states are degenerate. When a field of magnitude  $B$  is applied, the degeneracy is removed and the three states with  $m_l = +1$  move up in energy by  $\mu_B B$ , the state with  $m_l = 0$  is unchanged, and the state with  $m_l = -1$  moves down in energy by  $\mu_B B$ , where  $\mu_B = e\hbar/2m_e = 9.274 \times 10^{-24} \text{ J T}^{-1}$  is the Bohr magneton (see Section 13.1). Therefore, a

## Molecular modelling and computational chemistry

Over the past two decades computational chemistry has evolved from a highly specialized tool, available to relatively few researchers, into a powerful and practical alternative to experimentation, accessible to all chemists. The driving force behind this evolution is the remarkable progress in computer

technology. Calculations that previously required hours or days on giant mainframe computers may now be completed in a fraction of time on a personal computer. It is natural and necessary that computational chemistry finds its way into the undergraduate chemistry curriculum as a hands-on experience, just as teaching experimental chemistry requires a laboratory experience. With these developments in the chemistry curriculum in mind, the text's website features a range of computational problems, which are intended to be performed with special software that can handle 'quantum chemical calculations'. Specifically, the problems have been designed with the student edition of Wavefunction's *Spartan* program (*Spartan Student*<sup>TM</sup>) in mind, although they could be completed with any electronic structure

program that allows Hartree-Fock, density functional and MP2 calculations.

It is necessary for students to recognize that calculations are not the same as experiments, and that each 'chemical model' built from calculations has its own strengths and shortcomings. With this caveat in mind, it is important that some of the problems yield results that can be compared directly with experimental data. However, most problems are intended to stand on their own, allowing computational chemistry to serve as an exploratory tool.

Students can visit [www.wavefun.com/cart/spartaned.html](http://www.wavefun.com/cart/spartaned.html) and enter promotional code WHFPCHEM to download the *Spartan Student*<sup>TM</sup> program at a special 20% discount.

# About the Book Companion Site

The Book Companion Site to accompany *Physical Chemistry* 9e provides teaching and learning resources to augment the printed book. It is free of charge, and provides additional material for download, much of which can be incorporated into a virtual learning environment.

The Book Companion Site can be accessed by visiting

[www.whfreeman.com/pchem](http://www.whfreeman.com/pchem)

Note that instructor resources are available only to registered adopters of the textbook. To register, simply visit [www.whfreeman.com/pchem](http://www.whfreeman.com/pchem) and follow the appropriate links. You will be given the opportunity to select your own username and password, which will be activated once your adoption has been verified.

Student resources are openly available to all, without registration.

## For students

### Living graphs

A *Living graph* can be used to explore how a property changes as a variety of parameters are changed. To encourage the use of this resource (and the more extensive *Explorations in physical chemistry*; see below), we have included a suggested *interActivity* to many of the illustrations in the text.

### Group theory tables

Comprehensive group theory tables are available for downloading.

## For Instructors

### Artwork

An instructor may wish to use the figures from this text in a lecture. Almost all the figures are available in electronic format and can be used for lectures without charge (but not for commercial purposes without specific permission).

### Tables of data

All the tables of data that appear in the chapter text are available and may be used under the same conditions as the figures.

## Other resources

### *Explorations in Physical Chemistry* by Valerie Walters, Julio de Paula, and Peter Atkins

*Explorations in Physical Chemistry* consists of interactive Mathcad® worksheets, interactive Excel® workbooks, and stimulating exercises. They motivate students to simulate physical, chemical, and biochemical phenomena with their personal computers. Students can manipulate over 75 graphics, alter simulation parameters, and solve equations, to gain deeper insight into physical chemistry.

*Explorations in Physical Chemistry* is available as an integrated part of the eBook version of the text (see below). It can also be purchased online at <http://www.whfreeman.com/explorations>.

### *Physical Chemistry, Ninth Edition* eBook

The eBook, which is a complete online version of the textbook itself, provides a rich learning experience by taking full advantage of the electronic medium. It brings together a range of student resources alongside additional functionality unique to the eBook. The eBook also offers lecturers unparalleled flexibility and customization options. The eBook can be purchased at [www.whfreeman.com/pchem](http://www.whfreeman.com/pchem).

Key features of the eBook include:

- Easy access from any Internet-connected computer via a standard Web browser.
- Quick, intuitive navigation to any section or subsection, as well as any printed book page number.
- Living Graph animations.
- Integration of *Explorations in Physical Chemistry*.
- Text highlighting, down to the level of individual phrases.
- A book marking feature that allows for quick reference to any page.
- A powerful Notes feature that allows students or instructors to add notes to any page.
- A full index.
- Full-text search, including an option to search the glossary and index.
- Automatic saving of all notes, highlighting, and bookmarks.

Additional features for instructors:

- Custom chapter selection: Instructors can choose the chapters that correspond with their syllabus, and students will get a custom version of the eBook with the selected chapters only.

- Instructor notes: Instructors can choose to create an annotated version of the eBook with their notes on any page. When students in their course log in, they will see the instructor's version.

- Custom content: Instructor notes can include text, web links, and images, allowing instructors to place any content they choose exactly where they want it.

## Physical Chemistry, 9e is available in two volumes!

For maximum flexibility in your physical chemistry course, this text is now offered as a traditional, full text or in two volumes. The chapters from Physical Chemistry, 9e, that appear each volume are as follows:

Volume 1: Thermodynamics and Kinetics (1-4292-3127-0)

Chapter 0: Fundamentals

Chapter 1: The properties of gases

Chapter 2: The First Law

Chapter 3: The Second Law

Chapter 4: Physical transformations of pure substances

Chapter 5: Simple mixtures

Chapter 6: Chemical equilibrium

Chapter 20: Molecules in motion

Chapter 21: The rates of chemical reactions

Chapter 22: Reaction dynamics

Chapter 23: Catalysis

Volume 2: Quantum Chemistry, Spectroscopy, and Statistical Thermodynamics (1-4292-3126-2)

Chapter 7: Quantum theory: introduction and principles

Chapter 8: Quantum theory: techniques and applications

Chapter 9: Atomic structure and spectra

Chapter 10: Molecular structure

Chapter 11: Molecular symmetry

Chapter 12: Molecular spectroscopy 1: rotational and vibrational spectra

Chapter 13: Molecular spectroscopy 2: electronic transitions

Chapter 14: Molecular spectroscopy 3: magnetic resonance

Chapter 15: Statistical thermodynamics 1: the concepts

Chapter 16: Statistical thermodynamics 2: applications

Chapters 17, 18, and 19 are not contained in the two volumes, but can be made available on-line on request.

## Solutions manuals

As with previous editions, Charles Trapp, Carmen Giunta, and Marshall Cady have produced the solutions manuals to accompany this book. A *Student's Solutions Manual* (978-1-4292-3128-2) provides full solutions to the 'b' exercises and the odd-numbered problems. An *Instructor's Solutions Manual* (978-1-4292-5032-0) provides full solutions to the 'a' exercises and the even-numbered problems.

## About the authors

---



Professor Peter Atkins is a fellow of Lincoln College, University of Oxford, and the author of more than sixty books for students and a general audience. His texts are market leaders around the globe. A frequent lecturer in the United States and throughout the world, he has held visiting professorships in France, Israel, Japan, China, and New Zealand. He was the founding chairman of the Committee on Chemistry Education of the International Union of Pure and Applied Chemistry and a member of IUPAC's Physical and Biophysical Chemistry Division.



Julio de Paula is Professor of Chemistry at Lewis and Clark College. A native of Brazil, Professor de Paula received a B.A. degree in chemistry from Rutgers, The State University of New Jersey, and a Ph.D. in biophysical chemistry from Yale University. His research activities encompass the areas of molecular spectroscopy, biophysical chemistry, and nanoscience. He has taught courses in general chemistry, physical chemistry, biophysical chemistry, instrumental analysis, and writing.

# Acknowledgements

---

A book as extensive as this could not have been written without significant input from many individuals. We would like to reiterate our thanks to the hundreds of people who contributed to the first eight editions.

Many people gave their advice based on the eighth edition of the text, and others reviewed the draft chapters for the ninth edition as they emerged. We would like to thank the following colleagues:

Adedoyin Adeyiga, Cheyney University of Pennsylvania  
David Andrews, University of East Anglia  
Richard Ansell, University of Leeds  
Colin Bain, University of Durham  
Godfrey Beddard, University of Leeds  
Magnus Bergstrom, Royal Institute of Technology, Stockholm, Sweden  
Mark Bier, Carnegie Mellon University  
Robert Bohn, University of Connecticut  
Stefan Bon, University of Warwick  
Fernando Bresme, Imperial College, London  
Melanie Britton, University of Birmingham  
Ten Brinke, Groningen, Netherlands  
Ria Broer, Groningen, Netherlands  
Alexander Burin, Tulane University  
Philip J. Camp, University of Edinburgh  
David Cedeno, Illinois State University  
Alan Chadwick, University of Kent  
Li-Heng Chen, Aquinas College  
Aurora Clark, Washington State University  
Nigel Clarke, University of Durham  
Ron Clarke, University of Sydney  
David Cooper, University of Liverpool  
Garry Crosson, University of Dayton  
John Cullen, University of Manitoba  
Rajeev Dabke, Columbus State University  
Keith Davidson, University of Lancaster  
Guy Dennault, University of Southampton  
Caroline Dessent, University of York  
Thomas DeVore, James Madison University  
Michael Doescher, Benedictine University  
Randy Dumont, McMaster University  
Karen Edler, University of Bath  
Timothy Ehler, Buena Vista University  
Andrew Ellis, University of Leicester  
Cherice Evans, The City University of New York  
Ashleigh Fletcher, University of Newcastle  
Jiali Gao, University of Minnesota  
Sophya Garashchuk, University of South Carolina in Columbia  
Benjamin Gherman, California State University  
Peter Griffiths, Cardiff, University of Wales  
Nick Greeves, University of Liverpool

Gerard Grobner, University of Umeå, Sweden  
Anton Guliaev, San Francisco State University  
Arun Gupta, University of Alabama  
Leonid Gurevich, Aalborg, Denmark  
Georg Harhner, St Andrews University  
Ian Hamley, University of Reading  
Chris Hardacre, Queens University Belfast  
Anthony Harriman, University of Newcastle  
Torsten Hegmann, University of Manitoba  
Richard Henchman, University of Manchester  
Ulf Henriksson, Royal Institute of Technology, Stockholm, Sweden  
Harald Høiland, Bergen, Norway  
Paul Hodgkinson, University of Durham  
Phillip John, Heriot-Watt University  
Robert Hillman, University of Leicester  
Pat Holt, Bellarmine University  
Andrew Horn, University of Manchester  
Ben Horrocks, University of Newcastle  
Rob A. Jackson, University of Keele  
Seogjoo Jang, The City University of New York  
Don Jenkins, University of Warwick  
Matthew Johnson, Copenhagen, Denmark  
Mats Johnsson, Royal Institute of Technology, Stockholm, Sweden  
Milton Johnston, University of South Florida  
Peter Karadakov, University of York  
Dale Keefe, Cape Breton University  
Jonathan Kenny, Tufts University  
Peter Knowles, Cardiff, University of Wales  
Ranjit Koodali, University Of South Dakota  
Evguenii Kozliak, University of North Dakota  
Krish Krishnan, California State University  
Peter Kroll, University of Texas at Arlington  
Kari Laasonen, University of Oulu, Finland  
Ian Lane, Queens University Belfast  
Stanley Latesky, University of the Virgin Islands  
Daniel Lawson, University of Michigan  
Adam Lee, University of York  
Donál Leech, Galway, Ireland  
Graham Leggett, University of Sheffield  
Dewi Lewis, University College London  
Goran Lindblom, University of Umeå, Sweden  
Lesley Lloyd, University of Birmingham  
John Lombardi, City College of New York  
Zan Luthey-Schulten, University of Illinois at Urbana-Champaign  
Michael Lyons, Trinity College Dublin  
Alexander Lyubartsev, University of Stockholm  
Jeffrey Mack, California State University  
Paul Madden, University of Edinburgh  
Arnold Maliniak, University of Stockholm  
Herve Marand, Virginia Tech

Louis Massa, Hunter College  
 Andrew Masters, University of Manchester  
 Joe McDouall, University of Manchester  
 Gordon S. McDougall, University of Edinburgh  
 David McGarvey, University of Keele  
 Anthony Meijer, University of Sheffield  
 Robert Metzger, University of Alabama  
 Sergey Mikhalovsky, University of Brighton  
 Marcelo de Miranda, University of Leeds  
 Gerald Morine, Bemidji State University  
 Damien Murphy, Cardiff, University of Wales  
 David Newman, Bowling Green State University  
 Gareth Parkes, University of Huddersfield  
 Ruben Parra, DePaul University  
 Enrique Peacock-Lopez, Williams College  
 Nils-Ola Persson, Linköping University  
 Barry Pickup, University of Sheffield  
 Ivan Powis, University of Nottingham  
 Will Price, University of Wollongong, New South Wales, Australia  
 Robert Quandt, Illinois State University  
 Chris Rego, University of Leicester  
 Scott Reid, Marquette University  
 Gavin Reid, University of Leeds  
 Steve Roser, University of Bath  
 David Rowley, University College London  
 Alan Ryder, Galway, Ireland  
 Karl Ryder, University of Leicester  
 Stephen Saeur, Copenhagen, Denmark  
 Sven Schroeder, University of Manchester  
 Jeffrey Shepherd, Laurentian University  
 Paul Siders, University of Minnesota Duluth  
 Richard Singer, University of Kingston  
 Carl Soennischsen, The Johannes Gutenberg University of Mainz  
 Jie Song, University of Michigan  
 David Steytler, University of East Anglia  
 Michael Stockenhuber, Nottingham-Trent University

Sven Stolen, University of Oslo  
 Emile Charles Sykes, Tufts University  
 Greg Szulczevski, University of Alabama  
 Annette Taylor, University of Leeds  
 Peter Taylor, University of Warwick  
 Jeremy Titman, University of Nottingham  
 Jeroen Van-Duijneveldt, University of Bristol  
 Joop van Lenthe, University of Utrecht  
 Peter Varnai, University of Sussex  
 Jay Wadhawan, University of Hull  
 Palle Waage Jensen, University of Southern Denmark  
 Darren Walsh, University of Nottingham  
 Kjell Waltersson, Malarden University, Sweden  
 Richard Wells, University of Aberdeen  
 Ben Whitaker, University of Leeds  
 Kurt Winkelmann, Florida Institute of Technology  
 Timothy Wright, University of Nottingham  
 Yuanzheng Yue, Aalborg, Denmark  
 David Zax, Cornell University

We would like to thank two colleagues for their special contribution. Kerry Karaktis (Harvey Mudd College) provided many useful suggestions that focused on applications of the material presented in the text. David Smith (University of Bristol) made detailed comments on many of the chapters.

We also thank Claire Eisenhandler and Valerie Walters, who read through the proofs with meticulous attention to detail and caught in private what might have been a public grief. Our warm thanks also go to Charles Trapp, Carmen Giunta, and Marshall Cady who have produced the *Solutions manuals* that accompany this book.

Last, but by no means least, we would also like to thank our two publishers, Oxford University Press and W.H. Freeman & Co., for their constant encouragement, advice, and assistance, and in particular our editors Jonathan Crowe and Jessica Fiorillo. Authors could not wish for a more congenial publishing environment.

*This page intentionally left blank*

# Summary of contents

---

Fundamentals	1
<b>PART 1 Equilibrium</b>	<b>17</b>
1 The properties of gases	19
Mathematical background 1: Differentiation and integration	42
2 The First Law	44
Mathematical background 2: Multivariate calculus	91
3 The Second Law	94
4 Physical transformations of pure substances	135
5 Simple mixtures	156
6 Chemical equilibrium	209
<b>PART 2 Structure</b>	<b>247</b>
7 Quantum theory: introduction and principles	249
Mathematical background 3: Complex numbers	286
8 Quantum theory: techniques and applications	288
Mathematical background 4: Differential equations	322
9 Atomic structure and spectra	324
Mathematical background 5: Vectors	368
10 Molecular structure	371
Mathematical background 6: Matrices	414
11 Molecular symmetry	417
12 Molecular spectroscopy 1: rotational and vibrational spectra	445
13 Molecular spectroscopy 2: electronic transitions	489
14 Molecular spectroscopy 3: magnetic resonance	520
15 Statistical thermodynamics 1: the concepts	564
16 Statistical thermodynamics 2: applications	592
17 Molecular interactions	622
18 Materials 1: macromolecules and self-assembly	659
19 Materials 2: solids	695
Mathematical background 7: Fourier series and Fourier transforms	740
<b>PART 3 Change</b>	<b>743</b>
20 Molecules in motion	745
21 The rates of chemical reactions	782
22 Reaction dynamics	831
23 Catalysis	876
Resource section	909
Answers to exercises and odd-numbered problems	948
Index	959

*This page intentionally left blank*

# Contents

---

<b>Fundamentals</b>	<b>1</b>	<b>Thermochemistry</b>	<b>65</b>
<b>F.1</b> Atoms	1	<b>2.7</b> Standard enthalpy changes	65
<b>F.2</b> Molecules	2	<b>I2.1</b> Impact on biology: Food and energy reserves	70
<b>F.3</b> Bulk matter	4	<b>2.8</b> Standard enthalpies of formation	71
<b>F.4</b> Energy	6	<b>2.9</b> The temperature dependence of reaction enthalpies	73
<b>F.5</b> The relation between molecular and bulk properties	7		
<b>F.6</b> The electromagnetic field	9		
<b>F.7</b> Units	10		
Exercises	13		
<b>PART 1 Equilibrium</b>	<b>17</b>	<b>State functions and exact differentials</b>	<b>74</b>
<b>1 The properties of gases</b>	<b>19</b>	<b>2.10</b> Exact and inexact differentials	74
<b>The perfect gas</b>	<b>19</b>	<b>2.11</b> Changes in internal energy	75
<b>1.1</b> The states of gases	19	<b>2.12</b> The Joule–Thomson effect	79
<b>1.2</b> The gas laws	23		
<b>I1.1</b> Impact on environmental science: The gas laws and the weather	28		
<b>Real gases</b>	<b>29</b>	Checklist of key equations	83
<b>1.3</b> Molecular interactions	30	Further information 2.1: Adiabatic processes	84
<b>1.4</b> The van der Waals equation	33	Further information 2.2: The relation between heat capacities	84
Checklist of key equations	37	Discussion questions	85
Discussion questions	38	Exercises	85
Exercises	38	Problems	88
<b>Mathematical background 1: Differentiation and integration</b>	<b>42</b>		
<b>2 The First Law</b>	<b>44</b>	<b>Mathematical background 2: Multivariate calculus</b>	<b>91</b>
<b>The basic concepts</b>	<b>44</b>	<b>MB2.1</b> Partial derivatives	91
<b>2.1</b> Work, heat, and energy	45	<b>MB2.2</b> Exact differentials	92
<b>2.2</b> The internal energy	47		
<b>2.3</b> Expansion work	49		
<b>2.4</b> Heat transactions	53		
<b>2.5</b> Enthalpy	56		
<b>I2.1</b> Impact on biochemistry and materials science: Differential scanning calorimetry	62		
<b>2.6</b> Adiabatic changes	63		
<b>3 The Second Law</b>	<b>94</b>		
<b>The direction of spontaneous change</b>	<b>95</b>		
<b>3.1</b> The dispersal of energy	95		
<b>3.2</b> Entropy	96		
<b>I3.1</b> Impact on engineering: Refrigeration	103		
<b>3.3</b> Entropy changes accompanying specific processes	104		
<b>3.4</b> The Third Law of thermodynamics	109		
<b>I3.2</b> Impact on materials chemistry: Crystal defects	112		
<b>Concentrating on the system</b>	<b>113</b>		
<b>3.5</b> The Helmholtz and Gibbs energies	113		
<b>3.6</b> Standard molar Gibbs energies	118		
<b>Combining the First and Second Laws</b>	<b>121</b>		
<b>3.7</b> The fundamental equation	121		
<b>3.8</b> Properties of the internal energy	121		
<b>3.9</b> Properties of the Gibbs energy	124		
Checklist of key equations	128		
Further information 3.1: The Born equation	128		
Further information 3.2: The fugacity	129		

Discussion questions	130	<b>6 Chemical equilibrium</b>	<b>209</b>
Exercises	131		
Problems	132		
<b>4 Physical transformations of pure substances</b>	<b>135</b>		
<b>Phase diagrams</b>	<b>135</b>	<b>Spontaneous chemical reactions</b>	<b>209</b>
<b>4.1</b> The stabilities of phases	135	<b>6.1</b> The Gibbs energy minimum	210
<b>4.2</b> Phase boundaries	137	<b>16.1</b> Impact on biochemistry: Energy conversion in biological cells	211
<b>4.3</b> Three representative phase diagrams	140	<b>6.2</b> The description of equilibrium	213
<b>I4.1</b> Impact on technology: Supercritical fluids	142		
<b>Thermodynamic aspects of phase transitions</b>	<b>143</b>	<b>The response of equilibria to the conditions</b>	<b>221</b>
<b>4.4</b> The dependence of stability on the conditions	143	<b>6.3</b> How equilibria respond to changes of pressure	221
<b>4.5</b> The location of phase boundaries	146	<b>6.4</b> The response of equilibria to changes of temperature	223
<b>4.6</b> The Ehrenfest classification of phase transitions	149	<b>16.2</b> Impact on technology: Supramolecular chemistry	226
Checklist of key equations	152		
Discussion questions	152	<b>Equilibrium electrochemistry</b>	<b>227</b>
Exercises	153	<b>6.5</b> Half-reactions and electrodes	228
Problems	154	<b>6.6</b> Varieties of cells	229
<b>5 Simple mixtures</b>	<b>156</b>	<b>6.7</b> The cell potential	230
<b>The thermodynamic description of mixtures</b>	<b>156</b>	<b>6.8</b> Standard electrode potentials	233
<b>5.1</b> Partial molar quantities	157	<b>6.9</b> Applications of standard potentials	235
<b>5.2</b> The thermodynamics of mixing	161	<b>16.3</b> Impact on technology: Species-selective electrodes	239
<b>5.3</b> The chemical potentials of liquids	164		
<b>The properties of solutions</b>	<b>167</b>	Checklist of key equations	240
<b>5.4</b> Liquid mixtures	167	Discussion questions	241
<b>5.5</b> Colligative properties	169	Exercises	241
<b>I5.1</b> Impact on biology: Osmosis in physiology and biochemistry	175	Problems	243
<b>Phase diagrams of binary systems</b>	<b>176</b>	<b>PART 2 Structure</b>	<b>247</b>
<b>5.6</b> Vapour pressure diagrams	176		
<b>5.7</b> Temperature–composition diagrams	179		
<b>5.8</b> Liquid–liquid phase diagrams	181		
<b>5.9</b> Liquid–solid phase diagrams	185		
<b>I5.2</b> Impact on materials science: Liquid crystals	188		
<b>Activities</b>	<b>190</b>	<b>7 Quantum theory: introduction and principles</b>	<b>249</b>
<b>5.10</b> The solvent activity	190	<b>The origins of quantum mechanics</b>	<b>249</b>
<b>5.11</b> The solute activity	191	<b>7.1</b> Energy quantization	250
<b>5.12</b> The activities of regular solutions	194	<b>7.2</b> Wave–particle duality	255
<b>5.13</b> The activities of ions in solution	195	<b>17.1</b> Impact on biology: Electron microscopy	259
Checklist of key equations	198	<b>The dynamics of microscopic systems</b>	<b>260</b>
Further information 5.1: The Debye–Hückel theory of ionic solutions	199	<b>7.3</b> The Schrödinger equation	260
Discussion questions	200	<b>7.4</b> The Born interpretation of the wavefunction	262
Exercises	201	<b>Quantum mechanical principles</b>	<b>266</b>
Problems	204	<b>7.5</b> The information in a wavefunction	266
		<b>7.6</b> The uncertainty principle	276
		<b>7.7</b> The postulates of quantum mechanics	279
		Checklist of key equations	280
		Further information 7.1: Classical mechanics	280
		Discussion questions	283
		Exercises	283
		Problems	284

<b>Mathematical background 3: Complex numbers</b>	<b>286</b>	Further information 9.2: The energy of spin–orbit interaction	363
<b>MB3.1</b> Definitions	286	Discussion questions	363
<b>MB3.2</b> Polar representation	286	Exercises	364
<b>MB3.3</b> Operations	287	Problems	365
<b>8 Quantum theory: techniques and applications</b>	<b>288</b>	<b>Mathematical background 5: Vectors</b>	<b>368</b>
<b>Translational motion</b>	<b>288</b>	<b>MB5.1</b> Addition and subtraction	368
<b>8.1</b> A particle in a box	289	<b>MB5.2</b> Multiplication	369
<b>8.2</b> Motion in two and more dimensions	293	<b>MB5.3</b> Differentiation	369
<b>I8.1</b> Impact on nanoscience: Quantum dots	295		
<b>8.3</b> Tunnelling	297		
<b>I8.2</b> Impact on nanoscience: Scanning probe microscopy	299		
<b>Vibrational motion</b>	<b>300</b>	<b>10 Molecular structure</b>	<b>371</b>
<b>8.4</b> The energy levels	301	<b>The Born–Oppenheimer approximation</b>	<b>372</b>
<b>8.5</b> The wavefunctions	302	<b>Valence-bond theory</b>	<b>372</b>
<b>Rotational motion</b>	<b>306</b>	<b>10.1</b> Homonuclear diatomic molecules	372
<b>8.6</b> Rotation in two dimensions: a particle on a ring	306	<b>10.2</b> Polyatomic molecules	374
<b>8.7</b> Rotation in three dimensions: the particle on a sphere	310	<b>Molecular orbital theory</b>	<b>378</b>
<b>8.8</b> Spin	315	<b>10.3</b> The hydrogen molecule-ion	378
Checklist of key equations	317	<b>10.4</b> Homonuclear diatomic molecules	382
Discussion questions	317	<b>10.5</b> Heteronuclear diatomic molecules	388
Exercises	317	<b>I10.1</b> Impact on biochemistry: The biochemical reactivity of O <sub>2</sub> , N <sub>2</sub> , and NO	394
Problems	319	<b>Molecular orbitals for polyatomic systems</b>	<b>395</b>
<b>Mathematical background 4: Differential equations</b>	<b>322</b>	<b>10.6</b> The Hückel approximation	395
<b>MB4.1</b> The structure of differential equations	322	<b>10.7</b> Computational chemistry	401
<b>MB4.2</b> The solution of ordinary differential equations	322	<b>10.8</b> The prediction of molecular properties	405
<b>MB4.3</b> The solution of partial differential equations	323	Checklist of key equations	407
<b>9 Atomic structure and spectra</b>	<b>324</b>	Further information 10.1: Details of the Hartree–Fock method	408
<b>The structure and spectra of hydrogenic atoms</b>	<b>324</b>	Discussion questions	409
<b>9.1</b> The structure of hydrogenic atoms	325	Exercises	409
<b>9.2</b> Atomic orbitals and their energies	330	Problems	410
<b>9.3</b> Spectroscopic transitions and selection rules	339		
<b>The structures of many-electron atoms</b>	<b>340</b>	<b>Mathematical background 6: Matrices</b>	<b>414</b>
<b>9.4</b> The orbital approximation	341	<b>MB6.1</b> Definitions	414
<b>9.5</b> Self-consistent field orbitals	349	<b>MB6.2</b> Matrix addition and multiplication	414
<b>The spectra of complex atoms</b>	<b>350</b>	<b>MB6.3</b> Eigenvalue equations	415
<b>9.6</b> Linewidths	350		
<b>9.7</b> Quantum defects and ionization limits	352		
<b>9.8</b> Singlet and triplet states	353		
<b>9.9</b> Spin–orbit coupling	354		
<b>9.10</b> Term symbols and selection rules	357		
<b>I9.1</b> Impact on astrophysics: Spectroscopy of stars	361		
Checklist of key equations	362	<b>11 Molecular symmetry</b>	<b>417</b>
Further information 9.1: The separation of motion	362		
		<b>The symmetry elements of objects</b>	<b>417</b>
		<b>11.1</b> Operations and symmetry elements	418
		<b>11.2</b> The symmetry classification of molecules	420
		<b>11.3</b> Some immediate consequences of symmetry	425
		<b>Applications to molecular orbital theory and spectroscopy</b>	<b>427</b>
		<b>11.4</b> Character tables and symmetry labels	427
		<b>11.5</b> Vanishing integrals and orbital overlap	433
		<b>11.6</b> Vanishing integrals and selection rules	439

Checklist of key equations	441	<b>The fates of electronically excited states</b>	<b>503</b>
Discussion questions	441	<b>13.4</b> Fluorescence and phosphorescence	503
Exercises	441	<b>I13.2</b> Impact on biochemistry: Fluorescence microscopy	507
Problems	442	<b>13.5</b> Dissociation and predissociation	507
		<b>13.6</b> Laser action	508
<b>12 Molecular spectroscopy 1: rotational and vibrational spectra</b>	<b>445</b>	Checklist of key equations	512
<b>General features of molecular spectroscopy</b>	<b>446</b>	Further information 13.1: Examples of practical lasers	513
<b>12.1</b> Experimental techniques	446	Discussion questions	515
<b>12.2</b> Selection rules and transition moments	447	Exercises	515
<b>I12.1</b> Impact on astrophysics: Rotational and vibrational spectroscopy of interstellar species	447	Problems	517
<b>Pure rotation spectra</b>	<b>449</b>	<b>14 Molecular spectroscopy 3: magnetic resonance</b>	<b>520</b>
<b>12.3</b> Moments of inertia	449	<b>The effect of magnetic fields on electrons and nuclei</b>	<b>520</b>
<b>12.4</b> The rotational energy levels	452	<b>14.1</b> The energies of electrons in magnetic fields	521
<b>12.5</b> Rotational transitions	456	<b>14.2</b> The energies of nuclei in magnetic fields	522
<b>12.6</b> Rotational Raman spectra	459	<b>14.3</b> Magnetic resonance spectroscopy	523
<b>12.7</b> Nuclear statistics and rotational states	460	<b>Nuclear magnetic resonance</b>	<b>524</b>
<b>The vibrations of diatomic molecules</b>	<b>462</b>	<b>14.4</b> The NMR spectrometer	525
<b>12.8</b> Molecular vibrations	462	<b>14.5</b> The chemical shift	526
<b>12.9</b> Selection rules	464	<b>14.6</b> The fine structure	532
<b>12.10</b> Anharmonicity	465	<b>14.7</b> Conformational conversion and exchange processes	539
<b>12.11</b> Vibration–rotation spectra	468	<b>Pulse techniques in NMR</b>	<b>540</b>
<b>12.12</b> Vibrational Raman spectra of diatomic molecules	469	<b>14.8</b> The magnetization vector	540
<b>The vibrations of polyatomic molecules</b>	<b>470</b>	<b>14.9</b> Spin relaxation	542
<b>12.13</b> Normal modes	471	<b>I14.1</b> Impact on medicine: Magnetic resonance imaging	546
<b>12.14</b> Infrared absorption spectra of polyatomic molecules	472	<b>14.10</b> Spin decoupling	548
<b>I12.2</b> Impact on environmental science: Climate change	473	<b>14.11</b> The nuclear Overhauser effect	548
<b>12.15</b> Vibrational Raman spectra of polyatomic molecules	475	<b>14.12</b> Two-dimensional NMR	550
<b>12.16</b> Symmetry aspects of molecular vibrations	476	<b>14.13</b> Solid-state NMR	551
Checklist of key equations	479	<b>Electron paramagnetic resonance</b>	<b>553</b>
Further information 12.1: Spectrometers	479	<b>14.14</b> The EPR spectrometer	553
Further information 12.2: Selection rules for rotational and vibrational spectroscopy	482	<b>14.15</b> The g-value	553
Discussion questions	484	<b>14.16</b> Hyperfine structure	555
Exercises	484	<b>I14.2</b> Impact on biochemistry and nanoscience: Spin probes	557
Problems	486	Checklist of key equations	559
<b>13 Molecular spectroscopy 2: electronic transitions</b>	<b>489</b>	Further information 14.1: Fourier transformation of the FID curve	559
<b>The characteristics of electronic transitions</b>	<b>489</b>	Discussion questions	559
<b>13.1</b> Measurements of intensity	490	Exercises	560
<b>13.2</b> The electronic spectra of diatomic molecules	491	Problems	561
<b>13.3</b> The electronic spectra of polyatomic molecules	498		
<b>I13.1</b> Impact on biochemistry: Vision	501		
		<b>15 Statistical thermodynamics 1: the concepts</b>	<b>564</b>
		<b>The distribution of molecular states</b>	<b>565</b>
		<b>15.1</b> Configurations and weights	565
		<b>15.2</b> The molecular partition function	568

<b>The internal energy and the entropy</b>	<b>574</b>	<b>17.6</b> Repulsive and total interactions	642
<b>15.3</b> The internal energy	574	<b>17.2</b> Impact on materials science: Hydrogen storage in molecular clathrates	643
<b>15.4</b> The statistical entropy	576		
<b>I15.1</b> Impact on technology: Reaching very low temperatures	578		
<b>The canonical partition function</b>	<b>579</b>	<b>Gases and liquids</b>	<b>643</b>
<b>15.5</b> The canonical ensemble	579	<b>17.7</b> Molecular interactions in gases	644
<b>15.6</b> The thermodynamic information in the partition function	581	<b>17.8</b> The liquid–vapour interface	645
<b>15.7</b> Independent molecules	582	<b>17.9</b> Surface films	649
Checklist of key equations	585	<b>17.10</b> Condensation	652
Further information 15.1: The Boltzmann distribution	585	Checklist of key equations	653
Further information 15.2: The Boltzmann formula	587	Further information 17.1: The dipole–dipole interaction	654
Discussion questions	588	Further information 17.2: The basic principles of molecular beams	654
Exercises	588	Discussion questions	655
Problems	590	Exercises	655
		Problems	656
<b>16 Statistical thermodynamics 2: applications</b>	<b>592</b>	<b>18 Materials 1: macromolecules and self-assembly</b>	<b>659</b>
<b>Fundamental relations</b>	<b>592</b>	<b>Structure and dynamics</b>	<b>659</b>
<b>16.1</b> The thermodynamic functions	592	<b>18.1</b> The different levels of structure	660
<b>16.2</b> The molecular partition function	594	<b>18.2</b> Random coils	660
<b>Using statistical thermodynamics</b>	<b>601</b>	<b>18.3</b> The mechanical properties of polymers	665
<b>16.3</b> Mean energies	601	<b>18.4</b> The electrical properties of polymers	667
<b>16.4</b> Heat capacities	602	<b>18.5</b> The structures of biological macromolecules	667
<b>16.5</b> Equations of state	605		
<b>16.6</b> Molecular interactions in liquids	607	<b>Aggregation and self-assembly</b>	<b>671</b>
<b>16.7</b> Residual entropies	609	<b>18.6</b> Colloids	671
<b>16.8</b> Equilibrium constants	610	<b>18.7</b> Micelles and biological membranes	674
<b>I16.1</b> Impact on biochemistry: The helix–coil transition in polypeptides	615		
Checklist of key equations	616	<b>Determination of size and shape</b>	<b>677</b>
Further information 16.1: The rotational partition function of a symmetric rotor	617	<b>18.8</b> Mean molar masses	678
Discussion questions	618	<b>18.9</b> The techniques	680
Exercises	618	Checklist of key equations	688
Problems	619	Further information 18.1: Random and nearly random coils	689
		Discussion questions	690
		Exercises	690
		Problems	691
<b>17 Molecular interactions</b>	<b>622</b>	<b>19 Materials 2: solids</b>	<b>695</b>
<b>Electric properties of molecules</b>	<b>622</b>	<b>Crystallography</b>	<b>695</b>
<b>17.1</b> Electric dipole moments	622	<b>19.1</b> Lattices and unit cells	695
<b>17.2</b> Polarizabilities	625	<b>19.2</b> The identification of lattice planes	697
<b>17.3</b> Polarization	626	<b>19.3</b> The investigation of structure	699
<b>17.4</b> Relative permittivities	628	<b>19.4</b> Neutron and electron diffraction	708
<b>Interactions between molecules</b>	<b>631</b>	<b>19.5</b> Metallic solids	709
<b>17.5</b> Interactions between dipoles	631	<b>19.6</b> Ionic solids	711
<b>I17.1</b> Impact on medicine: Molecular recognition and drug design	640	<b>19.7</b> Molecular solids and covalent networks	714
		<b>I19.1</b> Impact on biochemistry: X-ray crystallography of biological macromolecules	715

<b>The properties of solids</b>	<b>717</b>	<b>21 The rates of chemical reactions</b>	<b>782</b>
19.8 Mechanical properties	717		
19.9 Electrical properties	719		
I19.2 Impact on nanoscience: Nanowires	723		
19.10 Optical properties	724		
19.11 Magnetic properties	728		
19.12 Superconductors	731		
Checklist of key equations	733		
Further information 19.1: Solid state lasers and light-emitting diodes	733		
Discussion questions	734		
Exercises	735		
Problems	737		
<b>Mathematical background 7: Fourier series and Fourier transforms</b>	<b>740</b>		
MB7.1 Fourier series	740		
MB7.2 Fourier transforms	741		
MB7.3 The convolution theorem	742		
<b>PART 3 Change</b>	<b>743</b>		
<b>20 Molecules in motion</b>	<b>745</b>		
<b>Molecular motion in gases</b>	<b>745</b>		
20.1 The kinetic model of gases	746		
I20.1 Impact on astrophysics: The Sun as a ball of perfect gas	752		
20.2 Collisions with walls and surfaces	753		
20.3 The rate of effusion	754		
20.4 Transport properties of a perfect gas	755		
<b>Molecular motion in liquids</b>	<b>758</b>		
20.5 Experimental results	758		
20.6 The conductivities of electrolyte solutions	759		
20.7 The mobilities of ions	760		
I20.2 Impact on biochemistry: Ion channels	764		
<b>Diffusion</b>	<b>766</b>		
20.8 The thermodynamic view	766		
20.9 The diffusion equation	770		
20.10 Diffusion probabilities	772		
20.11 The statistical view	773		
Checklist of key equations	774		
Further information 20.1: The transport characteristics of a perfect gas	775		
Discussion questions	776		
Exercises	777		
Problems	779		
<b>21 The rates of chemical reactions</b>	<b>782</b>		
<b>Empirical chemical kinetics</b>	<b>782</b>		
21.1 Experimental techniques	783		
21.2 The rates of reactions	786		
21.3 Integrated rate laws	790		
21.4 Reactions approaching equilibrium	796		
21.5 The temperature dependence of reaction rates	799		
<b>Accounting for the rate laws</b>	<b>802</b>		
21.6 Elementary reactions	802		
21.7 Consecutive elementary reactions	803		
<b>Examples of reaction mechanisms</b>	<b>809</b>		
21.8 Unimolecular reactions	809		
21.9 Polymerization kinetics	811		
21.10 Photochemistry	815		
I21.1 Impact on biochemistry: Harvesting of light during plant photosynthesis	822		
Checklist of key equations	825		
Discussion questions	825		
Exercises	826		
Problems	828		
<b>22 Reaction dynamics</b>	<b>831</b>		
<b>Reactive encounters</b>	<b>831</b>		
22.1 Collision theory	832		
22.2 Diffusion-controlled reactions	839		
22.3 The material balance equation	842		
<b>Transition state theory</b>	<b>843</b>		
22.4 The Eyring equation	844		
22.5 Thermodynamic aspects	848		
<b>The dynamics of molecular collisions</b>	<b>851</b>		
22.6 Reactive collisions	851		
22.7 Potential energy surfaces	852		
22.8 Some results from experiments and calculations	853		
<b>The dynamics of electron transfer</b>	<b>856</b>		
22.9 Electron transfer in homogeneous systems	857		
22.10 Electron transfer processes at electrodes	861		
I22.1 Impact on technology: Fuel cells	867		
Checklist of key equations	868		
Further information 22.1: The Gibbs energy of activation of electron transfer	868		
Further information 22.2: The Butler–Volmer equation	869		
Discussion questions	871		
Exercises	871		
Problems	873		

<b>23 Catalysis</b>	<b>876</b>	
<hr/>		
<b>Homogeneous catalysis</b>	<b>876</b>	<b>I23.1</b> Impact on technology: Catalysis in the chemical industry
<b>23.1</b> Features of homogeneous catalysis	876	Checklist of key equations
<b>23.2</b> Enzymes	878	Further information 23.1: The BET isotherm
<hr/>		
<b>Heterogeneous catalysis</b>	<b>884</b>	Discussion questions
<b>23.3</b> The growth and structure of solid surfaces	885	Exercises
<b>23.4</b> The extent of adsorption	888	Problems
<b>23.5</b> The rates of surface processes	894	Resource section
<b>23.6</b> Mechanisms of heterogeneous catalysis	897	Answers to exercises and odd-numbered problems
<b>23.7</b> Catalytic activity at surfaces	899	Index
900		
903		
903		
904		
904		
906		
909		
948		
959		

*This page intentionally left blank*

# List of impact sections

---

## Impact on astrophysics

I9.1	Spectroscopy of stars	361
I12.1	Rotational and vibrational spectroscopy of interstellar species	447
I20.1	The Sun as a ball of perfect gas	752

## Impact on biochemistry

I2.1	Differential scanning calorimetry	62
I6.1	Energy conversion in biological cells	211
I10.1	The biochemical reactivity of O <sub>2</sub> , N <sub>2</sub> , and NO	394
I13.1	Vision	501
I13.2	Fluorescence microscopy	507
I14.2	Spin probes	557
I16.1	The helix–coil transition in polypeptides	615
I19.1	X-ray crystallography of biological macromolecules	715
I20.2	Ion channels	764
I21.1	Harvesting of light during plant photosynthesis	822

## Impact on biology

I2.2	Food and energy reserves	70
I5.1	Osmosis in physiology and biochemistry	175
I7.1	Electron microscopy	259

## Impact on engineering

I3.1	Refrigeration	103
------	---------------	-----

## Impact on environmental science

I1.1	The gas laws and the weather	28
I12.2	Climate change	473

## Impact on materials science

I3.2	Crystal defects	112
I5.2	Liquid crystals	188
I17.2	Hydrogen storage in molecular clathrates	643

## Impact on medicine

I14.1	Magnetic resonance imaging	546
I17.1	Molecular recognition and drug design	640

## Impact on nanoscience

I8.1	Quantum dots	295
I8.2	Scanning probe microscopy	299
I19.2	Nanowires	723

## Impact on technology

I4.1	Supercritical fluids	142
I6.2	Supramolecular chemistry	226
I6.3	Species-selective electrodes	239
I15.1	Reaching very low temperatures	578
I22.1	Fuel cells	867
I23.1	Catalysis in the chemical industry	900

# Fundamentals



Chemistry is the science of matter and the changes it can undergo. **Physical chemistry** is the branch of chemistry that establishes and develops the principles of the subject in terms of the underlying concepts of physics and the language of mathematics. It provides the basis for developing new spectroscopic techniques and their interpretation, for understanding the structures of molecules and the details of their electron distributions, and for relating the bulk properties of matter to their constituent atoms. Physical chemistry also provides a window on to the world of chemical reactions and allows us to understand in detail how they take place. In fact, the subject underpins the whole of chemistry, providing the principles in terms we use to understand structure and change and providing the basis of all techniques of investigation.

Throughout the text we shall draw on a number of concepts, most of which should already be familiar from introductory chemistry. This section reviews them. In almost every case the following chapters will provide a deeper discussion, but we are presuming that we can refer to these concepts at any stage of the presentation. Because physical chemistry lies at the interface between physics and chemistry, we also need to review some of the concepts from elementary physics that we need to draw on in the text.

## F.1 Atoms

**Key points** (a) The nuclear model is the basis for discussion of atomic structure: negatively charged electrons occupy atomic orbitals, which are arranged in shells around a positively charged nucleus. (b) The periodic table highlights similarities in electronic configurations of atoms, which in turn lead to similarities in their physical and chemical properties. (c) Monatomic ions are electrically charged atoms and are characterized by their oxidation numbers.

Matter consists of atoms. The atom of an element is characterized by its **atomic number**,  $Z$ , which is the number of protons in its nucleus. The number of neutrons in a nucleus is variable to a small extent, and the **nucleon number** (which is also commonly called the *mass number*),  $A$ , is the total number of protons and neutrons, which are collectively called **nucleons**, in the nucleus. Atoms of the same atomic number but different nucleon number are the **isotopes** of the element.

According to the **nuclear model**, an atom of atomic number  $Z$  consists of a nucleus of charge  $+Ze$  surrounded by  $Z$  electrons each of charge  $-e$  ( $e$  is the fundamental charge: see inside the front cover for its value and the values of the other fundamental constants). These electrons occupy **atomic orbitals**, which are regions of space where they are most likely to be found, with no more than two electrons in any one orbital. The atomic orbitals are arranged in **shells** around the nucleus, each shell being characterized by the **principal quantum number**,  $n = 1, 2, \dots$ . A shell consists of  $n^2$

## F.1 Atoms

### F.2 Molecules

### F.3 Bulk matter

### F.4 Energy

### F.5 The relation between molecular and bulk properties

#### (a) The Boltzmann distribution

#### (b) Equipartition

### F.6 The electromagnetic field

### F.7 Units

## Exercises

individual orbitals, which are grouped together into  $n$  subshells; these subshells, and the orbitals they contain, are denoted s, p, d, and f. For all neutral atoms other than hydrogen, the subshells of a given shell have slightly different energies.

The sequential occupation of the orbitals in successive shells results in periodic similarities in the **electronic configurations**, the specification of the occupied orbitals, of atoms when they are arranged in order of their atomic number, which leads to the formulation of the **periodic table** (a version is shown inside the back cover). The vertical columns of the periodic table are called **groups** and (in the modern convention) numbered from 1 to 18. Successive rows of the periodic table are called **periods**, the number of the period being equal to the principal quantum number of the **valence shell**, the outermost shell of the atom. The periodic table is divided into s, p, d, and f blocks, according to the subshell that is last to be occupied in the formulation of the electronic configuration of the atom. The members of the d block (specifically the members of Groups 3–11 in the d block) are also known as the **transition metals**; those of the f block (which is not divided into numbered groups) are sometimes called the **inner transition metals**. The upper row of the f block (Period 6) consists of the **lanthanoids** (still commonly the ‘lanthanides’) and the lower row (Period 7) consists of the **actinoids** (still commonly the ‘actinides’). Some of the groups also have familiar names: Group 1 consists of the **alkali metals**, Group 2 (more specifically, calcium, strontium, and barium) of the **alkaline earth metals**, Group 17 of the **halogens**, and Group 18 of the **noble gases**. Broadly speaking, the elements towards the left of the periodic table are **metals** and those towards the right are **nonmetals**; the two classes of substance meet at a diagonal line running from boron to polonium, which constitute the **metalloids**, with properties intermediate between those of metals and nonmetals.

A monatomic ion is an electrically charged atom. When an atom gains one or more electrons it becomes a negatively charged **anion**; when it loses one or more electrons it becomes a positively charged **cation**. The charge number of an ion is called the **oxidation number** of the element in that state (thus, the oxidation number of magnesium in  $Mg^{2+}$  is +2 and that of oxygen in  $O^{2-}$  is -2). It is appropriate, but not always done, to distinguish between the oxidation number and the **oxidation state**, the latter being the physical state of the atom with a specified oxidation number. Thus, the oxidation number of magnesium is +2 when it is present as  $Mg^{2+}$ , and it is present in the oxidation state  $Mg^{2+}$ . The elements form ions that are characteristic of their location in the periodic table: metallic elements typically form cations by losing the electrons of their outermost shell and acquiring the electronic configuration of the preceding noble gas. Nonmetals typically form anions by gaining electrons and attaining the electronic configuration of the following noble gas.

## F.2 Molecules

---

**Key points** (a) Covalent compounds consist of discrete molecules in which atoms are linked by covalent bonds. (b) Ionic compounds consist of cations and anions in a crystalline array. (c) Lewis structures are useful models of the pattern of bonding in molecules. (d) The valence-shell electron pair repulsion theory (VSEPR theory) is used to predict the three-dimensional structures of molecules from their Lewis structures. (e) The electrons in polar covalent bonds are shared unevenly between the bonded nuclei.

---

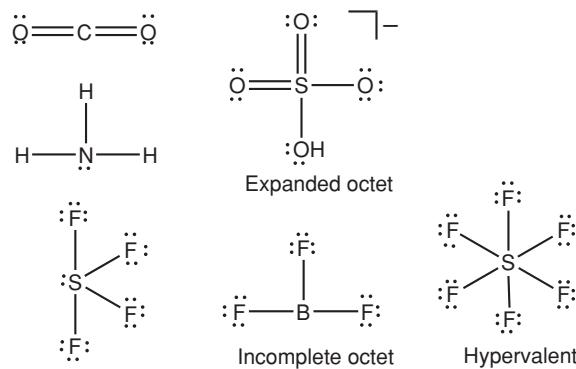
A **chemical bond** is the link between atoms. Compounds that contain a metallic element typically, but far from universally, form **ionic compounds** that consist of cations and anions in a crystalline array. The ‘chemical bonds’ in an ionic compound

are due to the Coulombic interactions (Section F.4) between all the ions in the crystal, and it is inappropriate to refer to a bond between a specific pair of neighbouring ions. The smallest unit of an ionic compound is called a **formula unit**. Thus  $\text{NaNO}_3$ , consisting of a  $\text{Na}^+$  cation and a  $\text{NO}_3^-$  anion, is the formula unit of sodium nitrate. Compounds that do not contain a metallic element typically form **covalent compounds** consisting of discrete molecules. In this case, the bonds between the atoms of a molecule are **covalent**, meaning that they consist of shared pairs of electrons.

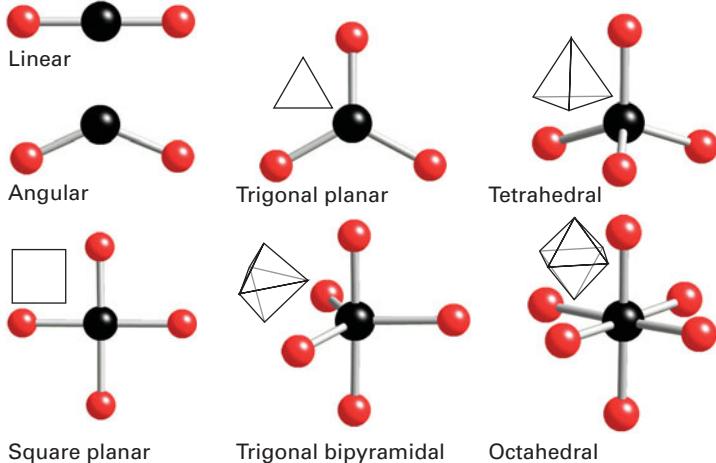
The pattern of bonds between neighbouring atoms is displayed by drawing a **Lewis structure**, in which bonds are shown as lines and **lone pairs** of electrons, pairs of valence electrons that are not used in bonding, are shown as dots. Lewis structures are constructed by allowing each atom to share electrons until it has acquired an octet of eight electrons (for hydrogen, a *duplet* of two electrons). A shared pair of electrons is a **single bond**, two shared pairs constitute a **double bond**, and three shared pairs constitute a **triple bond**. Atoms of elements of Period 3 and later can accommodate more than eight electrons in their valence shell and ‘expand their octet’ to become **hypervalent**, that is, form more bonds than the octet rule would allow (for example,  $\text{SF}_6$ ), or form more bonds to a small number of atoms (for example, a Lewis structure of  $\text{SO}_4^{2-}$  with one or more double bonds). When more than one Lewis structure can be written for a given arrangement of atoms, it is supposed that **resonance**, a blending of the structures, may occur and distribute multiple-bond character over the molecule (for example, the two Kekulé structures of benzene). Examples of these aspects of Lewis structures are shown in Fig. F.1.

Except in the simplest cases, a Lewis structure does not express the three-dimensional structure of a molecule. The simplest approach to the prediction of molecular shape is **valence-shell electron pair repulsion theory** (VSEPR theory). In this approach, the regions of high electron density, as represented by bonds—whether single or multiple—and lone pairs, take up orientations around the central atom that maximize their separations. Then the position of the attached atoms (not the lone pairs) is noted and used to classify the shape of the molecule. Thus, four regions of electron density adopt a tetrahedral arrangement; if an atom is at each of these locations (as in  $\text{CH}_4$ ), then the molecule is tetrahedral; if there is an atom at only three of these locations (as in  $\text{NH}_3$ ), then the molecule is trigonal pyramidal; and so on. The names of the various shapes that are commonly found are shown in Fig. F.2. In a refinement of the theory, lone pairs are assumed to repel bonding pairs more strongly than bonding pairs repel each other. The shape a molecule then adopts, if it is not

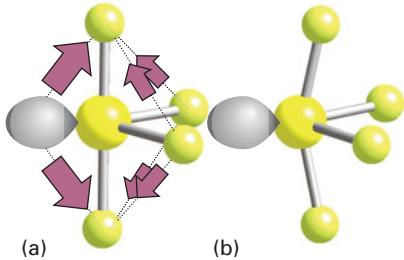
**A note on good practice** Some chemists use the term ‘molecule’ to denote the smallest unit of a compound with the composition of the bulk material regardless of whether it is an ionic or covalent compound and thus speak of ‘a molecule of  $\text{NaCl}$ ’. We use the term ‘molecule’ to denote a discrete covalently bonded entity (as in  $\text{H}_2\text{O}$ ); for an ionic compound we use ‘formula unit’.



**Fig. F.1** A collection of typical Lewis structures for simple molecules and ions. The structures show the bonding patterns and lone pairs and, except in simple cases, do not express the shape of the species.



**Fig. F.2** The names of the shapes of the geometrical figures used to describe symmetrical polyatomic molecules and ions.



**Fig. F.3** (a) The influences on the shape of the SF<sub>4</sub> molecule according to the VSEPR model. (b) As a result the molecule adopts a bent see-saw shape.

determined fully by symmetry, is such as to minimize repulsions from lone pairs. Thus, in SF<sub>4</sub> the lone pair adopts an equatorial position and the two axial S–F bonds bend away from it slightly, to give a bent see-saw shaped molecule (Fig. F.3).

Covalent bonds may be **polar**, or correspond to an unequal sharing of the electron pair, with the result that one atom has a partial positive charge (denoted  $\delta+$ ) and the other a partial negative charge ( $\delta-$ ). The ability of an atom to attract electrons to itself when part of a molecule is measured by the **electronegativity**,  $\chi$  (chi), of the element. The juxtaposition of equal and opposite partial charges constitutes an **electric dipole**. If those charges are  $+Q$  and  $-Q$  and they are separated by a distance  $d$ , the magnitude of the **electric dipole moment** is  $\mu = Qd$ . Whether or not a molecule as a whole is polar depends on the arrangement of its bonds, for in highly symmetrical molecules there may be no net dipole. Thus, although the linear CO<sub>2</sub> molecule (which is structurally OCO) has polar CO bonds, their effects cancel and the molecule as a whole is nonpolar.

### F.3 Bulk matter

**Key points** (a) The physical states of bulk matter are solid, liquid, or gas. (b) The state of a sample of bulk matter is defined by specifying its properties, such as mass, volume, amount, pressure, and temperature. (c) The perfect gas law is a relation between the pressure, volume, amount, and temperature of an idealized gas.

**Bulk matter** consists of large numbers of atoms, molecules, or ions. Its physical state may be solid, liquid, or gas:

A **solid** is a form of matter that adopts and maintains a shape that is independent of the container it occupies.

A **liquid** is a form of matter that adopts the shape of the part of the container it occupies (in a gravitational field, the lower part) and is separated from the unoccupied part of the container by a definite surface.

A **gas** is a form of matter that immediately fills any container it occupies.

A liquid and a solid are examples of a **condensed state** of matter. A liquid and a gas are examples of a **fluid** form of matter; they flow in response to forces (such as gravity) that are applied.

The state of a bulk sample of matter is defined by specifying the values of various properties. Among them are:

The **mass**,  $m$ , a measure of the quantity of matter present (unit: kilogram, kg).

The **volume**,  $V$ , a measure of the quantity of space the sample occupies (unit: cubic metre, m<sup>3</sup>).

The **amount of substance**,  $n$ , a measure of the number of specified entities (atoms, molecules, or formula units) present (unit: mole, mol).

An **extensive property** of bulk matter is a property that depends on the amount of substance present in the sample; an **intensive property** is a property that is independent of the amount of substance. The volume is extensive; the mass density,  $\rho$  (rho), the mass of a sample divided by its volume,  $\rho = m/V$ , is intensive.

The amount of substance,  $n$  (colloquially, ‘the number of moles’), is a measure of the number of specified entities present in the sample. ‘Amount of substance’ is the official name of the quantity; it is commonly simplified to ‘chemical amount’ or simply ‘amount’. The unit 1 mol is defined as the number of carbon atoms in exactly 12 g of carbon-12. The number of entities per mole is called **Avogadro’s constant**,  $N_A$ ; the currently accepted value is  $6.022 \times 10^{23} \text{ mol}^{-1}$  (note that  $N_A$  is a constant with units, not a pure number). The **molar mass of a substance**,  $M$  (units: formally kilograms per mole but commonly grams per mole, g mol<sup>-1</sup>) is the mass per mole of its atoms, its molecules, or its formula units. The amount of substance of specified entities in a sample can readily be calculated from its mass, by noting that

$$n = \frac{m}{M} \quad (\text{F.1})$$

A sample of matter may be subjected to a **pressure**,  $p$  (unit: pascal, Pa; 1 Pa = 1 kg m<sup>-1</sup> s<sup>-2</sup>), which is defined as the force,  $F$ , it is subjected to, divided by the area,  $A$ , to which that force is applied. A sample of gas exerts a pressure on the walls of its container because the molecules of gas are in ceaseless, random motion and exert a force when they strike the walls. The frequency of the collisions is normally so great that the force, and therefore the pressure, is perceived as being steady. Although pascal is the SI unit of pressure (Section F.6), it is also common to express pressure in bar (1 bar = 10<sup>5</sup> Pa) or atmospheres (1 atm = 101 325 Pa exactly), both of which correspond to typical atmospheric pressure. We shall see that, because many physical properties depend on the pressure acting on a sample, it is appropriate to select a certain value of the pressure to report their values. The **standard pressure** for reporting physical quantities is currently defined as  $p^\circ = 1 \text{ bar}$  exactly. We shall see the role of the standard pressure starting in Chapter 2.

To specify the state of a sample fully it is also necessary to give its **temperature**,  $T$ . The temperature is formally a property that determines in which direction energy will flow as heat when two samples are placed in contact through thermally conducting walls: energy flows from the sample with the higher temperature to the sample with the lower temperature. The symbol  $T$  is used to denote the **thermodynamic temperature**, which is an absolute scale with  $T = 0$  as the lowest point. Temperatures above  $T = 0$  are then most commonly expressed by using the **Kelvin scale**, in which the gradations of temperature are called **kelvin** (K). The Kelvin scale is defined by setting the triple point of water (the temperature at which ice, liquid water, and water vapour are in mutual equilibrium) at exactly 273.16 K. The freezing point of water (the melting point of ice) at 1 atm is then found experimentally to lie 0.01 K below the triple point, so the freezing point of water is 273.15 K. The Kelvin scale is unsuitable for everyday

**A note on good practice** Be careful to distinguish atomic or molecular mass (the mass of a single atom or molecule; units kg) from molar mass (the mass per mole of atoms or molecules; units kg mol<sup>-1</sup>). Relative molecular masses of atoms and molecules,  $M_r = m/m_u$ , where  $m$  is the mass of the atom or molecule and  $m_u$  is the atomic mass constant, are still widely called ‘atomic weights’ and ‘molecular weights’ even though they are dimensionless quantities and not weights (the gravitational force exerted on an object). Even IUPAC continues to use the terms ‘for historical reasons’.

**A note on good practice** Note that we write  $T = 0$ , not  $T = 0 \text{ K}$ . General statements in science should be expressed without reference to a specific set of units. Moreover, because  $T$  (unlike  $\theta$ ) is absolute, the lowest point is 0 regardless of the scale used to express higher temperatures (such as the Kelvin scale or the Rankine scale). Similarly, we write  $m = 0$ , not  $m = 0 \text{ kg}$  and  $l = 0$ , not  $l = 0 \text{ m}$ .

measurements of temperature, and it is common to use the Celsius scale, which is defined in terms of the Kelvin scale as

$$\theta/^\circ\text{C} = T/\text{K} - 273.15$$

Definition of  
Celsius scale

(F.2)

Thus, the freezing point of water is  $0^\circ\text{C}$  and its boiling point (at 1 atm) is found to be  $100^\circ\text{C}$  (more precisely  $99.974^\circ\text{C}$ ). Note that in this text  $T$  invariably denotes the thermodynamic (absolute) temperature and that temperatures on the Celsius scale are denoted  $\theta$  (theta).

The properties that define the state of a system are not in general independent of one another. The most important example of a relation between them is provided by the idealized fluid known as a **perfect gas** (also, commonly, an ‘ideal gas’)

$$pV = nRT$$

Perfect gas  
equation

(F.3)

Here  $R$  is the **gas constant**, a universal constant (in the sense of being independent of the chemical identity of the gas) with the value  $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ . Equation F.3 is central to the development of the description of gases in Chapter 1.

#### F.4 Energy

**Key points** (a) Energy is the capacity to do work. (b) The total energy of a particle is the sum of its kinetic and potential energies. The kinetic energy of a particle is the energy it possesses as a result of its motion. The potential energy of a particle is the energy it possesses as a result of its position. (c) The Coulomb potential energy between two charges separated by a distance  $r$  varies as  $1/r$ .

Much of chemistry is concerned with transfers and transformations of energy, and it is appropriate to define this familiar quantity precisely: **energy** is the capacity to do work. In turn, work is defined as motion against an opposing force. The SI unit of energy is the **joule** (J), with

$$1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$$

(see Section F.7).

A body may possess two kinds of energy, kinetic energy and potential energy. The **kinetic energy**,  $E_k$ , of a body is the energy the body possesses as a result of its motion. For a body of mass  $m$  travelling at a speed  $v$

$$E_k = \frac{1}{2}mv^2$$

Kinetic energy

(F.4)

The **potential energy**,  $E_p$  or more commonly  $V$ , of a body is the energy it possesses as a result of its position. No universal expression for the potential energy can be given because it depends on the type of force that the body experiences. For a particle of mass  $m$  at an altitude  $h$  close to the surface of the Earth, the gravitational potential energy is

$$V(h) = V(0) + mgh$$

Gravitational  
potential energy

(F.5)

where  $g$  is the **acceleration of free fall** ( $g = 9.81 \text{ m s}^{-2}$ ). The zero of potential energy is arbitrary, and in this case it is common to set  $V(0) = 0$ .

One of the most important forms of potential energy in chemistry is the **Coulomb potential energy**, the potential energy of the electrostatic interaction between two point electric charges. For a point charge  $Q_1$  at a distance  $r$  in a vacuum from another point charge  $Q_2$

$$V(r) = \frac{Q_1 Q_2}{4\pi\epsilon_0 r} \quad (\text{Coulomb potential energy}) \quad (\text{F.6})$$

It is conventional (as here) to set the potential energy equal to zero at infinite separation of charges. Then two opposite charges have a negative potential energy at finite separations, whereas two like charges have a positive potential energy. Charge is expressed in coulombs (C), often as a multiple of the fundamental charge,  $e$ . Thus, the charge of an electron is  $-e$  and that of a proton is  $+e$ ; the charge of an ion is  $ze$ , with  $z$  the **charge number** (positive for cations, negative for anions). The constant  $\epsilon_0$  (epsilon zero) is the **vacuum permittivity**, a fundamental constant with the value  $8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$ . In a medium other than a vacuum, the potential energy of interaction between two charges is reduced, and the vacuum permittivity is replaced by the **permittivity**,  $\epsilon$ , of the medium. The permittivity is commonly expressed as a multiple of the vacuum permittivity

$$\epsilon = \epsilon_r \epsilon_0 \quad (\text{F.7})$$

with  $\epsilon_r$  the dimensionless **relative permittivity** (formerly, the *dielectric constant*).

The **total energy** of a particle is the sum of its kinetic and potential energies

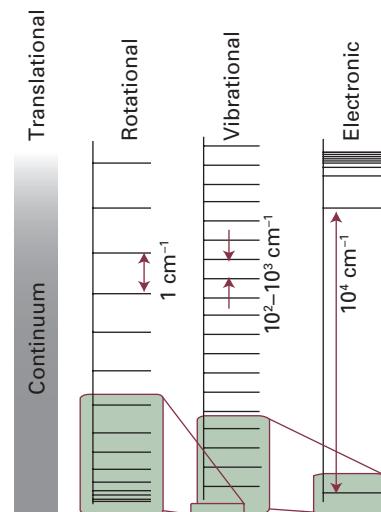
$$E = E_k + E_p \quad (\text{F.8})$$

We make frequent use of the apparently universal law of nature that *energy is conserved*; that is, energy can neither be created nor destroyed. Although energy can be transferred from one location to another and transformed from one form to another, the total energy is constant.

## F.5 The relation between molecular and bulk properties

**Key points** (a) The energy levels of confined particles are quantized. (b) The Boltzmann distribution is a formula for calculating the relative populations of states of various energies. (c) The equipartition theorem provides a way to calculate the energy of some systems.

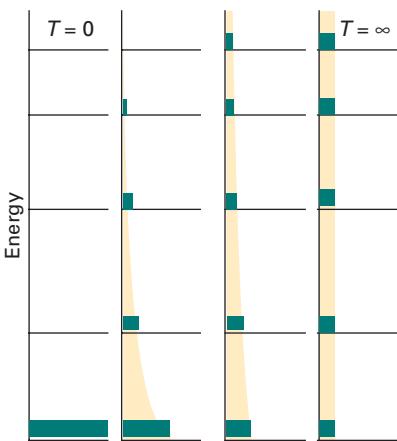
The energy of a molecule, atom, or subatomic particle that is confined to a region of space is **quantized**, or restricted to certain discrete values. These permitted energies are called **energy levels**. The values of the permitted energies depend on the characteristics of the particle (for instance, its mass) and the extent of the region to which it is confined. The quantization of energy is most important—in the sense that the allowed energies are widest apart—for particles of small mass confined to small regions of space. Consequently, quantization is very important for electrons in atoms and molecules, but usually unimportant for macroscopic bodies. For particles in containers of macroscopic dimensions the separation of energy levels is so small that for all practical purposes the motion of the particles through space—their translational motion—is unquantized and can be varied virtually continuously. As we shall see in detail in Chapter 7, quantization becomes increasingly important as we change focus from rotational to vibrational and then to electronic motion. The separation of rotational energy levels (in small molecules, about  $10^{-23} \text{ J}$  or  $0.01 \text{ zJ}$ , corresponding to about  $0.01 \text{ kJ mol}^{-1}$ ) is smaller than that of vibrational energy levels (about  $10 \text{ kJ mol}^{-1}$ ), which itself is smaller than that of electronic energy levels (about  $10^{-18} \text{ J}$  or  $1 \text{ aJ}$ , corresponding to about  $10^3 \text{ kJ mol}^{-1}$ ). Figure F.4 depicts these typical energy level separations.



**Fig. F.4** The energy level separations (expressed as wavenumbers) typical of four types of system.

### A brief comment

The uncommon but useful prefixes z (for zepto) and a (for atto) are explained in Section F.7 on the use of units.



**Fig. F.5** The Boltzmann distribution of populations for a system of five energy levels as the temperature is raised from zero to infinity.

### (a) The Boltzmann distribution

The continuous thermal agitation that the molecules experience in a sample when  $T > 0$  ensures that they are distributed over the available energy levels. One particular molecule may be in a state corresponding to a low energy level at one instant, and then be excited into a high energy state a moment later. Although we cannot keep track of the state of a single molecule, we can speak of the *average* numbers of molecules in each state. Even though individual molecules may be changing their states as a result of collisions, the average number in each state is constant (provided the temperature remains the same).

The average number of molecules in a state is called the **population** of the state. Only the lowest energy state is occupied at  $T = 0$ . Raising the temperature excites some molecules into higher energy states, and more and more states become accessible as the temperature is raised further (Fig. F.5). The formula for calculating the relative populations of states of various energies is called the **Boltzmann distribution** and was derived by the Austrian scientist Ludwig Boltzmann towards the end of the nineteenth century. Although we shall derive and discuss this distribution in more detail in Chapter 15, at this point it is important to know that it gives the ratio of the numbers of particles in states with energies  $E_i$  and  $E_j$  as

$$\frac{N_i}{N_j} = e^{-(E_i - E_j)/kT} \quad (\text{F.9})$$

Boltzmann distribution

where  $k$  is **Boltzmann's constant**, a fundamental constant with the value  $k = 1.381 \times 10^{-23} \text{ J K}^{-1}$ . This constant occurs throughout physical chemistry, often in a disguised (molar) form as the gas constant, for

$$R = N_A k \quad (\text{F.10})$$

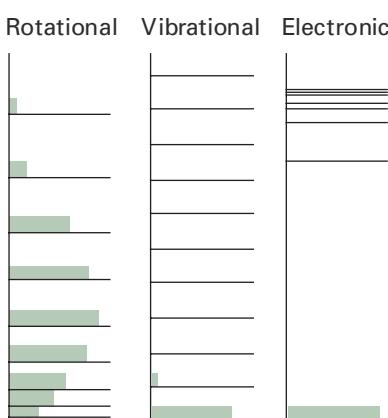
where  $N_A$  is Avogadro's constant. We shall see in Chapter 15 that the Boltzmann distribution provides the crucial link for expressing the macroscopic properties of bulk matter in terms of the behaviour of its constituent atoms.

The important features of the Boltzmann distribution to bear in mind are:

- The higher the energy of a state, the lower its population.
- The higher the temperature, the more likely it is that a state of high energy is populated.
- More levels are significantly populated if they are close together in comparison with  $kT$  (like rotational and translational states), than if they are far apart (like vibrational and electronic states).

Figure F.6 summarizes the form of the Boltzmann distribution for some typical sets of energy levels. The peculiar shape of the population of rotational levels stems from the fact that eqn F.9 applies to *individual states*, and for molecular rotation the number of rotational states corresponding to a given energy increases with energy. Broadly speaking, the number of planes of rotation increases with energy. Therefore, although the population of each *state* decreases with energy, the population of the *levels* goes through a maximum.

One of the simplest examples of the relation between microscopic and bulk properties is provided by **kinetic molecular theory**, a model of a perfect gas. In this model, it is assumed that the molecules, imagined as particles of negligible size, are in ceaseless, random motion and do not interact except during their brief collisions. Different speeds correspond to different kinetic energies, so the Boltzmann formula can be used to predict the proportions of molecules having a specific speed at a particular temperature. The expression giving the fraction of molecules that have a particular speed is



**Fig. F.6** The Boltzmann distribution of populations for rotation, vibration, and electronic energy levels at room temperature.

called the **Maxwell distribution**, and has the features summarized in Fig. F.7. The Maxwell distribution, which is derived, specified, and discussed more fully in Chapter 20, can be used to show that the average speed,  $v_{\text{mean}}$ , of the molecules depends on the temperature and their molar mass as

$$v_{\text{mean}} \propto \left( \frac{T}{M} \right)^{1/2} \quad (\text{F.11})$$

That is, the average speed increases as the square-root of the temperature and decreases as the square-root of the molar mass. Thus, the average speed is high for light molecules at high temperatures. The distribution itself gives more information than the average value. For instance, the tail towards high speeds is longer at high temperatures than at low, which indicates that at high temperatures more molecules in a sample have speeds much higher than average.

### (b) Equipartition

The Boltzmann distribution can be used to calculate the average energy associated with each mode of motion of a molecule (as we shall see in detail in Chapters 15 and 16). However, for certain modes of motion (which in practice means translation of any molecule and the rotation of all except the lightest molecules) there is a short cut, called the **equipartition theorem**. This theorem (which is derived from the Boltzmann distribution) states:

In a sample at a temperature  $T$ , all quadratic contributions to the total energy have the same mean value, namely  $\frac{1}{2}kT$ .

Equipartition theorem

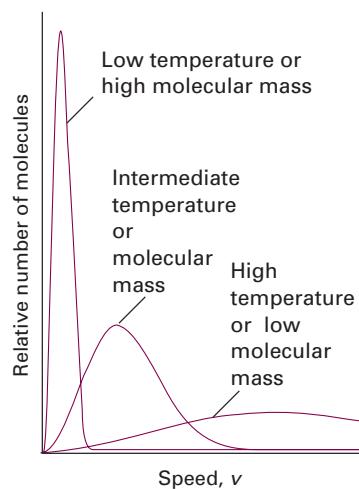
A ‘quadratic contribution’ simply means a contribution that depends on the square of the position or the velocity (or momentum). For example, because the kinetic energy of a body of mass  $m$  free to undergo translation in three dimensions is  $E_k = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$ , there are three quadratic terms. The theorem implies that the average kinetic energy of motion parallel to the  $x$ -axis is the same as the average kinetic energy of motion parallel to the  $y$ -axis and to the  $z$ -axis. That is, in a normal sample (one at thermal equilibrium throughout), the total energy is equally ‘partitioned’ over all the available modes of motion. One mode of motion is not especially rich in energy at the expense of another. Because the average contribution of each mode is  $\frac{1}{2}kT$ , the average kinetic energy of a molecule free to move in three dimensions is  $\frac{3}{2}kT$ , as there are three quadratic contributions to the kinetic energy.

We shall often use the equipartition theorem to make quick assessments of molecular properties and to judge the outcome of the competition of the ordering effects of intermolecular interactions and the disordering effects of thermal motion.

## F.6 The electromagnetic field

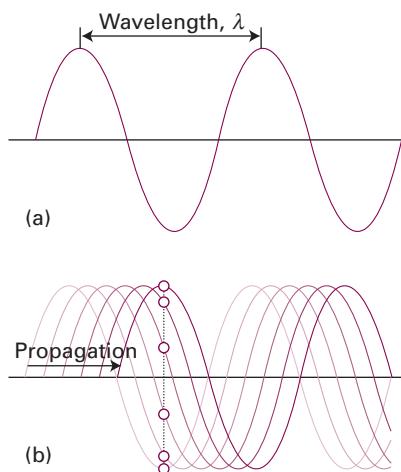
**Key point** Electromagnetic radiation is characterized by its direction of propagation, its wavelength, frequency, and wavenumber, and its state of polarization.

Light is a form of electromagnetic radiation. In classical physics, electromagnetic radiation is understood in terms of the **electromagnetic field**, an oscillating electric and magnetic disturbance that spreads as a harmonic wave through empty space, the vacuum. The wave travels at a constant speed called the *speed of light*,  $c$ , which is about  $3 \times 10^8 \text{ m s}^{-1}$ . As its name suggests, an electromagnetic field has two components, an electric field that acts on charged particles (whether stationary or moving) and a magnetic field that acts only on moving charged particles. The electromagnetic field,



**Fig. F.7** The distribution of molecular speeds with temperature and molar mass. Note that the most probable speed (corresponding to the peak of the distribution) increases with temperature and with decreasing molar mass, and simultaneously the distribution becomes broader.

**interActivity** (a) Plot different distributions by keeping the molar mass constant at  $100 \text{ g mol}^{-1}$  and varying the temperature of the sample between 200 K and 2000 K. (b) Use mathematical software or the *Living graph* applet from the text’s web site to evaluate numerically the fraction of molecules with speeds in the range  $100 \text{ m s}^{-1}$  to  $200 \text{ m s}^{-1}$  at 300 K and 1000 K. (c) Based on your observations, provide a molecular interpretation of temperature.



**Fig. F.8** (a) The wavelength,  $\lambda$ , of a wave is the peak-to-peak distance. (b) The wave is shown travelling to the right at a speed  $c$ . At a given location, the instantaneous amplitude of the wave changes through a complete cycle (the six dots show half a cycle) as it passes a given point. The frequency,  $v$ , is the number of cycles per second that occur at a given point. Wavelength and frequency are related by  $\lambda v = c$ .

**A note on good practice** You will hear people speaking of ‘a frequency of so many wavenumbers’. That is doubly wrong. First, wavenumber and frequency are two different physical observables. Second, wavenumber is a physical quantity, not a unit. The dimensions of wavenumber are  $1/\text{length}$  and it is commonly reported in reciprocal centimetres,  $\text{cm}^{-1}$ .

like any periodic wave, is characterized by a **wavelength**,  $\lambda$  (lambda), the distance between the neighbouring peaks of the wave, and its **frequency**,  $v$  (nu), the number of times in a given time interval at which its displacement at a fixed point returns to its original value divided by the length of the time interval, normally in seconds (Fig. F.8). The frequency is measured in **hertz**, where  $1 \text{ Hz} = 1 \text{ s}^{-1}$ . The wavelength and frequency of an electromagnetic wave are related by

$$\lambda v = c \quad (\text{F.12})$$

Therefore, the shorter the wavelength, the higher the frequency. The characteristics of a wave are also reported by giving the **wavenumber**,  $\tilde{v}$  (nu tilde), of the radiation, where

$$\tilde{v} = \frac{v}{c} = \frac{1}{\lambda} \quad (\text{F.13})$$

A wavenumber can be interpreted as the number of complete wavelengths in a given length. Wavenumbers are normally reported in reciprocal centimetres ( $\text{cm}^{-1}$ ), so a wavenumber of  $5 \text{ cm}^{-1}$  indicates that there are 5 complete wavelengths in 1 cm. A typical wavenumber of visible light is about  $15\,000 \text{ cm}^{-1}$ , corresponding to 15 000 complete wavelengths in each centimetre. The classification of the electromagnetic field according to its frequency and wavelength is summarized in Fig. F.9.

Electromagnetic radiation is **plane-polarized** if the electric and magnetic fields each oscillate in a single plane (Fig. F.10). The plane of polarization may be orientated in any direction around the direction of propagation with the electric and magnetic fields perpendicular to that direction (and perpendicular to each other). An alternative mode of polarization is **circular polarization**, in which the electric and magnetic fields rotate around the direction of propagation in either a clockwise or a counter-clockwise sense but remain perpendicular to it and each other.

According to classical electromagnetic theory, the intensity of electromagnetic radiation is proportional to the square of the amplitude of the wave. For example, the radiation detectors used in spectroscopy are based on the interaction between the electric field of the incident radiation and the detecting element, so light intensities are proportional to the square of the amplitude of the waves.

## F.7 Units

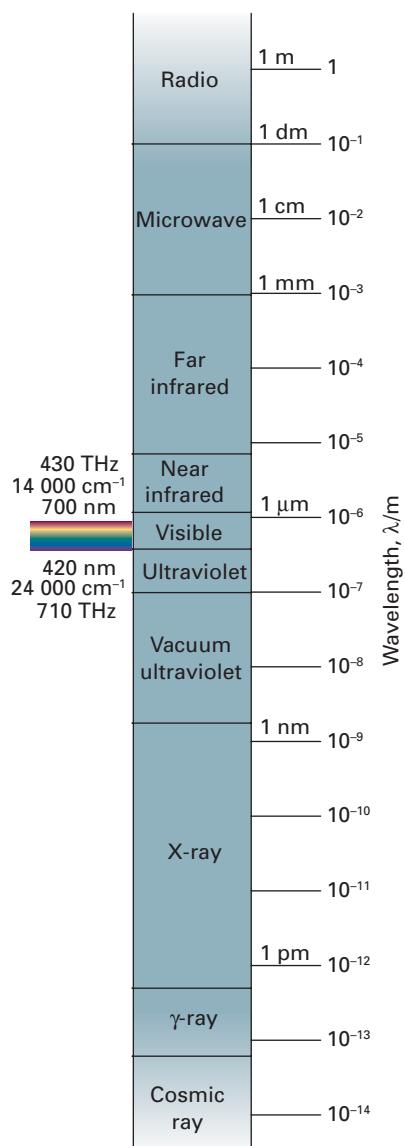
**Key points** (a) The measurement of a physical property is expressed as the product of a numerical value and a unit. (b) In the International System of units (SI), the units are formed from seven base units, and all other physical quantities may be expressed as combinations of these physical quantities and reported in terms of derived units.

The measurement of a physical property is expressed as

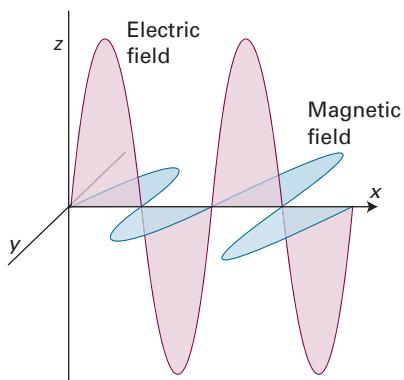
$$\text{Physical property} = \text{numerical value} \times \text{unit}$$

For example, a length ( $l$ ) may be reported as  $l = 5.1 \text{ m}$ , if it is found to be 5.1 times as great as a defined unit of length, namely, 1 metre (1 m). Units are treated as algebraic quantities, and may be multiplied and divided. Thus, the same length could be reported as  $l/\text{m} = 5.1$ . The symbols for physical properties are always italic (sloping; thus  $V$  for volume, not  $V$ ), including Greek symbols (thus,  $\mu$  for electric dipole moment, not  $\mu$ ), but available typefaces are not always so obliging.

In the **International System of units** (SI, from the French *Système International d'Unités*), the units are formed from seven **base units** listed in Table F.1. All other physical quantities may be expressed as combinations of these physical quantities and



**Fig. F.9** The regions of the electromagnetic spectrum. The boundaries are only approximate.



**Fig. F.10** Electromagnetic radiation consists of a wave of electric and magnetic fields perpendicular to the direction of propagation (in this case the  $x$ -direction), and mutually perpendicular to each other. This illustration shows a plane-polarized wave, with the electric and magnetic fields oscillating in the  $xz$ - and  $xy$ -planes, respectively.

**Table F.1** The SI base units

Physical quantity	Symbol for quantity	Base unit
Length	$l$	metre, m
Mass	$m$	kilogram, kg
Time	$t$	second, s
Electric current	$I$	ampere, A
Thermodynamic temperature	$T$	kelvin, K
Amount of substance	$n$	mole, mol
Luminous intensity	$I_v$	candela, cd

**Table F.2** A selection of derived units

Physical quantity	Derived unit*	Name of derived unit
Force	$1 \text{ kg m s}^{-2}$	newton, N
Pressure	$1 \text{ kg m}^{-1} \text{ s}^{-2}$ $1 \text{ N m}^{-2}$	pascal, Pa
Energy	$1 \text{ kg m}^2 \text{ s}^{-2}$ $1 \text{ N m}$ $1 \text{ Pa m}^3$	joule, J
Power	$1 \text{ kg m}^2 \text{ s}^{-3}$ $1 \text{ J s}^{-1}$	watt, W

\* Equivalent definitions in terms of derived units are given following the definition in terms of base units.

**Table F.3** Common SI prefixes

Prefix	y	z	a	f	p	n	$\mu$	m	c	d
Name	yocto	zepto	atto	femto	pico	nano	micro	milli	centi	deci
Factor	$10^{-24}$	$10^{-21}$	$10^{-18}$	$10^{-15}$	$10^{-12}$	$10^{-9}$	$10^{-6}$	$10^{-3}$	$10^{-2}$	$10^{-1}$
Prefix	da	h	k	M	G	T	P	E	Z	Y
Name	deca	hecto	kilo	mega	giga	tera	peta	exa	zeta	yotta
Factor	10	$10^2$	$10^3$	$10^6$	$10^9$	$10^{12}$	$10^{15}$	$10^{18}$	$10^{21}$	$10^{24}$

reported in terms of **derived units**. Thus, volume is  $(\text{length})^3$  and may be reported as a multiple of 1 metre cubed ( $1 \text{ m}^3$ ), and density, which is mass/volume, may be reported as a multiple of 1 kilogram per metre cubed ( $1 \text{ kg m}^{-3}$ ).

A number of derived units have special names and symbols. The names of units derived from names of people are lower case (as in torr, joule, pascal, and kelvin), but their symbols are upper case (as in Torr, J, Pa, and K). The most important for our purposes are listed in Table F.2.

In all cases (both for base and derived quantities), the units may be modified by a prefix that denotes a factor of a power of 10. The Greek prefixes of units are upright (as in  $\mu\text{m}$ , not  $\mu\text{m}$ ). Among the most common prefixes are those listed in Table F.3. Examples of the use of these prefixes are

$$1 \text{ nm} = 10^{-9} \text{ m} \quad 1 \text{ ps} = 10^{-12} \text{ s} \quad 1 \mu\text{mol} = 10^{-6} \text{ mol}$$

The kilogram (kg) is anomalous: although it is a base unit, it is interpreted as  $10^3 \text{ g}$ , and prefixes are attached to the gram (as in  $1 \text{ mg} = 10^{-3} \text{ g}$ ). Powers of units apply to the prefix as well as the unit they modify

$$1 \text{ cm}^3 = 1 (\text{cm})^3 = 1 (10^{-2} \text{ m})^3 = 10^{-6} \text{ m}^3$$

Note that  $1 \text{ cm}^3$  does not mean  $1 \text{ c(m}^3\text{)}$ . When carrying out numerical calculations, it is usually safest to write out the numerical value of an observable as a power of 10.

There are a number of units that are in wide use but are not a part of the International System. Some are exactly equal to multiples of SI units. These include the *litre* (L), which is exactly  $10^3 \text{ cm}^3$  (or  $1 \text{ dm}^3$ ) and the *atmosphere* (atm), which is exactly 101.325 kPa. Others rely on the values of fundamental constants, and hence are liable to change when the values of the fundamental constants are modified by more accurate

**Table F.4** Some common units

Physical quantity	Name of unit	Symbol for unit	Value*
Time	minute	min	60 s
	hour	h	3600 s
	day	d	86 400 s
	year	a	31 556 952 s
Length	ångström	Å	$10^{-10}$ m
Volume	litre	L, l	1 dm <sup>3</sup>
Mass	tonne	t	$10^3$ kg
Pressure	bar	bar	$10^5$ Pa
	atmosphere	atm	101.325 kPa
Energy	electronvolt	eV	$1.602\ 176\ 53 \times 10^{-19}$ J
			96.485 31 kJ mol <sup>-1</sup>

\* All values in the final column are exact, except for the definition of 1 eV, which depends on the measured value of  $e$ , and the year, which is not a constant and depends on a variety of astronomical assumptions.

or more precise measurements. Thus, the size of the energy unit *electronvolt* (eV), the energy acquired by an electron that is accelerated through a potential difference of exactly 1 V, depends on the value of the charge of the electron, and the present (2008) conversion factor is  $1 \text{ eV} = 1.602\ 176\ 53 \times 10^{-19}$  J. Table F.4 gives the conversion factors for a number of these convenient units.

## Exercises

### F.1 Atoms

**F1.1(a)** Summarize the nuclear model of the atom.

**F1.1(b)** Define the terms atomic number, nucleon number, mass number.

**F1.2(a)** Express the typical ground-state electron configuration of an atom of an element in (a) Group 2, (b) Group 7, (c) Group 15 of the periodic table.

**F1.2(b)** Express the typical ground-state electron configuration of an atom of an element in (a) Group 3, (b) Group 5, (c) Group 13 of the periodic table.

**F1.3(a)** Identify the oxidation numbers of the elements in (a) MgCl<sub>2</sub>, (b) FeO, (c) Hg<sub>2</sub>Cl<sub>2</sub>.

**F1.3(b)** Identify the oxidation numbers of the elements in (a) CaH<sub>2</sub>, (b) CaC<sub>2</sub>, (c) LiN<sub>3</sub>.

**F1.4(a)** Where in the periodic table are metals and nonmetals found?

**F1.4(b)** Where in the periodic table are transition metals, lanthanoids, and actinoids found?

### F.2 Molecules

**F2.1(a)** Summarize what is meant by a single and multiple bond.

**F2.1(b)** Identify a molecule with (a) one, (b) two, (c) three lone pairs on the central atom.

**F2.2(a)** Draw the Lewis (electron dot) structures of (a) SO<sub>3</sub><sup>2-</sup>, (b) XeF<sub>4</sub>, (c) P<sub>4</sub>.

**F2.2(b)** Draw the Lewis (electron dot) structures of (a) O<sub>3</sub>, (b) ClF<sub>3</sub><sup>+</sup>, (c) N<sub>3</sub><sup>-</sup>.

**F2.3(a)** Summarize the principal concepts of the VSEPR theory of molecular shape.

**F2.3(b)** Identify four hypervalent compounds.

**F2.4(a)** Use VSEPR theory to predict the structures of (a) PCl<sub>3</sub>, (b) PCl<sub>5</sub>, (c) XeF<sub>2</sub>, (d) XeF<sub>4</sub>.

**F2.4(b)** Use VSEPR theory to predict the structures of (a) H<sub>2</sub>O<sub>2</sub>, (b) FSO<sub>3</sub><sup>-</sup>, (c) KrF<sub>2</sub>, (d) PCl<sub>4</sub><sup>+</sup>.

**F2.5(a)** Identify the polarities (by attaching partial charges  $\delta+$  and  $\delta-$ ) of the bonds (a) C–Cl, (b) P–H, (c) N–O.

**F2.5(b)** Identify the polarities (by attaching partial charges  $\delta+$  and  $\delta-$ ) of the bonds (a) C–H, (b) P–S, (c) N–Cl.

**F2.6(a)** State whether you expect the following molecules to be polar or nonpolar: (a) CO<sub>2</sub>, (b) SO<sub>2</sub>, (c) N<sub>2</sub>O, (d) SF<sub>4</sub>.

**F2.6(b)** State whether you expect the following molecules to be polar or nonpolar: (a) O<sub>3</sub>, (b) XeF<sub>2</sub>, (c) NO<sub>2</sub>, (d) C<sub>6</sub>H<sub>14</sub>.

**F2.7(a)** Arrange the molecules in Exercise F2.6a by increasing dipole moment.

**F2.7(b)** Arrange the molecules in Exercise F2.6b by increasing dipole moment.

### F.3 Bulk matter

**F3.1(a)** Compare and contrast the properties of the solid, liquid, and gas states of matter.

**F3.1(b)** Compare and contrast the properties of the condensed and gaseous states of matter.

**F3.2(a)** Classify the following properties as extensive or intensive: (a) mass, (b) mass density, (c) temperature, (d) number density.

**F3.2(b)** Classify the following properties as extensive or intensive: (a) pressure, (b) specific heat capacity, (c) weight, (d) molality.

**F3.3(a)** Calculate (a) the amount of  $\text{C}_2\text{H}_5\text{OH}$  (in moles) and (b) the number of molecules present in 25.0 g of ethanol.

**F3.3(b)** Calculate (a) the amount of  $\text{C}_6\text{H}_{12}\text{O}_6$  (in moles) and (b) the number of molecules present in 5.0 g of glucose.

**F3.4(a)** Express a pressure of 1.45 atm in (a) pascal, (b) bar.

**F3.4(b)** Express a pressure of 222 atm in (a) pascal, (b) bar.

**F3.5(a)** Convert blood temperature,  $37.0^\circ\text{C}$ , to the Kelvin scale.

**F3.5(b)** Convert the boiling point of oxygen, 90.18 K, to the Celsius scale.

**F3.6(a)** Equation F.2 is a relation between the Kelvin and Celsius scales.

Devise the corresponding equation relating the Fahrenheit and Celsius scales and use it to express the boiling point of ethanol ( $78.5^\circ\text{C}$ ) in degrees Fahrenheit.

**F3.6(b)** The Rankine scale is a version of the thermodynamic temperature scale in which the degrees ( $^\circ\text{R}$ ) are the same size as degrees Fahrenheit. Derive an expression relating the Rankine and Kelvin scales and express the freezing point of water in degrees Rankine.

**F3.7(a)** A sample of hydrogen gas was found to have a pressure of 110 kPa when the temperature was  $20.0^\circ\text{C}$ . What is its pressure expected to be when the temperature is  $7.0^\circ\text{C}$ ?

**F3.7(b)** A sample of 325 mg of neon occupies  $2.00 \text{ dm}^3$  at  $20.0^\circ\text{C}$ . Use the perfect gas law to calculate the pressure of the gas.

### F.4 Energy

**F4.1(a)** Define energy and work.

**F4.1(b)** Distinguish between kinetic and potential energy.

**F4.2(a)** Consider a region of the atmosphere of volume  $25 \text{ dm}^3$  that at  $20^\circ\text{C}$  contains about 1.0 mol of molecules. Take the average molar mass of the molecules as  $29 \text{ g mol}^{-1}$  and their average speed as about  $400 \text{ m s}^{-1}$ . Estimate the energy stored as molecular kinetic energy in this volume of air.

**F4.2(b)** Calculate the minimum energy that a bird of mass 25 g must expend in order to reach a height of 50 m.

**F4.3(a)** The potential energy of a charge  $Q_1$  in the presence of another charge  $Q_2$  can be expressed in terms of the *Coulomb potential*,  $\phi$  (phi):

$$V = Q_1 \phi \quad \phi = \frac{Q_2}{4\pi\epsilon_0 r}$$

The units of potential are joules per coulomb,  $\text{J C}^{-1}$  so, when  $\phi$  is multiplied by a charge in coulombs, the result is in joules. The combination joules per coulomb occurs widely and is called a volt (V), with  $1 \text{ V} = 1 \text{ J C}^{-1}$ . Calculate the Coulomb potential due to the nuclei at a point in a LiH molecule located at 200 pm from the Li nucleus and 150 pm from the H nucleus.

**F4.3(b)** Plot the Coulomb potential due to the nuclei at a point in a  $\text{Na}^+\text{Cl}^-$  ion pair located on a line halfway between the nuclei (the internuclear

separation is 283 pm) as the point approaches from infinity and ends at the midpoint between the nuclei.

### F.5 The relation between molecular and bulk properties

**F5.1(a)** What is meant by quantization of energy?

**F5.1(b)** In what circumstances are the effects of quantization most important for microscopic systems?

**F5.2(a)** The unit 1 electronvolt (1 eV) is defined as the energy acquired by an electron as it moves through a potential difference of 1 V. Suppose two states differ in energy by 1.0 eV. What is the ratio of their populations at (a) 300 K, (b) 3000 K?

**F5.2(b)** Suppose two states differ in energy by 1.0 eV, what can be said about their populations when  $T = 0$  and when the temperature is infinite?

**F5.3(a)** What are the assumptions of the kinetic molecular theory?

**F5.3(b)** What are the main features of the Maxwell distribution of speeds?

**F5.4(a)** Suggest a reason why most molecules survive for long periods at room temperature.

**F5.4(b)** Suggest a reason why the rates of chemical reactions typically increase with increasing temperature.

**F5.5(a)** Calculate the relative mean speeds of  $\text{N}_2$  molecules in air at  $0^\circ\text{C}$  and  $40^\circ\text{C}$ .

**F5.5(b)** Calculate the relative mean speeds of  $\text{CO}_2$  molecules in air at  $20^\circ\text{C}$  and  $30^\circ\text{C}$ .

**F5.6(a)** Use the equipartition theorem to calculate the contribution of translational motion to the total energy of 5.0 g of argon at  $25^\circ\text{C}$ .

**F5.6(b)** Use the equipartition theorem to calculate the contribution of translational motion to the total energy of 10.0 g of helium at  $30^\circ\text{C}$ .

**F5.7(a)** Use the equipartition theorem to calculate the contribution to the total energy of a sample of 10.0 g of (a) carbon dioxide, (b) methane at  $20^\circ\text{C}$ ; take into account translation and rotation but not vibration.

**F5.7(b)** Use the equipartition theorem to calculate the contribution to the total internal energy of a sample of 10.0 g of lead at  $20^\circ\text{C}$ , taking into account the vibrations of the atoms.

### F.6 The electromagnetic field

**F6.1(a)** Express a wavelength of 230 nm as a frequency.

**F6.1(b)** Express a wavelength of 720 nm as a frequency.

**F6.2(a)** Express a frequency of 560 THz as a wavenumber.

**F6.2(b)** Express a frequency of 160 MHz as a wavenumber.

**F6.3(a)** A radio station broadcasts at a frequency of 91.7 MHz. What is (a) the wavelength, (b) the wavenumber of the radiation?

**F6.3(b)** A spectroscopic technique uses microwave radiation of wavelength 3.0 cm. What is (a) the wavenumber, (b) the frequency of the radiation?

### F.7 Units

**F7.1(a)** Express a volume of  $1.45 \text{ cm}^3$  in cubic metres.

**F7.1(b)** Express a volume of  $1.45 \text{ dm}^3$  in cubic centimetres.

**F7.2(a)** Express a mass density of  $11.2 \text{ g cm}^{-3}$  in kilograms per cubic metre.

**F7.2(b)** Express a mass density of  $1.12 \text{ g dm}^{-3}$  in kilograms per cubic metre.

**F7.3(a)** Express pascal per joule in base units.

**F7.3(b)** Express  $(\text{joule})^2$  per  $(\text{newton})^3$  in base units.

**F7.4(a)** The expression  $kT/hc$  sometimes appears in physical chemistry. Evaluate this expression at 298 K in reciprocal centimetres ( $\text{cm}^{-1}$ ).

**F7.4(b)** The expression  $kT/e$  sometimes appears in physical chemistry. Evaluate this expression at 298 K in millielectronvolts (meV).

**F7.5(a)** Given that  $R = 8.3144 \text{ J K}^{-1} \text{ mol}^{-1}$ , express  $R$  in decimetre cubed atmospheres per kelvin per mole.

**F7.5(b)** Given that  $R = 8.3144 \text{ J K}^{-1} \text{ mol}^{-1}$ , express  $R$  in pascal centimetre cubed per kelvin per molecule.

**F7.6(a)** Convert  $1 \text{ dm}^3 \text{ atm}$  into joules.

**F7.6(b)** Convert  $1 \text{ J}$  into litre-atmospheres.

**F7.7(a)** Determine the SI units of  $e^2/\epsilon_0 r^2$ . Express them in (a) base units, (b) units containing newtons.

**F7.7(b)** Determine the SI units of  $\mu_B^2/\mu_0 r^3$ , where  $\mu_B$  is the Bohr magneton ( $\mu_B = e\hbar/2m_e$ ) and  $\mu_0$  is the vacuum permeability (see inside front cover). Express them in (a) base units, (b) units containing joules.

*This page intentionally left blank*



# PART 1 Equilibrium

Part 1 of the text develops the concepts that are needed for the discussion of equilibria in chemistry. Equilibria include physical change, such as fusion and vaporization, and chemical change, including electrochemistry. The discussion is in terms of thermodynamics, and particularly in terms of enthalpy and entropy. We see that we can obtain a unified view of equilibrium and the direction of spontaneous change in terms of the chemical potentials of substances. The chapters in Part 1 deal with the bulk properties of matter; those of Part 2 will show how these properties stem from the behaviour of individual atoms.

## 1 The properties of gases

Mathematical background 1: Differentiation and integration

## 2 The First Law

Mathematical background 2: Multivariate calculus

## 3 The Second Law

## 4 Physical transformations of pure substances

## 5 Simple mixtures

## 6 Chemical equilibrium

*This page intentionally left blank*

# The properties of gases

# 1

This chapter establishes the properties of gases that will be used throughout the text. It begins with an account of an idealized version of a gas, a perfect gas, and shows how its equation of state may be assembled experimentally. We then see how the properties of real gases differ from those of a perfect gas, and construct an approximate equation of state that describes their properties.

The simplest state of matter is a **gas**, a form of matter that fills any container it occupies. Initially we consider only pure gases, but later in the chapter we see that the same ideas and equations apply to mixtures of gases too.

## The perfect gas

We shall find it helpful to picture a gas as a collection of molecules (or atoms) in continuous random motion, with average speeds that increase as the temperature is raised. A gas differs from a liquid in that, except during collisions, the molecules of a gas are widely separated from one another and move in paths that are largely unaffected by intermolecular forces.

### 1.1 The states of gases

**Key points** Each substance is described by an equation of state. (a) Pressure, force divided by area, provides a criterion of mechanical equilibrium for systems free to change their volume. (b) Pressure is measured with a barometer. (c) Through the Zeroth Law of thermodynamics, temperature provides a criterion of thermal equilibrium.

The **physical state** of a sample of a substance, its physical condition, is defined by its physical properties. Two samples of a substance that have the same physical properties are in the same state. The state of a pure gas, for example, is specified by giving its volume,  $V$ , amount of substance (number of moles),  $n$ , pressure,  $p$ , and temperature,  $T$ . However, it has been established experimentally that it is sufficient to specify only three of these variables, for then the fourth variable is fixed. That is, it is an experimental fact that each substance is described by an **equation of state**, an equation that interrelates these four variables.

The general form of an equation of state is

$$p = f(T, V, n)$$

General form of  
an equation of state (1.1)

## The perfect gas

### 1.1 The states of gases

#### 1.2 The gas laws

#### 1.1 Impact on environmental science: The gas laws and the weather

## Real gases

### 1.3 Molecular interactions

### 1.4 The van der Waals equation

Checklist of key equations

Exercises

Problems



This equation tells us that, if we know the values of  $n$ ,  $T$ , and  $V$  for a particular substance, then the pressure has a fixed value. Each substance is described by its own equation of state, but we know the explicit form of the equation in only a few special cases. One very important example is the equation of state of a ‘perfect gas’, which has the form  $p = nRT/V$ , where  $R$  is a constant (Section F.3). Much of the rest of this chapter will examine the origin of this equation of state and its applications.

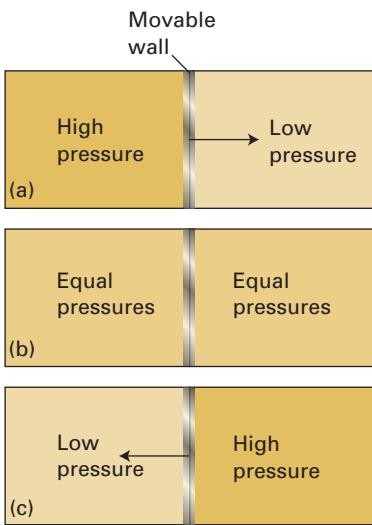
### (a) Pressure

Pressure,  $p$ , is defined as force,  $F$ , divided by the area,  $A$ , to which the force is applied:

$$p = \frac{F}{A}$$

Definition of pressure

[1.2]



**Fig. 1.1** When a region of high pressure is separated from a region of low pressure by a movable wall, the wall will be pushed into one region or the other, as in (a) and (c). However, if the two pressures are identical, the wall will not move (b). The latter condition is one of mechanical equilibrium between the two regions.

That is, the greater the force acting on a given area, the greater the pressure. The origin of the force exerted by a gas is the incessant battering of the molecules on the walls of its container. The collisions are so numerous that they exert an effectively steady force, which is experienced as a steady pressure. The SI unit of pressure, the *pascal* ( $\text{Pa}$ ,  $1 \text{ Pa} = 1 \text{ N m}^{-2}$ ) was introduced in Section F.7. As we saw there, several other units are still widely used (Table 1.1). A pressure of 1 bar is the standard pressure for reporting data; we denote it  $p^*$ .

**Self-test 1.1** Calculate the pressure (in pascals and atmospheres) exerted by a mass of  $1.0 \text{ kg}$  pressing through the point of a pin of area  $1.0 \times 10^{-2} \text{ mm}^2$  at the surface of the Earth. Hint. The force exerted by a mass  $m$  due to gravity at the surface of the Earth is  $mg$ , where  $g$  is the acceleration of free fall (see inside the front cover for its standard value).

[ $0.98 \text{ GPa}$ ,  $9.7 \times 10^3 \text{ atm}$ ]

If two gases are in separate containers that share a common movable wall (a ‘piston’, Fig. 1.1), the gas that has the higher pressure will tend to compress (reduce the volume of) the gas that has lower pressure. The pressure of the high-pressure gas will fall as it expands and that of the low-pressure gas will rise as it is compressed. There will come a stage when the two pressures are equal and the wall has no further tendency to move. This condition of equality of pressure on either side of a movable wall is a state of **mechanical equilibrium** between the two gases. The pressure of a gas is therefore an indication of whether a container that contains the gas will be in mechanical equilibrium with another gas with which it shares a movable wall.

**Table 1.1** Pressure units

Name	Symbol	Value
pascal	1 Pa	$1 \text{ N m}^{-2}$ , $1 \text{ kg m}^{-1} \text{ s}^{-2}$
bar	1 bar	$10^5 \text{ Pa}$
atmosphere	1 atm	101.325 kPa
torr	1 Torr	$(101\ 325/760) \text{ Pa} = 133.32 \dots \text{ Pa}$
millimetres of mercury	1 mmHg	133.322 ... Pa
pound per square inch	1 psi	$6.894\ 757 \dots \text{ kPa}$

### (b) The measurement of pressure

The pressure exerted by the atmosphere is measured with a **barometer**. The original version of a barometer (which was invented by Torricelli, a student of Galileo) was an inverted tube of mercury sealed at the upper end. When the column of mercury is in mechanical equilibrium with the atmosphere, the pressure at its base is equal to that exerted by the atmosphere. It follows that the height of the mercury column is proportional to the external pressure.

#### Example 1.1 Calculating the pressure exerted by a column of liquid

Derive an equation for the pressure at the base of a column of liquid of mass density  $\rho$  (rho) and height  $h$  at the surface of the Earth. The pressure exerted by a column of liquid is commonly called the ‘hydrostatic pressure’.

**Method** Use the definition of pressure in eqn 1.2 with  $F = mg$ . To calculate  $F$  we need to know the mass  $m$  of the column of liquid, which is its mass density,  $\rho$ , multiplied by its volume,  $V$ :  $m = \rho V$ . The first step, therefore, is to calculate the volume of a cylindrical column of liquid.

**Answer** Let the column have cross-sectional area  $A$ ; then its volume is  $Ah$  and its mass is  $m = \rho Ah$ . The force the column of this mass exerts at its base is

$$F = mg = \rho Ahg$$

The pressure at the base of the column is therefore

$$p = \frac{F}{A} = \frac{\rho Ahg}{A} = \rho gh \quad \boxed{1} \quad \text{Hydrostatic pressure} \quad (1.3)$$

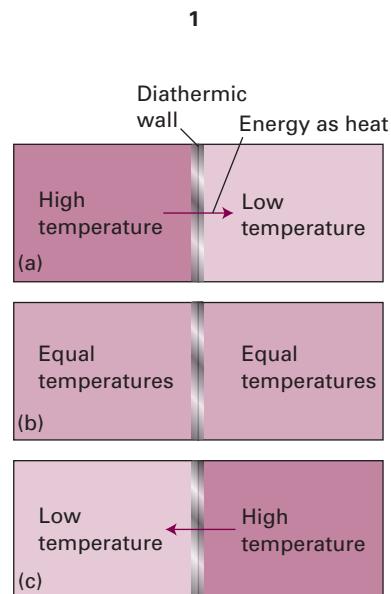
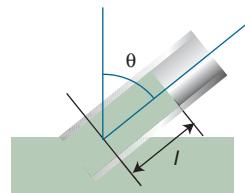
Note that the hydrostatic pressure is independent of the shape and cross-sectional area of the column. The mass of the column of a given height increases as the area, but so does the area on which the force acts, so the two cancel.

**Self-test 1.2** Derive an expression for the pressure at the base of a column of liquid of length  $l$  held at an angle  $\theta$  (theta) to the vertical (1).  $[p = \rho gl \cos \theta]$

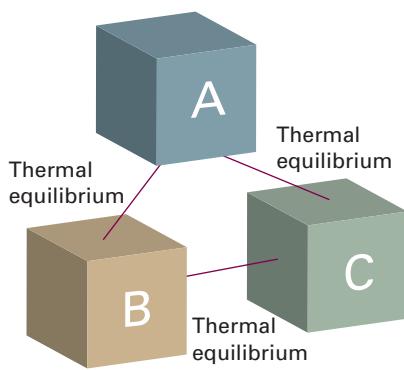
The pressure of a sample of gas inside a container is measured by using a pressure gauge, which is a device with electrical properties that depend on the pressure. For instance, a *Bayard–Alpert pressure gauge* is based on the ionization of the molecules present in the gas and the resulting current of ions is interpreted in terms of the pressure. In a *capacitance manometer*, the deflection of a diaphragm relative to a fixed electrode is monitored through its effect on the capacitance of the arrangement. Certain semiconductors also respond to pressure and are used as transducers in solid-state pressure gauges.

### (c) Temperature

The concept of temperature springs from the observation that a change in physical state (for example, a change of volume) can occur when two objects are in contact with one another, as when a red-hot metal is plunged into water. Later (Section 2.1) we shall see that the change in state can be interpreted as arising from a flow of energy as heat from one object to another. The **temperature**,  $T$ , is the property that indicates the direction of the flow of energy through a thermally conducting, rigid wall. If energy flows from A to B when they are in contact, then we say that A has a higher temperature than B (Fig. 1.2).



**Fig. 1.2** Energy flows as heat from a region at a higher temperature to one at a lower temperature if the two are in contact through a diathermic wall, as in (a) and (c). However, if the two regions have identical temperatures, there is no net transfer of energy as heat even though the two regions are separated by a diathermic wall (b). The latter condition corresponds to the two regions being at thermal equilibrium.



**Fig. 1.3** The experience summarized by the Zeroth Law of thermodynamics is that, if an object A is in thermal equilibrium with B and B is in thermal equilibrium with C, then C is in thermal equilibrium with A.

It will prove useful to distinguish between two types of boundary that can separate the objects. A boundary is **diathermic** (thermally conducting; ‘dia’ is from the Greek word for ‘through’) if a change of state is observed when two objects at different temperatures are brought into contact. A metal container has diathermic walls. A boundary is **adiabatic** (thermally insulating) if no change occurs even though the two objects have different temperatures. A vacuum flask is an approximation to an adiabatic container.

The temperature is a property that indicates whether two objects would be in ‘thermal equilibrium’ if they were in contact through a diathermic boundary. **Thermal equilibrium** is established if no change of state occurs when two objects A to B are in contact through a diathermic boundary. Suppose an object A (which we can think of as a block of iron) is in thermal equilibrium with an object B (a block of copper), and that B is also in thermal equilibrium with another object C (a flask of water). Then it has been found experimentally that A and C will also be in thermal equilibrium when they are put in contact (Fig. 1.3). This observation is summarized by the **Zeroth Law of thermodynamics**:

If A is in thermal equilibrium with B, and B is in thermal equilibrium with C, then C is also in thermal equilibrium with A.

Zeroth Law of thermodynamics

The Zeroth Law justifies the concept of temperature and the use of a **thermometer**, a device for measuring the temperature. Thus, suppose that B is a glass capillary containing a liquid, such as mercury, that expands significantly as the temperature increases. Then, when A is in contact with B, the mercury column in the latter has a certain length. According to the Zeroth Law, if the mercury column in B has the same length when it is placed in thermal contact with another object C, then we can predict that no change of state of A and C will occur when they are in thermal contact. Moreover, we can use the length of the mercury column as a measure of the temperatures of A and C.

In the early days of thermometry (and still in laboratory practice today), temperatures were related to the length of a column of liquid, and the difference in lengths shown when the thermometer was first in contact with melting ice and then with boiling water was divided into 100 steps called ‘degrees’, the lower point being labelled 0. This procedure led to the **Celsius scale** of temperature. In this text, temperatures on the Celsius scale are denoted  $\theta$  (theta) and expressed in *degrees Celsius* ( $^{\circ}\text{C}$ ). However, because different liquids expand to different extents, and do not always expand uniformly over a given range, thermometers constructed from different materials showed different numerical values of the temperature between their fixed points. The pressure of a gas, however, can be used to construct a **perfect-gas temperature scale** that is independent of the identity of the gas. The perfect-gas scale turns out to be identical to the **thermodynamic temperature scale** to be introduced in Section 3.2d, so we shall use the latter term from now on to avoid a proliferation of names. On the thermodynamic temperature scale, temperatures are denoted  $T$  and are normally reported in *kelvins* (K; not  $^{\circ}\text{K}$ ). Thermodynamic and Celsius temperatures are related by the exact expression

$$T/\text{K} = \theta/\text{ }^{\circ}\text{C} + 273.15$$

Definition of Celsius scale

(1.4)

This relation is the current definition of the Celsius scale in terms of the more fundamental Kelvin scale. It implies that a difference in temperature of  $1^{\circ}\text{C}$  is equivalent to a difference of 1 K.

**A note on good practice** We write  $T = 0$ , not  $T = 0\text{ K}$  for the zero temperature on the thermodynamic temperature scale. This scale is absolute, and the lowest temperature is 0 regardless of the size of the divisions on the scale (just as we write  $p = 0$  for zero pressure, regardless of the size of the units we adopt, such as bar or pascal). However, we write  $0^{\circ}\text{C}$  because the Celsius scale is not absolute.

### • A brief illustration

To express 25.00°C as a temperature in kelvins, we use eqn 1.4 to write

$$T/K = (25.00^\circ\text{C})/\text{°C} + 273.15 = 25.00 + 273.15 = 298.15$$

Note how the units (in this case, °C) are cancelled like numbers. This is the procedure called ‘quantity calculus’ in which a physical quantity (such as the temperature) is the product of a numerical value (25.00) and a unit (1°C); see Section F.7. Multiplication of both sides by the unit K then gives  $T = 298.15 \text{ K}$ . •

**A note on good practice** When the units need to be specified in an equation, the approved procedure, which avoids any ambiguity, is to write (physical quantity)/units, which is a dimensionless number, just as  $(25.00^\circ\text{C})/\text{°C} = 25.00$  in this *brief illustration*. Units may be multiplied and cancelled just like numbers.

## 1.2 The gas laws

**Key points** (a) The perfect gas law, a limiting law valid in the limit of zero pressure, summarizes Boyle’s and Charles’s laws and Avogadro’s principle. (b) The kinetic theory of gases, in which molecules are in ceaseless random motion, provides a model that accounts for the gas laws and a relation between average speed and temperature. (c) A mixture of perfect gases behaves like a single perfect gas; its components each contribute their partial pressure to the total pressure.

The equation of state of a gas at low pressure was established by combining a series of empirical laws.

### (a) The perfect gas law

We assume that the following individual gas laws are familiar:

$$\text{Boyle's law: } pV = \text{constant, at constant } n, T \quad (1.5)^{\circ}$$

$$\text{Charles's law: } V = \text{constant} \times T, \text{ at constant } n, p \quad (1.6a)^{\circ}$$

$$p = \text{constant} \times T, \text{ at constant } n, V \quad (1.6b)^{\circ}$$

$$\text{Avogadro's principle: } V = \text{constant} \times n \text{ at constant } p, T \quad (1.7)^{\circ}$$

Boyle’s and Charles’s laws are examples of a **limiting law**, a law that is strictly true only in a certain limit, in this case  $p \rightarrow 0$ . Equations valid in this limiting sense will be signalled by a ° on the equation number, as in these expressions. Avogadro’s principle is commonly expressed in the form ‘equal volumes of gases at the same temperature and pressure contain the same numbers of molecules’. In this form, it is increasingly true as  $p \rightarrow 0$ . Although these relations are strictly true only at  $p = 0$ , they are reasonably reliable at normal pressures ( $p \approx 1 \text{ bar}$ ) and are used widely throughout chemistry.

Figure 1.4 depicts the variation of the pressure of a sample of gas as the volume is changed. Each of the curves in the graph corresponds to a single temperature and hence is called an **isotherm**. According to Boyle’s law, the isotherms of gases are hyperbolas (a curve obtained by plotting  $y$  against  $x$  with  $xy = \text{constant}$ ). An alternative depiction, a plot of pressure against 1/volume, is shown in Fig. 1.5. The linear variation of volume with temperature summarized by Charles’s law is illustrated in Fig. 1.6. The lines in this illustration are examples of **isobars**, or lines showing the variation of properties at constant pressure. Figure 1.7 illustrates the linear variation of pressure with temperature. The lines in this diagram are **isochores**, or lines showing the variation of properties at constant volume.

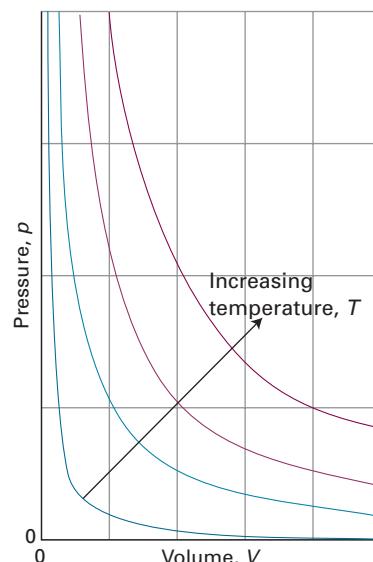
The empirical observations summarized by eqns 1.5–7 can be combined into a single expression

$$pV = \text{constant} \times nT$$

### A brief comment

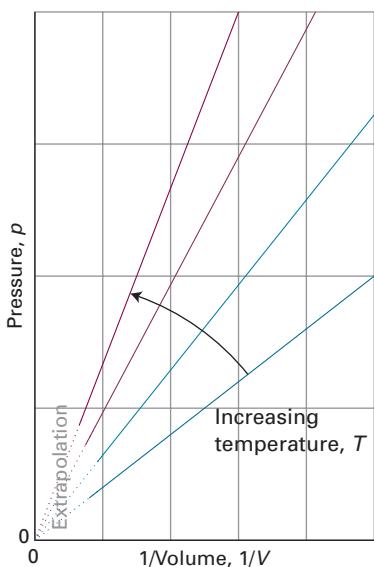
Avogadro’s principle is a principle rather than a law (a summary of experience) because it depends on the validity of a model, in this case the existence of molecules.

Despite there now being no doubt about the existence of molecules, it is still a model-based principle rather than a law.



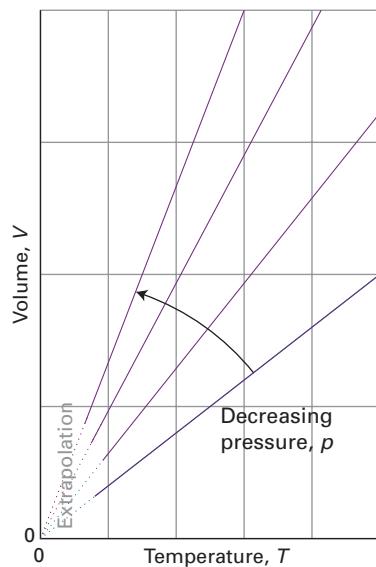
**Fig. 1.4** The pressure–volume dependence of a fixed amount of perfect gas at different temperatures. Each curve is a hyperbola ( $pV = \text{constant}$ ) and is called an isotherm.

**interActivity** Explore how the pressure of 1.5 mol CO<sub>2</sub>(g) varies with volume as it is compressed at (a) 273 K, (b) 373 K from 30 dm<sup>3</sup> to 15 dm<sup>3</sup>.



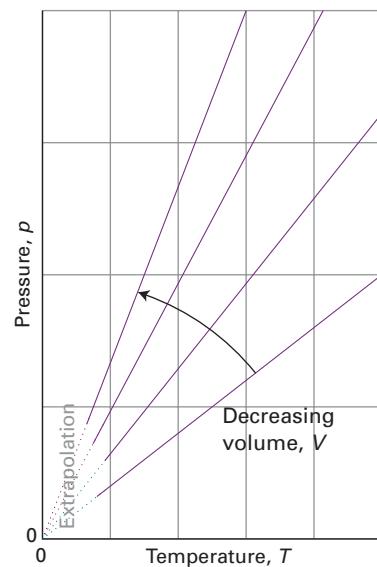
**Fig. 1.5** Straight lines are obtained when the pressure is plotted against  $1/V$  at constant temperature.

**interActivity** Repeat *interActivity 1.4*, but plot the data as  $p$  against  $1/V$ .



**Fig. 1.6** The variation of the volume of a fixed amount of gas with the temperature at constant pressure. Note that in each case the isobars extrapolate to zero volume at  $T = 0$  or  $\theta = -273^\circ\text{C}$ .

**interActivity** Explore how the volume of 1.5 mol  $\text{CO}_2(\text{g})$  in a container maintained at (a) 1.00 bar, (b) 0.50 bar varies with temperature as it is cooled from 373 K to 273 K.



**Fig. 1.7** The pressure also varies linearly with the temperature at constant volume, and extrapolates to zero at  $T = 0$  ( $-273^\circ\text{C}$ ).

**interActivity** Explore how the pressure of 1.5 mol  $\text{CO}_2(\text{g})$  in a container of volume (a)  $30 \text{ dm}^3$ , (b)  $15 \text{ dm}^3$  varies with temperature as it is cooled from 373 K to 273 K.

**A note on good practice** To test the validity of a relation between two quantities, it is best to plot them in such a way that they should give a straight line, for deviations from a straight line are much easier to detect than deviations from a curve.

This expression is consistent with Boyle's law ( $pV = \text{constant}$ ) when  $n$  and  $T$  are constant, with both forms of Charles's law ( $p \propto T$ ,  $V \propto T$ ) when  $n$  and either  $V$  or  $p$  are held constant, and with Avogadro's principle ( $V \propto n$ ) when  $p$  and  $T$  are constant. The constant of proportionality, which is found experimentally to be the same for all gases, is denoted  $R$  and called the **gas constant**. The resulting expression

$$pV = nRT$$

Perfect gas law (1.8)<sup>°</sup>

is the **perfect gas law** (or *perfect gas equation of state*). It is the approximate equation of state of any gas, and becomes increasingly exact as the pressure of the gas approaches zero. A gas that obeys eqn 1.8 exactly under all conditions is called a **perfect gas** (or *ideal gas*). A **real gas**, an actual gas, behaves more like a perfect gas the lower the pressure, and is described exactly by eqn 1.8 in the limit of  $p \rightarrow 0$ . The gas constant  $R$  can be determined by evaluating  $R = pV/nT$  for a gas in the limit of zero pressure (to guarantee that it is behaving perfectly). However, a more accurate value can be obtained by measuring the speed of sound in a low-pressure gas (argon is used in practice) and extrapolating its value to zero pressure. Table 1.2 lists the values of  $R$  in a variety of units.

The surface in Fig. 1.8 is a plot of the pressure of a fixed amount of perfect gas against its volume and thermodynamic temperature as given by eqn 1.8. The surface depicts the only possible states of a perfect gas: the gas cannot exist in states that do not correspond to points on the surface. The graphs in Figs. 1.4, 1.6, and 1.7 correspond to the sections through the surface (Fig. 1.9).

**Table 1.2** The gas constant

$R$	
8.314 47	$\text{J K}^{-1} \text{ mol}^{-1}$
$8.205\ 74 \times 10^{-2}$	$\text{dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$
$8.314\ 47 \times 10^{-2}$	$\text{dm}^3 \text{ bar K}^{-1} \text{ mol}^{-1}$
8.314 47	$\text{Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1}$
62.364	$\text{dm}^3 \text{ Torr K}^{-1} \text{ mol}^{-1}$
1.987 21	$\text{cal K}^{-1} \text{ mol}^{-1}$

**Example 1.2** Using the perfect gas law

In an industrial process, nitrogen is heated to 500 K in a vessel of constant volume. If it enters the vessel at 100 atm and 300 K, what pressure would it exert at the working temperature if it behaved as a perfect gas?

**Method** We expect the pressure to be greater on account of the increase in temperature. The perfect gas law in the form  $pV/nT = R$  implies that, if the conditions are changed from one set of values to another, then, because  $pV/nT$  is equal to a constant, the two sets of values are related by the ‘combined gas law’

$$\frac{p_1 V_1}{n_1 T_1} = \frac{p_2 V_2}{n_2 T_2} \quad \text{Combined gas law} \quad (1.9)^{\circ}$$

This expression is easily rearranged to give the unknown quantity (in this case  $p_2$ ) in terms of the known. The known and unknown data are summarized in (2).

**Answer** Cancellation of the volumes (because  $V_1 = V_2$ ) and amounts (because  $n_1 = n_2$ ) on each side of the combined gas law results in

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

which can be rearranged into

$$p_2 = \frac{T_2}{T_1} \times p_1$$

Substitution of the data then gives

$$p_2 = \frac{500 \text{ K}}{300 \text{ K}} \times (100 \text{ atm}) = 167 \text{ atm}$$

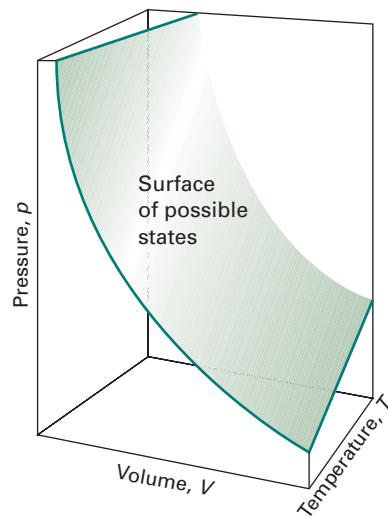
Experiment shows that the pressure is actually 183 atm under these conditions, so the assumption that the gas is perfect leads to a 10 per cent error.

**Self-test 1.3** What temperature would result in the same sample exerting a pressure of 300 atm? [900 K]

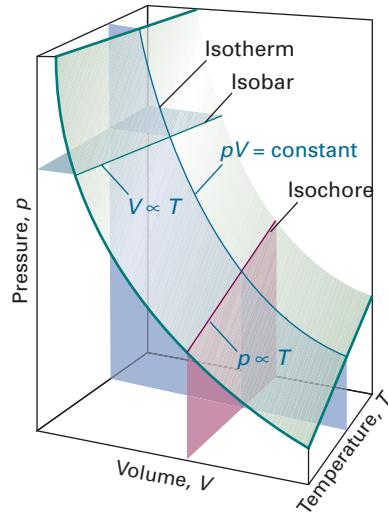
The perfect gas law is of the greatest importance in physical chemistry because it is used to derive a wide range of relations that are used throughout thermodynamics. However, it is also of considerable practical utility for calculating the properties of a gas under a variety of conditions. For instance, the molar volume,  $V_m = V/n$ , of a perfect gas under the conditions called **standard ambient temperature and pressure** (SATP), which means 298.15 K and 1 bar (that is, exactly 10<sup>5</sup> Pa), is easily calculated from  $V_m = RT/p$  to be 24.789 dm<sup>3</sup> mol<sup>-1</sup>. An earlier definition, **standard temperature and pressure** (STP), was 0°C and 1 atm; at STP, the molar volume of a perfect gas is 22.414 dm<sup>3</sup> mol<sup>-1</sup>.

**(b) The kinetic model of gases**

The molecular explanation of Boyle’s law is that, if a sample of gas is compressed to half its volume, then twice as many molecules strike the walls in a given period of time than before it was compressed. As a result, the average force exerted on the walls is



**Fig. 1.8** A region of the  $p, V, T$  surface of a fixed amount of perfect gas. The points forming the surface represent the only states of the gas that can exist.



**Fig. 1.9** Sections through the surface shown in Fig. 1.8 at constant temperature give the isotherms shown in Fig. 1.4 and the isobars shown in Fig. 1.6.

	$n$	$p$	$V$	$T$
Initial	Same	100	Same	300
Final	Same	?	Same	500

doubled. Hence, when the volume is halved the pressure of the gas is doubled, and  $p \times V$  is a constant. Boyle's law applies to all gases regardless of their chemical identity (provided the pressure is low) because at low pressures the average separation of molecules is so great that they exert no influence on one another and hence travel independently. The molecular explanation of Charles's law lies in the fact that raising the temperature of a gas increases the average speed of its molecules. The molecules collide with the walls more frequently and with greater impact. Therefore they exert a greater pressure on the walls of the container.

These qualitative concepts are expressed quantitatively in terms of the kinetic model of gases, which is described more fully in Chapter 20. Briefly, the kinetic model is based on three assumptions:

1. The gas consists of molecules of mass  $m$  in ceaseless random motion.
2. The size of the molecules is negligible, in the sense that their diameters are much smaller than the average distance travelled between collisions.
3. The molecules interact only through brief, infrequent, and elastic collisions.

An *elastic collision* is a collision in which the total translational kinetic energy of the molecules is conserved. From the very economical assumptions of the kinetic model, it can be deduced (as we show in detail in Chapter 20) that the pressure and volume of the gas are related by

$$pV = \frac{1}{3}nMc^2 \quad (1.10)^{\circ}$$

where  $M = mN_A$ , the molar mass of the molecules, and  $c$  is the *root mean square speed* of the molecules, the square root of the mean of the squares of the speeds,  $v$ , of the molecules:

$$c = \langle v^2 \rangle^{1/2} \quad (1.11)$$

We see that, if the root mean square speed of the molecules depends only on the temperature, then at constant temperature  $pV = \text{constant}$ , which is the content of Boyle's law. Moreover, for eqn 1.10 to be the equation of state of a perfect gas, its right-hand side must be equal to  $nRT$ . It follows that the root mean square speed of the molecules in a gas at a temperature  $T$  must be

$$c = \left( \frac{3RT}{M} \right)^{1/2} \quad \boxed{\begin{array}{l} \text{Relation between molecular} \\ \text{speed and temperature} \end{array}} \quad (1.12)^{\circ}$$

We can conclude that *the root mean square speed of the molecules of a gas is proportional to the square root of the temperature and inversely proportional to the square root of the molar mass*. That is, the higher the temperature, the higher the root mean square speed of the molecules, and, at a given temperature, heavy molecules travel more slowly than light molecules. The root mean square speed of  $\text{N}_2$  molecules, for instance, is found from eqn 1.12 to be  $515 \text{ m s}^{-1}$  at  $298 \text{ K}$ .

### (c) Mixtures of gases

When dealing with gaseous mixtures, we often need to know the contribution that each component makes to the total pressure of the sample. The **partial pressure**,  $p_J$ , of a gas J in a mixture (any gas, not just a perfect gas), is defined as

$$p_J = x_J p$$

Definition of  
partial pressure

[1.13]

where  $x_J$  is the mole fraction of the component J, the amount of J expressed as a fraction of the total amount of molecules,  $n$ , in the sample:

$$x_J = \frac{n_J}{n} \quad n = n_A + n_B + \dots$$

Definition of  
mole fraction [1.14]

When no J molecules are present,  $x_J = 0$ ; when only J molecules are present,  $x_J = 1$ . It follows from the definition of  $x_J$  that, whatever the composition of the mixture,  $x_A + x_B + \dots = 1$  and therefore that the sum of the partial pressures is equal to the total pressure

$$p_A + p_B + \dots = (x_A + x_B + \dots)p = p \quad (1.15)$$

This relation is true for both real and perfect gases.

When all the gases are perfect, the partial pressure as defined in eqn 1.13 is also the pressure that each gas would exert if it occupied the same container alone at the same temperature. The latter is the original meaning of ‘partial pressure’. That identification was the basis of the original formulation of Dalton’s law:

The pressure exerted by a mixture of gases is the sum of the pressures that each one would exert if it occupied the container alone.

Dalton's  
law

Now, however, the relation between partial pressure (as defined in eqn 1.13) and total pressure (as given by eqn 1.15) is true for all gases and the identification of partial pressure with the pressure that the gas would exert on its own is valid only for a perfect gas.

### Example 1.3 Calculating partial pressures

The mass percentage composition of dry air at sea level is approximately N<sub>2</sub>: 75.5; O<sub>2</sub>: 23.2; Ar: 1.3. What is the partial pressure of each component when the total pressure is 1.20 atm?

**Method** We expect species with a high mole fraction to have a proportionally high partial pressure. Partial pressures are defined by eqn 1.13. To use the equation, we need the mole fractions of the components. To calculate mole fractions, which are defined by eqn 1.14, we use the fact that the amount of molecules J of molar mass  $M_J$  in a sample of mass  $m_J$  is  $n_J = m_J/M_J$ . The mole fractions are independent of the total mass of the sample, so we can choose the latter to be exactly 100 g (which makes the conversion from mass percentages very easy). Thus, the mass of N<sub>2</sub> present is 75.5 per cent of 100 g, which is 75.5 g.

**Answer** The amounts of each type of molecule present in 100 g of air, in which the masses of N<sub>2</sub>, O<sub>2</sub>, and Ar are 75.5 g, 23.2 g, and 1.3 g, respectively, are

$$n(N_2) = \frac{75.5 \text{ g}}{28.02 \text{ g mol}^{-1}} = \frac{75.5}{28.02} \text{ mol}$$

$$n(O_2) = \frac{23.2 \text{ g}}{32.00 \text{ g mol}^{-1}} = \frac{23.2}{32.00} \text{ mol}$$

$$n(\text{Ar}) = \frac{1.3 \text{ g}}{39.95 \text{ g mol}^{-1}} = \frac{1.3}{39.95} \text{ mol}$$

These three amounts work out as 2.69 mol, 0.725 mol, and 0.033 mol, respectively, for a total of 3.45 mol. The mole fractions are obtained by dividing each of the above amounts by 3.45 mol and the partial pressures are then obtained by multiplying the mole fraction by the total pressure (1.20 atm):

	N <sub>2</sub>	O <sub>2</sub>	Ar
Mole fraction:	0.780	0.210	0.0096
Partial pressure/atm:	0.936	0.252	0.012

We have not had to assume that the gases are perfect: partial pressures are defined as  $p_j = x_j p$  for any kind of gas.

**Self-test 1.4** When carbon dioxide is taken into account, the mass percentages are 75.52 (N<sub>2</sub>), 23.15 (O<sub>2</sub>), 1.28 (Ar), and 0.046 (CO<sub>2</sub>). What are the partial pressures when the total pressure is 0.900 atm? [0.703, 0.189, 0.0084, 0.00027 atm]

#### IMPACT ON ENVIRONMENTAL SCIENCE

##### I1.1 The gas laws and the weather

The biggest sample of gas readily accessible to us is the atmosphere, a mixture of gases with the composition summarized in Table 1.3. The composition is maintained moderately constant by diffusion and convection (winds, particularly the local turbulence called *eddies*) but the pressure and temperature vary with altitude and with the local conditions, particularly in the troposphere (the ‘sphere of change’), the layer extending up to about 11 km.

In the troposphere the average temperature is 15°C at sea level, falling to -57°C at the bottom of the tropopause at 11 km. This variation is much less pronounced when expressed on the Kelvin scale, ranging from 288 K to 216 K, an average of 268 K. If we suppose that the temperature has its average value all the way up to the tropopause, then the pressure varies with altitude, *h*, according to the *barometric formula*

**Table 1.3** The composition of dry air at sea level

Component	Percentage	
	By volume	By mass
Nitrogen, N <sub>2</sub>	78.08	75.53
Oxygen, O <sub>2</sub>	20.95	23.14
Argon, Ar	0.93	1.28
Carbon dioxide, CO <sub>2</sub>	0.031	0.047
Hydrogen, H <sub>2</sub>	$5.0 \times 10^{-3}$	$2.0 \times 10^{-4}$
Neon, Ne	$1.8 \times 10^{-3}$	$1.3 \times 10^{-3}$
Helium, He	$5.2 \times 10^{-4}$	$7.2 \times 10^{-5}$
Methane, CH <sub>4</sub>	$2.0 \times 10^{-4}$	$1.1 \times 10^{-4}$
Krypton, Kr	$1.1 \times 10^{-4}$	$3.2 \times 10^{-4}$
Nitric oxide, NO	$5.0 \times 10^{-5}$	$1.7 \times 10^{-6}$
Xenon, Xe	$8.7 \times 10^{-6}$	$1.2 \times 10^{-5}$
Ozone, O <sub>3</sub> ; summer	$7.0 \times 10^{-6}$	$1.2 \times 10^{-5}$
winter	$2.0 \times 10^{-6}$	$3.3 \times 10^{-6}$

$$p = p_0 e^{-h/H} \quad (1.16)$$

where  $p_0$  is the pressure at sea level and  $H$  is a constant approximately equal to 8 km. More specifically,  $H = RT/Mg$ , where  $M$  is the average molar mass of air and  $T$  is the temperature. This formula represents the outcome of the competition between the potential energy of the molecules in the gravitational field of the Earth and the stirring effects of thermal motion; it is derived on the basis of the Boltzmann distribution (Section F.5a). The barometric formula fits the observed pressure distribution quite well even for regions well above the troposphere (Fig. 1.10). It implies that the pressure of the air falls to half its sea-level value at  $h = H \ln 2$ , or 6 km.

Local variations of pressure, temperature, and composition in the troposphere are manifest as ‘weather’. A small region of air is termed a *parcel*. First, we note that a parcel of warm air is less dense than the same parcel of cool air. As a parcel rises, it expands adiabatically (that is, without transfer of heat from its surroundings), so it cools. Cool air can absorb lower concentrations of water vapour than warm air, so the moisture forms clouds. Cloudy skies can therefore be associated with rising air and clear skies are often associated with descending air.

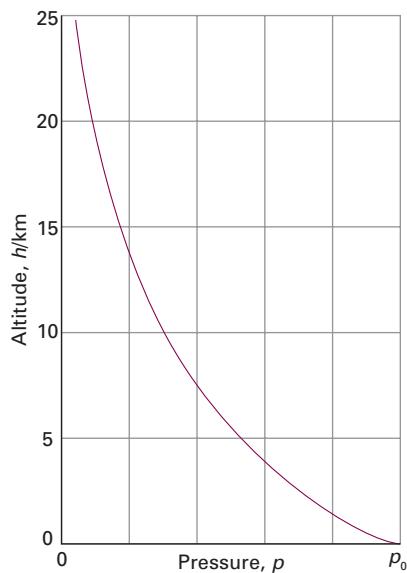
The motion of air in the upper altitudes may lead to an accumulation in some regions and a loss of molecules from other regions. The former result in the formation of regions of high pressure ('highs' or anticyclones) and the latter result in regions of low pressure ('lows', depressions, or cyclones). On a weather map, such as that shown in Fig. 1.11, the lines of constant pressure marked on it are called *isobars*. Elongated regions of high and low pressure are known, respectively, as *ridges* and *troughs*.

Horizontal pressure differentials result in the flow of air that we call *wind* (Fig. 1.12). Winds coming from the north in the Northern hemisphere and from the south in the Southern hemisphere are deflected towards the west as they migrate from a region where the Earth is rotating slowly (at the poles) to where it is rotating most rapidly (at the equator). Winds travel nearly parallel to the isobars, with low pressure to their left in the Northern hemisphere and to the right in the Southern hemisphere. At the surface, where wind speeds are lower, the winds tend to travel perpendicular to the isobars from high to low pressure. This differential motion results in a spiral outward flow of air clockwise in the Northern hemisphere around a high and an inward counterclockwise flow around a low.

The air lost from regions of high pressure is restored as an influx of air converges into the region and descends. As we have seen, descending air is associated with clear skies. It also becomes warmer by compression as it descends, so regions of high pressure are associated with high surface temperatures. In winter, the cold surface air may prevent the complete fall of air, and result in a temperature *inversion*, with a layer of warm air over a layer of cold air. Geographical conditions may also trap cool air, as in Los Angeles, and the photochemical pollutants we know as *smog* may be trapped under the warm layer.

## Real gases

Real gases do not obey the perfect gas law exactly except in the limit of  $p \rightarrow 0$ . Deviations from the law are particularly important at high pressures and low temperatures, especially when a gas is on the point of condensing to liquid.

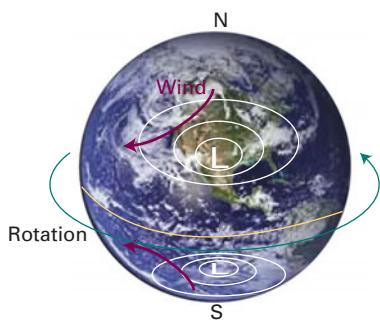


**Fig. 1.10** The variation of atmospheric pressure with altitude, as predicted by the barometric formula and as suggested by the ‘US Standard Atmosphere’, which takes into account the variation of temperature with altitude.

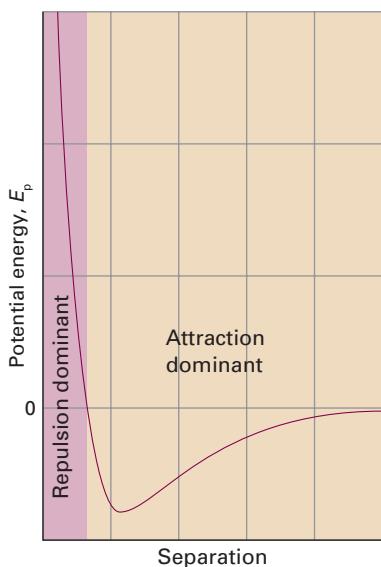
 **interActivity** How would the graph shown in the illustration change if the temperature variation with altitude were taken into account? Construct a graph allowing for a linear decrease in temperature with altitude.



**Fig. 1.11** A typical weather map; in this case, for the North Atlantic and neighbouring regions on 16 December 2008.



**Fig. 1.12** The flow of air ('wind') around regions of high and low pressure in the Northern and Southern hemispheres.



**Fig. 1.13** The variation of the potential energy of two molecules on their separation. High positive potential energy (at very small separations) indicates that the interactions between them are strongly repulsive at these distances. At intermediate separations, where the potential energy is negative, the attractive interactions dominate. At large separations (on the right) the potential energy is zero and there is no interaction between the molecules.

### 1.3 Molecular interactions

**Key points** (a) The extent of deviations from perfect behaviour is summarized by introducing the compression factor. (b) The virial equation is an empirical extension of the perfect gas equation that summarizes the behaviour of real gases over a range of conditions. (c) The isotherms of a real gas introduce the concept of vapour pressure and critical behaviour. (d) A gas can be liquefied by pressure alone only if its temperature is at or below its critical temperature.

Real gases show deviations from the perfect gas law because molecules interact with one another. A point to keep in mind is that repulsive forces between molecules assist expansion and attractive forces assist compression.

Repulsive forces are significant only when molecules are almost in contact: they are short-range interactions, even on a scale measured in molecular diameters (Fig. 1.13). Because they are short-range interactions, repulsions can be expected to be important only when the average separation of the molecules is small. This is the case at high pressure, when many molecules occupy a small volume. On the other hand, attractive intermolecular forces have a relatively long range and are effective over several molecular diameters. They are important when the molecules are fairly close together but not necessarily touching (at the intermediate separations in Fig. 1.13). Attractive forces are ineffective when the molecules are far apart (well to the right in Fig. 1.13). Intermolecular forces are also important when the temperature is so low that the molecules travel with such low mean speeds that they can be captured by one another.

At low pressures, when the sample occupies a large volume, the molecules are so far apart for most of the time that the intermolecular forces play no significant role, and the gas behaves virtually perfectly. At moderate pressures, when the average separation of the molecules is only a few molecular diameters, the attractive forces dominate the repulsive forces. In this case, the gas can be expected to be more compressible than a perfect gas because the forces help to draw the molecules together. At high pressures, when the average separation of the molecules is small, the repulsive forces dominate and the gas can be expected to be less compressible because now the forces help to drive the molecules apart.

#### (a) The compression factor

The compression factor,  $Z$ , of a gas is the ratio of its measured molar volume,  $V_m = V/n$ , to the molar volume of a perfect gas,  $V_m^0$ , at the same pressure and temperature:

$$Z = \frac{V_m}{V_m^0}$$

Definition of compression factor

[1.17]

Because the molar volume of a perfect gas is equal to  $RT/p$ , an equivalent expression is  $Z = pV_m/RT$ , which we can write as

$$pV_m = RTZ \quad (1.18)$$

Because, for a perfect gas  $Z = 1$  under all conditions, deviation of  $Z$  from 1 is a measure of departure from perfect behaviour.

Some experimental values of  $Z$  are plotted in Fig. 1.14. At very low pressures, all the gases shown have  $Z \approx 1$  and behave nearly perfectly. At high pressures, all the gases have  $Z > 1$ , signifying that they have a larger molar volume than a perfect gas. Repulsive forces are now dominant. At intermediate pressures, most gases have  $Z < 1$ , indicating that the attractive forces are reducing the molar volume relative to that of a perfect gas.

### (b) Virial coefficients

Figure 1.15 shows the experimental isotherms for carbon dioxide. At large molar volumes and high temperatures the real-gas isotherms do not differ greatly from perfect-gas isotherms. The small differences suggest that the perfect gas law is in fact the first term in an expression of the form

$$pV_m = RT(1 + B'p + C'p^2 + \dots) \quad (1.19a)$$

This expression is an example of a common procedure in physical chemistry, in which a simple law that is known to be a good first approximation (in this case  $pV = nRT$ ) is treated as the first term in a series in powers of a variable (in this case  $p$ ). A more convenient expansion for many applications is

$$pV_m = RT \left( 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots \right) \quad \text{Virial equation of state} \quad (1.19b)$$

These two expressions are two versions of the **virial equation of state**.<sup>1</sup> By comparing the expression with eqn 1.18 we see that the term in parentheses in eqn 1.19b is just the compression factor,  $Z$ .

The coefficients  $B, C, \dots$ , which depend on the temperature, are the second, third, ... virial coefficients (Table 1.4); the first virial coefficient is 1. The third virial coefficient,  $C$ , is usually less important than the second coefficient,  $B$ , in the sense that at typical molar volumes  $C/V_m^2 \ll B/V_m$ . The values of the virial coefficients of a gas are determined from measurements of its compression factor.

An important point is that, although the equation of state of a real gas may coincide with the perfect gas law as  $p \rightarrow 0$ , not all its properties necessarily coincide with those of a perfect gas in that limit. Consider, for example, the value of  $dZ/dp$ , the slope of the graph of compression factor against pressure. For a perfect gas  $dZ/dp = 0$  (because  $Z = 1$  at all pressures), but for a real gas from eqn 1.19a we obtain

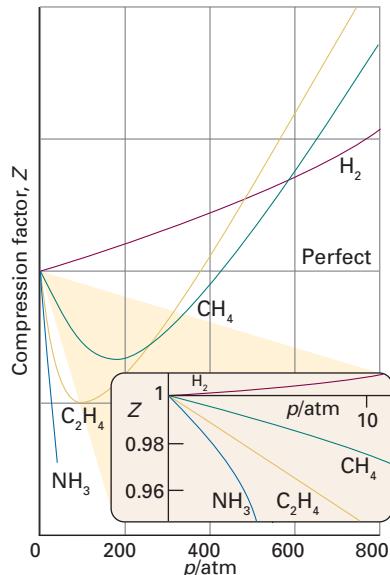
$$\frac{dZ}{dp} = B' + 2pC' + \dots \rightarrow B' \quad \text{as } p \rightarrow 0 \quad (1.20a)$$

However,  $B'$  is not necessarily zero, so the slope of  $Z$  with respect to  $p$  does not necessarily approach 0 (the perfect gas value), as we can see in Fig. 1.14. Because several physical properties of gases depend on derivatives, the properties of real gases do not always coincide with the perfect gas values at low pressures. By a similar argument

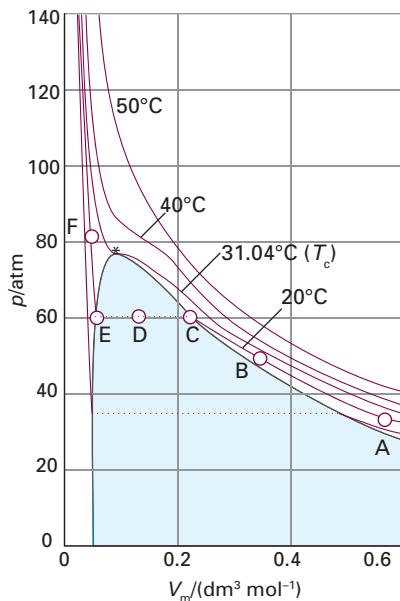
$$\frac{dZ}{d\left(\frac{1}{V_m}\right)} \rightarrow B \quad \text{as } V_m \rightarrow \infty \quad (1.20b)$$

Because the virial coefficients depend on the temperature, there may be a temperature at which  $Z \rightarrow 1$  with zero slope at low pressure or high molar volume (Fig. 1.16). At this temperature, which is called the **Boyle temperature**,  $T_B$ , the properties of the real gas do coincide with those of a perfect gas as  $p \rightarrow 0$ . According to eqn 1.20a,  $Z$  has zero slope as  $p \rightarrow 0$  if  $B = 0$ , so we can conclude that  $B = 0$  at the Boyle temperature. It then follows from eqn 1.18 that  $pV_m \approx RT_B$  over a more extended range of pressures than at other temperatures because the first term after 1 (that is,  $B/V_m$ ) in the virial equation is zero and  $C/V_m^2$  and higher terms are negligibly small. For helium  $T_B = 22.64$  K; for air  $T_B = 346.8$  K; more values are given in Table 1.5.

<sup>1</sup> The name comes from the Latin word for force. The coefficients are sometimes denoted  $B_2, B_3, \dots$



**Fig. 1.14** The variation of the compression factor,  $Z$ , with pressure for several gases at 0°C. A perfect gas has  $Z = 1$  at all pressures. Notice that, although the curves approach 1 as  $p \rightarrow 0$ , they do so with different slopes.



**Fig. 1.15** Experimental isotherms of carbon dioxide at several temperatures. The ‘critical isotherm’, the isotherm at the critical temperature, is at 31.04°C. The critical point is marked with a star.

**Table 1.4\*** Second virial coefficients,  $B/(cm^3 mol^{-1})$ 

	Temperature	
	273 K	600 K
Ar	-21.7	11.9
CO <sub>2</sub>	-142	-12.4
N <sub>2</sub>	-10.5	21.7
Xe	-153.7	-19.6

\* More values are given in the *Data section*.

**Table 1.5\*** Critical constants of gases

	$p_c/atm$	$V_c/(cm^3 mol^{-1})$	$T_c/K$	$Z_c$	$T_B/K$
Ar	48.0	75.3	150.7	0.292	411.5
CO <sub>2</sub>	72.9	94.0	304.2	0.274	714.8
He	2.26	57.8	5.2	0.305	22.64
O <sub>2</sub>	50.14	78.0	154.8	0.308	405.9

\* More values are given in the *Data section*.

### (c) Condensation

Now consider what happens when we compress (reduce the volume of) a sample of gas initially in the state marked A in Fig. 1.15 at constant temperature by pushing in a piston. Near A, the pressure of the gas rises in approximate agreement with Boyle's law. Serious deviations from that law begin to appear when the volume has been reduced to B.

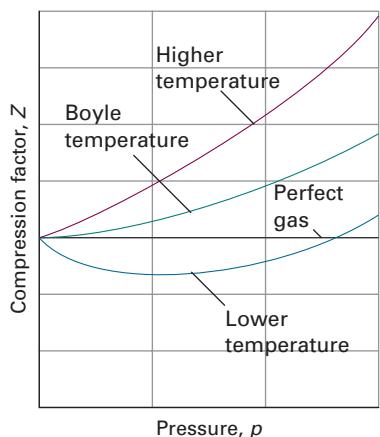
At C (which corresponds to about 60 atm for carbon dioxide), all similarity to perfect behaviour is lost, for suddenly the piston slides in without any further rise in pressure: this stage is represented by the horizontal line CDE. Examination of the contents of the vessel shows that just to the left of C a liquid appears, and there are two phases separated by a sharply defined surface. As the volume is decreased from C through D to E, the amount of liquid increases. There is no additional resistance to the piston because the gas can respond by condensing. The pressure corresponding to the line CDE, when both liquid and vapour are present in equilibrium, is called the **vapour pressure** of the liquid at the temperature of the experiment.

At E, the sample is entirely liquid and the piston rests on its surface. Any further reduction of volume requires the exertion of considerable pressure, as is indicated by the sharply rising line to the left of E. Even a small reduction of volume from E to F requires a great increase in pressure.

### (d) Critical constants

The isotherm at the temperature  $T_c$  (304.19 K, or 31.04°C for CO<sub>2</sub>) plays a special role in the theory of the states of matter. An isotherm slightly below  $T_c$  behaves as we have already described: at a certain pressure, a liquid condenses from the gas and is distinguishable from it by the presence of a visible surface. If, however, the compression takes place at  $T_c$  itself, then a surface separating two phases does not appear and the volumes at each end of the horizontal part of the isotherm have merged to a single point, the **critical point** of the gas. The temperature, pressure, and molar volume at the critical point are called, respectively, the **critical temperature**,  $T_c$ , **critical pressure**,  $p_c$ , and **critical molar volume**,  $V_c$ , of the substance. Collectively,  $p_c$ ,  $V_c$ , and  $T_c$  are the **critical constants** of a substance (Table 1.5).

At and above  $T_c$ , the sample has a single phase that occupies the entire volume of the container. Such a phase is, by definition, a gas. Hence, the liquid phase of a substance does not form above the critical temperature. The critical temperature of oxygen, for instance, signifies that it is impossible to produce liquid oxygen by compression alone if its temperature is greater than 155 K: to liquefy oxygen—to obtain a fluid phase that does not occupy the entire volume—the temperature must first be lowered to below 155 K, and then the gas compressed isothermally. The single phase that fills the entire volume when  $T > T_c$  may be much denser than we normally consider typical of gases, and the name **supercritical fluid** is preferred.



**Fig. 1.16** The compression factor,  $Z$ , approaches 1 at low pressures, but does so with different slopes. For a perfect gas, the slope is zero, but real gases may have either positive or negative slopes, and the slope may vary with temperature. At the Boyle temperature, the slope is zero and the gas behaves perfectly over a wider range of conditions than at other temperatures.

## 1.4 The van der Waals equation

**Key points** (a) The van der Waals equation is a model equation of state for a real gas expressed in terms of two parameters, one corresponding to molecular attractions and the other to molecular repulsions. (b) The van der Waals equation captures the general features of the behaviour of real gases, including their critical behaviour. (c) The properties of real gases are coordinated by expressing their equations of state in terms of reduced variables.

We can draw conclusions from the virial equations of state only by inserting specific values of the coefficients. It is often useful to have a broader, if less precise, view of all gases. Therefore, we introduce the approximate equation of state suggested by J.D. van der Waals in 1873. This equation is an excellent example of an expression that can be obtained by thinking scientifically about a mathematically complicated but physically simple problem; that is, it is a good example of ‘model building’.

### (a) Formulation of the equation

The van der Waals equation is

$$p = \frac{nRT}{V - nb} - a \frac{n^2}{V^2} \quad \text{van der Waals equation of state} \quad (1.21a)$$

and a derivation is given in the following *Justification*. The equation is often written in terms of the molar volume  $V_m = V/n$  as

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad (1.21b)$$

The constants  $a$  and  $b$  are called the **van der Waals coefficients**. As can be understood from the following *Justification*,  $a$  represents the strength of attractive interactions and  $b$  that of the repulsive interactions between the molecules. They are characteristic of each gas but independent of the temperature (Table 1.6). Although  $a$  and  $b$  are not precisely defined molecular properties, they correlate with physical properties such as critical temperature, vapor pressure, and enthalpy of vaporization that reflect the strength of intermolecular interactions. Correlations have also been sought where intermolecular forces might play a role. For example, the potencies of certain general anaesthetics show a correlation in the sense that a higher activity is observed with lower values of  $a$  (Fig. 1.17).

#### Justification 1.1 The van der Waals equation of state

The repulsive interactions between molecules are taken into account by supposing that they cause the molecules to behave as small but impenetrable spheres. The non-zero volume of the molecules implies that instead of moving in a volume  $V$  they are restricted to a smaller volume  $V - nb$ , where  $nb$  is approximately the total volume taken up by the molecules themselves. This argument suggests that the perfect gas law  $p = nRT/V$  should be replaced by

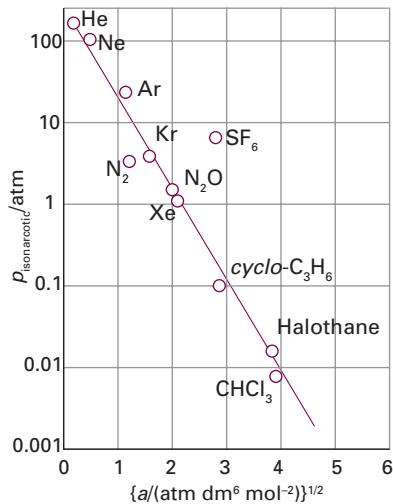
$$p = \frac{nRT}{V - nb}$$

when repulsions are significant. To calculate the excluded volume we note that the closest distance of two hard-sphere molecules of radius  $r$ , and volume  $V_{\text{molecule}} = \frac{4}{3}\pi r^3$ , is  $2r$ , so the volume excluded is  $\frac{4}{3}\pi(2r)^3$ , or  $8V_{\text{molecule}}$ . The volume excluded per molecule is one-half this volume, or  $4V_{\text{molecule}}$ , so  $b \approx 4V_{\text{molecule}}N_A$ .

**Table 1.6\*** van der Waals coefficients

	$a/(\text{atm dm}^6 \text{ mol}^{-2})$	$b/(10^{-2} \text{ dm}^3 \text{ mol}^{-1})$
Ar	1.337	3.20
CO <sub>2</sub>	3.610	4.29
He	0.0341	2.38
Xe	4.137	5.16

\* More values are given in the *Data section*.



**Fig. 1.17** The correlation of the effectiveness of a gas as an anaesthetic and the van der Waals parameter  $a$ . (Based on R.J. Wulf and R.M. Featherstone, *Anesthesiology*, 18, 97 (1957).) The isonarcotic pressure is the pressure required to bring about the same degree of anaesthesia.

The pressure depends on both the frequency of collisions with the walls and the force of each collision. Both the frequency of the collisions and their force are reduced by the attractive interactions, which act with a strength proportional to the molar concentration,  $n/V$ , of molecules in the sample. Therefore, because both the frequency and the force of the collisions are reduced by the attractive interactions, the pressure is reduced in proportion to the square of this concentration. If the reduction of pressure is written as  $-a(n/V)^2$ , where  $a$  is a positive constant characteristic of each gas, the combined effect of the repulsive and attractive forces is the van der Waals equation of state as expressed in eqn 1.21.

In this *Justification* we have built the van der Waals equation using vague arguments about the volumes of molecules and the effects of forces. The equation can be derived in other ways, but the present method has the advantage that it shows how to derive the form of an equation from general ideas. The derivation also has the advantage of keeping imprecise the significance of the coefficients  $a$  and  $b$ : they are much better regarded as empirical parameters that represent attractions and repulsions, respectively, rather than as precisely defined molecular properties.

**Example 1.4** Using the van der Waals equation to estimate a molar volume

Estimate the molar volume of  $\text{CO}_2$  at 500 K and 100 atm by treating it as a van der Waals gas.

**Method** We need to find an expression for the molar volume by solving the van der Waals equation, eqn 1.21b. To do so, we multiply both sides of the equation by  $(V_m - b)V_m^2$ , to obtain

$$(V_m - b)V_m^2 p = RT V_m^2 - (V_m - b)a$$

Then, after division by  $p$ , collect powers of  $V_m$  to obtain

$$V_m^3 - \left( b + \frac{RT}{p} \right) V_m^2 + \left( \frac{a}{p} \right) V_m - \frac{ab}{p} = 0$$

Although closed expressions for the roots of a cubic equation can be given, they are very complicated. Unless analytical solutions are essential, it is usually more expedient to solve such equations with commercial software; graphing calculators can also be used to help identify the acceptable root.

**Answer** According to Table 1.6,  $a = 3.610 \text{ dm}^6 \text{ atm mol}^{-2}$  and  $b = 4.29 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$ . Under the stated conditions,  $RT/p = 0.410 \text{ dm}^3 \text{ mol}^{-1}$ . The coefficients in the equation for  $V_m$  are therefore

$$b + RT/p = 0.453 \text{ dm}^3 \text{ mol}^{-1}$$

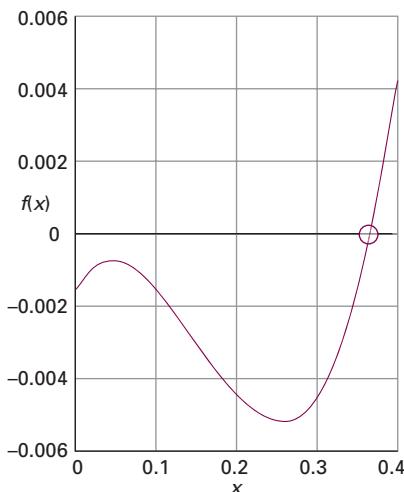
$$a/p = 3.61 \times 10^{-2} (\text{dm}^3 \text{ mol}^{-1})^2$$

$$ab/p = 1.55 \times 10^{-3} (\text{dm}^3 \text{ mol}^{-1})^3$$

Therefore, on writing  $x = V_m/(\text{dm}^3 \text{ mol}^{-1})$ , the equation to solve is

$$x^3 - 0.453x^2 + (3.61 \times 10^{-2})x - (1.55 \times 10^{-3}) = 0$$

The acceptable root is  $x = 0.366$  (Fig. 1.18), which implies that  $V_m = 0.366 \text{ dm}^3 \text{ mol}^{-1}$ . For a perfect gas under these conditions, the molar volume is  $0.410 \text{ dm}^3 \text{ mol}^{-1}$ .



**Fig. 1.18** The graphical solution of the cubic equation for  $V$  in Example 1.4.

**Self-test 1.5** Calculate the molar volume of argon at 100°C and 100 atm on the assumption that it is a van der Waals gas. [0.298  $\text{dm}^3 \text{ mol}^{-1}$ ]

**Table 1.7** Selected equations of state

Equation	Reduced form*	Critical constants		
		$p_c$	$V_c$	$T_c$
Perfect gas	$p = \frac{RT}{V_m}$			
van der Waals	$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$	$p = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2}$	$\frac{a}{27b^2}$	$3b$
Berthelot	$p = \frac{RT}{V_m - b} - \frac{a}{TV_m^2}$	$p = \frac{8T_r}{3V_r - 1} - \frac{3}{T_r V_r^2}$	$\frac{1}{12} \left( \frac{2aR}{3b^3} \right)^{1/2}$	$3b$
Dieterici	$p = \frac{RT e^{-a/RTV_m}}{V_m - b}$	$p = \frac{e^2 T_r e^{-2/T_r V_r}}{2V_r - 1}$	$\frac{a}{4e^2 b^2}$	$2b$
Virial	$p = \frac{RT}{V_m} \left\{ 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \dots \right\}$			$\frac{a}{4bR}$

\* Reduced variables are defined in Section 1.4c.

### (b) The features of the equation

We now examine to what extent the van der Waals equation predicts the behaviour of real gases. It is too optimistic to expect a single, simple expression to be the true equation of state of all substances, and accurate work on gases must resort to the virial equation, use tabulated values of the coefficients at various temperatures, and analyse the systems numerically. The advantage of the van der Waals equation, however, is that it is analytical (that is, expressed symbolically) and allows us to draw some general conclusions about real gases. When the equation fails we must use one of the other equations of state that have been proposed (some are listed in Table 1.7), invent a new one, or go back to the virial equation.

That having been said, we can begin to judge the reliability of the equation by comparing the isotherms it predicts with the experimental isotherms in Fig. 1.15. Some calculated isotherms are shown in Fig. 1.19 and Fig. 1.20. Apart from the oscillations below the critical temperature, they do resemble experimental isotherms quite well. The oscillations, the van der Waals loops, are unrealistic because they suggest that under some conditions an increase of pressure results in an increase of volume. Therefore they are replaced by horizontal lines drawn so the loops define equal areas above and below the lines: this procedure is called the Maxwell construction (3). The van der Waals coefficients, such as those in Table 1.6, are found by fitting the calculated curves to the experimental curves.

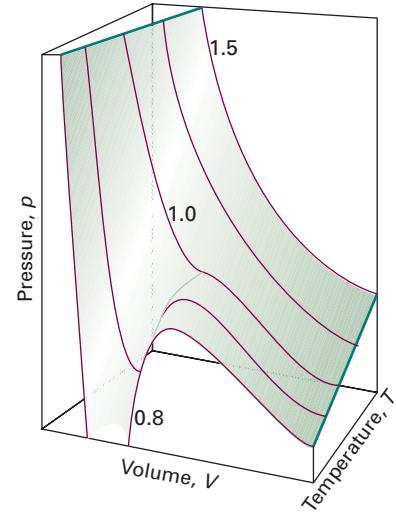
The principal features of the van der Waals equation can be summarized as follows.

- (1) Perfect gas isotherms are obtained at high temperatures and large molar volumes.

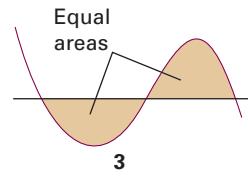
When the temperature is high,  $RT$  may be so large that the first term in eqn 1.21b greatly exceeds the second. Furthermore, if the molar volume is large in the sense  $V_m \gg b$ , then the denominator  $V_m - b \approx V_m$ . Under these conditions, the equation reduces to  $p = RT/V_m$ , the perfect gas equation.

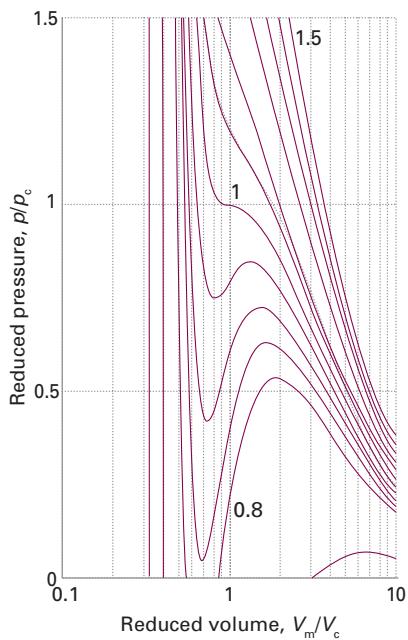
- (2) Liquids and gases coexist when cohesive and dispersing effects are in balance.

The van der Waals loops occur when both terms in eqn 1.21b have similar magnitudes. The first term arises from the kinetic energy of the molecules and their repulsive interactions; the second represents the effect of the attractive interactions.



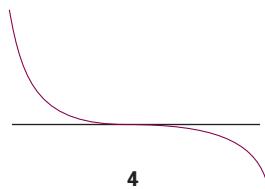
**Fig. 1.19** The surface of possible states allowed by the van der Waals equation. Compare this surface with that shown in Fig. 1.8.





**Fig. 1.20** Van der Waals isotherms at several values of  $T/T_c$ . Compare these curves with those in Fig. 1.15. The van der Waals loops are normally replaced by horizontal straight lines. The critical isotherm is the isotherm for  $T/T_c = 1$ .

 **interActivity** Calculate the molar volume of chlorine gas on the basis of the van der Waals equation of state at 250 K and 150 kPa and calculate the percentage difference from the value predicted by the perfect gas equation.



### (3) The critical constants are related to the van der Waals coefficients.

For  $T < T_c$ , the calculated isotherms oscillate, and each one passes through a minimum followed by a maximum. These extrema converge as  $T \rightarrow T_c$  and coincide at  $T = T_c$ ; at the critical point the curve has a flat inflection (4). From the properties of curves, we know that an inflection of this type occurs when both the first and second derivatives are zero. Hence, we can find the critical constants by calculating these derivatives and setting them equal to zero

$$\frac{dp}{dV_m} = -\frac{RT}{(V_m - b)^2} + \frac{2a}{V_m^3} = 0$$

$$\frac{d^2p}{dV_m^2} = \frac{2RT}{(V_m - b)^3} - \frac{6a}{V_m^4} = 0$$

at the critical point. The solutions of these two equations (and using eqn 1.21b to calculate  $p_c$  from  $V_c$  and  $T_c$ ) are

$$V_c = 3b \quad p_c = \frac{a}{27b^2} \quad T_c = \frac{8a}{27Rb} \quad (1.22)$$

These relations provide an alternative route to the determination of  $a$  and  $b$  from the values of the critical constants. They can be tested by noting that the **critical compression factor**,  $Z_c$ , is predicted to be equal to

$$Z_c = \frac{p_c V_c}{RT_c} = \frac{3}{8} \quad (1.23)$$

for all gases that are described by the van der Waals equation near the critical point. We see from Table 1.5 that, although  $Z_c < \frac{3}{8} = 0.375$ , it is approximately constant (at 0.3) and the discrepancy is reasonably small.

### (c) The principle of corresponding states

An important general technique in science for comparing the properties of objects is to choose a related fundamental property of the same kind and to set up a relative scale on that basis. We have seen that the critical constants are characteristic properties of gases, so it may be that a scale can be set up by using them as yardsticks. We therefore introduce the dimensionless **reduced variables** of a gas by dividing the actual variable by the corresponding critical constant:

$$V_r = \frac{V_m}{V_c} \quad p_r = \frac{p}{p_c} \quad T_r = \frac{T}{T_c}$$

Definition of reduced variables

[1.24]

If the reduced pressure of a gas is given, we can easily calculate its actual pressure by using  $p = p_r p_c$ , and likewise for the volume and temperature. van der Waals, who first tried this procedure, hoped that gases confined to the same reduced volume,  $V_r$ , at the same reduced temperature,  $T_r$ , would exert the same reduced pressure,  $p_r$ . The hope was largely fulfilled (Fig. 1.21). The illustration shows the dependence of the compression factor on the reduced pressure for a variety of gases at various reduced temperatures. The success of the procedure is strikingly clear: compare this graph with Fig. 1.14, where similar data are plotted without using reduced variables. The observation that real gases at the same reduced volume and reduced temperature exert the same reduced pressure is called the **principle of corresponding states**. The principle is only an approximation. It works best for gases composed of spherical molecules; it fails, sometimes badly, when the molecules are non-spherical or polar.

The van der Waals equation sheds some light on the principle. First, we express eqn 1.21b in terms of the reduced variables, which gives

$$p_r p_c = \frac{RT_r T_c}{V_r V_c - b} - \frac{a}{V_r^2 V_c^2}$$

Then we express the critical constants in terms of  $a$  and  $b$  by using eqn 1.22:

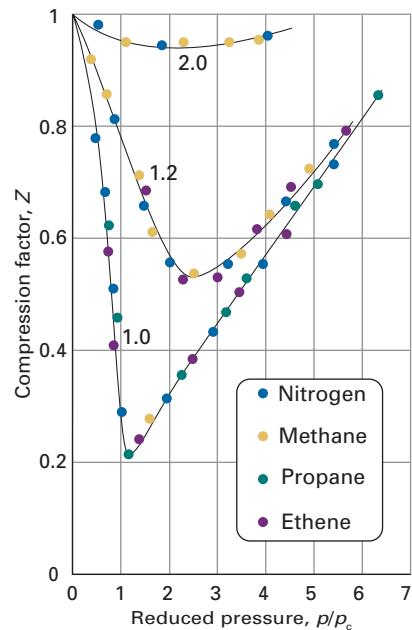
$$\frac{ap_r}{27b^2} = \frac{8aT_r}{27b(3bV_r - b)} - \frac{a}{9b^2 V_r^2}$$

which can be reorganized into

$$p_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2} \quad (1.25)$$

This equation has the same form as the original, but the coefficients  $a$  and  $b$ , which differ from gas to gas, have disappeared. It follows that, if the isotherms are plotted in terms of the reduced variables (as we did in fact in Fig. 1.20 without drawing attention to the fact), then the same curves are obtained whatever the gas. This is precisely the content of the principle of corresponding states, so the van der Waals equation is compatible with it.

Looking for too much significance in this apparent triumph is mistaken, because other equations of state also accommodate the principle (Table 1.7). In fact, all we need are two parameters playing the roles of  $a$  and  $b$ , for then the equation can always be manipulated into reduced form. The observation that real gases obey the principle approximately amounts to saying that the effects of the attractive and repulsive interactions can each be approximated in terms of a single parameter. The importance of the principle is then not so much its theoretical interpretation but the way in which it enables the properties of a range of gases to be coordinated on to a single diagram (for example, Fig. 1.21 instead of Fig. 1.14).



**Fig. 1.21** The compression factors of four gases plotted using reduced variables. The curves are labelled with the reduced temperature  $T_r = T/T_c$ . The use of reduced variables organizes the data on to single curves.

 **interActivity** Is there a set of conditions at which the compression factor of a van der Waals gas passes through a minimum? If so, how do the location and value of the minimum value of  $Z$  depend on the coefficients  $a$  and  $b$ ?

## Checklist of key equations

Property	Equation	Comment
Equation of state	$p = f(n, V, T)$	
Perfect gas law	$pV = nRT$	Valid for real gases in the limit $p \rightarrow 0$
Relation between temperature scales	$T/K = \theta/^\circ\text{C} + 273.15$	273.15 is exact temperature scales
Partial pressure	$p_j = x_j p$	Valid for all gases
Virial equation of state	$pV_m = RT(1 + B/V_m + C/V_m^2 + \dots)$	$B, C$ depend on temperature
van der Waals equation of state	$p = nRT/(V - nb) - a(n/V)^2$	$a$ parametrizes attractions; $b$ parametrizes repulsions

→ For a chart of the relations between principal equations, see the **Road map section** of the Resource section.

## Discussion questions

- 1.1** Explain how the perfect gas equation of state arises by combination of Boyle's law, Charles's law, and Avogadro's principle.
- 1.2** Explain the term 'partial pressure' and explain why Dalton's law is a limiting law.
- 1.3** Explain how the compression factor varies with pressure and temperature and describe how it reveals information about intermolecular interactions in real gases.

## Exercises

**1.1(a)** (a) Could 131 g of xenon gas in a vessel of volume 1.0 dm<sup>3</sup> exert a pressure of 20 atm at 25°C if it behaved as a perfect gas? If not, what pressure would it exert? (b) What pressure would it exert if it behaved as a van der Waals gas?

**1.1(b)** (a) Could 25 g of argon gas in a vessel of volume 1.5 dm<sup>3</sup> exert a pressure of 2.0 bar at 30°C if it behaved as a perfect gas? If not, what pressure would it exert? (b) What pressure would it exert if it behaved as a van der Waals gas?

**1.2(a)** A perfect gas undergoes isothermal compression, which reduces its volume by 2.20 dm<sup>3</sup>. The final pressure and volume of the gas are 5.04 bar and 4.65 dm<sup>3</sup>, respectively. Calculate the original pressure of the gas in (a) bar, (b) atm.

**1.2(b)** A perfect gas undergoes isothermal compression, which reduces its volume by 1.80 dm<sup>3</sup>. The final pressure and volume of the gas are 1.97 bar and 2.14 dm<sup>3</sup>, respectively. Calculate the original pressure of the gas in (a) bar, (b) Torr.

**1.3(a)** A car tyre (i.e. an automobile tire) was inflated to a pressure of 24 lb in<sup>-2</sup> (1.00 atm = 14.7 lb in<sup>-2</sup>) on a winter's day when the temperature was -5°C. What pressure will be found, assuming no leaks have occurred and that the volume is constant, on a subsequent summer's day when the temperature is 35°C? What complications should be taken into account in practice?

**1.3(b)** A sample of hydrogen gas was found to have a pressure of 125 kPa when the temperature was 23°C. What can its pressure be expected to be when the temperature is 11°C?

**1.4(a)** A sample of 255 mg of neon occupies 3.00 dm<sup>3</sup> at 122 K. Use the perfect gas law to calculate the pressure of the gas.

**1.4(b)** A homeowner uses  $4.00 \times 10^3$  m<sup>3</sup> of natural gas in a year to heat a home. Assume that natural gas is all methane, CH<sub>4</sub>, and that methane is a perfect gas for the conditions of this problem, which are 1.00 atm and 20°C. What is the mass of gas used?

**1.5(a)** A diving bell has an air space of 3.0 m<sup>3</sup> when on the deck of a boat. What is the volume of the air space when the bell has been lowered to a depth of 50 m? Take the mean density of sea water to be 1.025 g cm<sup>-3</sup> and assume that the temperature is the same as on the surface.

**1.5(b)** What pressure difference must be generated across the length of a 15 cm vertical drinking straw in order to drink a water-like liquid of density 1.0 g cm<sup>-3</sup>?

**1.6(a)** A manometer consists of a U-shaped tube containing a liquid. One side is connected to the apparatus and the other is open to the atmosphere. The pressure inside the apparatus is then determined from the difference in heights of the liquid. Suppose the liquid is water, the external pressure is 770 Torr, and the open side is 10.0 cm lower than the side connected to the

**1.4** What is the significance of the critical constants?

**1.5** Describe the formulation of the van der Waals equation and suggest a rationale for one other equation of state in Table 1.7.

**1.6** Explain how the van der Waals equation accounts for critical behaviour.

apparatus. What is the pressure in the apparatus? (The density of water at 25°C is 0.997 07 g cm<sup>-3</sup>.)

**1.6(b)** A manometer like that described in Exercise 1.6a contained mercury in place of water. Suppose the external pressure is 760 Torr, and the open side is 10.0 cm higher than the side connected to the apparatus. What is the pressure in the apparatus? (The density of mercury at 25°C is 13.55 g cm<sup>-3</sup>.)

**1.7(a)** In an attempt to determine an accurate value of the gas constant, R, a student heated a container of volume 20.000 dm<sup>3</sup> filled with 0.251 32 g of helium gas to 500°C and measured the pressure as 206.402 cm of water in a manometer at 25°C. Calculate the value of R from these data. (The density of water at 25°C is 0.997 07 g cm<sup>-3</sup>; the construction of a manometer is described in Exercise 1.6a.)

**1.7(b)** The following data have been obtained for oxygen gas at 273.15 K. Calculate the best value of the gas constant R from them and the best value of the molar mass of O<sub>2</sub>.

p/atm	0.750 000	0.500 000	0.250 000
V <sub>m</sub> /(dm <sup>3</sup> mol <sup>-1</sup> )	29.8649	44.8090	89.6384

**1.8(a)** At 500°C and 93.2 kPa, the mass density of sulfur vapour is 3.710 kg m<sup>-3</sup>. What is the molecular formula of sulfur under these conditions?

**1.8(b)** At 100°C and 16.0 kPa, the mass density of phosphorus vapour is 0.6388 kg m<sup>-3</sup>. What is the molecular formula of phosphorus under these conditions?

**1.9(a)** Calculate the mass of water vapour present in a room of volume 400 m<sup>3</sup> that contains air at 27°C on a day when the relative humidity is 60 per cent.

**1.9(b)** Calculate the mass of water vapour present in a room of volume 250 m<sup>3</sup> that contains air at 23°C on a day when the relative humidity is 53 per cent.

**1.10(a)** Given that the density of air at 0.987 bar and 27°C is 1.146 kg m<sup>-3</sup>, calculate the mole fraction and partial pressure of nitrogen and oxygen assuming that (a) air consists only of these two gases, (b) air also contains 1.0 mole per cent Ar.

**1.10(b)** A gas mixture consists of 320 mg of methane, 175 mg of argon, and 225 mg of neon. The partial pressure of neon at 300 K is 8.87 kPa. Calculate (a) the volume and (b) the total pressure of the mixture.

**1.11(a)** The density of a gaseous compound was found to be 1.23 kg m<sup>-3</sup> at 330 K and 20 kPa. What is the molar mass of the compound?

**1.11(b)** In an experiment to measure the molar mass of a gas, 250 cm<sup>3</sup> of the gas was confined in a glass vessel. The pressure was 152 Torr at 298 K and, after correcting for buoyancy effects, the mass of the gas was 33.5 mg. What is the molar mass of the gas?

**1.12(a)** The densities of air at  $-85^\circ\text{C}$ ,  $0^\circ\text{C}$ , and  $100^\circ\text{C}$  are  $1.877 \text{ g dm}^{-3}$ ,  $1.294 \text{ g dm}^{-3}$ , and  $0.946 \text{ g dm}^{-3}$ , respectively. From these data, and assuming that air obeys Charles's law, determine a value for the absolute zero of temperature in degrees Celsius.

**1.12(b)** A certain sample of a gas has a volume of  $20.00 \text{ dm}^3$  at  $0^\circ\text{C}$  and  $1.000 \text{ atm}$ . A plot of the experimental data of its volume against the Celsius temperature,  $\theta$ , at constant  $p$ , gives a straight line of slope  $0.0741 \text{ dm}^3 (\text{ }^\circ\text{C})^{-1}$ . From these data alone (without making use of the perfect gas law), determine the absolute zero of temperature in degrees Celsius.

**1.13(a)** Calculate the pressure exerted by  $1.0 \text{ mol C}_2\text{H}_6$  behaving as (a) a perfect gas, (b) a van der Waals gas when it is confined under the following conditions: (i) at  $273.15 \text{ K}$  in  $22.414 \text{ dm}^3$ , (ii) at  $1000 \text{ K}$  in  $100 \text{ cm}^3$ . Use the data in Table 1.6.

**1.13(b)** Calculate the pressure exerted by  $1.0 \text{ mol H}_2\text{S}$  behaving as (a) a perfect gas, (b) a van der Waals gas when it is confined under the following conditions: (i) at  $273.15 \text{ K}$  in  $22.414 \text{ dm}^3$ , (ii) at  $500 \text{ K}$  in  $150 \text{ cm}^3$ . Use the data in Table 1.6.

**1.14(a)** Express the van der Waals parameters  $a = 0.751 \text{ atm dm}^6 \text{ mol}^{-2}$  and  $b = 0.0226 \text{ dm}^3 \text{ mol}^{-1}$  in SI base units.

**1.14(b)** Express the van der Waals parameters  $a = 1.32 \text{ atm dm}^6 \text{ mol}^{-2}$  and  $b = 0.0436 \text{ dm}^3 \text{ mol}^{-1}$  in SI base units.

**1.15(a)** A gas at  $250 \text{ K}$  and  $15 \text{ atm}$  has a molar volume 12 per cent smaller than that calculated from the perfect gas law. Calculate (a) the compression factor under these conditions and (b) the molar volume of the gas. Which are dominating in the sample, the attractive or the repulsive forces?

**1.15(b)** A gas at  $350 \text{ K}$  and  $12 \text{ atm}$  has a molar volume 12 per cent larger than that calculated from the perfect gas law. Calculate (a) the compression factor under these conditions and (b) the molar volume of the gas. Which are dominating in the sample, the attractive or the repulsive forces?

**1.16(a)** In an industrial process, nitrogen is heated to  $500 \text{ K}$  at a constant volume of  $1.000 \text{ m}^3$ . The gas enters the container at  $300 \text{ K}$  and  $100 \text{ atm}$ . The mass of the gas is  $92.4 \text{ kg}$ . Use the van der Waals equation to determine the approximate pressure of the gas at its working temperature of  $500 \text{ K}$ . For nitrogen,  $a = 1.352 \text{ dm}^6 \text{ atm mol}^{-2}$ ,  $b = 0.0387 \text{ dm}^3 \text{ mol}^{-1}$ .

**1.16(b)** Cylinders of compressed gas are typically filled to a pressure of  $200 \text{ bar}$ . For oxygen, what would be the molar volume at this pressure and  $25^\circ\text{C}$  based on (a) the perfect gas equation, (b) the van der Waals equation. For oxygen,  $a = 1.364 \text{ dm}^6 \text{ atm mol}^{-2}$ ,  $b = 3.19 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$ .

**1.17(a)** Suppose that  $10.0 \text{ mol C}_2\text{H}_6(\text{g})$  is confined to  $4.860 \text{ dm}^3$  at  $27^\circ\text{C}$ . Predict the pressure exerted by the ethane from (a) the perfect gas and (b) the van der Waals equations of state. Calculate the compression factor based on these calculations. For ethane,  $a = 5.507 \text{ dm}^6 \text{ atm mol}^{-2}$ ,  $b = 0.0651 \text{ dm}^3 \text{ mol}^{-1}$ .

**1.17(b)** At  $300 \text{ K}$  and  $20 \text{ atm}$ , the compression factor of a gas is  $0.86$ . Calculate (a) the volume occupied by  $8.2 \text{ mmol}$  of the gas under these conditions and (b) an approximate value of the second virial coefficient  $B$  at  $300 \text{ K}$ .

**1.18(a)** A vessel of volume  $22.4 \text{ dm}^3$  contains  $2.0 \text{ mol H}_2$  and  $1.0 \text{ mol N}_2$  at  $273.15 \text{ K}$ . Calculate (a) the mole fractions of each component, (b) their partial pressures, and (c) their total pressure.

**1.18(b)** A vessel of volume  $22.4 \text{ dm}^3$  contains  $1.5 \text{ mol H}_2$  and  $2.5 \text{ mol N}_2$  at  $273.15 \text{ K}$ . Calculate (a) the mole fractions of each component, (b) their partial pressures, and (c) their total pressure.

**1.19(a)** The critical constants of methane are  $p_c = 45.6 \text{ atm}$ ,  $V_c = 98.7 \text{ cm}^3 \text{ mol}^{-1}$ , and  $T_c = 190.6 \text{ K}$ . Calculate the van der Waals parameters of the gas and estimate the radius of the molecules.

**1.19(b)** The critical constants of ethane are  $p_c = 48.20 \text{ atm}$ ,  $V_c = 148 \text{ cm}^3 \text{ mol}^{-1}$ , and  $T_c = 305.4 \text{ K}$ . Calculate the van der Waals parameters of the gas and estimate the radius of the molecules.

**1.20(a)** Use the van der Waals parameters for chlorine to calculate approximate values of (a) the Boyle temperature of chlorine and (b) the radius of a  $\text{Cl}_2$  molecule regarded as a sphere.

**1.20(b)** Use the van der Waals parameters for hydrogen sulfide (Table 1.6 in the *Data section*) to calculate approximate values of (a) the Boyle temperature of the gas and (b) the radius of a  $\text{H}_2\text{S}$  molecule regarded as a sphere.

**1.21(a)** Suggest the pressure and temperature at which  $1.0 \text{ mol}$  of (a)  $\text{NH}_3$ , (b)  $\text{Xe}$ , (c)  $\text{He}$  will be in states that correspond to  $1.0 \text{ mol H}_2$  at  $1.0 \text{ atm}$  and  $25^\circ\text{C}$ .

**1.21(b)** Suggest the pressure and temperature at which  $1.0 \text{ mol}$  of (a)  $\text{H}_2\text{S}$ , (b)  $\text{CO}_2$ , (c)  $\text{Ar}$  will be in states that correspond to  $1.0 \text{ mol N}_2$  at  $1.0 \text{ atm}$  and  $25^\circ\text{C}$ .

**1.22(a)** A certain gas obeys the van der Waals equation with  $a = 0.50 \text{ m}^6 \text{ Pa mol}^{-2}$ . Its volume is found to be  $5.00 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}$  at  $273 \text{ K}$  and  $3.0 \text{ MPa}$ . From this information calculate the van der Waals constant  $b$ . What is the compression factor for this gas at the prevailing temperature and pressure?

**1.22(b)** A certain gas obeys the van der Waals equation with  $a = 0.76 \text{ m}^6 \text{ Pa mol}^{-2}$ . Its volume is found to be  $4.00 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}$  at  $288 \text{ K}$  and  $4.0 \text{ MPa}$ . From this information calculate the van der Waals constant  $b$ . What is the compression factor for this gas at the prevailing temperature and pressure?

## Problems\*

### Numerical problems

**1.1** Recent communication with the inhabitants of Neptune has revealed that they have a Celsius-type temperature scale, but based on the melting point ( $0^\circ\text{N}$ ) and boiling point ( $100^\circ\text{N}$ ) of their most common substance, hydrogen. Further communications have revealed that the Neptunians know about perfect gas behaviour and they find that, in the limit of zero pressure, the value of  $pV$  is  $28 \text{ dm}^3 \text{ atm}$  at  $0^\circ\text{N}$  and  $40 \text{ dm}^3 \text{ atm}$  at  $100^\circ\text{N}$ . What is the value of the absolute zero of temperature on their temperature scale?

**1.2** Deduce the relation between the pressure and mass density,  $\rho$ , of a perfect gas of molar mass  $M$ . Confirm graphically, using the following data on

dimethyl ether at  $25^\circ\text{C}$ , that perfect behaviour is reached at low pressures and find the molar mass of the gas.

$p/\text{kPa}$	12.223	25.20	36.97	60.37	85.23	101.3
$\rho/(\text{kg m}^{-3})$	0.225	0.456	0.664	1.062	1.468	1.734

**1.3** Charles's law is sometimes expressed in the form  $V = V_0(1 + \alpha\theta)$ , where  $\theta$  is the Celsius temperature,  $\alpha$  is a constant, and  $V_0$  is the volume of the sample at  $0^\circ\text{C}$ . The following values for  $\alpha$  have been reported for nitrogen at  $0^\circ\text{C}$ :

$p/\text{Torr}$	749.7	599.6	333.1	98.6
$10^3\alpha/(\text{ }^\circ\text{C})^{-1}$	3.6717	3.6697	3.6665	3.6643

\* Problems denoted with the symbol \* were supplied by Charles Trapp, Carmen Giunta, and Marshall Cady.

For these data calculate the best value for the absolute zero of temperature on the Celsius scale.

**1.4** The molar mass of a newly synthesized fluorocarbon was measured in a gas microbalance. This device consists of a glass bulb forming one end of a beam, the whole surrounded by a closed container. The beam is pivoted, and the balance point is attained by raising the pressure of gas in the container, so increasing the buoyancy of the enclosed bulb. In one experiment, the balance point was reached when the fluorocarbon pressure was 327.10 Torr; for the same setting of the pivot, a balance was reached when  $\text{CHF}_3$  ( $M = 70.014 \text{ g mol}^{-1}$ ) was introduced at 423.22 Torr. A repeat of the experiment with a different setting of the pivot required a pressure of 293.22 Torr of the fluorocarbon and 427.22 Torr of the  $\text{CHF}_3$ . What is the molar mass of the fluorocarbon? Suggest a molecular formula.

**1.5** A constant-volume perfect gas thermometer indicates a pressure of 6.69 kPa at the triple point temperature of water (273.16 K). (a) What change of pressure indicates a change of 1.00 K at this temperature? (b) What pressure indicates a temperature of 100.00°C? (c) What change of pressure indicates a change of 1.00 K at the latter temperature?

**1.6** A vessel of volume 22.4 dm<sup>3</sup> contains 2.0 mol H<sub>2</sub> and 1.0 mol N<sub>2</sub> at 273.15 K initially. All the H<sub>2</sub> reacted with sufficient N<sub>2</sub> to form NH<sub>3</sub>. Calculate the partial pressures and the total pressure of the final mixture.

**1.7** Calculate the molar volume of chlorine gas at 350 K and 2.30 atm using (a) the perfect gas law and (b) the van der Waals equation. Use the answer to (a) to calculate a first approximation to the correction term for attraction and then use successive approximations to obtain a numerical answer for part (b).

**1.8** At 273 K measurements on argon gave  $B = -21.7 \text{ cm}^3 \text{ mol}^{-1}$  and  $C = 1200 \text{ cm}^6 \text{ mol}^{-2}$ , where  $B$  and  $C$  are the second and third virial coefficients in the expansion of  $Z$  in powers of  $1/V_m$ . Assuming that the perfect gas law holds sufficiently well for the estimation of the second and third terms of the expansion, calculate the compression factor of argon at 100 atm and 273 K. From your result, estimate the molar volume of argon under these conditions.

**1.9** Calculate the volume occupied by 1.00 mol N<sub>2</sub> using the van der Waals equation in the form of a virial expansion at (a) its critical temperature, (b) its Boyle temperature, and (c) its inversion temperature. Assume that the pressure is 10 atm throughout. At what temperature is the gas most perfect? Use the following data:  $T_c = 126.3 \text{ K}$ ,  $a = 1.390 \text{ dm}^6 \text{ atm mol}^{-2}$ ,  $b = 0.0391 \text{ dm}^3 \text{ mol}^{-1}$ .

**1.10‡** The second virial coefficient of methane can be approximated by the empirical equation  $B'(T) = a + b e^{-c/T^2}$ , where  $a = -0.1993 \text{ bar}^{-1}$ ,  $b = 0.2002 \text{ bar}^{-1}$ , and  $c = 1131 \text{ K}^2$  with  $300 \text{ K} < T < 600 \text{ K}$ . What is the Boyle temperature of methane?

**1.11** The mass density of water vapour at 327.6 atm and 776.4 K is 133.2 kg m<sup>-3</sup>. Given that for water  $T_c = 647.4 \text{ K}$ ,  $p_c = 218.3 \text{ atm}$ ,  $a = 5.464 \text{ dm}^6 \text{ atm mol}^{-2}$ ,  $b = 0.03049 \text{ dm}^3 \text{ mol}^{-1}$ , and  $M = 18.02 \text{ g mol}^{-1}$ , calculate (a) the molar volume. Then calculate the compression factor (b) from the data, (c) from the virial expansion of the van der Waals equation.

**1.12** The critical volume and critical pressure of a certain gas are 160 cm<sup>3</sup> mol<sup>-1</sup> and 40 atm, respectively. Estimate the critical temperature by assuming that the gas obeys the Berthelot equation of state. Estimate the radii of the gas molecules on the assumption that they are spheres.

**1.13** Estimate the coefficients  $a$  and  $b$  in the Dieterici equation of state from the critical constants of xenon. Calculate the pressure exerted by 1.0 mol Xe when it is confined to 1.0 dm<sup>3</sup> at 25°C.

### Theoretical problems

**1.14** Show that the van der Waals equation leads to values of  $Z < 1$  and  $Z > 1$ , and identify the conditions for which these values are obtained.

**1.15** Express the van der Waals equation of state as a virial expansion in powers of  $1/V_m$  and obtain expressions for  $B$  and  $C$  in terms of the parameters  $a$  and  $b$ . The expansion you will need is  $(1-x)^{-1} = 1+x+x^2+\dots$ . Measurements on argon gave  $B = -21.7 \text{ cm}^3 \text{ mol}^{-1}$  and  $C = 1200 \text{ cm}^6 \text{ mol}^{-2}$  for the virial coefficients at 273 K. What are the values of  $a$  and  $b$  in the corresponding van der Waals equation of state?

**1.16‡** Derive the relation between the critical constants and the Dieterici equation parameters. Show that  $Z_c = 2e^{-2}$  and derive the reduced form of the Dieterici equation of state. Compare the van der Waals and Dieterici predictions of the critical compression factor. Which is closer to typical experimental values?

**1.17** A scientist proposed the following equation of state:

$$p = \frac{RT}{V_m} - \frac{B}{V_m^2} + \frac{C}{V_m^3}$$

Show that the equation leads to critical behaviour. Find the critical constants of the gas in terms of  $B$  and  $C$  and an expression for the critical compression factor.

**1.18** Equations 1.19a and 1.19b are expansions in  $p$  and  $1/V_m$ , respectively. Find the relation between  $B$ ,  $C$  and  $B'$ ,  $C'$ .

**1.19** The second virial coefficient  $B'$  can be obtained from measurements of the density  $\rho$  of a gas at a series of pressures. Show that the graph of  $p/\rho$  against  $p$  should be a straight line with slope proportional to  $B'$ . Use the data on dimethyl ether in Problem 1.2 to find the values of  $B'$  and  $B$  at 25°C.

**1.20** The equation of state of a certain gas is given by  $p = RT/V_m + (a+bT)/V_m^2$ , where  $a$  and  $b$  are constants. Find  $(\partial V/\partial T)_p$ .

**1.21** The following equations of state are occasionally used for approximate calculations on gases: (gas A)  $pV_m = RT(1+b/V_m)$ , (gas B)  $p(V_m - b) = RT$ . Assuming that there were gases that actually obeyed these equations of state, would it be possible to liquefy either gas A or B? Would they have a critical temperature? Explain your answer.

**1.22** Derive an expression for the compression factor of a gas that obeys the equation of state  $p(V-nb) = nRT$ , where  $b$  and  $R$  are constants. If the pressure and temperature are such that  $V_m = 10b$ , what is the numerical value of the compression factor?

**1.23‡** The discovery of the element argon by Lord Rayleigh and Sir William Ramsay had its origins in Rayleigh's measurements of the density of nitrogen with an eye toward accurate determination of its molar mass. Rayleigh prepared some samples of nitrogen by chemical reaction of nitrogen-containing compounds; under his standard conditions, a glass globe filled with this 'chemical nitrogen' had a mass of 2.2990 g. He prepared other samples by removing oxygen, carbon dioxide, and water vapour from atmospheric air; under the same conditions, this 'atmospheric nitrogen' had a mass of 2.3102 g (Lord Rayleigh, *Royal Institution Proceedings* 14, 524 (1895)). With the hindsight of knowing accurate values for the molar masses of nitrogen and argon, compute the mole fraction of argon in the latter sample on the assumption that the former was pure nitrogen and the latter a mixture of nitrogen and argon.

**1.24‡** A substance as elementary and well known as argon still receives research attention. Stewart and Jacobsen have published a review of thermodynamic properties of argon (R.B. Stewart and R.T. Jacobsen, *J. Phys. Chem. Ref. Data* 18, 639 (1989)) which included the following 300 K isotherm.

$p/\text{MPa}$	0.4000	0.5000	0.6000	0.8000	1.000
$V_m/(\text{dm}^3 \text{ mol}^{-1})$	6.2208	4.9736	4.1423	3.1031	2.4795
$p/\text{MPa}$	1.500	2.000	2.500	3.000	4.000
$V_m/(\text{dm}^3 \text{ mol}^{-1})$	1.6483	1.2328	0.98357	0.81746	0.60998

(a) Compute the second virial coefficient,  $B$ , at this temperature. (b) Use nonlinear curve-fitting software to compute the third virial coefficient,  $C$ , at this temperature.

### Applications: to atmospheric science

**1.25** Atmospheric pollution is a problem that has received much attention. Not all pollution, however, is from industrial sources. Volcanic eruptions can be a significant source of air pollution. The Kilauea volcano in Hawaii emits 200–300 t of  $\text{SO}_2$  per day. If this gas is emitted at 800°C and 1.0 atm, what volume of gas is emitted?

**1.26** Ozone is a trace atmospheric gas that plays an important role in screening the Earth from harmful ultraviolet radiation. The abundance of ozone is commonly reported in *Dobson units*. One Dobson unit is the thickness, in thousandths of a centimetre, of a column of gas if it were collected as a pure gas at 1.00 atm and 0°C. What amount of  $\text{O}_3$  (in moles) is found in a column of atmosphere with a cross-sectional area of 1.00  $\text{dm}^2$  if the abundance is 250 Dobson units (a typical mid-latitude value)? In the seasonal Antarctic ozone hole, the column abundance drops below 100 Dobson units; how many moles of ozone are found in such a column of air above a 1.00  $\text{dm}^2$  area? Most atmospheric ozone is found between 10 and 50 km above the surface of the Earth. If that ozone is spread uniformly through this portion of the atmosphere, what is the average molar concentration corresponding to (a) 250 Dobson units, (b) 100 Dobson units?

**1.27** The barometric formula relates the pressure of a gas of molar mass  $M$  at an altitude  $h$  to its pressure  $p_0$  at sea level. Derive this relation by showing that the change in pressure  $dp$  for an infinitesimal change in altitude  $dh$  where the density is  $\rho$  is  $dp = -\rho g dh$ . Remember that  $\rho$  depends on the pressure. Evaluate (a) the pressure difference between the top and bottom of a

laboratory vessel of height 15 cm, and (b) the external atmospheric pressure at a typical cruising altitude of an aircraft (11 km) when the pressure at ground level is 1.0 atm.

**1.28** Balloons are still used to deploy sensors that monitor meteorological phenomena and the chemistry of the atmosphere. It is possible to investigate some of the technicalities of ballooning by using the perfect gas law. Suppose your balloon has a radius of 3.0 m and that it is spherical. (a) What amount of  $\text{H}_2$  (in moles) is needed to inflate it to 1.0 atm in an ambient temperature of 25°C at sea level? (b) What mass can the balloon lift at sea level, where the density of air is 1.22  $\text{kg m}^{-3}$ ? (c) What would be the payload if He were used instead of  $\text{H}_2$ ?

**1.29†** The preceding problem is most readily solved (see the *Solutions manual*) with the use of Archimedes' principle, which states that the lifting force is equal to the difference between the weight of the displaced air and the weight of the balloon. Prove Archimedes' principle for the atmosphere from the barometric formula. *Hint.* Assume a simple shape for the balloon, perhaps a right circular cylinder of cross-sectional area  $A$  and height  $h$ .

**1.30‡** Chlorofluorocarbons such as  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$  have been linked to ozone depletion in Antarctica. As of 1994, these gases were found in quantities of 261 and 509 parts per trillion ( $10^{12}$ ) by volume (World Resources Institute, *World resources 1996–97*). Compute the molar concentration of these gases under conditions typical of (a) the mid-latitude troposphere (10°C and 1.0 atm) and (b) the Antarctic stratosphere (200 K and 0.050 atm).

**1.31‡** The composition of the atmosphere is approximately 80 per cent nitrogen and 20 per cent oxygen by mass. At what height above the surface of the Earth would the atmosphere become 90 per cent nitrogen and 10 per cent oxygen by mass? Assume that the temperature of the atmosphere is constant at 25°C. What is the pressure of the atmosphere at that height?

**MATHEMATICAL BACKGROUND 1****Differentiation and integration**

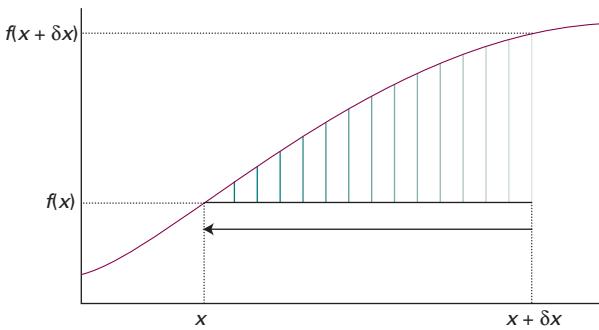
Rates of change of functions—slopes of their graphs—are best discussed in terms of infinitesimal calculus. The slope of a function, like the slope of a hill, is obtained by dividing the rise of the hill by the horizontal distance (Fig. MB1.1). However, because the slope may vary from point to point, we should make the horizontal distance between the points as small as possible. In fact, we let it become infinitesimally small—hence the name *infinitesimal* calculus. The values of a function  $f$  at two locations  $x$  and  $x + \delta x$  are  $f(x)$  and  $f(x + \delta x)$ , respectively. Therefore, the slope of the function  $f$  at  $x$  is the vertical distance, which we write  $\delta f$ , divided by the horizontal distance, which we write  $\delta x$ :

$$\text{Slope} = \frac{\text{rise in value}}{\text{horizontal distance}} = \frac{\delta f}{\delta x} = \frac{f(x + \delta x) - f(x)}{\delta x} \quad (\text{MB1.1})$$

The slope at  $x$  itself is obtained by letting the horizontal distance become zero, which we write  $\lim \delta x \rightarrow 0$ . In this limit, the  $\delta$  is replaced by a  $d$ , and we write

$$\text{Slope at } x = \frac{df}{dx} = \lim_{\delta x \rightarrow 0} \left( \frac{f(x + \delta x) - f(x)}{\delta x} \right) \quad (\text{MB1.2})$$

To work out the slope of any function, we work out the expression on the right: this process is called **differentiation** and the expression for  $df/dx$  is the **derivative** of the function  $f$  with respect to the variable  $x$ . Some important derivatives are given inside the front cover of the text. Most of the functions encountered in chemistry can be differentiated by using the following rules (noting that in these expressions, derivatives  $df/dx$  are written as  $df$ ).



**Fig. MB1.1** The slope of  $f(x)$  at  $x$ ,  $df/dx$ , is obtained by making a series of approximations to the value of  $f(x + \delta x) - f(x)$  divided by the change in  $x$ , denoted  $\delta x$ , and allowing  $\delta x$  to approach 0 (as indicated by the vertical lines getting closer to  $x$ ).

**Rule 1** For two functions  $f$  and  $g$ :

$$d(f+g) = df + dg \quad [\text{MB1.3}]$$

**Rule 2** (the product rule) For two functions  $f$  and  $g$ :

$$d(fg) = f dg + g df \quad [\text{MB1.4}]$$

**Rule 3** (the quotient rule) For two functions  $f$  and  $g$ :

$$d\frac{f}{g} = \frac{1}{g} df - \frac{f}{g^2} dg \quad [\text{MB1.5}]$$

**Rule no. 4** (the chain rule) For a function  $f = f(g)$ , where  $g = g(t)$ :

$$\frac{df}{dt} = \frac{df}{dg} \frac{dg}{dt} \quad [\text{MB1.6}]$$

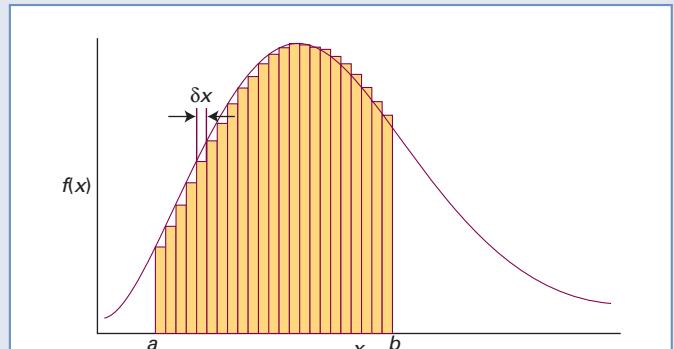
The area under a graph of any function  $f$  is found by the techniques of **integration**. For instance, the area under the graph of the function  $f$  drawn in Fig. MB1.2 can be written as the value of  $f$  evaluated at a point multiplied by the width of the region,  $\delta x$ , and then all those products  $f(x)\delta x$  summed over all the regions:

$$\text{Area between } a \text{ and } b = \sum f(x)\delta x$$

When we allow  $\delta x$  to become infinitesimally small, written  $dx$ , and sum an infinite number of strips, we write

$$\text{Area between } a \text{ and } b = \int_a^b f(x) dx \quad [\text{MB1.7}]$$

The elongated  $S$  symbol on the right is called the **integral** of the function  $f$ . When written as  $\int$  alone, it is the **indefinite integral** of the function. When written with limits (as in eqn MB1.7), it is the **definite integral** of the function. The definite integral is the indefinite integral evaluated at the upper limit ( $b$ ) minus the indefinite integral evaluated at the lower limit ( $a$ ). The **average value** (or *mean value*) of a function  $f(x)$  in the range  $x = a$  to  $x = b$  is



**Fig. MB1.2** The shaded area is equal to the definite integral of  $f(x)$  between the limits  $a$  and  $b$ .

$$\text{Average value of } f(x) \text{ from } a \text{ to } b = \frac{1}{b-a} \int_a^b f(x) dx \quad [\text{MB1.8}]$$

The **mean value theorem** states that a continuous function has its mean value at least once in the range.

Integration is the inverse of differentiation. That is, if we integrate a function and then differentiate the result, we get back the original function. Some important integrals are given inside the front cover of the text. Many other standard forms are found in tables and it is also possible to calculate definite and indefinite integrals with mathematical software. Two integration techniques are useful.

*Technique 1* (integration by parts) For two functions  $f$  and  $g$ :

$$\int f \frac{dg}{dx} dx = fg - \int g \frac{df}{dx} dx \quad [\text{MB1.9}]$$

*Technique 2* (method of partial fractions) To solve an integral of the form

$$\int \frac{1}{(a-x)(b-x)} dx$$

where  $a$  and  $b$  are constants, we write

$$\frac{1}{(a-x)(b-x)} = \frac{1}{b-a} \left( \frac{1}{a-x} - \frac{1}{b-x} \right)$$

and integrate the expression on the right. It follows that

$$\begin{aligned} \int \frac{dx}{(a-x)(b-x)} &= \frac{1}{b-a} \left[ \int \frac{dx}{a-x} - \int \frac{dx}{b-x} \right] \\ &= \frac{1}{b-a} \left( \ln \frac{1}{a-x} - \ln \frac{1}{b-x} \right) + \text{constant} \end{aligned} \quad [\text{MB1.10}]$$



# 2

# The First Law

## The basic concepts

**2.1** Work, heat, and energy

**2.2** The internal energy

**2.3** Expansion work

**2.4** Heat transactions

**2.5** Enthalpy

**I2.1** Impact on biochemistry and materials science: Differential scanning calorimetry

**2.6** Adiabatic changes

## Thermochemistry

**2.7** Standard enthalpy changes

**I2.2** Impact on biology: Food and energy reserves

**2.8** Standard enthalpies of formation

**2.9** The temperature dependence of reaction enthalpies

## State functions and exact differentials

**2.10** Exact and inexact differentials

**2.11** Changes in internal energy

**2.12** The Joule–Thomson effect

Checklist of key equations

Further information 2.1: Adiabatic processes

Further information 2.2: The relation between heat capacities

Discussion questions

Exercises

Problems

This chapter introduces some of the basic concepts of thermodynamics. It concentrates on the conservation of energy—the experimental observation that energy can be neither created nor destroyed—and shows how the principle of the conservation of energy can be used to assess the energy changes that accompany physical and chemical processes. Much of this chapter examines the means by which a system can exchange energy with its surroundings in terms of the work it may do or have done on it or the heat that it may produce or absorb. The target concept of the chapter is enthalpy, which is a very useful bookkeeping property for keeping track of the heat output (or requirements) of physical processes and chemical reactions at constant pressure. We also begin to unfold some of the power of thermodynamics by showing how to establish relations between different properties of a system. We shall see that one very useful aspect of thermodynamics is that a property can be measured indirectly by measuring others and then combining their values. The relations we derive also enable us to discuss the liquefaction of gases and to establish the relation between the heat capacities of a substance under different conditions.

The release of energy can be used to provide heat when a fuel burns in a furnace, to produce mechanical work when a fuel burns in an engine, and to generate electrical work when a chemical reaction pumps electrons through a circuit. In chemistry, we encounter reactions that can be harnessed to provide heat and work, reactions that liberate energy that is released unused but which give products we require, and reactions that constitute the processes of life. **Thermodynamics**, the study of the transformations of energy, enables us to discuss all these matters quantitatively and to make useful predictions.

## The basic concepts

For the purposes of thermodynamics, the universe is divided into two parts, the system and its surroundings. The **system** is the part of the world in which we have a special interest. It may be a reaction vessel, an engine, an electrochemical cell, a biological cell, and so on. The **surroundings** comprise the region outside the system and are where we make our measurements. The type of system depends on the characteristics of the boundary that divides it from the surroundings (Fig. 2.1). If matter can be transferred through the boundary between the system and its surroundings the system is classified as **open**. If matter cannot pass through the boundary the system is classified as **closed**. Both open and closed systems can exchange energy with their surroundings. For example, a closed system can expand and thereby raise a weight in the surroundings; a closed system may also transfer energy to the surroundings if they are

at a lower temperature. An **isolated system** is a closed system that has neither mechanical nor thermal contact with its surroundings.

## 2.1 Work, heat, and energy

**Key points** (a) Work is done to achieve motion against an opposing force; energy is the capacity to do work. (b) Heating is the transfer of energy that makes use of disorderly molecular motion; work is the transfer of energy that makes use of organized motion.

Although thermodynamics deals with observations on bulk systems, it is immeasurably enriched by understanding the molecular origins of these observations. In each case we shall set out the bulk observations on which thermodynamics is based and then describe their molecular interpretations.

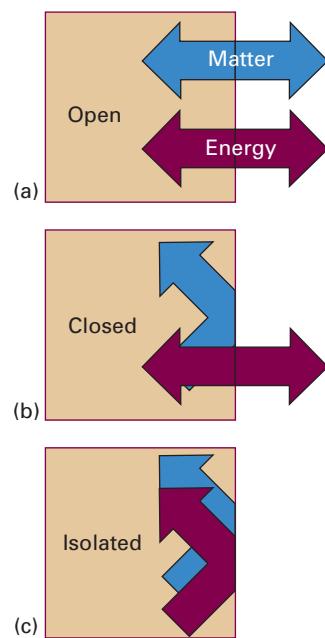
### (a) Operational definitions

The fundamental physical property in thermodynamics is work: **work** is done to achieve motion against an opposing force. A simple example is the process of raising a weight against the pull of gravity. A process does work if, in principle, it can be harnessed to raise a weight somewhere in the surroundings. An example of doing work is the expansion of a gas that pushes out a piston: the motion of the piston can in principle be used to raise a weight. A chemical reaction that drives an electric current through a resistance also does work, because the same current could be passed through a motor and used to raise a weight.

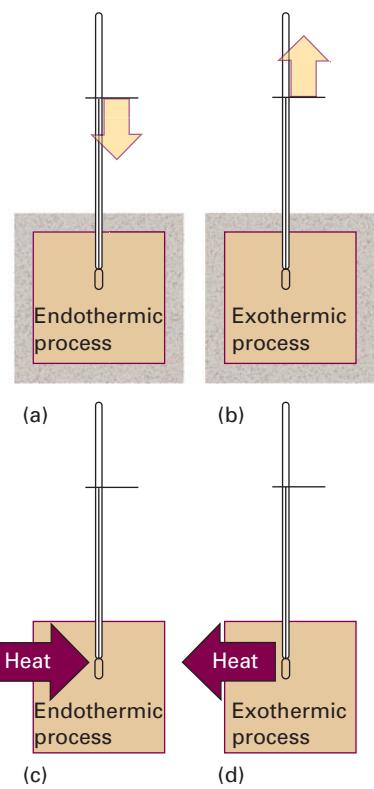
The **energy** of a system is its capacity to do work. When work is done on an otherwise isolated system (for instance, by compressing a gas or winding a spring), the capacity of the system to do work is increased; in other words, the energy of the system is increased. When the system does work (when the piston moves out or the spring unwinds), the energy of the system is reduced and it can do less work than before.

Experiments have shown that the energy of a system may be changed by means other than work itself. When the energy of a system changes as a result of a temperature difference between the system and its surroundings we say that energy has been transferred as **heat**. When a heater is immersed in a beaker of water (the system), the capacity of the system to do work increases because hot water can be used to do more work than the same amount of cold water. Not all boundaries permit the transfer of energy even though there is a temperature difference between the system and its surroundings. Boundaries that do permit the transfer of energy as heat are called **diathermic**; those that do not are called **adiabatic**.

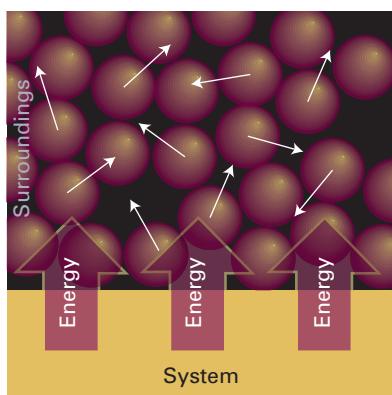
An **exothermic process** is a process that releases energy as heat into its surroundings. All combustion reactions are exothermic. An **endothermic process** is a process in which energy is acquired from its surroundings as heat. An example of an endothermic process is the vaporization of water. To avoid a lot of awkward language, we say that in an exothermic process energy is transferred ‘as heat’ to the surroundings and in an endothermic process energy is transferred ‘as heat’ from the surroundings into the system. However, it must never be forgotten that heat is a process (the transfer of energy as a result of a temperature difference), not an entity. An endothermic process in a diathermic container results in energy flowing into the system as heat to restore the temperature to that of the surroundings. An exothermic process in a similar diathermic container results in a release of energy as heat into the surroundings. When an endothermic process takes place in an adiabatic container, it results in a lowering of temperature of the system; an exothermic process results in a rise of temperature. These features are summarized in Fig. 2.2.



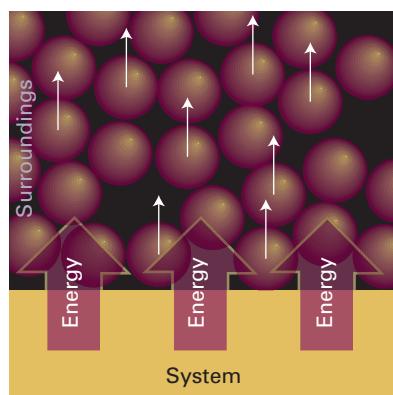
**Fig. 2.1** (a) An open system can exchange matter and energy with its surroundings. (b) A closed system can exchange energy with its surroundings, but it cannot exchange matter. (c) An isolated system can exchange neither energy nor matter with its surroundings.



**Fig. 2.2** (a) When an endothermic process occurs in an adiabatic system, the temperature falls; (b) if the process is exothermic, the temperature rises. (c) When an endothermic process occurs in a diathermic container, energy enters as heat from the surroundings, and the system remains at the same temperature. (d) If the process is exothermic, energy leaves as heat, and the process is isothermal.



**Fig. 2.3** When energy is transferred to the surroundings as heat, the transfer stimulates random motion of the atoms in the surroundings. Transfer of energy from the surroundings to the system makes use of random motion (thermal motion) in the surroundings.



**Fig. 2.4** When a system does work, it stimulates orderly motion in the surroundings. For instance, the atoms shown here may be part of a weight that is being raised. The ordered motion of the atoms in a falling weight does work on the system.

### (b) The molecular interpretation of heat and work

In molecular terms, heating is the transfer of energy that makes use of disorderly molecular motion in the surroundings. The disorderly motion of molecules is called **thermal motion**. The thermal motion of the molecules in the hot surroundings stimulates the molecules in the cooler system to move more vigorously and, as a result, the energy of the system is increased. When a system heats its surroundings, molecules of the system stimulate the thermal motion of the molecules in the surroundings (Fig. 2.3).

In contrast, work is the transfer of energy that makes use of organized motion in the surroundings (Fig. 2.4). When a weight is raised or lowered, its atoms move in an organized way (up or down). The atoms in a spring move in an orderly way when it is wound; the electrons in an electric current move in an orderly direction. When a system does work it causes atoms or electrons in its surroundings to move in an organized way. Likewise, when work is done on a system, molecules in the surroundings are used to transfer energy to it in an organized way, as the atoms in a weight are lowered or a current of electrons is passed.

The distinction between work and heat is made in the surroundings. The fact that a falling weight may stimulate thermal motion in the system is irrelevant to the distinction between heat and work: work is identified as energy transfer making use of the organized motion of atoms in the surroundings, and heat is identified as energy transfer making use of thermal motion in the surroundings. In the adiabatic compression of a gas, for instance, work is done on the system as the atoms of the compressing weight descend in an orderly way, but the effect of the incoming piston is to accelerate the gas molecules to higher average speeds. Because collisions between molecules quickly randomize their directions, the orderly motion of the atoms of the weight is in effect stimulating thermal motion in the gas. We observe the falling weight, the orderly descent of its atoms, and report that work is being done even though it is stimulating thermal motion.

## 2.2 The internal energy

**Key points** Internal energy, the total energy of a system, is a state function. (a) The equipartition theorem can be used to estimate the contribution to the internal energy of classical modes of motion. (b) The First Law states that the internal energy of an isolated system is constant.

In thermodynamics, the total energy of a system is called its **internal energy**,  $U$ . The internal energy is the total kinetic and potential energy of the molecules in the system. We denote by  $\Delta U$  the change in internal energy when a system changes from an initial state i with internal energy  $U_i$  to a final state f of internal energy  $U_f$ :

$$\Delta U = U_f - U_i \quad [2.1]$$

Throughout thermodynamics, we use the convention that  $\Delta X = X_f - X_i$ , where  $X$  is a property (a ‘state function’) of the system.

The internal energy is a **state function** in the sense that its value depends only on the current state of the system and is independent of how that state has been prepared. In other words, internal energy is a function of the properties that determine the current state of the system. Changing any one of the state variables, such as the pressure, results in a change in internal energy. That the internal energy is a state function has consequences of the greatest importance, as we shall start to unfold in Section 2.10.

The internal energy is an extensive property of a system (Section F.3) and is measured in joules ( $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$ , Section F.4). The molar internal energy,  $U_m$ , is the internal energy divided by the amount of substance in a system,  $U_m = U/n$ ; it is an intensive property and commonly reported in kilojoules per mole ( $\text{kJ mol}^{-1}$ ).

### (a) Molecular interpretation of internal energy

A molecule has a certain number of motional degrees of freedom, such as the ability to translate (the motion of its centre of mass through space), rotate around its centre of mass, or vibrate (as its bond lengths and angles change, leaving its centre of mass unmoved). Many physical and chemical properties depend on the energy associated with each of these modes of motion. For example, a chemical bond might break if a lot of energy becomes concentrated in it, for instance as vigorous vibration.

The ‘equipartition theorem’ of classical mechanics was introduced in Section F.5. According to it, the average energy of each quadratic contribution to the energy is  $\frac{1}{2}kT$ . As we saw in Section F.5, the mean energy of the atoms free to move in three dimensions is  $\frac{3}{2}kT$  and the total energy of a monatomic perfect gas is  $\frac{3}{2}NkT$ , or  $\frac{3}{2}nRT$  (because  $N = nN_A$  and  $R = N_A k$ ). We can therefore write

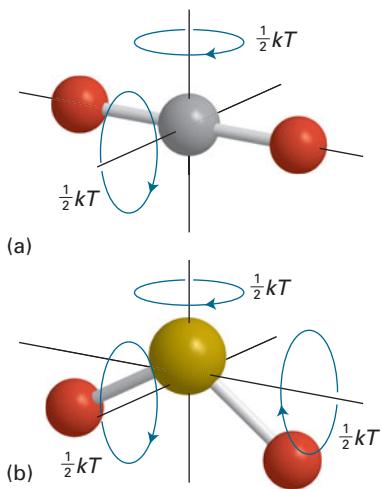
$$U_m(T) = U_m(0) + \frac{3}{2}RT \quad (\text{monatomic gas; translation only}) \quad (2.2a)$$

where  $U_m(0)$  is the molar internal energy at  $T = 0$ , when all translational motion has ceased and the sole contribution to the internal energy arises from the internal structure of the atoms. This equation shows that the internal energy of a perfect gas increases linearly with temperature. At  $25^\circ\text{C}$ ,  $\frac{3}{2}RT = 3.7 \text{ kJ mol}^{-1}$ , so translational motion contributes about  $4 \text{ kJ mol}^{-1}$  to the molar internal energy of a gaseous sample of atoms or molecules.

When the gas consists of molecules, we need to take into account the effect of rotation and vibration. A linear molecule, such as  $\text{N}_2$  and  $\text{CO}_2$ , can rotate around two axes perpendicular to the line of the atoms (Fig. 2.5), so it has two rotational modes of motion, each contributing a term  $\frac{1}{2}kT$  to the internal energy. Therefore, the mean rotational energy is  $kT$  and the rotational contribution to the molar internal energy is  $RT$ . By adding the translational and rotational contributions, we obtain

### A brief comment

The internal energy does not include the kinetic energy arising from the motion of the system as a whole, such as its kinetic energy as it accompanies the Earth on its orbit round the Sun. That is, the internal energy is the energy ‘internal’ to the system.



**Fig. 2.5** The rotational modes of molecules and the corresponding average energies at a temperature  $T$ . (a) A linear molecule can rotate about two axes perpendicular to the line of the atoms. (b) A nonlinear molecule can rotate about three perpendicular axes.

$$U_m(T) = U_m(0) + \frac{5}{2}RT \quad (\text{linear molecule; translation and rotation only}) \quad (2.2b)$$

A nonlinear molecule, such as CH<sub>4</sub> or H<sub>2</sub>O, can rotate around three axes and, again, each mode of motion contributes a term  $\frac{1}{2}kT$  to the internal energy. Therefore, the mean rotational energy is  $\frac{3}{2}kT$  and there is a rotational contribution of  $\frac{3}{2}RT$  to the molar internal energy. That is,

$$U_m(T) = U_m(0) + 3RT \quad (\text{nonlinear molecule; translation and rotation only}) \quad (2.2c)$$

The internal energy now increases twice as rapidly with temperature compared with the monatomic gas. Put another way: for a gas consisting of 1 mol of nonlinear molecules to undergo the same rise in temperature as 1 mol of monatomic gas, twice as much energy must be supplied. Molecules do not vibrate significantly at room temperature and, as a first approximation, the contribution of molecular vibrations to the internal energy is negligible except for very large molecules such as polymers and biological macromolecules.

None of the expressions we have derived depends on the volume occupied by the molecules: there are no intermolecular interactions in a perfect gas, so the distance between the molecules has no effect on the energy. That is, *the internal energy of a perfect gas is independent of the volume it occupies*. The internal energy of interacting molecules in condensed phases also has a contribution from the potential energy of their interaction. However, no simple expressions can be written down in general. Nevertheless, the crucial molecular point is that, as the temperature of a system is raised, the internal energy increases as the various modes of motion become more highly excited.

### (b) The formulation of the First Law

It has been found experimentally that the internal energy of a system may be changed either by doing work on the system or by heating it. Whereas we may know how the energy transfer has occurred (because we can see if a weight has been raised or lowered in the surroundings, indicating transfer of energy by doing work, or if ice has melted in the surroundings, indicating transfer of energy as heat), the system is blind to the mode employed. *Heat and work are equivalent ways of changing a system's internal energy*. A system is like a bank: it accepts deposits in either currency, but stores its reserves as internal energy. It is also found experimentally that, if a system is isolated from its surroundings, then no change in internal energy takes place. This summary of observations is now known as the **First Law of thermodynamics** and is expressed as follows:

The internal energy of an isolated system is constant.

First Law of thermodynamics

We cannot use a system to do work, leave it isolated, and then come back expecting to find it restored to its original state with the same capacity for doing work. The experimental evidence for this observation is that no ‘perpetual motion machine’, a machine that does work without consuming fuel or using some other source of energy, has ever been built.

These remarks may be summarized as follows. If we write  $w$  for the work done on a system,  $q$  for the energy transferred as heat to a system, and  $\Delta U$  for the resulting change in internal energy, then it follows that

$$\Delta U = q + w$$

Mathematical statement  
of the First Law

(2.3)

Equation 2.3 summarizes the equivalence of heat and work and the fact that the internal energy is constant in an isolated system (for which  $q = 0$  and  $w = 0$ ). The equation states that the change in internal energy of a closed system is equal to the energy that passes through its boundary as heat or work. It employs the ‘acquisitive convention’, in which  $w$  and  $q$  are positive if energy is transferred to the system as work or heat and are negative if energy is lost from the system. In other words, we view the flow of energy as work or heat from the system’s perspective.

• **A brief illustration**

If an electric motor produced 15 kJ of energy each second as mechanical work and lost 2 kJ as heat to the surroundings, then the change in the internal energy of the motor each second is

$$\Delta U = -2 \text{ kJ} - 15 \text{ kJ} = -17 \text{ kJ}$$

Suppose that, when a spring was wound, 100 J of work was done on it but 15 J escaped to the surroundings as heat. The change in internal energy of the spring is

$$\Delta U = 100 \text{ J} - 15 \text{ J} = +85 \text{ J} •$$

**A note on good practice** Always include the sign of  $\Delta U$  (and of  $\Delta X$  in general), even if it is positive.

## 2.3 Expansion work

**Key points** (a) Expansion work is proportional to the external pressure. (b) Free expansion (against zero pressure) does no work. (c) The work of expansion against constant pressure is proportional to that pressure and to the change in volume. (d) To achieve reversible expansion, the external pressure is matched at every stage to the pressure of the system. (e) The work of reversible, isothermal expansion of a perfect gas is a logarithmic function of the volume.

The way is opened to powerful methods of calculation by switching attention to infinitesimal changes of state (such as infinitesimal change in temperature) and infinitesimal changes in the internal energy  $dU$ . Then, if the work done on a system is  $dw$  and the energy supplied to it as heat is  $dq$ , in place of eqn 2.3 we have

$$dU = dq + dw \quad (2.4)$$

To use this expression we must be able to relate  $dq$  and  $dw$  to events taking place in the surroundings.

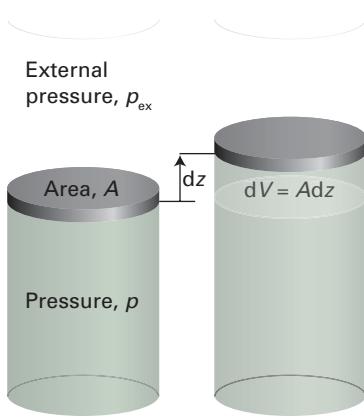
We begin by discussing **expansion work**, the work arising from a change in volume. This type of work includes the work done by a gas as it expands and drives back the atmosphere. Many chemical reactions result in the generation of gases (for instance, the thermal decomposition of calcium carbonate or the combustion of octane), and the thermodynamic characteristics of the reaction depend on the work that must be done to make room for the gas it has produced. The term ‘expansion work’ also includes work associated with negative changes of volume, that is, compression.

### (a) The general expression for work

The calculation of expansion work starts from the definition used in physics, which states that the work required to move an object a distance  $dz$  against an opposing force of magnitude  $F$  is

$$dw = -Fdz$$

General definition  
of work done [2.5]



**Fig. 2.6** When a piston of area  $A$  moves out through a distance  $dz$ , it sweeps out a volume  $dV = Adz$ . The external pressure  $p_{\text{ex}}$  is equivalent to a weight pressing on the piston, and the force opposing expansion is  $F = p_{\text{ex}}A$ .

The negative sign tells us that, when the system moves an object against an opposing force of magnitude  $F$ , and there are no other changes, then the internal energy of the system doing the work will decrease. That is, if  $dz$  is positive (motion to positive  $z$ ),  $dw$  is negative, and the internal energy decreases ( $dU$  in eqn 2.4 is negative provided that  $dq = 0$ ).

Now consider the arrangement shown in Fig. 2.6, in which one wall of a system is a massless, frictionless, rigid, perfectly fitting piston of area  $A$ . If the external pressure is  $p_{\text{ex}}$ , the magnitude of the force acting on the outer face of the piston is  $F = p_{\text{ex}}A$ . When the system expands through a distance  $dz$  against an external pressure  $p_{\text{ex}}$ , it follows that the work done is  $dw = -p_{\text{ex}}Adz$ . The quantity  $Adz$  is the change in volume,  $dV$ , in the course of the expansion. Therefore, the work done when the system expands by  $dV$  against a pressure  $p_{\text{ex}}$  is

$$dw = -p_{\text{ex}}dV \quad (\text{Expansion work} \quad (2.6a))$$

To obtain the total work done when the volume changes from an initial value  $V_i$  to a final value  $V_f$  we integrate this expression between the initial and final volumes:

$$w = - \int_{V_i}^{V_f} p_{\text{ex}}dV \quad (2.6b)$$

The force acting on the piston,  $p_{\text{ex}}A$ , is equivalent to the force arising from a weight that is raised as the system expands. If the system is compressed instead, then the same weight is lowered in the surroundings and eqn 2.6 can still be used, but now  $V_f < V_i$ . It is important to note that it is still the external pressure that determines the magnitude of the work. This somewhat perplexing conclusion seems to be inconsistent with the fact that the gas *inside* the container is opposing the compression. However, when a gas is compressed, the ability of the *surroundings* to do work is diminished by an amount determined by the weight that is lowered, and it is this energy that is transferred into the system.

Other types of work (for example, electrical work), which we shall call either **non-expansion work** or **additional work**, have analogous expressions, with each one the product of an intensive factor (the pressure, for instance) and an extensive factor (the change in volume). Some are collected in Table 2.1. For the present we continue with the work associated with changing the volume, the expansion work, and see what we can extract from eqn 2.6.

**Table 2.1** Varieties of work\*

Type of work	$dw$	Comments	Units†
Expansion	$-p_{\text{ex}}dV$	$p_{\text{ex}}$ is the external pressure $dV$ is the change in volume	$\text{Pa m}^3$
Surface expansion	$\gamma d\sigma$	$\gamma$ is the surface tension $d\sigma$ is the change in area	$\text{N m}^{-1} \text{m}^2$
Extension	$f dl$	$f$ is the tension $dl$ is the change in length	$\text{N m}$
Electrical	$\phi dQ$	$\phi$ is the electric potential $dQ$ is the change in charge	$\text{V C}$

\* In general, the work done on a system can be expressed in the form  $dw = -Fdz$ , where  $F$  is a ‘generalized force’ and  $dz$  is a ‘generalized displacement’.

† For work in joules (J). Note that  $1 \text{ N m} = 1 \text{ J}$  and  $1 \text{ V C} = 1 \text{ J}$ .

### (b) Free expansion

Free expansion is expansion against zero opposing force. It occurs when  $p_{\text{ex}} = 0$ . According to eqn 2.6a,  $dw = 0$  for each stage of the expansion. Hence, overall:

$$w = 0$$

Work of free expansion

(2.7)

That is, no work is done when a system expands freely. Expansion of this kind occurs when a gas expands into a vacuum.

### (c) Expansion against constant pressure

Now suppose that the external pressure is constant throughout the expansion. For example, the piston may be pressed on by the atmosphere, which exerts the same pressure throughout the expansion. A chemical example of this condition is the expansion of a gas formed in a chemical reaction in a container that can expand. We can evaluate eqn 2.6b by taking the constant  $p_{\text{ex}}$  outside the integral:

$$w = -p_{\text{ex}} \int_{V_i}^{V_f} dV = -p_{\text{ex}}(V_f - V_i)$$

Therefore, if we write the change in volume as  $\Delta V = V_f - V_i$ ,

$$w = -p_{\text{ex}} \Delta V$$

Expansion work against constant external pressure

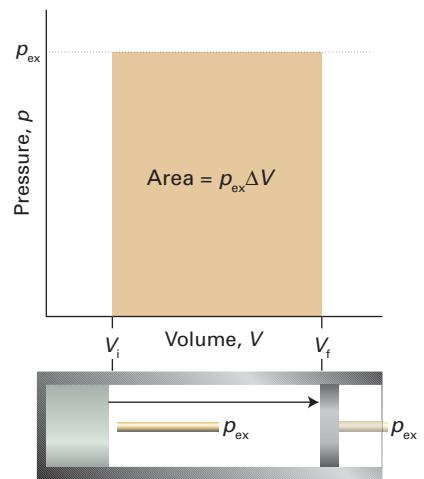
(2.8)

This result is illustrated graphically in Fig. 2.7, which makes use of the fact that an integral can be interpreted as an area. The magnitude of  $w$ , denoted  $|w|$ , is equal to the area beneath the horizontal line at  $p = p_{\text{ex}}$  lying between the initial and final volumes. A  $p,V$ -graph used to illustrate expansion work is called an **indicator diagram**; James Watt first used one to indicate aspects of the operation of his steam engine.

### (d) Reversible expansion

A reversible change in thermodynamics is a change that can be reversed by an infinitesimal modification of a variable. The key word ‘infinitesimal’ sharpens the everyday meaning of the word ‘reversible’ as something that can change direction. One example of reversibility that we have encountered already is the thermal equilibrium of two systems with the same temperature. The transfer of energy as heat between the two is reversible because, if the temperature of either system is lowered infinitesimally, then energy flows into the system with the lower temperature. If the temperature of either system at thermal equilibrium is raised infinitesimally, then energy flows out of the hotter system. There is obviously a very close relationship between reversibility and equilibrium: systems at equilibrium are poised to undergo reversible change.

Suppose a gas is confined by a piston and that the external pressure,  $p_{\text{ex}}$ , is set equal to the pressure,  $p$ , of the confined gas. Such a system is in mechanical equilibrium with its surroundings because an infinitesimal change in the external pressure in either direction causes changes in volume in opposite directions. If the external pressure is reduced infinitesimally, the gas expands slightly. If the external pressure is increased infinitesimally, the gas contracts slightly. In either case the change is reversible in the thermodynamic sense. If, on the other hand, the external pressure differs measurably from the internal pressure, then changing  $p_{\text{ex}}$  infinitesimally will not decrease it below the pressure of the gas, so will not change the direction of the process. Such a system is not in mechanical equilibrium with its surroundings and the expansion is thermodynamically irreversible.

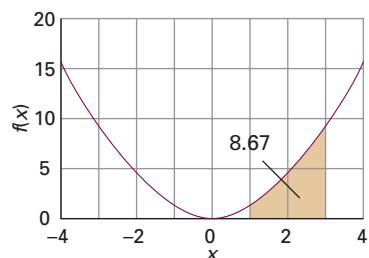


**Fig. 2.7** The work done by a gas when it expands against a constant external pressure,  $p_{\text{ex}}$ , is equal to the shaded area in this example of an indicator diagram.

#### A brief comment

The value of the integral  $\int_a^b f(x)dx$  is equal to the area under the graph of  $f(x)$  between  $x = a$  and  $x = b$ . For instance, the area under the curve  $f(x) = x^2$  shown in the illustration that lies between  $x = 1$  and  $3$  is

$$\begin{aligned} \int_1^3 x^2 dx &= (\frac{1}{3}x^3 + \text{constant}) \Big|_1^3 \\ &= \frac{1}{3}(3^3 - 1^3) = \frac{26}{3} \approx 8.67 \end{aligned}$$



To achieve reversible expansion we set  $p_{\text{ex}}$  equal to  $p$  at each stage of the expansion. In practice, this equalization could be achieved by gradually removing weights from the piston so that the downward force due to the weights always matches the changing upward force due to the pressure of the gas. When we set  $p_{\text{ex}} = p$ , eqn 2.6a becomes

$$dw = -p_{\text{ex}} dV = -pdV \quad \boxed{\text{Reversible expansion work}} \quad (2.9a)_{\text{rev}}$$

(Equations valid only for reversible processes are labelled with a subscript rev.) Although the pressure inside the system appears in this expression for the work, it does so only because  $p_{\text{ex}}$  has been set equal to  $p$  to ensure reversibility. The total work of reversible expansion from an initial volume  $V_i$  to a final volume  $V_f$  is therefore

$$w = - \int_{V_i}^{V_f} pdV \quad (2.9b)_{\text{rev}}$$

We can evaluate the integral once we know how the pressure of the confined gas depends on its volume. Equation 2.9 is the link with the material covered in Chapter 1 for, if we know the equation of state of the gas, then we can express  $p$  in terms of  $V$  and evaluate the integral.

### (e) Isothermal reversible expansion

Consider the isothermal, reversible expansion of a perfect gas. The expansion is made isothermal by keeping the system in thermal contact with its surroundings (which may be a constant-temperature bath). Because the equation of state is  $pV = nRT$ , we know that at each stage  $p = nRT/V$ , with  $V$  the volume at that stage of the expansion. The temperature  $T$  is constant in an isothermal expansion, so (together with  $n$  and  $R$ ) it may be taken outside the integral. It follows that the work of reversible isothermal expansion of a perfect gas from  $V_i$  to  $V_f$  at a temperature  $T$  is

$$w = -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i} \quad \boxed{\text{Reversible, isothermal expansion work of a perfect gas}} \quad (2.10)^\circ_{\text{rev}}$$

**A brief comment**  
An integral that occurs throughout thermodynamics is

$$\int \frac{1}{x} dx = \ln x + \text{constant},$$

$$\text{so } \int_a^b \frac{1}{x} dx = \ln \frac{b}{a}$$

When the final volume is greater than the initial volume, as in an expansion, the logarithm in eqn 2.10 is positive and hence  $w < 0$ . In this case, the system has done work on the surroundings and there is a corresponding reduction in its internal energy. (Note the cautious language: we shall see later that there is a compensating influx of energy as heat, so overall the internal energy is constant for the isothermal expansion of a perfect gas.) The equations also show that more work is done for a given change of volume when the temperature is increased: at a higher temperature the greater pressure of the confined gas needs a higher opposing pressure to ensure reversibility and the work done is correspondingly greater.

We can express the result of the calculation as an indicator diagram, for the magnitude of the work done is equal to the area under the isotherm  $p = nRT/V$  (Fig. 2.8). Superimposed on the diagram is the rectangular area obtained for irreversible expansion against constant external pressure fixed at the same final value as that reached in the reversible expansion. More work is obtained when the expansion is reversible (the area is greater) because matching the external pressure to the internal pressure at each stage of the process ensures that none of the system's pushing power is wasted. We cannot obtain more work than for the reversible process because increasing the external pressure even infinitesimally at any stage results in compression. We may infer from this discussion that, because some pushing power is wasted when  $p > p_{\text{ex}}$ , the maximum work available from a system operating between specified initial and final states and passing along a specified path is obtained when the change takes place reversibly.

We have introduced the connection between reversibility and maximum work for the special case of a perfect gas undergoing expansion. Later (in Section 3.5) we shall see that it applies to all substances and to all kinds of work.

### Example 2.1 Calculating the work of gas production

Calculate the work done when 50 g of iron reacts with hydrochloric acid to produce  $\text{FeCl}_2(\text{aq})$  and hydrogen in (a) a closed vessel of fixed volume, (b) an open beaker at 25°C.

**Method** We need to judge the magnitude of the volume change and then to decide how the process occurs. If there is no change in volume, there is no expansion work however the process takes place. If the system expands against a constant external pressure, the work can be calculated from eqn 2.8. A general feature of processes in which a condensed phase changes into a gas is that the volume of the former may usually be neglected relative to that of the gas it forms.

**Answer** In (a) the volume cannot change, so no expansion work is done and  $w=0$ . In (b) the gas drives back the atmosphere and therefore  $w=-p_{\text{ex}}\Delta V$ . We can neglect the initial volume because the final volume (after the production of gas) is so much larger and  $\Delta V=V_f-V_i \approx V_f=nRT/p_{\text{ex}}$ , where  $n$  is the amount of  $\text{H}_2$  produced. Therefore,

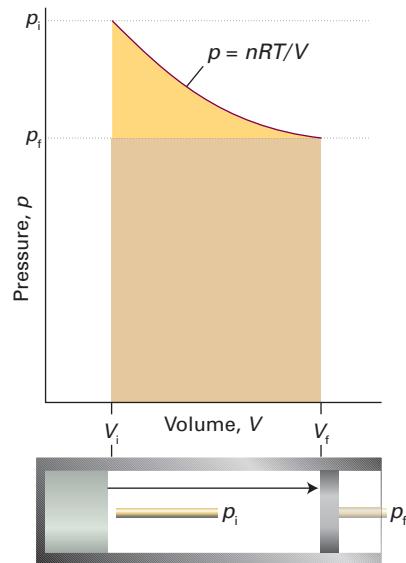
$$w=-p_{\text{ex}}\Delta V \approx -p_{\text{ex}} \times \frac{nRT}{p_{\text{ex}}} = -nRT$$

Because the reaction is  $\text{Fe}(\text{s}) + 2 \text{ HCl}(\text{aq}) \rightarrow \text{FeCl}_2(\text{aq}) + \text{H}_2(\text{g})$ , we know that 1 mol  $\text{H}_2$  is generated when 1 mol Fe is consumed, and  $n$  can be taken as the amount of Fe atoms that react. Because the molar mass of Fe is 55.85 g mol<sup>-1</sup>, it follows that

$$w \approx -\frac{50 \text{ g}}{55.85 \text{ g mol}^{-1}} \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \\ \approx -2.2 \text{ kJ}$$

The system (the reaction mixture) does 2.2 kJ of work driving back the atmosphere. Note that (for this perfect gas system) the magnitude of the external pressure does not affect the final result: the lower the pressure, the larger the volume occupied by the gas, so the effects cancel.

**Self-test 2.1** Calculate the expansion work done when 50 g of water is electrolysed under constant pressure at 25°C. [−10 kJ]



**Fig. 2.8** The work done by a perfect gas when it expands reversibly and isothermally is equal to the area under the isotherm  $p=nRT/V$ . The work done during the irreversible expansion against the same final pressure is equal to the rectangular area shown slightly darker. Note that the reversible work is greater than the irreversible work.

 **interActivity** Calculate the work of isothermal reversible expansion of 1.0 mol  $\text{CO}_2(\text{g})$  at 298 K from 1.0 m<sup>3</sup> to 3.0 m<sup>3</sup> on the basis that it obeys the van der Waals equation of state.

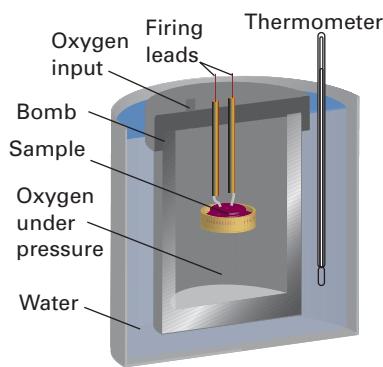
## 2.4 Heat transactions

**Key points** The energy transferred as heat at constant volume is equal to the change in internal energy of the system. (a) Calorimetry is the measurement of heat transactions. (b) The heat capacity at constant volume is the slope of the internal energy with respect to temperature.

In general, the change in internal energy of a system is

$$dU = dq + dw_{\text{exp}} + dw_e \quad (2.11)$$

where  $dw_e$  is work in addition (e for ‘extra’) to the expansion work,  $dw_{\text{exp}}$ . For instance,  $dw_e$  might be the electrical work of driving a current through a circuit. A



**Fig. 2.9** A constant-volume bomb calorimeter. The ‘bomb’ is the central vessel, which is strong enough to withstand high pressures. The calorimeter (for which the heat capacity must be known) is the entire assembly shown here. To ensure adiabaticity, the calorimeter is immersed in a water bath with a temperature continuously readjusted to that of the calorimeter at each stage of the combustion.

system kept at constant volume can do no expansion work, so  $dW_{\text{exp}} = 0$ . If the system is also incapable of doing any other kind of work (if it is not, for instance, an electrochemical cell connected to an electric motor), then  $dW_e = 0$  too. Under these circumstances:

$$dU = dq$$

Heat transferred at constant volume

(2.12a)

We express this relation by writing  $dU = dq_V$ , where the subscript implies a change at constant volume. For a measurable change,

$$\Delta U = q_V$$
(2.12b)

It follows that, by measuring the energy supplied to a constant-volume system as heat ( $q_V > 0$ ) or released from it as heat ( $q_V < 0$ ) when it undergoes a change of state, we are in fact measuring the change in its internal energy.

### (a) Calorimetry

Calorimetry is the study of heat transfer during physical and chemical processes. A **calorimeter** is a device for measuring energy transferred as heat. The most common device for measuring  $\Delta U$  is an **adiabatic bomb calorimeter** (Fig. 2.9). The process we wish to study—which may be a chemical reaction—is initiated inside a constant-volume container, the ‘bomb’. The bomb is immersed in a stirred water bath, and the whole device is the calorimeter. The calorimeter is also immersed in an outer water bath. The water in the calorimeter and of the outer bath are both monitored and adjusted to the same temperature. This arrangement ensures that there is no net loss of heat from the calorimeter to the surroundings (the bath) and hence that the calorimeter is adiabatic.

The change in temperature,  $\Delta T$ , of the calorimeter is proportional to the energy that the reaction releases or absorbs as heat. Therefore, by measuring  $\Delta T$  we can determine  $q_V$  and hence find  $\Delta U$ . The conversion of  $\Delta T$  to  $q_V$  is best achieved by calibrating the calorimeter using a process of known energy output and determining the **calorimeter constant**, the constant  $C$  in the relation

$$q = C\Delta T \quad (2.13)$$

The calorimeter constant may be measured electrically by passing a constant current,  $I$ , from a source of known potential difference,  $\Delta\phi$ , through a heater for a known period of time,  $t$ , for then

$$q = It\Delta\phi \quad (2.14)$$

#### A brief comment

Electrical charge is measured in **coulombs**,  $C$ . The motion of charge gives rise to an electric current,  $I$ , measured in coulombs per second, or **amperes**,  $A$ , where  $1 A = 1 C s^{-1}$ . If a constant current  $I$  flows through a potential difference  $\Delta\phi$  (measured in volts,  $V$ ), the total energy supplied in an interval  $t$  is  $It\Delta\phi$ . Because  $1 A V s = 1 (C s^{-1}) V s = 1 C V = 1 J$ , the energy is obtained in joules with the current in amperes, the potential difference in volts, and the time in seconds.

#### ● A brief illustration

If we pass a current of  $10.0 A$  from a  $12 V$  supply for  $300 s$ , then from eqn 2.14 the energy supplied as heat is

$$q = (10.0 A) \times (12 V) \times (300 s) = 3.6 \times 10^4 A V s = 36 kJ$$

because  $1 A V s = 1 J$ . If the observed rise in temperature is  $5.5 K$ , then the calorimeter constant is  $C = (36 kJ)/(5.5 K) = 6.5 kJ K^{-1}$ . ●

Alternatively,  $C$  may be determined by burning a known mass of substance (benzoic acid is often used) that has a known heat output. With  $C$  known, it is simple to interpret an observed temperature rise as a release of heat.

### (b) Heat capacity

The internal energy of a system increases when its temperature is raised. The increase depends on the conditions under which the heating takes place and for the present we suppose that the system has a constant volume. For example, it may be a gas in a container of fixed volume. If the internal energy is plotted against temperature, then a curve like that in Fig. 2.10 may be obtained. The slope of the tangent to the curve at any temperature is called the **heat capacity** of the system at that temperature. The **heat capacity at constant volume** is denoted  $C_V$  and is defined formally as

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V \quad [2.15]$$

Definition of heat capacity  
at constant volume

In this case, the internal energy varies with the temperature and the volume of the sample, but we are interested only in its variation with the temperature, the volume being held constant (Fig. 2.11).

#### • A brief illustration

The heat capacity of a monatomic perfect gas can be calculated by inserting the expression for the internal energy derived in Section 2.2a. There we saw that

$$U_m = U_m(0) + \frac{3}{2}RT$$

so from eqn 2.15

$$C_{V,m} = \frac{\partial}{\partial T} (U_m(0) + \frac{3}{2}RT) = \frac{3}{2}R$$

The numerical value is  $12.47 \text{ J K}^{-1} \text{ mol}^{-1}$ . ●

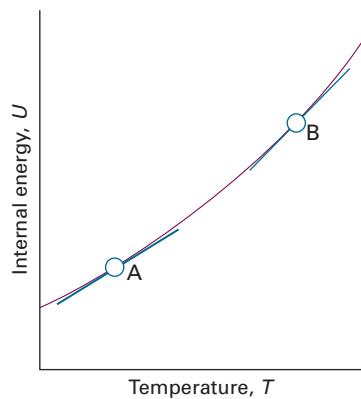
Heat capacities are extensive properties: 100 g of water, for instance, has 100 times the heat capacity of 1 g of water (and therefore requires 100 times the energy as heat to bring about the same rise in temperature). The **molar heat capacity at constant volume**,  $C_{V,m} = C_V/n$ , is the heat capacity per mole of substance, and is an intensive property (all molar quantities are intensive). Typical values of  $C_{V,m}$  for polyatomic gases are close to  $25 \text{ J K}^{-1} \text{ mol}^{-1}$ . For certain applications it is useful to know the **specific heat capacity** (more informally, the ‘specific heat’) of a substance, which is the heat capacity of the sample divided by the mass, usually in grams:  $C_{V,s} = C_V/m$ . The specific heat capacity of water at room temperature is close to  $4.2 \text{ J K}^{-1} \text{ g}^{-1}$ . In general, heat capacities depend on the temperature and decrease at low temperatures. However, over small ranges of temperature at and above room temperature, the variation is quite small and for approximate calculations heat capacities can be treated as almost independent of temperature.

The heat capacity is used to relate a change in internal energy to a change in temperature of a constant-volume system. It follows from eqn 2.15 that

$$dU = C_V dT \quad (\text{at constant volume}) \quad (2.16a)$$

That is, at constant volume, an infinitesimal change in temperature brings about an infinitesimal change in internal energy, and the constant of proportionality is  $C_V$ . If the heat capacity is independent of temperature over the range of temperatures of interest, a measurable change of temperature,  $\Delta T$ , brings about a measurable increase in internal energy,  $\Delta U$ , where

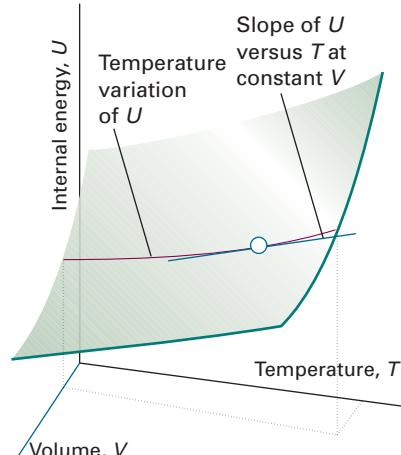
$$\Delta U = C_V \Delta T \quad (\text{at constant volume}) \quad (2.16b)$$



**Fig. 2.10** The internal energy of a system increases as the temperature is raised; this graph shows its variation as the system is heated at constant volume. The slope of the tangent to the curve at any temperature is the heat capacity at constant volume at that temperature. Note that, for the system illustrated, the heat capacity is greater at B than at A.

#### A brief comment

Partial derivatives are reviewed in *Mathematical background 2* following this chapter.



**Fig. 2.11** The internal energy of a system varies with volume and temperature, perhaps as shown here by the surface. The variation of the internal energy with temperature at one particular constant volume is illustrated by the curve drawn parallel to  $T$ . The slope of this curve at any point is the partial derivative  $(\partial U / \partial T)_V$ .

Because a change in internal energy can be identified with the heat supplied at constant volume (eqn 2.12b), the last equation can also be written

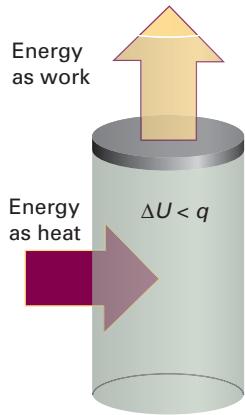
$$q_V = C_V \Delta T \quad (2.17)$$

This relation provides a simple way of measuring the heat capacity of a sample: a measured quantity of energy is transferred as heat to the sample (electrically, for example), and the resulting increase in temperature is monitored. The ratio of the energy transferred as heat to the temperature rise it causes ( $q_V/\Delta T$ ) is the constant-volume heat capacity of the sample.

A large heat capacity implies that, for a given quantity of energy transferred as heat, there will be only a small increase in temperature (the sample has a large capacity for heat). An infinite heat capacity implies that there will be no increase in temperature however much energy is supplied as heat. At a phase transition, such as at the boiling point of water, the temperature of a substance does not rise as energy is supplied as heat: the energy is used to drive the endothermic transition, in this case to vaporize the water, rather than to increase its temperature. Therefore, at the temperature of a phase transition, the heat capacity of a sample is infinite. The properties of heat capacities close to phase transitions are treated more fully in Section 4.6.

## 2.5 Enthalpy

**Key points** (a) Energy transferred as heat at constant pressure is equal to the change in enthalpy of a system. (b) Enthalpy changes are measured in a constant-pressure calorimeter. (c) The heat capacity at constant pressure is equal to the slope of enthalpy with temperature.



**Fig. 2.12** When a system is subjected to constant pressure and is free to change its volume, some of the energy supplied as heat may escape back into the surroundings as work. In such a case, the change in internal energy is smaller than the energy supplied as heat.

The change in internal energy is not equal to the energy transferred as heat when the system is free to change its volume. Under these circumstances some of the energy supplied as heat to the system is returned to the surroundings as expansion work (Fig. 2.12), so  $dU$  is less than  $dq$ . However, we shall now show that in this case the energy supplied as heat at constant pressure is equal to the change in another thermodynamic property of the system, the enthalpy.

### (a) The definition of enthalpy

The enthalpy,  $H$ , is defined as

$$H = U + pV$$

Definition of enthalpy

[2.18]

where  $p$  is the pressure of the system and  $V$  is its volume. Because  $U$ ,  $p$ , and  $V$  are all state functions, the enthalpy is a state function too. As is true of any state function, the change in enthalpy,  $\Delta H$ , between any pair of initial and final states is independent of the path between them.

Although the definition of enthalpy may appear arbitrary, it has important implications for thermochemistry. For instance, we show in the following *Justification* that eqn 2.18 implies that *the change in enthalpy is equal to the energy supplied as heat at constant pressure* (provided the system does no additional work):

$$dH = dq$$

Heat transferred at constant pressure

(2.19a)

For a measurable change

$$\Delta H = q_p$$

(2.19b)

**Justification 2.1** The relation  $\Delta H = q_p$ 

For a general infinitesimal change in the state of the system,  $U$  changes to  $U + dU$ ,  $p$  changes to  $p + dp$ , and  $V$  changes to  $V + dV$ , so from the definition in eqn 2.18,  $H$  changes from  $U + pV$  to

$$\begin{aligned} H + dH &= (U + dU) + (p + dp)(V + dV) \\ &= U + dU + pV + pdV + Vdp + dpdV \end{aligned}$$

The last term is the product of two infinitesimally small quantities and can therefore be neglected. As a result, after recognizing  $U + pV = H$  on the right, we find that  $H$  changes to

$$H + dH = H + dU + pdV + Vdp$$

and hence that

$$dH = dU + pdV + Vdp$$

If we now substitute  $dU = dq + dw$  into this expression, we get

$$dH = dq + dw + pdV + Vdp$$

If the system is in mechanical equilibrium with its surroundings at a pressure  $p$  and does only expansion work, we can write  $dw = -pdV$  and obtain

$$dH = dq + Vdp$$

Now we impose the condition that the heating occurs at constant pressure by writing  $dp = 0$ . Then

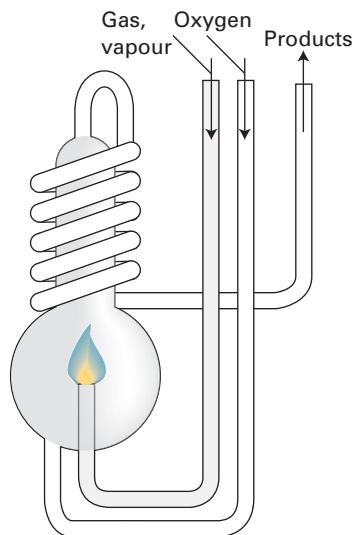
$$dH = dq \quad (\text{at constant pressure, no additional work})$$

as in eqn 2.19a.

The result expressed in eqn 2.19 states that, when a system is subjected to constant pressure and only expansion work can occur, the change in enthalpy is equal to the energy supplied as heat. For example, if we supply 36 kJ of energy through an electric heater immersed in an open beaker of water, then the enthalpy of the water increases by 36 kJ and we write  $\Delta H = +36 \text{ kJ}$ .

**(b) The measurement of an enthalpy change**

An enthalpy change can be measured calorimetrically by monitoring the temperature change that accompanies a physical or chemical change occurring at constant pressure. A calorimeter for studying processes at constant pressure is called an **isobaric calorimeter**. A simple example is a thermally insulated vessel open to the atmosphere: the heat released in the reaction is monitored by measuring the change in temperature of the contents. For a combustion reaction an **adiabatic flame calorimeter** may be used to measure  $\Delta T$  when a given amount of substance burns in a supply of oxygen (Fig. 2.13). Another route to  $\Delta H$  is to measure the internal energy change by using a bomb calorimeter, and then to convert  $\Delta U$  to  $\Delta H$ . Because solids and liquids have small molar volumes, for them  $pV_m$  is so small that the molar enthalpy and molar internal energy are almost identical ( $H_m = U_m + pV_m \approx U_m$ ). Consequently, if a process involves only solids or liquids, the values of  $\Delta H$  and  $\Delta U$  are almost identical. Physically, such processes are accompanied by a very small change in volume; the system does negligible work on the surroundings when the process occurs, so the energy supplied as heat stays entirely within the system. The most sophisticated way to measure enthalpy changes, however, is to use a **differential scanning calorimeter**



**Fig. 2.13** A constant-pressure flame calorimeter consists of this component immersed in a stirred water bath. Combustion occurs as a known amount of reactant is passed through to fuel the flame, and the rise of temperature is monitored.

(DSC). Changes in enthalpy and internal energy may also be measured by noncalorimetric methods (see Chapter 6).

**Example 2.2** Relating  $\Delta H$  and  $\Delta U$

The change in molar internal energy when  $\text{CaCO}_3(\text{s})$  as calcite converts to another form, aragonite, is  $+0.21 \text{ kJ mol}^{-1}$ . Calculate the difference between the molar enthalpy and internal energy changes when the pressure is 1.0 bar given that the densities of the polymorphs are  $2.71 \text{ g cm}^{-3}$  and  $2.93 \text{ g cm}^{-3}$ , respectively.

**Method** The starting point for the calculation is the relation between the enthalpy of a substance and its internal energy (eqn 2.18). The difference between the two quantities can be expressed in terms of the pressure and the difference of their molar volumes, and the latter can be calculated from their molar masses,  $M$ , and their mass densities,  $\rho$ , by using  $\rho = M/V_m$ .

**Answer** The change in enthalpy when the transition occurs is

$$\begin{aligned}\Delta H_m &= H_m(\text{aragonite}) - H_m(\text{calcite}) \\ &= \{U_m(a) + pV_m(a)\} - \{U_m(c) + pV_m(c)\} \\ &= \Delta U_m + p\{V_m(a) - V_m(c)\}\end{aligned}$$

where a denotes aragonite and c calcite. It follows by substituting  $V_m = M/\rho$  that

$$\Delta H_m - \Delta U_m = pM \left( \frac{1}{\rho(a)} - \frac{1}{\rho(c)} \right)$$

Substitution of the data, using  $M = 100 \text{ g mol}^{-1}$ , gives

$$\begin{aligned}\Delta H_m - \Delta U_m &= (1.0 \times 10^5 \text{ Pa}) \times (100 \text{ g mol}^{-1}) \times \left( \frac{1}{2.93 \text{ g cm}^{-3}} - \frac{1}{2.71 \text{ g cm}^{-3}} \right) \\ &= -2.8 \times 10^5 \text{ Pa cm}^3 \text{ mol}^{-1} = -0.28 \text{ Pa m}^3 \text{ mol}^{-1}\end{aligned}$$

Hence (because  $1 \text{ Pa m}^3 = 1 \text{ J}$ ),  $\Delta H_m - \Delta U_m = -0.28 \text{ J mol}^{-1}$ , which is only 0.1 per cent of the value of  $\Delta U_m$ . We see that it is usually justifiable to ignore the difference between the molar enthalpy and internal energy of condensed phases, except at very high pressures, when  $p\Delta V_m$  is no longer negligible.

**Self-test 2.2** Calculate the difference between  $\Delta H$  and  $\Delta U$  when 1.0 mol  $\text{Sn}(\text{s}, \text{grey})$  of density  $5.75 \text{ g cm}^{-3}$  changes to  $\text{Sn}(\text{s}, \text{white})$  of density  $7.31 \text{ g cm}^{-3}$  at 10.0 bar. At 298 K,  $\Delta H = +2.1 \text{ kJ}$ . [ $\Delta H - \Delta U = -4.4 \text{ J}$ ]

The enthalpy of a perfect gas is related to its internal energy by using  $pV = nRT$  in the definition of  $H$ :

$$H = U + pV = U + nRT \quad (2.20)^{\circ}$$

This relation implies that the change of enthalpy in a reaction that produces or consumes gas is

$$\Delta H = \Delta U + \Delta n_g RT \quad (2.21)^{\circ}$$

where  $\Delta n_g$  is the change in the amount of gas molecules in the reaction.

● **A brief illustration**

In the reaction  $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{l})$ , 3 mol of gas-phase molecules is replaced by 2 mol of liquid-phase molecules, so  $\Delta n_g = -3 \text{ mol}$ . Therefore, at 298 K, when  $RT = 2.48 \text{ kJ mol}^{-1}$ , the enthalpy and internal energy changes taking place in the system are related by

$$\Delta H_m - \Delta U_m = (-3 \text{ mol}) \times RT \approx -7.4 \text{ kJ mol}^{-1}$$

Note that the difference is expressed in kilojoules, not joules as in Example 2.2. The enthalpy change is smaller (in this case, less negative) than the change in internal energy because, although heat escapes from the system when the reaction occurs, the system contracts when the liquid is formed, so energy is restored to it from the surroundings. ●

**Example 2.3** Calculating a change in enthalpy

Water is heated to boiling under a pressure of 1.0 atm. When an electric current of 0.50 A from a 12 V supply is passed for 300 s through a resistance in thermal contact with it, it is found that 0.798 g of water is vaporized. Calculate the molar internal energy and enthalpy changes at the boiling point (373.15 K).

**Method** Because the vaporization occurs at constant pressure, the enthalpy change is equal to the heat supplied by the heater. Therefore, the strategy is to calculate the energy supplied as heat (from  $q = It\Delta\phi$ ), express that as an enthalpy change, and then convert the result to a molar enthalpy change by division by the amount of  $\text{H}_2\text{O}$  molecules vaporized. To convert from enthalpy change to internal energy change, we assume that the vapour is a perfect gas and use eqn 2.21.

**Answer** The enthalpy change is

$$\Delta H = q_p = (0.50 \text{ A}) \times (12 \text{ V}) \times (300 \text{ s}) = 0.50 \times 12 \times 300 \text{ J}$$

Here we have used  $1 \text{ A V s} = 1 \text{ J}$ . Because  $0.798 \text{ g}$  of water is  $(0.798 \text{ g})/(18.02 \text{ g mol}^{-1}) = (0.798/18.02) \text{ mol H}_2\text{O}$ , the enthalpy of vaporization per mole of  $\text{H}_2\text{O}$  is

$$\Delta H_m = +\frac{0.50 \times 12 \times 300 \text{ J}}{(0.798/18.02) \text{ mol}} = +41 \text{ kJ mol}^{-1}$$

In the process  $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$  the change in the amount of gas molecules is  $\Delta n_g = +1 \text{ mol}$ , so

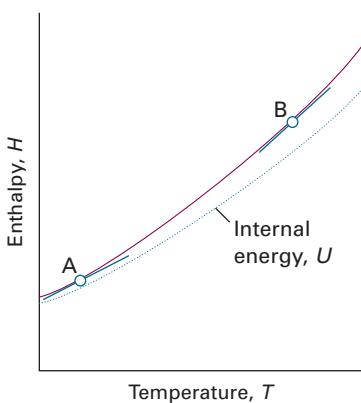
$$\Delta U_m = \Delta H_m - RT = +38 \text{ kJ mol}^{-1}$$

Notice that the internal energy change is smaller than the enthalpy change because energy has been used to drive back the surrounding atmosphere to make room for the vapour.

**Self-test 2.3** The molar enthalpy of vaporization of benzene at its boiling point (353.25 K) is  $30.8 \text{ kJ mol}^{-1}$ . What is the molar internal energy change? For how long would the same 12 V source need to supply a 0.50 A current in order to vaporize a 10 g sample?  $[+27.9 \text{ kJ mol}^{-1}, 6.6 \times 10^2 \text{ s}]$

**(c) The variation of enthalpy with temperature**

The enthalpy of a substance increases as its temperature is raised. The relation between the increase in enthalpy and the increase in temperature depends on the conditions (for example, constant pressure or constant volume). The most important



**Fig. 2.14** The constant-pressure heat capacity at a particular temperature is the slope of the tangent to a curve of the enthalpy of a system plotted against temperature (at constant pressure). For gases, at a given temperature the slope of enthalpy versus temperature is steeper than that of internal energy versus temperature, and  $C_{p,m}$  is larger than  $C_{V,m}$ .

condition is constant pressure, and the slope of the tangent to a plot of enthalpy against temperature at constant pressure is called the **heat capacity at constant pressure**,  $C_p$ , at a given temperature (Fig. 2.14). More formally:

$$C_p = \left( \frac{\partial H}{\partial T} \right)_p$$

Definition of heat capacity at constant pressure

[2.22]

The heat capacity at constant pressure is the analogue of the heat capacity at constant volume and is an extensive property. The **molar heat capacity at constant pressure**,  $C_{p,m}$ , is the heat capacity per mole of material; it is an intensive property.

The heat capacity at constant pressure is used to relate the change in enthalpy to a change in temperature. For infinitesimal changes of temperature

$$dH = C_p dT \quad (\text{at constant pressure}) \quad (2.23a)$$

If the heat capacity is constant over the range of temperatures of interest, then for a measurable increase in temperature

$$\Delta H = C_p \Delta T \quad (\text{at constant pressure}) \quad (2.23b)$$

Because an increase in enthalpy can be equated with the energy supplied as heat at constant pressure, the practical form of the latter equation is

$$q_p = C_p \Delta T \quad (2.24)$$

This expression shows us how to measure the heat capacity of a sample: a measured quantity of energy is supplied as heat under conditions of constant pressure (as in a sample exposed to the atmosphere and free to expand) and the temperature rise is monitored.

The variation of heat capacity with temperature can sometimes be ignored if the temperature range is small; this approximation is highly accurate for a monatomic perfect gas (for instance, one of the noble gases at low pressure). However, when it is necessary to take the variation into account, a convenient approximate empirical expression is

$$C_{p,m} = a + bT + \frac{c}{T^2} \quad (2.25)$$

The empirical parameters  $a$ ,  $b$ , and  $c$  are independent of temperature (Table 2.2) and are found by fitting this expression to experimental data.

**Table 2.2\*** Temperature variation of molar heat capacities,  $C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1}) = a + bT + c/T^2$

	$a$	$b/(10^{-3} \text{ K})$	$c/(10^5 \text{ K}^2)$
C(s, graphite)	16.86	4.77	-8.54
CO <sub>2</sub> (g)	44.22	8.79	-8.62
H <sub>2</sub> O(l)	75.29	0	0
N <sub>2</sub> (g)	28.58	3.77	-0.50

\* More values are given in the *Data section*.

**Example 2.4** Evaluating an increase in enthalpy with temperature

What is the change in molar enthalpy of N<sub>2</sub> when it is heated from 25°C to 100°C? Use the heat capacity information in Table 2.2.

**Method** The heat capacity of N<sub>2</sub> changes with temperature, so we cannot use eqn 2.23b (which assumes that the heat capacity of the substance is constant). Therefore, we must use eqn 2.23a, substitute eqn 2.25 for the temperature dependence of the heat capacity, and integrate the resulting expression from 25°C to 100°C.

**Answer** For convenience, we denote the two temperatures T<sub>1</sub> (298 K) and T<sub>2</sub> (373 K). The relation we require is

$$\int_{H(T_1)}^{H(T_2)} dH = \int_{T_1}^{T_2} \left( a + bT + \frac{c}{T^2} \right) dT$$

and the relevant integrals are

$$\int dx = x + \text{constant} \quad \int x dx = \frac{1}{2}x^2 + \text{constant} \quad \int \frac{dx}{x^2} = -\frac{1}{x} + \text{constant}$$

It follows that

$$H(T_2) - H(T_1) = a(T_2 - T_1) + \frac{1}{2}b(T_2^2 - T_1^2) - c\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Substitution of the numerical data results in

$$H(373 \text{ K}) = H(298 \text{ K}) + 2.20 \text{ kJ mol}^{-1}$$

If we had assumed a constant heat capacity of 29.14 J K<sup>-1</sup> mol<sup>-1</sup> (the value given by eqn 2.25 at 25°C), we would have found that the two enthalpies differed by 2.19 kJ mol<sup>-1</sup>.

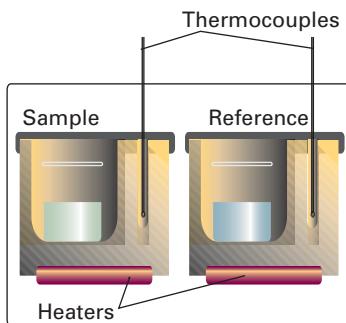
**Self-test 2.4** At very low temperatures the heat capacity of a solid is proportional to T<sup>3</sup>, and we can write C<sub>p</sub> = aT<sup>3</sup>. What is the change in enthalpy of such a substance when it is heated from 0 to a temperature T (with T close to 0)? [ΔH =  $\frac{1}{4}aT^4$ ]

Most systems expand when heated at constant pressure. Such systems do work on the surroundings and therefore some of the energy supplied to them as heat escapes back to the surroundings. As a result, the temperature of the system rises less than when the heating occurs at constant volume. A smaller increase in temperature implies a larger heat capacity, so we conclude that in most cases the heat capacity at constant pressure of a system is larger than its heat capacity at constant volume. We show later (Section 2.11) that there is a simple relation between the two heat capacities of a perfect gas:

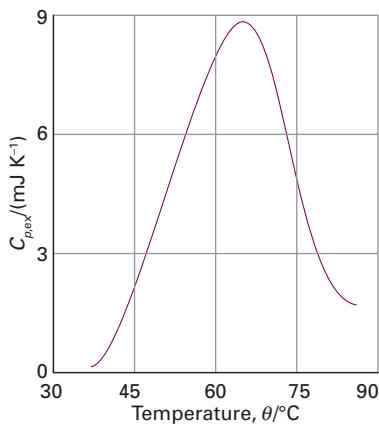
$$C_p - C_V = nR$$

Relation between heat capacities of a perfect gas (2.26)<sup>o</sup>

It follows that the molar heat capacity of a perfect gas is about 8 J K<sup>-1</sup> mol<sup>-1</sup> larger at constant pressure than at constant volume. Because the heat capacity at constant volume of a monatomic gas is about 12 J K<sup>-1</sup> mol<sup>-1</sup>, the difference is highly significant and must be taken into account.



**Fig. 2.15** A differential scanning calorimeter. The sample and a reference material are heated in separate but identical metal heat sinks. The output is the difference in power needed to maintain the heat sinks at equal temperatures as the temperature rises.



**Fig. 2.16** A thermogram for the protein ubiquitin at  $\text{pH} = 2.45$ . The protein retains its native structure up to about  $45^\circ\text{C}$  and then undergoes an endothermic conformational change. (Adapted from B. Chowdhry and S. LeHarne, *J. Chem. Educ.* 74, 236 (1997).)

## IMPACT ON BIOCHEMISTRY AND MATERIALS SCIENCE

### I2.1 Differential scanning calorimetry

A differential scanning calorimeter (DSC) measures the energy transferred as heat to or from a sample at constant pressure during a physical or chemical change. The term 'differential' refers to the fact that the behaviour of the sample is compared to that of a reference material that does not undergo a physical or chemical change during the analysis. The term 'scanning' refers to the fact that the temperatures of the sample and reference material are increased, or scanned, during the analysis.

A DSC consists of two small compartments that are heated electrically at a constant rate. The temperature,  $T$ , at time  $t$  during a linear scan is  $T = T_0 + \alpha t$ , where  $T_0$  is the initial temperature and  $\alpha$  is the temperature scan rate. A computer controls the electrical power supply that maintains the same temperature in the sample and reference compartments throughout the analysis (Fig. 2.15).

If no physical or chemical change occurs in the sample at temperature  $T$ , we write the heat transferred to the sample as  $q_p = C_p \Delta T$ , where  $\Delta T = T - T_0$  and we have assumed that  $C_p$  is independent of temperature. Because  $T = T_0 + \alpha t$ ,  $\Delta T = \alpha t$ . The chemical or physical process requires the transfer of  $q_p + q_{p,\text{ex}}$  where  $q_{p,\text{ex}}$  is the excess energy transferred as heat needed to attain the same change in temperature of the sample as the control. The quantity  $q_{p,\text{ex}}$  is interpreted in terms of an apparent change in the heat capacity at constant pressure of the sample,  $C_p$ , during the temperature scan:

$$C_{p,\text{ex}} = \frac{q_{p,\text{ex}}}{\Delta T} = \frac{q_{p,\text{ex}}}{\alpha t} = \frac{P_{\text{ex}}}{\alpha}$$

where  $P_{\text{ex}} = q_{p,\text{ex}}/t$  is the excess electrical power necessary to equalize the temperature of the sample and reference compartments. A DSC trace, also called a *thermogram*, consists of a plot of  $C_{p,\text{ex}}$  against  $T$  (Fig. 2.16). From eqn 2.23a, the enthalpy change associated with the process is

$$\Delta H = \int_{T_1}^{T_2} C_{p,\text{ex}} dT$$

where  $T_1$  and  $T_2$  are, respectively, the temperatures at which the process begins and ends. This relation shows that the enthalpy change is equal to the area under the plot of  $C_{p,\text{ex}}$  against  $T$ .

With a DSC, enthalpy changes may be determined in samples of masses as low as 0.5 mg, which is a significant advantage over conventional calorimeters, which require several grams of material. The technique is used in the chemical industry to characterize polymers in terms of their structural integrity, stability, and nanoscale organization. For example, it is possible to detect the ability of certain polymers such as ethylene oxide (EO) and propylene oxide (PO) to self-aggregate as their temperature is raised. These copolymers are widely used as surfactants and detergents with the amphiphilic (both water- and hydrocarbon-attracting) character provided by the hydrophobic central PO block and the more hydrophilic EO blocks attached on either side. They aggregate to form micelles (clusters) as the temperature is raised because the more hydrophobic central PO block becomes less soluble at higher temperature but the terminal EO blocks retain their strong interaction with water. This enhanced amphiphilic character of the molecules at higher temperature drives the copolymers to form micelles that are spherical in shape. The micellization process is strongly endothermic, reflecting the initial destruction of the hydrogen bonds of the PO block with water, and is readily detected by DSC. Further increases in temperature affect the shape of the micelle, changing from spherical to rod-like. A new but weaker DSC

signal at higher temperature reflects a small change in enthalpy as micelles aggregate to form the rod-like structure. The marked decrease in the heat capacity accompanying the sphere-to-rod transition presumably reflects an extensive decrease in the degree of hydration of the polymer.

The technique is also used to assess the stability of proteins, nucleic acids, and membranes. For example, the thermogram shown in Fig. 2.16 indicates that the protein ubiquitin undergoes an endothermic conformational change in which a large number of non-covalent interactions (such as hydrogen bonds) are broken simultaneously and result in denaturation, the loss of the protein's three-dimensional structure. The area under the curve represents the heat absorbed in this process and can be identified with the enthalpy change. The thermogram also reveals the formation of new intermolecular interactions in the denatured form. The increase in heat capacity accompanying the native → denatured transition reflects the change from a more compact native conformation to one in which the more exposed amino acid side chains in the denatured form have more extensive interactions with the surrounding water molecules.

## 2.6 Adiabatic changes

**Key point** For the reversible adiabatic expansion of a perfect gas, pressure and volume are related by an expression that depends on the ratio of heat capacities.

We are now equipped to deal with the changes that occur when a perfect gas expands adiabatically. A decrease in temperature should be expected: because work is done but no heat enters the system, the internal energy falls, and therefore the temperature of the working gas also falls. In molecular terms, the kinetic energy of the molecules falls as work is done, so their average speed decreases, and hence the temperature falls.

The change in internal energy of a perfect gas when the temperature is changed from  $T_i$  to  $T_f$  and the volume is changed from  $V_i$  to  $V_f$  can be expressed as the sum of two steps (Fig. 2.17). In the first step, only the volume changes and the temperature is held constant at its initial value. However, because the internal energy of a perfect gas is independent of the volume the molecules occupy, the overall change in internal energy arises solely from the second step, the change in temperature at constant volume. Provided the heat capacity is independent of temperature, this change is

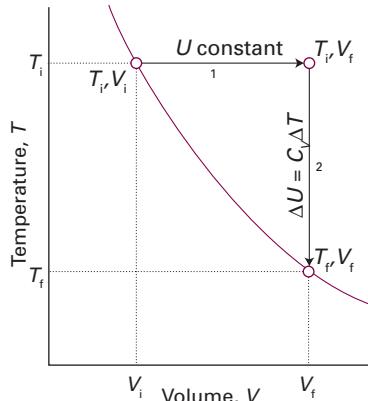
$$\Delta U = C_V(T_f - T_i) = C_V \Delta T$$

Because the expansion is adiabatic, we know that  $q = 0$ ; because  $\Delta U = q + w$ , it then follows that  $\Delta U = w_{\text{ad}}$ . The subscript 'ad' denotes an adiabatic process. Therefore, by equating the two expressions we have obtained for  $\Delta U$ , we obtain

$$w_{\text{ad}} = C_V \Delta T \quad (2.27)$$

That is, the work done during an adiabatic expansion of a perfect gas is proportional to the temperature difference between the initial and final states. That is exactly what we expect on molecular grounds, because the mean kinetic energy is proportional to  $T$ , so a change in internal energy arising from temperature alone is also expected to be proportional to  $\Delta T$ . In *Further information 2.1* we show that the initial and final temperatures of a perfect gas that undergoes reversible adiabatic expansion (reversible expansion in a thermally insulated container) can be calculated from

$$T_f = T_i \left( \frac{V_i}{V_f} \right)^{1/c} \quad (2.28a)_{\text{rev}}$$



**Fig. 2.17** To achieve a change of state from one temperature and volume to another temperature and volume, we may consider the overall change as composed of two steps. In the first step, the system expands at constant temperature; there is no change in internal energy if the system consists of a perfect gas. In the second step, the temperature of the system is reduced at constant volume. The overall change in internal energy is the sum of the changes for the two steps.

where  $c = C_{V,m}/R$ . By raising each side of this expression to the power  $c$ , an equivalent expression is

$$V_i T_i^c = V_f T_f^c \quad (2.28b)_{\text{rev}}^{\circ}$$

This result is often summarized in the form  $VT^c = \text{constant}$ .

● A brief illustration

Consider the adiabatic, reversible expansion of 0.020 mol Ar, initially at 25°C, from 0.50 dm<sup>3</sup> to 1.00 dm<sup>3</sup>. The molar heat capacity of argon at constant volume is 12.48 J K<sup>-1</sup> mol<sup>-1</sup>, so  $c = 1.501$ . Therefore, from eqn 2.28a,

$$T_f = (298 \text{ K}) \times \left( \frac{0.50 \text{ dm}^3}{1.00 \text{ dm}^3} \right)^{1/1.501} = 188 \text{ K}$$

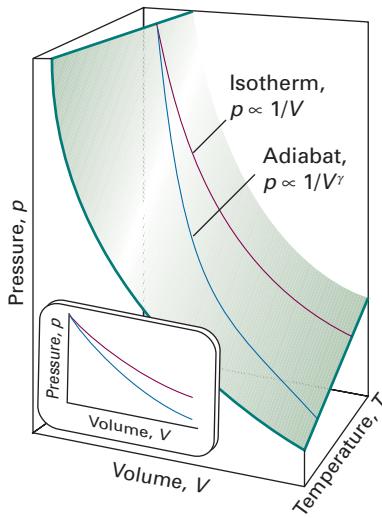
It follows that  $\Delta T = -110 \text{ K}$  and, therefore, from eqn 2.27, that

$$w = \{(0.020 \text{ mol}) \times (12.48 \text{ J K}^{-1} \text{ mol}^{-1})\} \times (-110 \text{ K}) = -27 \text{ J}$$

Note that temperature change is independent of the amount of gas but the work is not. ●

**Self-test 2.5** Calculate the final temperature, the work done, and the change of internal energy when ammonia is used in a reversible adiabatic expansion from 0.50 dm<sup>3</sup> to 2.00 dm<sup>3</sup>, the other initial conditions being the same.

[195 K, -56 J, -56 J]



**Fig. 2.18** An adiabat depicts the variation of pressure with volume when a gas expands adiabatically. Note that the pressure declines more steeply for an adiabat than it does for an isotherm because the temperature decreases in the former.

 **interActivity** Explore how the parameter  $\gamma$  affects the dependence of the pressure on the volume. Does the pressure–volume dependence become stronger or weaker with increasing volume?

We also show in *Further information 2.1* that the pressure of a perfect gas that undergoes reversible adiabatic expansion from a volume  $V_i$  to a volume  $V_f$  is related to its initial pressure by

$$p_f V_f^\gamma = p_i V_i^\gamma \quad \boxed{\text{Reversible adiabatic expansion of a perfect gas}} \quad (2.29)_{\text{rev}}^{\circ}$$

where  $\gamma = C_{p,m}/C_{V,m}$ . This result is commonly summarized in the form  $pV^\gamma = \text{constant}$ . For a monatomic perfect gas (Section 2.2a), and from eqn 2.26  $C_{p,m} = \frac{5}{2}R$ , so  $\gamma = \frac{5}{3}$ . For a gas of nonlinear polyatomic molecules (which can rotate as well as translate),  $C_{V,m} = 3R$ , so  $\gamma = \frac{4}{3}$ . The curves of pressure versus volume for adiabatic change are known as **adiabats**, and one for a reversible path is illustrated in Fig. 2.18. Because  $\gamma > 1$ , an adiabat falls more steeply ( $p \propto 1/V^\gamma$ ) than the corresponding isotherm ( $p \propto 1/V$ ). The physical reason for the difference is that, in an isothermal expansion, energy flows into the system as heat and maintains the temperature; as a result, the pressure does not fall as much as in an adiabatic expansion.

● A brief illustration

When a sample of argon (for which  $\gamma = \frac{5}{3}$ ) at 100 kPa expands reversibly and adiabatically to twice its initial volume the final pressure will be

$$p_f = \left( \frac{V_i}{V_f} \right)^\gamma p_i = \left( \frac{1}{2} \right)^{5/3} \times (100 \text{ kPa}) = 31.5 \text{ kPa}$$

For an isothermal doubling of volume, the final pressure would be 50 kPa. ●

## Thermochemistry

The study of the energy transferred as heat during the course of chemical reactions is called **thermochemistry**. Thermochemistry is a branch of thermodynamics because a reaction vessel and its contents form a system, and chemical reactions result in the exchange of energy between the system and the surroundings. Thus we can use calorimetry to measure the energy supplied or discarded as heat by a reaction, and can identify  $q$  with a change in internal energy if the reaction occurs at constant volume or with a change in enthalpy if the reaction occurs at constant pressure. Conversely, if we know  $\Delta U$  or  $\Delta H$  for a reaction, we can predict the heat the reaction can produce.

We have already remarked that a process that releases energy as heat into the surroundings is classified as exothermic and one that absorbs energy as heat from the surroundings is classified as endothermic. Because the release of heat signifies a decrease in the enthalpy of a system, we can now see that an exothermic process is one for which  $\Delta H < 0$ . Conversely, because the absorption of heat results in an increase in enthalpy, an endothermic process has  $\Delta H > 0$ :

exothermic process:  $\Delta H < 0$       endothermic process:  $\Delta H > 0$

### 2.7 Standard enthalpy changes

**Key points** (a) The standard enthalpy of transition is equal to the energy transferred as heat at constant pressure in the transition. (b) A thermochemical equation is a chemical equation and its associated change in enthalpy. (c) Hess's law states that the standard enthalpy of an overall reaction is the sum of the standard enthalpies of the individual reactions into which a reaction may be divided.

Changes in enthalpy are normally reported for processes taking place under a set of standard conditions. In most of our discussions we shall consider the **standard enthalpy change**,  $\Delta H^\circ$ , the change in enthalpy for a process in which the initial and final substances are in their standard states:

The **standard state** of a substance at a specified temperature is its pure form at 1 bar.

Specification of standard state

For example, the standard state of liquid ethanol at 298 K is pure liquid ethanol at 298 K and 1 bar; the standard state of solid iron at 500 K is pure iron at 500 K and 1 bar. The standard enthalpy change for a reaction or a physical process is the difference between the products in their standard states and the reactants in their standard states, all at the same specified temperature.

As an example of a standard enthalpy change, the *standard enthalpy of vaporization*,  $\Delta_{\text{vap}}H^\circ$ , is the enthalpy change per mole when a pure liquid at 1 bar vaporizes to a gas at 1 bar, as in



As implied by the examples, standard enthalpies may be reported for any temperature. However, the conventional temperature for reporting thermodynamic data is 298.15 K (corresponding to 25.00°C). Unless otherwise mentioned, all thermodynamic data in this text will refer to this conventional temperature.

#### (a) Enthalpies of physical change

The standard enthalpy change that accompanies a change of physical state is called the **standard enthalpy of transition** and is denoted  $\Delta_{\text{trs}}H^\circ$  (Table 2.3). The **standard**

#### A brief comment

The definition of standard state is more sophisticated for a real gas (*Further information 3.2*) and for solutions (Sections 5.10 and 5.11).

**A note on good practice** The attachment of the name of the transition to the symbol  $\Delta$ , as in  $\Delta_{\text{vap}}H$ , is the modern convention. However, the older convention,  $\Delta H_{\text{vap}}$ , is still widely used. The new convention is more logical because the subscript identifies the type of change, not the physical observable related to the change.

**Table 2.3\*** Standard enthalpies of fusion and vaporization at the transition temperature,  $\Delta_{\text{trs}}H^\ominus/(\text{kJ mol}^{-1})$ 

	$T_f/\text{K}$	Fusion	$T_b/\text{K}$	Vaporization
Ar	83.81	1.188	87.29	6.506
$\text{C}_6\text{H}_6$	278.61	10.59	353.2	30.8
$\text{H}_2\text{O}$	273.15	6.008	373.15	40.656 (44.016 at 298 K)
He	3.5	0.021	4.22	0.084

\* More values are given in the *Data section*.

**Table 2.4** Enthalpies of transition

Transition	Process	Symbol*
Transition	Phase $\alpha \rightarrow \beta$	$\Delta_{\text{trs}}H$
Fusion	$s \rightarrow l$	$\Delta_{\text{fus}}H$
Vaporization	$l \rightarrow g$	$\Delta_{\text{vap}}H$
Sublimation	$s \rightarrow g$	$\Delta_{\text{sub}}H$
Mixing	Pure $\rightarrow$ mixture	$\Delta_{\text{mix}}H$
Solution	Solute $\rightarrow$ solution	$\Delta_{\text{sol}}H$
Hydration	$X^\pm(g) \rightarrow X^\pm(aq)$	$\Delta_{\text{hyd}}H$
Atomization	Species(s, l, g) $\rightarrow$ atoms(g)	$\Delta_{\text{at}}H$
Ionization	$X(g) \rightarrow X^+(g) + e^-(g)$	$\Delta_{\text{ion}}H$
Electron gain	$X(g) + e^-(g) \rightarrow X^-(g)$	$\Delta_{\text{eg}}H$
Reaction	Reactants $\rightarrow$ products	$\Delta_rH$
Combustion	Compound(s, l, g) + $\text{O}_2(g) \rightarrow \text{CO}_2(g), \text{H}_2\text{O}(l, g)$	$\Delta_cH$
Formation	Elements $\rightarrow$ compound	$\Delta_fH$
Activation	Reactants $\rightarrow$ activated complex	$\Delta^\ddagger H$

\* IUPAC recommendations. In common usage, the transition subscript is often attached to  $\Delta H$ , as in  $\Delta H_{\text{trs}}$ .

enthalpy of vaporization,  $\Delta_{\text{vap}}H^\ominus$ , is one example. Another is the standard enthalpy of fusion,  $\Delta_{\text{fus}}H^\ominus$ , the standard enthalpy change accompanying the conversion of a solid to a liquid, as in

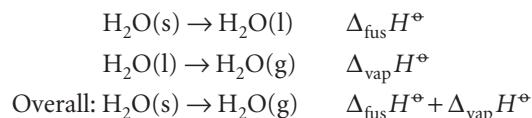


As in this case, it is sometimes convenient to know the standard enthalpy change at the transition temperature as well as at the conventional temperature of 298 K. The different types of enthalpies encountered in thermochemistry are summarized in Table 2.4. We shall meet them again in various locations throughout the text.

Because enthalpy is a state function, a change in enthalpy is independent of the path between the two states. This feature is of great importance in thermochemistry, for it implies that the same value of  $\Delta H^\ominus$  will be obtained however the change is brought about between the same initial and final states. For example, we can picture the conversion of a solid to a vapour either as occurring by sublimation (the direct conversion from solid to vapour)



or as occurring in two steps, first fusion (melting) and then vaporization of the resulting liquid:



Because the overall result of the indirect path is the same as that of the direct path, the overall enthalpy change is the same in each case (1), and we can conclude that (for processes occurring at the same temperature)

$$\Delta_{\text{sub}} H^\ominus = \Delta_{\text{fus}} H^\ominus + \Delta_{\text{vap}} H^\ominus \quad (2.30)$$

An immediate conclusion is that, because all enthalpies of fusion are positive, the enthalpy of sublimation of a substance is greater than its enthalpy of vaporization (at a given temperature).

Another consequence of  $H$  being a state function is that the standard enthalpy changes of a forward process and its reverse differ in sign (2):

$$\Delta H^\ominus(A \rightarrow B) = -\Delta H^\ominus(B \rightarrow A) \quad (2.31)$$

For instance, because the enthalpy of vaporization of water is  $+44 \text{ kJ mol}^{-1}$  at 298 K, its enthalpy of condensation at that temperature is  $-44 \text{ kJ mol}^{-1}$ .

The vaporization of a solid often involves a large increase in energy, especially when the solid is ionic and the strong Coulombic interaction of the ions must be overcome in a process such as



The **lattice enthalpy**,  $\Delta H_L$ , is the change in standard molar enthalpy for this process. The lattice enthalpy is equal to the lattice internal energy at  $T=0$ ; at normal temperatures they differ by only a few kilojoules per mole, and the difference is normally neglected.

Experimental values of the lattice enthalpy are obtained by using a **Born–Haber cycle**, a closed path of transformations starting and ending at the same point, one step of which is the formation of the solid compound from a gas of widely separated ions.

### • A brief illustration

A typical Born–Haber cycle, for potassium chloride, is shown in Fig. 2.19. It consists of the following steps (for convenience, starting at the elements):

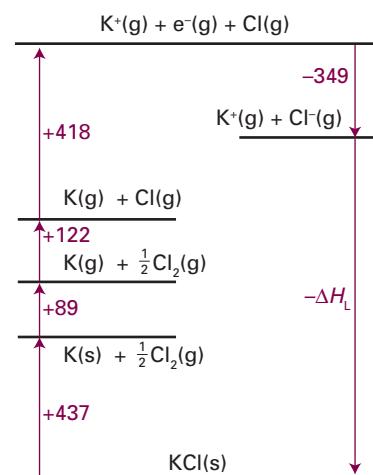
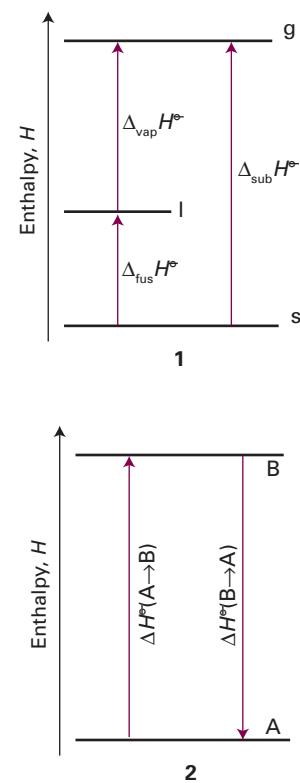
	$\Delta H^\ominus/( \text{kJ mol}^{-1})$
1. Sublimation of K(s)	+89 [dissociation enthalpy of K(s)]
2. Dissociation of $\frac{1}{2} \text{Cl}_2(g)$	+122 [ $\frac{1}{2} \times$ dissociation enthalpy of $\text{Cl}_2(g)$ ]
3. Ionization of K(g)	+418 [ionization enthalpy of K(g)]
4. Electron attachment to Cl(g)	-349 [electron gain enthalpy of Cl(g)]
5. Formation of solid from gas	$-\Delta H_L/( \text{kJ mol}^{-1})$
6. Decomposition of compound	+437 [negative of enthalpy of formation of KCl(s)]

Because the sum of these enthalpy changes is equal to zero, we can infer from

$$89 + 122 + 418 - 349 - \Delta H_L/( \text{kJ mol}^{-1}) + 437 = 0$$

that  $\Delta H_L = +717 \text{ kJ mol}^{-1}$ . •

Some lattice enthalpies obtained in the same way as in the *brief illustration* are listed in Table 2.5. They are large when the ions are highly charged and small, for then they are close together and attract each other strongly. We examine the quantitative relation between lattice enthalpy and structure in Section 19.6.



**Fig. 2.19** The Born–Haber cycle for KCl at 298 K. Enthalpy changes are in kilojoules per mole.

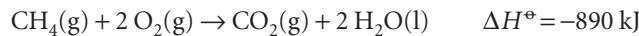
**Table 2.5\*** Lattice enthalpies at 298 K

	$\Delta H_L/(kJ\ mol^{-1})$
NaF	787
NaBr	751
MgO	3850
MgS	3406

\* More values are given in the *Data section*.

### (b) Enthalpies of chemical change

Now we consider enthalpy changes that accompany chemical reactions. There are two ways of reporting the change in enthalpy that accompanies a chemical reaction. One is to write the **thermochemical equation**, a combination of a chemical equation and the corresponding change in standard enthalpy:



$\Delta H^\circ$  is the change in enthalpy when reactants in their standard states change to products in their standard states:

Pure, separate reactants in their standard states

→ pure, separate products in their standard states

Except in the case of ionic reactions in solution, the enthalpy changes accompanying mixing and separation are insignificant in comparison with the contribution from the reaction itself. For the combustion of methane, the standard value refers to the reaction in which 1 mol  $\text{CH}_4$  in the form of pure methane gas at 1 bar reacts completely with 2 mol  $\text{O}_2$  in the form of pure oxygen gas at 1 bar to produce 1 mol  $\text{CO}_2$  as pure carbon dioxide gas at 1 bar and 2 mol  $\text{H}_2\text{O}$  as pure liquid water at 1 bar; the numerical value is for the reaction at 298.15 K.

Alternatively, we write the chemical equation and then report the **standard reaction enthalpy**,  $\Delta_r H^\circ$  (or ‘standard enthalpy of reaction’). Thus, for the combustion of methane, we write



For a reaction of the form  $2 \text{A} + \text{B} \rightarrow 3 \text{C} + \text{D}$  the standard reaction enthalpy would be

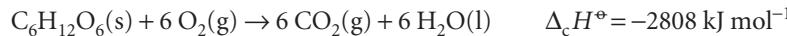
$$\Delta_r H^\circ = \{3H_m^\circ(\text{C}) + H_m^\circ(\text{D})\} - \{2H_m^\circ(\text{A}) + H_m^\circ(\text{B})\}$$

where  $H_m^\circ(J)$  is the standard molar enthalpy of species J at the temperature of interest. Note how the ‘per mole’ of  $\Delta_r H^\circ$  comes directly from the fact that molar enthalpies appear in this expression. We interpret the ‘per mole’ by noting the stoichiometric coefficients in the chemical equation. In this case ‘per mole’ in  $\Delta_r H^\circ$  means ‘per 2 mol A’, ‘per mole B’, ‘per 3 mol C’, or ‘per mol D’. In general,

$$\Delta_r H^\circ = \sum_{\text{Products}} vH_m^\circ - \sum_{\text{Reactants}} vH_m^\circ \quad \boxed{\begin{array}{l} \text{Definition of standard} \\ \text{reaction enthalpy} \end{array}} \quad [2.32]$$

where in each case the molar enthalpies of the species are multiplied by their (dimensionless and positive) stoichiometric coefficients,  $v$ .

Some standard reaction enthalpies have special names and a particular significance. For instance, the **standard enthalpy of combustion**,  $\Delta_c H^\circ$ , is the standard reaction enthalpy for the complete oxidation of an organic compound to  $\text{CO}_2$  gas and liquid  $\text{H}_2\text{O}$  if the compound contains C, H, and O, and to  $\text{N}_2$  gas if N is also present. An example is the combustion of glucose:



The value quoted shows that 2808 kJ of heat is released when 1 mol  $\text{C}_6\text{H}_{12}\text{O}_6$  burns under standard conditions (at 298 K). More values are given in Table 2.6.

### (c) Hess's law

Standard enthalpies of individual reactions can be combined to obtain the enthalpy of another reaction. This application of the First Law is called **Hess's law**:

**Table 2.6\*** Standard enthalpies of formation and combustion of organic compounds at 298 K

	$\Delta_f H^\ominus/(kJ\ mol^{-1})$	$\Delta_c H^\ominus/(kJ\ mol^{-1})$
Benzene, C <sub>6</sub> H <sub>6</sub> (l)	+49.0	-3268
Ethane, C <sub>2</sub> H <sub>6</sub> (g)	-84.7	-1560
Glucose, C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> (s)	-1274	-2808
Methane, CH <sub>4</sub> (g)	-74.8	-890
Methanol, CH <sub>3</sub> OH(l)	-238.7	-726

\* More values are given in the *Data section*.

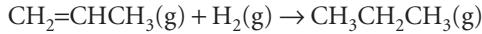
The standard enthalpy of an overall reaction is the sum of the standard enthalpies of the individual reactions into which a reaction may be divided.

Hess's law

The individual steps need not be realizable in practice: they may be hypothetical reactions, the only requirement being that their chemical equations should balance. The thermodynamic basis of the law is the path-independence of the value of  $\Delta_r H^\ominus$  and the implication that we may take the specified reactants, pass through any (possibly hypothetical) set of reactions to the specified products, and overall obtain the same change of enthalpy. The importance of Hess's law is that information about a reaction of interest, which may be difficult to determine directly, can be assembled from information on other reactions.

### Example 2.5 Using Hess's law

The standard reaction enthalpy for the hydrogenation of propene



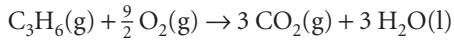
is  $-124\text{ kJ mol}^{-1}$ . The standard reaction enthalpy for the combustion of propane



is  $-2220\text{ kJ mol}^{-1}$ . Calculate the standard enthalpy of combustion of propene.

**Method** The skill to develop is the ability to assemble a given thermochemical equation from others. Add or subtract the reactions given, together with any others needed, so as to reproduce the reaction required. Then add or subtract the reaction enthalpies in the same way. Additional data are in Table 2.6.

**Answer** The combustion reaction we require is



This reaction can be recreated from the following sum:

	$\Delta_r H^\ominus/(kJ\ mol^{-1})$
C <sub>3</sub> H <sub>6</sub> (g) + H <sub>2</sub> (g) → C <sub>3</sub> H <sub>8</sub> (g)	-124
C <sub>3</sub> H <sub>8</sub> (g) + 5 O <sub>2</sub> (g) → 3 CO <sub>2</sub> (g) + 4 H <sub>2</sub> O(l)	-2220
H <sub>2</sub> O(l) → H <sub>2</sub> (g) + $\frac{1}{2}$ O <sub>2</sub> (g)	+286
C <sub>3</sub> H <sub>6</sub> (g) + $\frac{9}{2}$ O <sub>2</sub> (g) → 3 CO <sub>2</sub> (g) + 3 H <sub>2</sub> O(l)	-2058

**Self-test 2.6** Calculate the enthalpy of hydrogenation of benzene from its enthalpy of combustion and the enthalpy of combustion of cyclohexane. [-205 kJ mol<sup>-1</sup>]

**Table 2.7** Thermochemical properties of some fuels

Fuel	Combustion equation	$\Delta_c H^\circ/(\text{kJ mol}^{-1})$	Specific enthalpy/(\text{kJ g}^{-1})	Enthalpy density/(\text{kJ dm}^{-3})
Hydrogen	$\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$	-286	142	13
Methane	$\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	-890	55	40
Octane	$\text{C}_8\text{H}_{18}(\text{l}) + \frac{25}{2}\text{O}_2(\text{g}) \rightarrow 8\text{CO}_2(\text{g}) + 9\text{H}_2\text{O}(\text{l})$	-5471	48	$3.8 \times 10^4$
Methanol	$\text{CH}_3\text{OH}(\text{l}) + \frac{3}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	-726	23	$1.8 \times 10^4$

**IMPACT ON BIOLOGY****I2.2 Food and energy reserves**

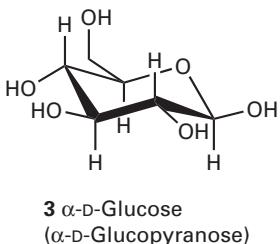
The thermochemical properties of fuels and foods are commonly discussed in terms of their *specific enthalpy*, the enthalpy of combustion per gram of material. Thus, if the standard enthalpy of combustion is  $\Delta_c H^\circ$  and the molar mass of the compound is  $M$ , then the specific enthalpy is  $\Delta_c H^\circ/M$ . Table 2.7 lists the specific enthalpies of several fuels.

A typical 18–20 year old man requires a daily input of about 12 MJ; a woman of the same age needs about 9 MJ. If the entire consumption were in the form of glucose (3; which has a specific enthalpy of 16 kJ g<sup>-1</sup>), that would require the consumption of 750 g of glucose for a man and 560 g for a woman. In fact, digestible carbohydrates have a slightly higher specific enthalpy (17 kJ g<sup>-1</sup>) than glucose itself, so a carbohydrate diet is slightly less daunting than a pure glucose diet, as well as being more appropriate in the form of fibre, the indigestible cellulose that helps move digestion products through the intestine.

Fats are long-chain esters like tristearin (beef fat). The enthalpy of combustion of a fat at around 38 kJ g<sup>-1</sup> is much greater than that of carbohydrates and only slightly less than that of the hydrocarbon oils used as fuel (48 kJ g<sup>-1</sup>). Fats are commonly used as an energy store, to be used only when the more readily accessible carbohydrates have fallen into short supply. In Arctic species, the stored fat also acts as a layer of insulation; in desert species (such as the camel), the fat is also a source of water, one of its oxidation products.

Proteins are also used as a source of energy, but their components, the amino acids, are often too valuable to squander in this way, and are used to construct other proteins instead. When proteins are oxidized (to urea,  $\text{CO}(\text{NH}_2)_2$ ), the equivalent enthalpy density is comparable to that of carbohydrates.

The heat released by the oxidation of foods needs to be discarded in order to maintain body temperature within its typical range of 35.6–37.8°C. A variety of mechanisms contribute to this aspect of homeostasis, the ability of an organism to counteract environmental changes with physiological responses. The general uniformity of temperature throughout the body is maintained largely by the flow of blood. When heat needs to be dissipated rapidly, warm blood is allowed to flow through the capillaries of the skin, so producing flushing. Radiation is one means of discarding heat; another is evaporation and the energy demands of the enthalpy of vaporization of water. Evaporation removes about 2.4 kJ per gram of water perspired. When vigorous exercise promotes sweating (through the influence of heat selectors on the hypothalamus), 1–2 dm<sup>3</sup> of perspired water can be produced per hour, corresponding to a heat loss of 2.4–5.0 MJ h<sup>-1</sup>.



## 2.8 Standard enthalpies of formation

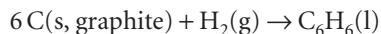
**Key points** Standard enthalpies of formation are defined in terms of the reference states of elements. (a) The standard reaction enthalpy is expressed as the difference of the standard enthalpies of formation of products and reactants. (b) Computer modelling is used to estimate standard enthalpies of formation.

The standard enthalpy of formation,  $\Delta_f H^\circ$ , of a substance is the standard reaction enthalpy for the formation of the compound from its elements in their reference states:

The reference state of an element is its most stable state at the specified temperature and 1 bar.

Specification of reference state

For example, at 298 K the reference state of nitrogen is a gas of  $N_2$  molecules, that of mercury is liquid mercury, that of carbon is graphite, and that of tin is the white (metallic) form. There is one exception to this general prescription of reference states: the reference state of phosphorus is taken to be white phosphorus despite this allotrope not being the most stable form but simply the more reproducible form of the element. Standard enthalpies of formation are expressed as enthalpies per mole of molecules or (for ionic substances) formula units of the compound. The standard enthalpy of formation of liquid benzene at 298 K, for example, refers to the reaction



and is  $+49.0 \text{ kJ mol}^{-1}$ . The standard enthalpies of formation of elements in their reference states are zero at all temperatures because they are the enthalpies of such ‘null’ reactions as  $\text{N}_2\text{(g)} \rightarrow \text{N}_2\text{(g)}$ . Some enthalpies of formation are listed in Tables 2.6 and 2.8.

The standard enthalpy of formation of ions in solution poses a special problem because it is impossible to prepare a solution of cations alone or of anions alone. This problem is solved by defining one ion, conventionally the hydrogen ion, to have zero standard enthalpy of formation at all temperatures:

$$\Delta_f H^\circ(\text{H}^+, \text{aq}) = 0$$

Convention for ions in solution [2.33]

Thus, if the enthalpy of formation of  $\text{HBr}(\text{aq})$  is found to be  $-122 \text{ kJ mol}^{-1}$ , then the whole of that value is ascribed to the formation of  $\text{Br}^-(\text{aq})$ , and we write  $\Delta_f H^\circ(\text{Br}^-, \text{aq}) = -122 \text{ kJ mol}^{-1}$ . That value may then be combined with, for instance, the enthalpy formation of  $\text{AgBr}(\text{aq})$  to determine the value of  $\Delta_f H^\circ(\text{Ag}^+, \text{aq})$ , and so on. In essence, this definition adjusts the actual values of the enthalpies of formation of ions by a fixed amount, which is chosen so that the standard value for one of them,  $\text{H}^+(\text{aq})$ , has the value zero.

### (a) The reaction enthalpy in terms of enthalpies of formation

Conceptually, we can regard a reaction as proceeding by decomposing the reactants into their elements and then forming those elements into the products. The value of  $\Delta_r H^\circ$  for the overall reaction is the sum of these ‘unforming’ and forming enthalpies. Because ‘unforming’ is the reverse of forming, the enthalpy of an unforming step is the negative of the enthalpy of formation (4). Hence, in the enthalpies of formation of substances, we have enough information to calculate the enthalpy of any reaction by using

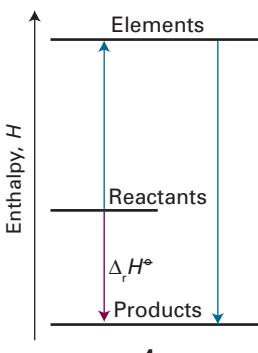
$$\Delta_r H^\circ = \sum_{\text{Products}} v\Delta_f H^\circ - \sum_{\text{Reactants}} v\Delta_f H^\circ$$

Procedure for calculating standard reaction enthalpy [2.34a]

**Table 2.8\*** Standard enthalpies of formation of inorganic compounds at 298 K

	$\Delta_f H^\circ / (\text{kJ mol}^{-1})$
$\text{H}_2\text{O(l)}$	-285.83
$\text{H}_2\text{O(g)}$	-241.82
$\text{NH}_3\text{(g)}$	-46.11
$\text{N}_2\text{H}_4\text{(l)}$	+50.63
$\text{NO}_2\text{(g)}$	+33.18
$\text{N}_2\text{O}_4\text{(g)}$	+9.16
$\text{NaCl(s)}$	-411.15
$\text{KCl(s)}$	-436.75

\* More values are given in the Data section.



**A brief comment**

Stoichiometric *numbers*, which have a sign, are denoted  $v_j$  or  $v(J)$ . Stoichiometric *coefficients*, which are all positive, are denoted simply  $v$  (with no subscript).

where in each case the enthalpies of formation of the species that occur are multiplied by their stoichiometric coefficients. A more sophisticated way of expressing the same result is to introduce the stoichiometric numbers  $v_j$  (as distinct from the stoichiometric coefficients) which are positive for products and negative for reactants. Then we can write

$$\Delta_r H^\ominus = \sum_j v_j \Delta_f H^\ominus (J) \quad (2.34b)$$

● **A brief illustration**

According to eqn 2.34a, the standard enthalpy of the reaction  $2 \text{HN}_3(\text{l}) + 2 \text{NO}(\text{g}) \rightarrow \text{H}_2\text{O}_2(\text{l}) + 4 \text{N}_2(\text{g})$  is calculated as follows:

$$\begin{aligned}\Delta_r H^\ominus &= \{\Delta_f H^\ominus (\text{H}_2\text{O}_2, \text{l}) + 4\Delta_f H^\ominus (\text{N}_2, \text{g})\} - \{2\Delta_f H^\ominus (\text{HN}_3, \text{l}) + 2\Delta_f H^\ominus (\text{NO}, \text{g})\} \\ &= \{-187.78 + 4(0)\} \text{ kJ mol}^{-1} - \{2(264.0) + 2(90.25)\} \text{ kJ mol}^{-1} \\ &= -896.3 \text{ kJ mol}^{-1}\end{aligned}$$

To use eqn 2.34b we identify  $v(\text{HN}_3) = -2$ ,  $v(\text{NO}) = -2$ ,  $v(\text{H}_2\text{O}_2) = +1$ , and  $v(\text{N}_2) = +4$ , and then write

$$\Delta_r H^\ominus = -2\Delta_f H^\ominus (\text{HN}_3, \text{l}) - 2\Delta_f H^\ominus (\text{NO}, \text{g}) + \Delta_f H^\ominus (\text{H}_2\text{O}_2, \text{l}) + 4\Delta_f H^\ominus (\text{N}_2, \text{g})$$

which gives the same result. ●

**(b) Enthalpies of formation and molecular modelling**

We have seen how to construct standard reaction enthalpies by combining standard enthalpies of formation. The question that now arises is whether we can construct standard enthalpies of formation from a knowledge of the chemical constitution of the species. The short answer is that there is no thermodynamically exact way of expressing enthalpies of formation in terms of contributions from individual atoms and bonds. In the past, approximate procedures based on **mean bond enthalpies**,  $\Delta H(A-B)$ , the average enthalpy change associated with the breaking of a specific A–B bond,



have been used. However, this procedure is notoriously unreliable, in part because the  $\Delta H(\text{A-B})$  are average values for a series of related compounds. Nor does the approach distinguish between geometrical isomers, where the same atoms and bonds may be present but experimentally the enthalpies of formation might be significantly different.

Computer-aided molecular modelling has largely displaced this more primitive approach. Commercial software packages use the principles developed in Chapter 10 to calculate the standard enthalpy of formation of a molecule drawn on the computer screen. These techniques can be applied to different conformations of the same molecule. In the case of methylcyclohexane, for instance, the calculated conformational energy difference ranges from 5.9 to 7.9 kJ mol<sup>-1</sup>, with the equatorial conformer having the lower standard enthalpy of formation. These estimates compare favourably with the experimental value of 7.5 kJ mol<sup>-1</sup>. However, good agreement between calculated and experimental values is relatively rare. Computational methods almost always predict correctly which conformer is more stable but do not always predict the correct magnitude of the conformational energy difference. The most reliable technique for the determination of enthalpies of formation remains calorimetry, typically by using enthalpies of combustion.

## 2.9 The temperature dependence of reaction enthalpies

**Key point** The temperature dependence of a reaction enthalpy is expressed by Kirchhoff's law.

The standard enthalpies of many important reactions have been measured at different temperatures. However, in the absence of this information, standard reaction enthalpies at different temperatures may be calculated from heat capacities and the reaction enthalpy at some other temperature (Fig. 2.20). In many cases heat capacity data are more accurate than reaction enthalpies. Therefore, providing the information is available, the procedure we are about to describe is more accurate than the direct measurement of a reaction enthalpy at an elevated temperature.

It follows from eqn 2.23a that, when a substance is heated from  $T_1$  to  $T_2$ , its enthalpy changes from  $H(T_1)$  to

$$H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p dT \quad (2.35)$$

(We have assumed that no phase transition takes place in the temperature range of interest.) Because this equation applies to each substance in the reaction, the standard reaction enthalpy changes from  $\Delta_r H^\circ(T_1)$  to

$$\Delta_r H^\circ(T_2) = \Delta_r H^\circ(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^\circ dT \quad \boxed{\text{Kirchhoff's law}} \quad (2.36a)$$

where  $\Delta_r C_p^\circ$  is the difference of the molar heat capacities of products and reactants under standard conditions weighted by the stoichiometric coefficients that appear in the chemical equation:

$$\Delta_r C_p^\circ = \sum_{\text{Products}} v C_{p,m}^\circ - \sum_{\text{Reactants}} v C_{p,m}^\circ \quad (2.36b)$$

Equation 2.36a is known as Kirchhoff's law. It is normally a good approximation to assume that  $\Delta_r C_p^\circ$  is independent of the temperature, at least over reasonably limited ranges. Although the individual heat capacities may vary, their difference varies less significantly. In some cases the temperature dependence of heat capacities is taken into account by using eqn 2.25.

### Example 2.6 Using Kirchhoff's law

The standard enthalpy of formation of  $\text{H}_2\text{O(g)}$  at 298 K is  $-241.82 \text{ kJ mol}^{-1}$ . Estimate its value at 100°C given the following values of the molar heat capacities at constant pressure:  $\text{H}_2\text{O(g)}$ :  $33.58 \text{ J K}^{-1} \text{ mol}^{-1}$ ;  $\text{H}_2\text{g}$ :  $28.82 \text{ J K}^{-1} \text{ mol}^{-1}$ ;  $\text{O}_2\text{g}$ :  $29.36 \text{ J K}^{-1} \text{ mol}^{-1}$ . Assume that the heat capacities are independent of temperature.

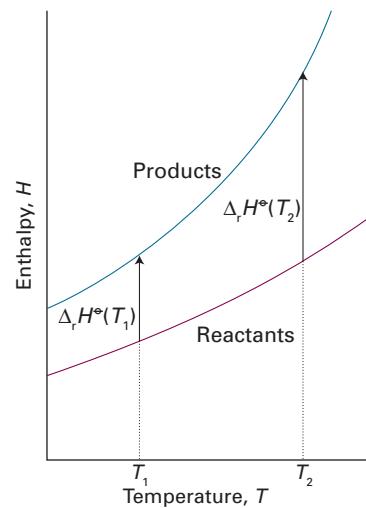
**Method** When  $\Delta C_p^\circ$  is independent of temperature in the range  $T_1$  to  $T_2$ , the integral in eqn 2.36a evaluates to  $(T_2 - T_1)\Delta_r C_p^\circ$ . Therefore,

$$\Delta_r H^\circ(T_2) = \Delta_r H^\circ(T_1) + (T_2 - T_1)\Delta_r C_p^\circ$$

To proceed, write the chemical equation, identify the stoichiometric coefficients, and calculate  $\Delta_r C_p^\circ$  from the data.

**Answer** The reaction is  $\text{H}_2\text{g} + \frac{1}{2}\text{O}_2\text{g} \rightarrow \text{H}_2\text{O(g)}$ , so

$$\Delta_r C_p^\circ = C_{p,m}^\circ(\text{H}_2\text{O,g}) - \{C_{p,m}^\circ(\text{H}_2\text{g}) + \frac{1}{2}C_{p,m}^\circ(\text{O}_2\text{g})\} = -9.92 \text{ J K}^{-1} \text{ mol}^{-1}$$



**Fig. 2.20** An illustration of the content of Kirchhoff's law. When the temperature is increased, the enthalpy of the products and the reactants both increase, but may do so to different extents. In each case, the change in enthalpy depends on the heat capacities of the substances. The change in reaction enthalpy reflects the difference in the changes of the enthalpies.

It then follows that

$$\Delta_f H^\circ(373 \text{ K}) = -241.82 \text{ kJ mol}^{-1} + (75 \text{ K}) \times (-9.92 \text{ J K}^{-1} \text{ mol}^{-1}) = -242.6 \text{ kJ mol}^{-1}$$

**Self-test 2.7** Estimate the standard enthalpy of formation of cyclohexane,  $C_6H_{12}(l)$ , at 400 K from the data in Table 2.6. [−163 kJ mol<sup>−1</sup>]

## State functions and exact differentials

We saw in Section 2.2 that a state function is a property that depends only on the current state of a system and is independent of its history. The internal energy and enthalpy are two examples of state functions. Physical quantities that do depend on the path between two states are called **path functions**. Examples of path functions are the work and the heating that are done when preparing a state. We do not speak of a system in a particular state as possessing work or heat. In each case, the energy transferred as work or heat relates to the path being taken between states, not the current state itself.

A part of the richness of thermodynamics is that it uses the mathematical properties of state functions to draw far-reaching conclusions about the relations between physical properties and thereby establish connections that may be completely unexpected. The practical importance of this ability is that we can combine measurements of different properties to obtain the value of a property we require.

### 2.10 Exact and inexact differentials

**Key points** The quantity  $dU$  is an exact differential;  $dw$  and  $dq$  are not.

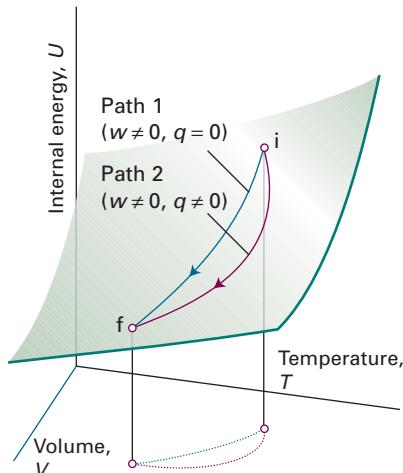
Consider a system undergoing the changes depicted in Fig. 2.21. The initial state of the system is  $i$  and in this state the internal energy is  $U_i$ . Work is done by the system as it expands adiabatically to a state  $f$ . In this state the system has an internal energy  $U_f$  and the work done on the system as it changes along Path 1 from  $i$  to  $f$  is  $w$ . Notice our use of language:  $U$  is a property of the state;  $w$  is a property of the path. Now consider another process, Path 2, in which the initial and final states are the same as those in Path 1 but in which the expansion is not adiabatic. The internal energy of both the initial and the final states are the same as before (because  $U$  is a state function). However, in the second path an energy  $q'$  enters the system as heat and the work  $w'$  is not the same as  $w$ . The work and the heat are path functions.

If a system is taken along a path (for example, by heating it),  $U$  changes from  $U_i$  to  $U_f$ , and the overall change is the sum (integral) of all the infinitesimal changes along the path:

$$\Delta U = \int_i^f dU \quad (2.37)$$

The value of  $\Delta U$  depends on the initial and final states of the system but is independent of the path between them. This path independence of the integral is expressed by saying that  $dU$  is an ‘exact differential’. In general, an **exact differential** is an infinitesimal quantity that, when integrated, gives a result that is independent of the path between the initial and final states.

When a system is heated, the total energy transferred as heat is the sum of all individual contributions at each point of the path:



**Fig. 2.21** As the volume and temperature of a system are changed, the internal energy changes. An adiabatic and a non-adiabatic path are shown as Path 1 and Path 2, respectively: they correspond to different values of  $q$  and  $w$  but to the same value of  $\Delta U$ .

$$q = \int_{i, \text{path}}^f dq \quad (2.38)$$

Notice the differences between this equation and eqn 2.37. First, we do not write  $\Delta q$ , because  $q$  is not a state function and the energy supplied as heat cannot be expressed as  $q_f - q_i$ . Secondly, we must specify the path of integration because  $q$  depends on the path selected (for example, an adiabatic path has  $q = 0$ , whereas a non-adiabatic path between the same two states would have  $q \neq 0$ ). This path-dependence is expressed by saying that  $dq$  is an ‘inexact differential’. In general, an **inexact differential** is an infinitesimal quantity that, when integrated, gives a result that depends on the path between the initial and final states. Often  $dq$  is written  $dq$  to emphasize that it is inexact and requires the specification of a path.

The work done on a system to change it from one state to another depends on the path taken between the two specified states; for example, in general the work is different if the change takes place adiabatically and non-adiabatically. It follows that  $dw$  is an inexact differential. It is often written  $dw$ .

#### **Example 2.7** Calculating work, heat, and change in internal energy

Consider a perfect gas inside a cylinder fitted with a piston. Let the initial state be  $T, V_i$  and the final state be  $T, V_f$ . The change of state can be brought about in many ways, of which the two simplest are the following: Path 1, in which there is free expansion against zero external pressure; Path 2, in which there is reversible, isothermal expansion. Calculate  $w$ ,  $q$ , and  $\Delta U$  for each process.

**Method** To find a starting point for a calculation in thermodynamics, it is often a good idea to go back to first principles and to look for a way of expressing the quantity we are asked to calculate in terms of other quantities that are easier to calculate. We saw in Section 2.2a that the internal energy of a perfect gas depends only on the temperature and is independent of the volume those molecules occupy, so for any isothermal change,  $\Delta U = 0$ . We also know that in general  $\Delta U = q + w$ . The question depends on being able to combine the two expressions. We have already derived a number of expressions for the work done in a variety of processes, and here we need to select the appropriate ones.

**Answer** Because  $\Delta U = 0$  for both paths and  $\Delta U = q + w$ , in each case  $q = -w$ . The work of free expansion is zero (Section 2.3b), so in Path 1,  $w = 0$  and therefore  $q = 0$  too. For Path 2, the work is given by eqn 2.10, so  $w = -nRT \ln(V_f/V_i)$  and consequently  $q = nRT \ln(V_f/V_i)$ .

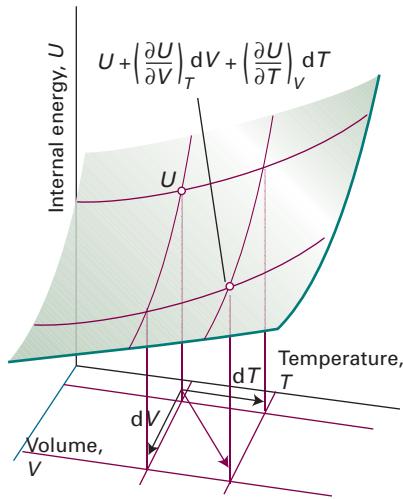
#### **Self-test 2.8** Calculate the values of $q$ , $w$ , and $\Delta U$ for an irreversible isothermal expansion of a perfect gas against a constant non-zero external pressure.

$$[q = p_{\text{ex}} \Delta V, w = -p_{\text{ex}} \Delta V, \Delta U = 0]$$

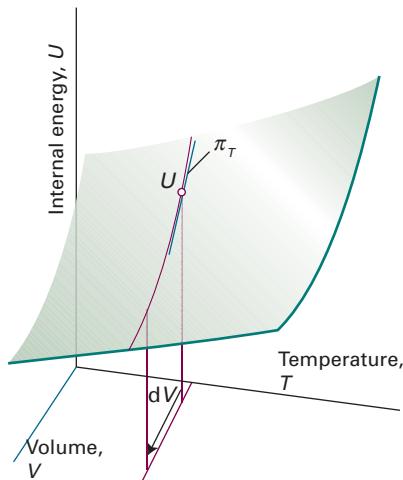
## 2.11 Changes in internal energy

**Keypoints** (a) The change in internal energy may be expressed in terms of changes in temperature and volume. The internal pressure is the variation of internal energy with volume at constant temperature. (b) Joule’s experiment showed that the internal pressure of a perfect gas is zero. (c) The change in internal energy with volume and temperature is expressed in terms of the internal pressure and the heat capacity and leads to a general expression for the relation between heat capacities.

We begin to unfold the consequences of  $dU$  being an exact differential by exploring a closed system of constant composition (the only type of system considered in the rest of this chapter). The internal energy  $U$  can be regarded as a function of  $V$ ,  $T$ , and  $p$ , but, because there is an equation of state, stating the values of two of the variables fixes the value of the third. Therefore, it is possible to write  $U$  in terms of just two independent variables:  $V$  and  $T$ ,  $p$  and  $T$ , or  $p$  and  $V$ . Expressing  $U$  as a function of volume and temperature fits the purpose of our discussion.



**Fig. 2.22** An overall change in  $U$ , which is denoted  $dU$ , arises when both  $V$  and  $T$  are allowed to change. If second-order infinitesimals are ignored, the overall change is the sum of changes for each variable separately.



**Fig. 2.23** The internal pressure,  $\pi_T$ , is the slope of  $U$  with respect to  $V$  with the temperature  $T$  held constant.

### (a) General considerations

Because the internal energy is a function of the volume and the temperature, when these two quantities change, the internal energy changes by

$$dU = \left( \frac{\partial U}{\partial V} \right)_T dV + \left( \frac{\partial U}{\partial T} \right)_V dT \quad [2.39]$$

General expression  
for a change in  $U$   
with  $T$  and  $V$

The interpretation of this equation is that, in a closed system of constant composition, any infinitesimal change in the internal energy is proportional to the infinitesimal changes of volume and temperature, the coefficients of proportionality being the two partial derivatives (Fig. 2.22).

In many cases partial derivatives have a straightforward physical interpretation, and thermodynamics gets shapeless and difficult only when that interpretation is not kept in sight. In the present case, we have already met  $(\partial U / \partial T)_V$  in eqn 2.15, where we saw that it is the constant-volume heat capacity,  $C_V$ . The other coefficient,  $(\partial U / \partial V)_T$ , plays a major role in thermodynamics because it is a measure of the variation of the internal energy of a substance as its volume is changed at constant temperature (Fig. 2.23). We shall denote it  $\pi_T$  and, because it has the same dimensions as pressure but arises from the interactions between the molecules within the sample, call it the **internal pressure**:

$$\pi_T = \left( \frac{\partial U}{\partial V} \right)_T \quad [2.40]$$

Definition of  
internal pressure

In terms of the notation  $C_V$  and  $\pi_T$ , eqn 2.39 can now be written

$$dU = \pi_T dV + C_V dT \quad [2.41]$$

### (b) The Joule experiment

When there are no interactions between the molecules, the internal energy is independent of their separation and hence independent of the volume of the sample (Section 2.2a). Therefore, for a perfect gas we can write  $\pi_T = 0$ . The statement  $\pi_T = 0$  (that is, the internal energy is independent of the volume occupied by the sample) can be taken to be the definition of a perfect gas, for later we shall see that it implies the equation of state  $pV \propto T$ . If the attractive forces between the particles dominate the repulsive forces, then the internal energy increases ( $dU > 0$ ) as the volume of the sample increases ( $dV > 0$ ) and the molecules attract each other less strongly; in this case a plot of internal energy against volume slopes upwards and  $\pi_T > 0$  (Fig. 2.24).

James Joule thought that he could measure  $\pi_T$  by observing the change in temperature of a gas when it is allowed to expand into a vacuum. He used two metal vessels immersed in a water bath (Fig. 2.25). One was filled with air at about 22 atm and the

other was evacuated. He then tried to measure the change in temperature of the water of the bath when a stopcock was opened and the air expanded into a vacuum. He observed no change in temperature.

The thermodynamic implications of the experiment are as follows. No work was done in the expansion into a vacuum, so  $w = 0$ . No energy entered or left the system (the gas) as heat because the temperature of the bath did not change, so  $q = 0$ . Consequently, within the accuracy of the experiment,  $\Delta U = 0$ . Joule concluded that  $U$  does not change when a gas expands isothermally and therefore that  $\pi_T = 0$ . His experiment, however, was crude. In particular, the heat capacity of the apparatus was so large that the temperature change that gases do in fact cause was too small to measure. Nevertheless, from his experiment Joule had extracted an essential limiting property of a gas, a property of a perfect gas, without detecting the small deviations characteristic of real gases.

### (c) Changes in internal energy at constant pressure

Partial derivatives have many useful properties and some that we shall draw on frequently are reviewed in *Mathematical background 2*. Skilful use of them can often turn some unfamiliar quantity into a quantity that can be recognized, interpreted, or measured.

As an example, suppose we want to find out how the internal energy varies with temperature when the pressure rather than the volume of the system is kept constant. If we divide both sides of eqn 2.41 ( $dU = \pi_T dV + C_V dT$ ) by  $dT$  and impose the condition of constant pressure on the resulting differentials, so that  $dU/dT$  on the left becomes  $(\partial U/\partial T)_p$ , we obtain

$$\left(\frac{\partial U}{\partial T}\right)_p = \pi_T \left(\frac{\partial V}{\partial T}\right)_p + C_V$$

It is usually sensible in thermodynamics to inspect the output of a manipulation like this to see if it contains any recognizable physical quantity. The partial derivative on the right in this expression is the slope of the plot of volume against temperature (at constant pressure). This property is normally tabulated as the **expansion coefficient**,  $\alpha$ , of a substance, which is defined as

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p$$

Definition of the  
expansion coefficient

[2.42]

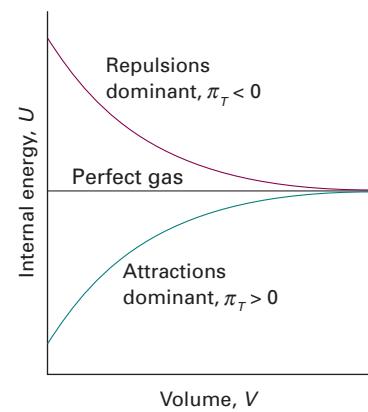
and physically is the fractional change in volume that accompanies a rise in temperature. A large value of  $\alpha$  means that the volume of the sample responds strongly to changes in temperature. Table 2.9 lists some experimental values of  $\alpha$ . For future reference, it also lists the **isothermal compressibility**,  $\kappa_T$  (kappa), which is defined as

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T$$

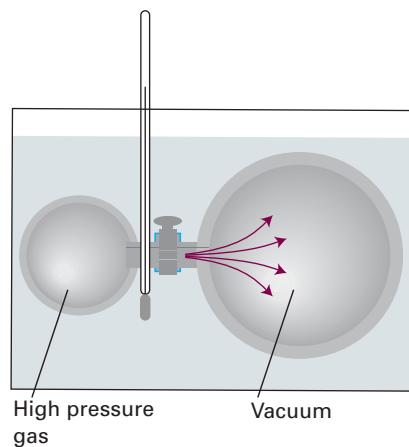
Definition of the  
isothermal compressibility

[2.43]

The isothermal compressibility is a measure of the fractional change in volume when the pressure is increased by a small amount; the negative sign in the definition ensures that the compressibility is a positive quantity, because an increase of pressure, implying a positive  $dp$ , brings about a reduction of volume, a negative  $dV$ .



**Fig. 2.24** For a perfect gas, the internal energy is independent of the volume (at constant temperature). If attractions are dominant in a real gas, the internal energy increases with volume because the molecules become farther apart on average. If repulsions are dominant, the internal energy decreases as the gas expands.



**Fig. 2.25** A schematic diagram of the apparatus used by Joule in an attempt to measure the change in internal energy when a gas expands isothermally. The heat absorbed by the gas is proportional to the change in temperature of the bath.

**Table 2.9\*** Expansion coefficients ( $\alpha$ ) and isothermal compressibilities ( $\kappa_T$ ) at 298 K

	$\alpha/(10^{-4} \text{ K}^{-1})$	$\kappa_T/(10^{-6} \text{ bar}^{-1})$
Benzene	12.4	90.9
Diamond	0.030	0.185
Lead	0.861	2.18
Water	2.1	49.0

\* More values are given in the *Data section*.

### Example 2.8 Calculating the expansion coefficient of a gas

Derive an expression for the expansion coefficient of a perfect gas.

**Method** The expansion coefficient is defined in eqn 2.42. To use this expression, substitute the expression for  $V$  in terms of  $T$  obtained from the equation of state for the gas. As implied by the subscript in eqn 2.42, the pressure,  $p$ , is treated as a constant.

**Answer** Because  $pV = nRT$ , we can write

$$\alpha = \frac{1}{V} \left( \frac{\partial(nRT/p)}{\partial T} \right)_p = \frac{1}{V} \times \frac{nR}{p} \frac{dT}{dT} = \frac{nR}{pV} = \frac{1}{T}$$

The higher the temperature, the less responsive is the volume of a perfect gas to a change in temperature.

**Self-test 2.9** Derive an expression for the isothermal compressibility of a perfect gas.  $[\kappa_T = 1/p]$

When we introduce the definition of  $\alpha$  into the equation for  $(\partial U/\partial T)_p$ , we obtain

$$\left( \frac{\partial U}{\partial T} \right)_p = \alpha \pi_T V + C_V \quad (2.44)$$

This equation is entirely general (provided the system is closed and its composition is constant). It expresses the dependence of the internal energy on the temperature at constant pressure in terms of  $C_V$ , which can be measured in one experiment, in terms of  $\alpha$ , which can be measured in another, and in terms of the quantity  $\pi_T$ . For a perfect gas,  $\pi_T = 0$ , so then

$$\left( \frac{\partial U}{\partial T} \right)_p = C_V \quad (2.45)^\circ$$

That is, although the constant-volume heat capacity of a perfect gas is defined as the slope of a plot of internal energy against temperature at constant volume, for a perfect gas  $C_V$  is also the slope at constant pressure.

Equation 2.45 provides an easy way to derive the relation between  $C_p$  and  $C_V$  for a perfect gas. Thus, we can use it to express both heat capacities in terms of derivatives at constant pressure:

$$C_p - C_V = \left( \frac{\partial H}{\partial T} \right)_p - \left( \frac{\partial U}{\partial T} \right)_V = \left( \frac{\partial H}{\partial T} \right)_p - \left( \frac{\partial U}{\partial T} \right)_p \quad (2.46)^\circ$$

Then we introduce  $H = U + pV = U + nRT$  into the first term, which results in

$$C_p - C_V = \left( \frac{\partial U}{\partial T} \right)_p + nR - \left( \frac{\partial U}{\partial T} \right)_p = nR \quad (2.47)^\circ$$

which is eqn 2.26. We show in *Further information 2.2* that in general

$$C_p - C_V = \frac{\alpha^2 TV}{\kappa_T} \quad (2.48)$$

Equation 2.48 applies to any substance (that is, it is ‘universally true’). It reduces to eqn 2.47 for a perfect gas when we set  $\alpha = 1/T$  and  $\kappa_T = 1/p$ . Because expansion coefficients  $\alpha$  of liquids and solids are small, it is tempting to deduce from eqn 2.48 that for them  $C_p \approx C_V$ . But this is not always so, because the compressibility  $\kappa_T$  might also be small, so  $\alpha^2/\kappa_T$  might be large. That is, although only a little work need be done to push back the atmosphere, a great deal of work may have to be done to pull atoms apart from one another as the solid expands. As an illustration, for water at 25°C, eqn 2.48 gives  $C_{p,m} = 75.3 \text{ J K}^{-1} \text{ mol}^{-1}$  compared with  $C_{V,m} = 74.8 \text{ J K}^{-1} \text{ mol}^{-1}$ . In some cases, the two heat capacities differ by as much as 30 per cent.

## 2.12 The Joule–Thomson effect

**Key point** The Joule–Thomson effect is the change in temperature of a gas when it undergoes isenthalpic expansion.

We can carry out a similar set of operations on the enthalpy,  $H = U + pV$ . The quantities  $U$ ,  $p$ , and  $V$  are all state functions; therefore  $H$  is also a state function and  $dH$  is an exact differential. It turns out that  $H$  is a useful thermodynamic function when the pressure is under our control: we saw a sign of that in the relation  $\Delta H = q_p$  (eqn 2.19b). We shall therefore regard  $H$  as a function of  $p$  and  $T$ , and adapt the argument in Section 2.11 to find an expression for the variation of  $H$  with temperature at constant volume. As explained in the following *Justification*, we find that for a closed system of constant composition

$$dH = -\mu C_p dp + C_p dT \quad (2.49)$$

where the Joule–Thomson coefficient,  $\mu$  (mu), is defined as

$$\mu = \left( \frac{\partial T}{\partial p} \right)_H \quad \begin{array}{l} \text{Definition of the} \\ \text{Joule–Thomson} \\ \text{coefficient} \end{array} \quad [2.50]$$

This relation will prove useful for relating the heat capacities at constant pressure and volume and for a discussion of the liquefaction of gases.

### Justification 2.2 The variation of enthalpy with pressure and temperature

Because  $H$  is a function of  $p$  and  $T$  we can write, when these two quantities change by an infinitesimal amount, that the enthalpy changes by

$$dH = \left( \frac{\partial H}{\partial p} \right)_T dp + \left( \frac{\partial H}{\partial T} \right)_p dT \quad (2.51)$$

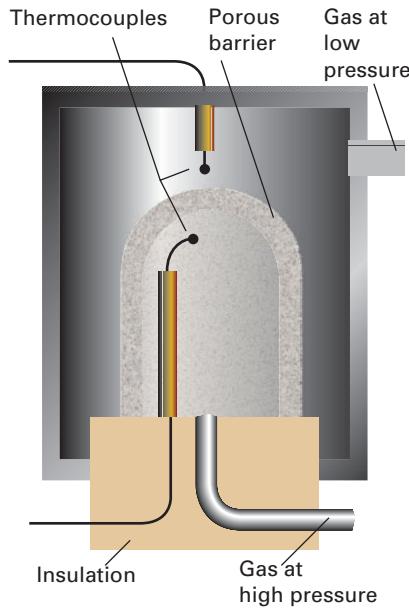
The second partial derivative is  $C_p$ ; our task here is to express  $(\partial H/\partial p)_T$  in terms of recognizable quantities. If the enthalpy is constant,  $dH = 0$  and this expression then requires that

$$\left( \frac{\partial H}{\partial p} \right)_T dp = -C_p dT \quad \text{at constant } H$$

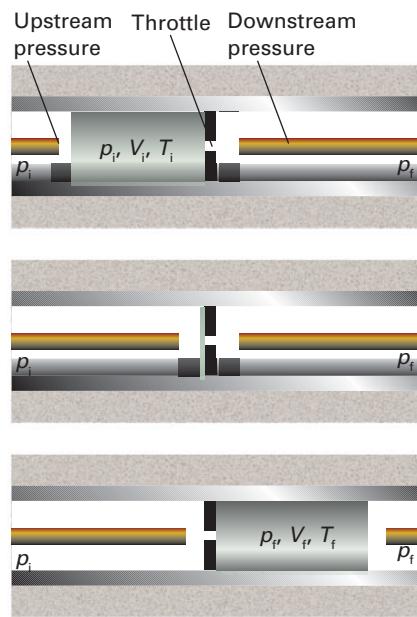
Division of both sides by  $dp$  then gives

$$\left( \frac{\partial H}{\partial p} \right)_T = -C_p \left( \frac{\partial T}{\partial p} \right)_H = -C_p \mu$$

Equation 2.49 now follows directly.



**Fig. 2.26** The apparatus used for measuring the Joule–Thomson effect. The gas expands through the porous barrier, which acts as a throttle, and the whole apparatus is thermally insulated. As explained in the text, this arrangement corresponds to an isenthalpic expansion (expansion at constant enthalpy). Whether the expansion results in a heating or a cooling of the gas depends on the conditions.



**Fig. 2.27** The thermodynamic basis of Joule–Thomson expansion. The pistons represent the upstream and downstream gases, which maintain constant pressures either side of the throttle. The transition from the top diagram to the bottom diagram, which represents the passage of a given amount of gas through the throttle, occurs without change of enthalpy.

### (a) Observation of the Joule–Thomson effect

The analysis of the Joule–Thomson coefficient is central to the technological problems associated with the liquefaction of gases. We need to be able to interpret it physically and to measure it. As shown in the following *Justification*, the cunning required to impose the constraint of constant enthalpy, so that the process is isenthalpic, was supplied by Joule and William Thomson (later Lord Kelvin). They let a gas expand through a porous barrier from one constant pressure to another and monitored the difference of temperature that arose from the expansion (Fig. 2.26). The whole apparatus was insulated so that the process was adiabatic. They observed a lower temperature on the low pressure side, the difference in temperature being proportional to the pressure difference they maintained. This cooling by isenthalpic expansion is now called the Joule–Thomson effect.

#### Justification 2.3 *The Joule–Thomson effect*

Here we show that the experimental arrangement results in expansion at constant enthalpy. Because all changes to the gas occur adiabatically,  $q=0$  implies that  $\Delta U=w$ . Next, consider the work done as the gas passes through the barrier. We focus on the passage of a fixed amount of gas from the high pressure side, where the pressure is  $p_i$ , the temperature  $T_i$ , and the gas occupies a volume  $V_i$  (Fig. 2.27). The gas emerges on the low pressure side, where the same amount of gas has a pressure  $p_f$ , a temperature  $T_f$ , and occupies a volume  $V_f$ . The gas on the left is compressed

isothermally by the upstream gas acting as a piston. The relevant pressure is  $p_i$  and the volume changes from  $V_i$  to 0; therefore, the work done on the gas is

$$w_1 = -p_i(0 - V_i) = p_i V_i$$

The gas expands isothermally on the right of the barrier (but possibly at a different constant temperature) against the pressure  $p_f$  provided by the downstream gas acting as a piston to be driven out. The volume changes from 0 to  $V_f$ , so the work done on the gas in this stage is

$$w_2 = -p_f(V_f - 0) = -p_f V_f$$

The total work done on the gas is the sum of these two quantities, or

$$w = w_1 + w_2 = p_i V_i - p_f V_f$$

It follows that the change of internal energy of the gas as it moves adiabatically from one side of the barrier to the other is

$$U_f - U_i = w = p_i V_i - p_f V_f$$

Reorganization of this expression gives

$$U_f + p_f V_f = U_i + p_i V_i \quad \text{or} \quad H_f = H_i$$

Therefore, the expansion occurs without change of enthalpy.

The property measured in the experiment is the ratio of the temperature change to the change of pressure,  $\Delta T/\Delta p$ . Adding the constraint of constant enthalpy and taking the limit of small  $\Delta p$  implies that the thermodynamic quantity measured is  $(\partial T/\partial p)_H$ , which is the Joule–Thomson coefficient,  $\mu$ . In other words, the physical interpretation of  $\mu$  is that it is the ratio of the change in temperature to the change in pressure when a gas expands under conditions that ensure there is no change in enthalpy.

The modern method of measuring  $\mu$  is indirect, and involves measuring the **isothermal Joule–Thomson coefficient**, the quantity

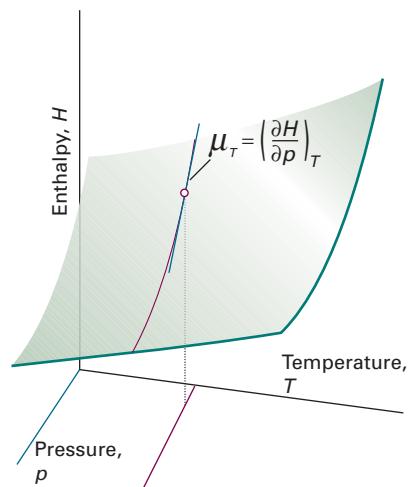
$$\mu_T = \left( \frac{\partial H}{\partial p} \right)_T \quad \boxed{\text{Definition of the isothermal Joule–Thomson coefficient}} \quad [2.52]$$

which is the slope of a plot of enthalpy against pressure at constant temperature (Fig. 2.28). Comparing eqns 2.51 and 2.52, we see that the two coefficients are related by

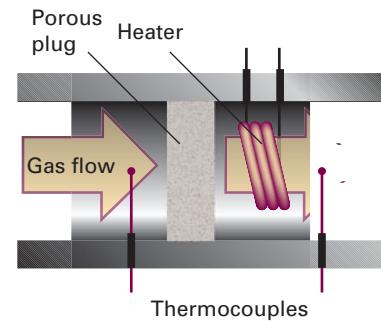
$$\mu_T = -C_p \mu \quad [2.53]$$

To measure  $\mu_T$ , the gas is pumped continuously at a steady pressure through a heat exchanger, which brings it to the required temperature, and then through a porous plug inside a thermally insulated container. The steep pressure drop is measured and the cooling effect is exactly offset by an electric heater placed immediately after the plug (Fig. 2.29). The energy provided by the heater is monitored. Because  $\Delta H = q_p$ , the energy transferred as heat can be identified with the value of  $\Delta H$ . The pressure change  $\Delta p$  is known, so we can find  $\mu_T$  from the limiting value of  $\Delta H/\Delta p$  as  $\Delta p \rightarrow 0$  and then convert it to  $\mu$ . Table 2.10 lists some values obtained in this way.

Real gases have nonzero Joule–Thomson coefficients. Depending on the identity of the gas, the pressure, the relative magnitudes of the attractive and repulsive intermolecular forces, and the temperature, the sign of the coefficient may be either positive or negative (Fig. 2.30). A positive sign implies that  $dT$  is negative when  $dp$  is negative, in which case the gas cools on expansion. Gases that show a heating effect ( $\mu < 0$ ) at one temperature show a cooling effect ( $\mu > 0$ ) when the temperature is below their upper inversion temperature,  $T_I$  (Table 2.10, Fig. 2.31). As indicated in



**Fig. 2.28** The isothermal Joule–Thomson coefficient is the slope of the enthalpy with respect to changing pressure, the temperature being held constant.

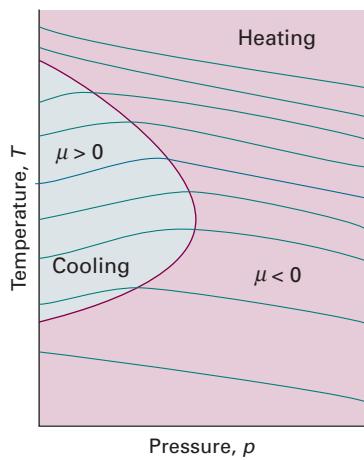


**Fig. 2.29** A schematic diagram of the apparatus used for measuring the isothermal Joule–Thomson coefficient. The electrical heating required to offset the cooling arising from expansion is interpreted as  $\Delta H$  and used to calculate  $(\partial H/\partial p)_T$ , which is then converted to  $\mu$  as explained in the text.

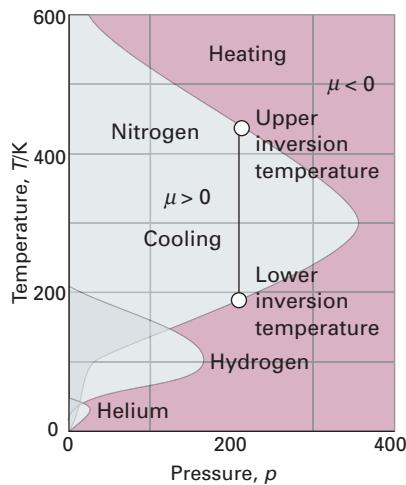
**Table 2.10\*** Inversion temperatures ( $T_I$ ), normal freezing ( $T_f$ ) and boiling ( $T_b$ ) points, and Joule–Thomson coefficient ( $\mu$ ) at 1 atm and 298 K

	$T_I/K$	$T_f/K$	$T_b/K$	$\mu/(K \text{ bar}^{-1})$
Ar	723	83.8	87.3	
$\text{CO}_2$	1500	194.7	+1.10	
He	40	4.2	-0.060	
$\text{N}_2$	621	63.3	77.4	+0.25

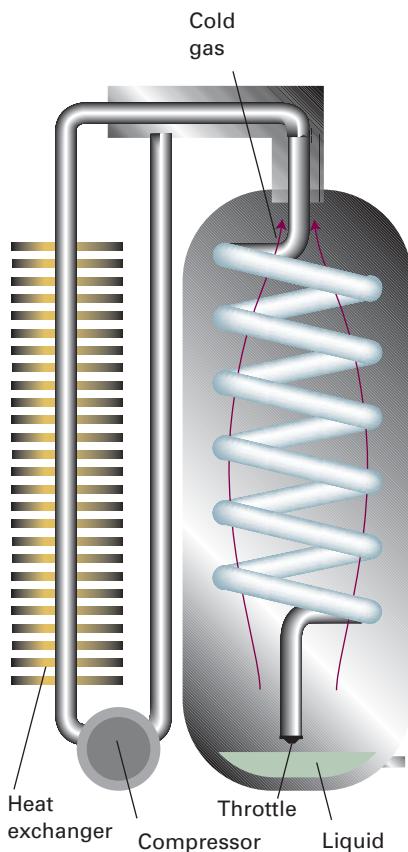
\* More values are given in the Data section.



**Fig. 2.30** The sign of the Joule–Thomson coefficient,  $\mu$ , depends on the conditions. Inside the boundary, the blue area, it is positive and outside it is negative. The temperature corresponding to the boundary at a given pressure is the ‘inversion temperature’ of the gas at that pressure. For a given pressure, the temperature must be below a certain value if cooling is required but, if it becomes too low, the boundary is crossed again and heating occurs. Reduction of pressure under adiabatic conditions moves the system along one of the isenthalps, or curves of constant enthalpy. The inversion temperature curve runs through the points of the isenthalps where their slope changes from negative to positive.



**Fig. 2.31** The inversion temperatures for three real gases, nitrogen, hydrogen, and helium.



**Fig. 2.32** The principle of the Linde refrigerator is shown in this diagram. The gas is recirculated, and, so long as it is beneath its inversion temperature, it cools on expansion through the throttle. The cooled gas cools the high-pressure gas, which cools still further as it expands. Eventually liquefied gas drips from the throttle.

Fig. 2.31, a gas typically has two inversion temperatures, one at high temperature and the other at low.

The ‘Linde refrigerator’ makes use of Joule–Thompson expansion to liquefy gases (Fig. 2.32). The gas at high pressure is allowed to expand through a throttle; it cools and is circulated past the incoming gas. That gas is cooled, and its subsequent expansion cools it still further. There comes a stage when the circulating gas becomes so cold that it condenses to a liquid.

For a perfect gas,  $\mu = 0$ ; hence, the temperature of a perfect gas is unchanged by Joule–Thompson expansion. (Simple adiabatic expansion does cool a perfect gas, because the gas does work, Section 2.6.) This characteristic points clearly to the involvement of intermolecular forces in determining the size of the effect. However, the Joule–Thompson coefficient of a real gas does not necessarily approach zero as the pressure is reduced even though the equation of state of the gas approaches that of a perfect gas. The coefficient behaves like the properties discussed in Section 1.3b in the sense that it depends on derivatives and not on  $p$ ,  $V$ , and  $T$  themselves.

### (b) The molecular interpretation of the Joule–Thomson effect

The kinetic model of gases (Section 1.2b) and the equipartition theorem (Section F.5) jointly imply that the mean kinetic energy of molecules in a gas is proportional to the temperature. It follows that reducing the average speed of the molecules is equivalent to cooling the gas. If the speed of the molecules can be reduced to the point that neighbours can capture each other by their intermolecular attractions, then the cooled gas will condense to a liquid.

To slow the gas molecules, we make use of an effect similar to that seen when a ball is thrown into the air: as it rises it slows in response to the gravitational attraction of the Earth and its kinetic energy is converted into potential energy. We saw in Section 1.3 that molecules in a real gas attract each other (the attraction is not gravitational, but the effect is the same). It follows that, if we can cause the molecules to move apart from each other, like a ball rising from a planet, then they should slow. It is very easy to move molecules apart from each other: we simply allow the gas to expand, which increases the average separation of the molecules. To cool a gas, therefore, we allow it to expand without allowing any energy to enter from outside as heat. As the gas expands, the molecules move apart to fill the available volume, struggling as they do so against the attraction of their neighbours. Because some kinetic energy must be converted into potential energy to reach greater separations, the molecules travel more slowly as their separation increases. This sequence of molecular events explains the Joule–Thomson effect: the cooling of a real gas by adiabatic expansion. The cooling effect, which corresponds to  $\mu > 0$ , is observed under conditions when attractive interactions are dominant ( $Z < 1$ , eqn 1.17), because the molecules have to climb apart against the attractive force in order for them to travel more slowly. For molecules under conditions when repulsions are dominant ( $Z > 1$ ), the Joule–Thomson effect results in the gas becoming warmer, or  $\mu < 0$ .

## Checklist of key equations

Property	Equation	Comment
First Law of thermodynamics	$\Delta U = q + w$	Acquisitive convention
Work of expansion	$dw = -p_{\text{ex}} dV$	
Work of expansion against a constant external pressure	$w = -p_{\text{ex}} \Delta V$	$p_{\text{ex}} = 0$ corresponds to free expansion
Work of isothermal reversible expansion of a perfect gas	$w = -nRT \ln(V_f/V_i)$	Isothermal, reversible, perfect gas
Heat capacity at constant volume	$C_V = (\partial U / \partial T)_V$	Definition
Heat capacity at constant pressure	$C_p = (\partial H / \partial T)_p$	Definition
Relation between heat capacities	$C_p - C_V = nR$	Perfect gas
Enthalpy	$H = U + pV$	Definition
The standard reaction enthalpy	$\Delta_f H^\circ = \sum_{\text{Products}} vH_m^\circ - \sum_{\text{Reactants}} vH_m^\circ$	
Kirchhoff's law	$\Delta_f H^\circ(T_2) = \Delta_f H^\circ(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^\circ dT$	
Internal pressure	$\pi_T = (\partial U / \partial V)_T$	For a perfect gas, $\pi_T = 0$
Joule–Thomson coefficient	$\mu = (\partial T / \partial p)_H$	For a perfect gas, $\mu = 0$

→ For a chart of the relations between principal equations, see the [Road map section](#) of the Resource section.

## Further information

### Further information 2.1 Adiabatic processes

Consider a stage in a reversible adiabatic expansion when the pressure inside and out is  $p$ . The work done when the gas expands by  $dV$  is  $dw = -pdV$ ; however, for a perfect gas,  $dU = C_V dT$ . Therefore, because for an adiabatic change ( $dq = 0$ )  $dU = dw + dq = dw$ , we can equate these two expressions for  $dU$  and write

$$C_V dT = -pdV$$

We are dealing with a perfect gas, so we can replace  $p$  by  $nRT/V$  and obtain

$$\frac{C_V dT}{T} = -\frac{nR dV}{V}$$

To integrate this expression we note that  $T$  is equal to  $T_i$  when  $V$  is equal to  $V_i$ , and is equal to  $T_f$  when  $V$  is equal to  $V_f$  at the end of the expansion. Therefore,

$$C_V \int_{T_i}^{T_f} \frac{dT}{T} = -nR \int_{V_i}^{V_f} \frac{dV}{V}$$

(We are taking  $C_V$  to be independent of temperature.) Then, because  $\int dx/x = \ln x + \text{constant}$ , we obtain

$$C_V \ln \frac{T_f}{T_i} = -nR \ln \frac{V_f}{V_i}$$

Because  $\ln(x/y) = -\ln(y/x)$ , this expression rearranges to

$$\frac{C_V}{nR} \ln \frac{T_f}{T_i} = \ln \frac{V_i}{V_f}$$

With  $c = C_V/nR$  we obtain (because  $\ln x^a = a \ln x$ )

$$\ln \left( \frac{T_f}{T_i} \right)^c = \ln \left( \frac{V_i}{V_f} \right)$$

which implies that  $(T_f/T_i)^c = (V_i/V_f)$  and, upon rearrangement, eqn 2.28.

The initial and final states of a perfect gas satisfy the perfect gas law regardless of how the change of state takes place, so we can use  $pV = nRT$  to write

$$\frac{p_i V_i}{p_f V_f} = \frac{T_i}{T_f}$$

However, we have just shown that

$$\frac{T_i}{T_f} = \left( \frac{V_f}{V_i} \right)^{1/c} = \left( \frac{V_f}{V_i} \right)^{\gamma-1}$$

where we use the definition of the heat capacity ratio where  $\gamma = C_{p,m}/C_{V,m}$  and the fact that, for a perfect gas,  $C_{p,m} - C_{V,m} = R$

(the molar version of eqn 2.26). Then we combine the two expressions, to obtain

$$\frac{p_i}{p_f} = \frac{V_f}{V_i} \times \left( \frac{V_f}{V_i} \right)^{\gamma-1} = \left( \frac{V_f}{V_i} \right)^\gamma$$

which rearranges to  $p_i V_i^\gamma = p_f V_f^\gamma$ , which is eqn 2.29.

### Further information 2.2 The relation between heat capacities

A useful rule when doing a problem in thermodynamics is to go back to first principles. In the present problem we do this twice, first by expressing  $C_p$  and  $C_V$  in terms of their definitions and then by inserting the definition  $H = U + pV$ :

$$\begin{aligned} C_p - C_V &= \left( \frac{\partial H}{\partial T} \right)_p - \left( \frac{\partial U}{\partial T} \right)_V \\ &= \left( \frac{\partial U}{\partial T} \right)_p + \left( \frac{\partial (pV)}{\partial T} \right)_p - \left( \frac{\partial U}{\partial T} \right)_V \end{aligned}$$

We have already calculated the difference of the first and third terms on the right, and eqn 2.44 lets us write this difference as  $\alpha \pi_T V$ . The factor  $\alpha V$  gives the change in volume when the temperature is raised, and  $\pi_T = (\partial U/\partial V)_T$  converts this change in volume into a change in internal energy. We can simplify the remaining term by noting that, because  $p$  is constant,

$$\left( \frac{\partial (pV)}{\partial T} \right)_p = p \left( \frac{\partial V}{\partial T} \right)_p = \alpha p V$$

The middle term of this expression identifies it as the contribution to the work of pushing back the atmosphere:  $(\partial V/\partial T)_p$  is the change of volume caused by a change of temperature, and multiplication by  $p$  converts this expansion into work.

Collecting the two contributions gives

$$C_p - C_V = \alpha(p + \pi_T)V \quad (2.54)$$

As just remarked, the first term on the right,  $\alpha p V$ , is a measure of the work needed to push back the atmosphere; the second term on the right,  $\alpha \pi_T V$ , is the work required to separate the molecules composing the system.

At this point we can go further by using the result we prove in Section 3.8 that

$$\pi_T = T \left( \frac{\partial p}{\partial T} \right)_V - p$$

When this expression is inserted in the last equation we obtain

$$C_p - C_V = \alpha TV \left( \frac{\partial p}{\partial T} \right)_V \quad (2.55)$$

We now transform the remaining partial derivative. With  $V$  regarded as a function of  $p$  and  $T$ , when these two quantities change the resulting change in  $V$  is

$$dV = \left( \frac{\partial V}{\partial T} \right)_p dT + \left( \frac{\partial V}{\partial p} \right)_T dp \quad (2.56)$$

If (as in eqn 2.56) we require the volume to be constant,  $dV = 0$  implies that

$$\left( \frac{\partial V}{\partial T} \right)_p dT = - \left( \frac{\partial V}{\partial p} \right)_T dp \quad \text{at constant volume} \quad (2.57)$$

On division by  $dT$ , this relation becomes

$$\left( \frac{\partial V}{\partial T} \right)_p = - \left( \frac{\partial V}{\partial p} \right)_T \left( \frac{\partial p}{\partial T} \right)_V \quad (2.58)$$

and therefore

$$\left( \frac{\partial p}{\partial T} \right)_V = - \frac{(\partial V/\partial T)_p}{(\partial V/\partial p)_T} = \frac{\alpha}{\kappa_T} \quad (2.59)$$

Insertion of this relation into eqn 2.55 produces eqn 2.48.

## Discussion questions

- 2.1** Provide mechanical and molecular definitions of work and heat.
- 2.2** Consider the reversible expansion of a perfect gas. Provide a physical interpretation for the fact that  $pV^\gamma = \text{constant}$  for an adiabatic change, whereas  $pV = \text{constant}$  for an isothermal change.
- 2.3** Explain the difference between the change in internal energy and the change in enthalpy accompanying a chemical or physical process.

- 2.4** Explain the significance of a physical observable being a state function and compile a list of as many state functions as you can identify.
- 2.5** Explain the significance of the Joule and Joule–Thomson experiments. What would Joule observe in a more sensitive apparatus?
- 2.6** Suggest (with explanation) how the internal energy of a van der Waals gas should vary with volume at constant temperature.

## Exercises

Assume all gases are perfect unless stated otherwise. Unless otherwise stated, thermodynamic data are for 298.15 K.

- 2.1(a)** Calculate the work needed for a 65 kg person to climb through 4.0 m on the surface of (a) the Earth and (b) the Moon ( $g = 1.60 \text{ m s}^{-2}$ ).
- 2.1(b)** Calculate the work needed for a bird of mass 120 g to fly to a height 50 m from the surface of the Earth.
- 2.2(a)** A chemical reaction takes place in a container of cross-sectional area  $100 \text{ cm}^2$ . As a result of the reaction, a piston is pushed out through 10 cm against an external pressure of 1.0 atm. Calculate the work done by the system.
- 2.2(b)** A chemical reaction takes place in a container of cross-sectional area  $50.0 \text{ cm}^2$ . As a result of the reaction, a piston is pushed out through 15 cm against an external pressure of 121 kPa. Calculate the work done by the system.
- 2.3(a)** A sample consisting of 1.00 mol Ar is expanded isothermally at  $0^\circ\text{C}$  from  $22.4 \text{ dm}^3$  to  $44.8 \text{ dm}^3$  (a) reversibly, (b) against a constant external pressure equal to the final pressure of the gas, and (c) freely (against zero external pressure). For the three processes calculate  $q$ ,  $w$ ,  $\Delta U$ , and  $\Delta H$ .

- 2.3(b)** A sample consisting of 2.00 mol He is expanded isothermally at  $22^\circ\text{C}$  from  $22.8 \text{ dm}^3$  to  $31.7 \text{ dm}^3$  (a) reversibly, (b) against a constant external pressure equal to the final pressure of the gas, and (c) freely (against zero external pressure). For the three processes calculate  $q$ ,  $w$ ,  $\Delta U$ , and  $\Delta H$ .

- 2.4(a)** A sample consisting of 1.00 mol of perfect gas atoms, for which  $C_{V,m} = \frac{3}{2}R$ , initially at  $p_1 = 1.00 \text{ atm}$  and  $T_1 = 300 \text{ K}$ , is heated reversibly to 400 K at constant volume. Calculate the final pressure,  $\Delta U$ ,  $q$ , and  $w$ .

- 2.4(b)** A sample consisting of 2.00 mol of perfect gas molecules, for which  $C_{V,m} = \frac{5}{2}R$ , initially at  $p_1 = 111 \text{ kPa}$  and  $T_1 = 277 \text{ K}$ , is heated reversibly to 356 K at constant volume. Calculate the final pressure,  $\Delta U$ ,  $q$ , and  $w$ .

- 2.5(a)** A sample of 4.50 g of methane occupies  $12.7 \text{ dm}^3$  at 310 K.  
(a) Calculate the work done when the gas expands isothermally against a constant external pressure of 200 Torr until its volume has increased by  $3.3 \text{ dm}^3$ . (b) Calculate the work that would be done if the same expansion occurred reversibly.

- 2.5(b)** A sample of argon of mass 6.56 g occupies  $18.5 \text{ dm}^3$  at 305 K.  
(a) Calculate the work done when the gas expands isothermally against a constant external pressure of 7.7 kPa until its volume has increased by  $2.5 \text{ dm}^3$ . (b) Calculate the work that would be done if the same expansion occurred reversibly.

- 2.6(a)** A sample of 1.00 mol  $\text{H}_2\text{O(g)}$  is condensed isothermally and reversibly to liquid water at  $100^\circ\text{C}$ . The standard enthalpy of vaporization of water at  $100^\circ\text{C}$  is  $40.656 \text{ kJ mol}^{-1}$ . Find  $w$ ,  $q$ ,  $\Delta U$ , and  $\Delta H$  for this process.

- 2.6(b)** A sample of 2.00 mol  $\text{CH}_3\text{OH(g)}$  is condensed isothermally and reversibly to liquid at  $64^\circ\text{C}$ . The standard enthalpy of vaporization of methanol at  $64^\circ\text{C}$  is  $35.3 \text{ kJ mol}^{-1}$ . Find  $w$ ,  $q$ ,  $\Delta U$ , and  $\Delta H$  for this process.

- 2.7(a)** A strip of magnesium of mass 15 g is placed in a beaker of dilute hydrochloric acid. Calculate the work done by the system as a result of the reaction. The atmospheric pressure is 1.0 atm and the temperature  $25^\circ\text{C}$ .

- 2.7(b)** A piece of zinc of mass 5.0 g is placed in a beaker of dilute hydrochloric acid. Calculate the work done by the system as a result of the reaction. The atmospheric pressure is 1.1 atm and the temperature  $23^\circ\text{C}$ .

**2.8(a)** The constant-pressure heat capacity of a sample of a perfect gas was found to vary with temperature according to the expression  $C_p/(J\ K^{-1}) = 20.17 + 0.3665(T/K)$ . Calculate  $q$ ,  $w$ ,  $\Delta U$ , and  $\Delta H$  when the temperature is raised from 25°C to 200°C (a) at constant pressure, (b) at constant volume.

**2.8(b)** The constant-pressure heat capacity of a sample of a perfect gas was found to vary with temperature according to the expression  $C_p/(J\ K^{-1}) = 20.17 + 0.4001(T/K)$ . Calculate  $q$ ,  $w$ ,  $\Delta U$ , and  $\Delta H$  when the temperature is raised from 0°C to 100°C (a) at constant pressure, (b) at constant volume.

**2.9(a)** Calculate the final temperature of a sample of argon of mass 12.0 g that is expanded reversibly and adiabatically from  $1.0\ dm^3$  at 273.15 K to  $3.0\ dm^3$ .

**2.9(b)** Calculate the final temperature of a sample of carbon dioxide of mass 16.0 g that is expanded reversibly and adiabatically from  $500\ cm^3$  at 298.15 K to  $2.00\ dm^3$ .

**2.10(a)** A sample of carbon dioxide of mass 2.45 g at 27.0°C is allowed to expand reversibly and adiabatically from  $500\ cm^3$  to  $3.00\ dm^3$ . What is the work done by the gas?

**2.10(b)** A sample of nitrogen of mass 3.12 g at 23.0°C is allowed to expand reversibly and adiabatically from  $400\ cm^3$  to  $2.00\ dm^3$ . What is the work done by the gas?

**2.11(a)** Calculate the final pressure of a sample of carbon dioxide that expands reversibly and adiabatically from 57.4 kPa and  $1.0\ dm^3$  to a final volume of  $2.0\ dm^3$ . Take  $\gamma = 1.4$ .

**2.11(b)** Calculate the final pressure of a sample of water vapour that expands reversibly and adiabatically from 87.3 Torr and  $500\ cm^3$  to a final volume of  $3.0\ dm^3$ . Take  $\gamma = 1.3$ .

**2.12(a)** When 229 J of energy is supplied as heat to 3.0 mol Ar(g) at constant pressure, the temperature of the sample increases by 2.55 K. Calculate the molar heat capacities at constant volume and constant pressure of the gas.

**2.12(b)** When 178 J of energy is supplied as heat to 1.9 mol of gas molecules at constant pressure, the temperature of the sample increases by 1.78 K. Calculate the molar heat capacities at constant volume and constant pressure of the gas.

**2.13(a)** When 3.0 mol O<sub>2</sub> is heated at a constant pressure of 3.25 atm, its temperature increases from 260 K to 285 K. Given that the molar heat capacity of O<sub>2</sub>(g) at constant pressure is  $29.4\ J\ K^{-1}\ mol^{-1}$ , calculate  $q$ ,  $\Delta H$ , and  $\Delta U$ .

**2.13(b)** When 2.0 mol CO<sub>2</sub> is heated at a constant pressure of 1.25 atm, its temperature increases from 250 K to 277 K. Given that the molar heat capacity of CO<sub>2</sub>(g) at constant pressure is  $37.11\ J\ K^{-1}\ mol^{-1}$ , calculate  $q$ ,  $\Delta H$ , and  $\Delta U$ .

**2.14(a)** A sample of 4.0 mol O<sub>2</sub>(g) is originally confined in  $20\ dm^3$  at 270 K and then undergoes adiabatic expansion against a constant pressure of 600 Torr until the volume has increased by a factor of 3.0. Calculate  $q$ ,  $w$ ,  $\Delta T$ ,  $\Delta U$ , and  $\Delta H$ . (The final pressure of the gas is not necessarily 600 Torr.)

**2.14(b)** A sample of 5.0 mol CO<sub>2</sub>(g) is originally confined in  $15\ dm^3$  at 280 K and then undergoes adiabatic expansion against a constant pressure of 78.5 kPa until the volume has increased by a factor of 4.0. Calculate  $q$ ,  $w$ ,  $\Delta T$ ,  $\Delta U$ , and  $\Delta H$ . (The final pressure of the gas is not necessarily 78.5 kPa.)

**2.15(a)** A sample consisting of 1.0 mol of perfect gas molecules with  $C_V = 20.8\ J\ K^{-1}$  is initially at 3.25 atm and 310 K. It undergoes reversible adiabatic expansion until its pressure reaches 2.50 atm. Calculate the final volume and temperature and the work done.

**2.15(b)** A sample consisting of 1.5 mol of perfect gas molecules with  $C_{p,m} = 20.8\ J\ K^{-1}\ mol^{-1}$  is initially at 230 kPa and 315 K. It undergoes reversible adiabatic expansion until its pressure reaches 170 kPa. Calculate the final volume and temperature and the work done.

**2.16(a)** A certain liquid has  $\Delta_{vap}H^\circ = 26.0\ kJ\ mol^{-1}$ . Calculate  $q$ ,  $w$ ,  $\Delta H$ , and  $\Delta U$  when 0.50 mol is vaporized at 250 K and 750 Torr.

**2.16(b)** A certain liquid has  $\Delta_{vap}H^\circ = 32.0\ kJ\ mol^{-1}$ . Calculate  $q$ ,  $w$ ,  $\Delta H$ , and  $\Delta U$  when 0.75 mol is vaporized at 260 K and 765 Torr.

**2.17(a)** Calculate the lattice enthalpy of SrI<sub>2</sub> from the following data:

	$\Delta H/(kJ\ mol^{-1})$
Sublimation of Sr(s)	+164
Ionization of Sr(g) to Sr <sup>2+</sup> (g)	+1626
Sublimation of I <sub>2</sub> (s)	+62
Dissociation of I <sub>2</sub> (g)	+151
Electron attachment to I(g)	−304
Formation of SrI <sub>2</sub> (s) from Sr(s) and I <sub>2</sub> (s)	−558

**2.17(b)** Calculate the lattice enthalpy of MgBr<sub>2</sub> from the following data:

	$\Delta H/(kJ\ mol^{-1})$
Sublimation of Mg(s)	+148
Ionization of Mg(g) to Mg <sup>2+</sup> (g)	+2187
Vaporization of Br <sub>2</sub> (l)	+31
Dissociation of Br <sub>2</sub> (g)	+193
Electron attachment to Br(g)	−331
Formation of MgBr <sub>2</sub> (s) from Mg(s) and Br <sub>2</sub> (l)	−524

**2.18(a)** The standard enthalpy of formation of ethylbenzene is  $−12.5\ kJ\ mol^{-1}$ . Calculate its standard enthalpy of combustion.

**2.18(b)** The standard enthalpy of formation of phenol is  $−165.0\ kJ\ mol^{-1}$ . Calculate its standard enthalpy of combustion.

**2.19(a)** The standard enthalpy of combustion of cyclopropane is  $−2091\ kJ\ mol^{-1}$  at 25°C. From this information and enthalpy of formation data for CO<sub>2</sub>(g) and H<sub>2</sub>O(g), calculate the enthalpy of formation of cyclopropane. The enthalpy of formation of propene is  $+20.42\ kJ\ mol^{-1}$ . Calculate the enthalpy of isomerization of cyclopropane to propene.

**2.19(b)** From the following data, determine  $\Delta_fH^\circ$  for diborane, B<sub>2</sub>H<sub>6</sub>(g), at 298 K:

- |  |  |
|--|--|
| (1) B <sub>2</sub> H <sub>6</sub> (g) + 3 O <sub>2</sub> (g) → B <sub>2</sub> O <sub>3</sub> (s) + 3 H <sub>2</sub> O(g) | $\Delta_fH^\circ = −2036\ kJ\ mol^{-1}$  |
| (2) 2 B(s) + $\frac{3}{2}$ O <sub>2</sub> (g) → B <sub>2</sub> O <sub>3</sub> (s)  | $\Delta_fH^\circ = −1274\ kJ\ mol^{-1}$  |
| (3) H <sub>2</sub> (g) + $\frac{1}{2}$ O <sub>2</sub> (g) → H <sub>2</sub> O(g)  | $\Delta_fH^\circ = −241.8\ kJ\ mol^{-1}$ |

**2.20(a)** When 120 mg of naphthalene, C<sub>10</sub>H<sub>8</sub>(s), was burned in a bomb calorimeter the temperature rose by 3.05 K. Calculate the calorimeter constant. By how much will the temperature rise when 10 mg of phenol, C<sub>6</sub>H<sub>5</sub>OH(s), is burned in the calorimeter under the same conditions?

**2.20(b)** When 2.25 mg of anthracene, C<sub>14</sub>H<sub>10</sub>(s), was burned in a bomb calorimeter the temperature rose by 1.35 K. Calculate the calorimeter constant. By how much will the temperature rise when 135 mg of phenol, C<sub>6</sub>H<sub>5</sub>OH(s), is burned in the calorimeter under the same conditions? ( $\Delta_cH^\circ(C_{14}H_{10},s) = −7061\ kJ\ mol^{-1}$ )

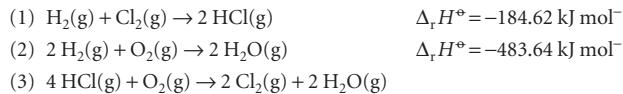
**2.21(a)** Calculate the standard enthalpy of solution of AgCl(s) in water from the enthalpies of formation of the solid and the aqueous ions.

**2.21(b)** Calculate the standard enthalpy of solution of AgBr(s) in water from the enthalpies of formation of the solid and the aqueous ions.

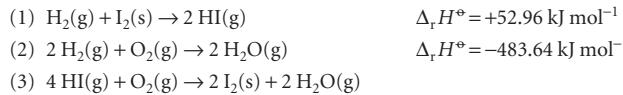
**2.22(a)** The standard enthalpy of decomposition of the yellow complex H<sub>3</sub>NSO<sub>2</sub> into NH<sub>3</sub> and SO<sub>2</sub> is  $+40\ kJ\ mol^{-1}$ . Calculate the standard enthalpy of formation of H<sub>3</sub>NSO<sub>2</sub>.

**2.22(b)** Given that the standard enthalpy of combustion of graphite is  $-393.51 \text{ kJ mol}^{-1}$  and that of diamond is  $-395.41 \text{ kJ mol}^{-1}$ , calculate the enthalpy of the graphite-to-diamond transition.

**2.23(a)** Given the reactions (1) and (2) below, determine (a)  $\Delta_f H^\circ$  and  $\Delta_f U^\circ$  for reaction (3), (b)  $\Delta_f H^\circ$  for both  $\text{HCl(g)}$  and  $\text{H}_2\text{O(g)}$  all at 298 K.



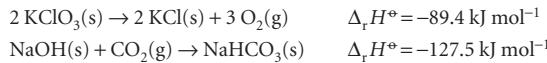
**2.23(b)** Given the reactions (1) and (2) below, determine (a)  $\Delta_f H^\circ$  and  $\Delta_f U^\circ$  for reaction (3), (b)  $\Delta_f H^\circ$  for both  $\text{HI(g)}$  and  $\text{H}_2\text{O(g)}$  all at 298 K.



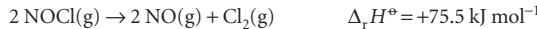
**2.24(a)** For the reaction  $\text{C}_2\text{H}_5\text{OH(l)} + 3 \text{O}_2(\text{g}) \rightarrow 2 \text{CO}_2(\text{g}) + 3 \text{H}_2\text{O(g)}$ ,  $\Delta_f U^\circ = -1373 \text{ kJ mol}^{-1}$  at 298 K, calculate  $\Delta_f H^\circ$ .

**2.24(b)** For the reaction  $2 \text{C}_6\text{H}_5\text{COOH(s)} + 13 \text{O}_2(\text{g}) \rightarrow 12 \text{CO}_2(\text{g}) + 6 \text{H}_2\text{O(g)}$ ,  $\Delta_f U^\circ = -772.7 \text{ kJ mol}^{-1}$  at 298 K, calculate  $\Delta_f H^\circ$ .

**2.25(a)** Calculate the standard enthalpies of formation of (a)  $\text{KClO}_3(\text{s})$  from the enthalpy of formation of  $\text{KCl}$ , (b)  $\text{NaHCO}_3(\text{s})$  from the enthalpies of formation of  $\text{CO}_2$  and  $\text{NaOH}$  together with the following information:



**2.25(b)** Calculate the standard enthalpy of formation of  $\text{NOCl(g)}$  from the enthalpy of formation of  $\text{NO}$  given in Table 2.8, together with the following information:



**2.26(a)** Use the information in Table 2.8 to predict the standard reaction enthalpy of  $2 \text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$  at 100°C from its value at 25°C.

**2.26(b)** Use the information in Table 2.8 to predict the standard reaction enthalpy of  $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O(l)}$  at 100°C from its value at 25°C.

**2.27(a)** From the data in Table 2.8, calculate  $\Delta_f H^\circ$  and  $\Delta_f U^\circ$  at (a) 298 K, (b) 378 K for the reaction  $\text{C(graphite)} + \text{H}_2\text{O(g)} \rightarrow \text{CO(g)} + \text{H}_2(\text{g})$ . Assume all heat capacities to be constant over the temperature range of interest.

**2.27(b)** Calculate  $\Delta_f H^\circ$  and  $\Delta_f U^\circ$  at 298 K and  $\Delta_f H^\circ$  at 348 K for the hydrogenation of ethyne (acetylene) to ethene (ethylene) from the enthalpy of combustion and heat capacity data in Tables 2.6 and 2.8. Assume the heat capacities to be constant over the temperature range involved.

**2.28(a)** Calculate  $\Delta_f H^\circ$  for the reaction  $\text{Zn(s)} + \text{CuSO}_4(\text{aq}) \rightarrow \text{ZnSO}_4(\text{aq}) + \text{Cu(s)}$  from the information in Table 2.8 in the *Data section*.

**2.28(b)** Calculate  $\Delta_f H^\circ$  for the reaction  $\text{NaCl(aq)} + \text{AgNO}_3(\text{aq}) \rightarrow \text{AgCl(s)} + \text{NaNO}_3(\text{aq})$  from the information in Table 2.8 in the *Data section*.

**2.29(a)** Set up a thermodynamic cycle for determining the enthalpy of hydration of  $\text{Mg}^{2+}$  ions using the following data: enthalpy of sublimation of  $\text{Mg(s)}$ ,  $+167.2 \text{ kJ mol}^{-1}$ ; first and second ionization enthalpies of  $\text{Mg(g)}$ ,

$7.646 \text{ eV}$  and  $15.035 \text{ eV}$ ; dissociation enthalpy of  $\text{Cl}_2(\text{g})$ ,  $+241.6 \text{ kJ mol}^{-1}$ ; electron gain enthalpy of  $\text{Cl(g)}$ ,  $-3.78 \text{ eV}$ ; enthalpy of solution of  $\text{MgCl}_2(\text{s})$ ,  $-150.5 \text{ kJ mol}^{-1}$ ; enthalpy of hydration of  $\text{Cl}^-(\text{g})$ ,  $-383.7 \text{ kJ mol}^{-1}$ .

**2.29(b)** Set up a thermodynamic cycle for determining the enthalpy of hydration of  $\text{Ca}^{2+}$  ions using the following data: enthalpy of sublimation of  $\text{Ca(s)}$ ,  $+178.2 \text{ kJ mol}^{-1}$ ; first and second ionization enthalpies of  $\text{Ca(g)}$ ,  $589.7 \text{ kJ mol}^{-1}$  and  $1145 \text{ kJ mol}^{-1}$ ; enthalpy of vaporization of bromine,  $30.91 \text{ kJ mol}^{-1}$ ; dissociation enthalpy of  $\text{Br}_2(\text{g})$ ,  $+192.9 \text{ kJ mol}^{-1}$ ; electron gain enthalpy of  $\text{Br(g)}$ ,  $-331.0 \text{ kJ mol}^{-1}$ ; enthalpy of solution of  $\text{CaBr}_2(\text{s})$ ,  $-103.1 \text{ kJ mol}^{-1}$ ; enthalpy of hydration of  $\text{Br}^-(\text{g})$ ,  $-97.5 \text{ kJ mol}^{-1}$ .

**2.30(a)** When a certain freon used in refrigeration was expanded adiabatically from an initial pressure of 32 atm and 0°C to a final pressure of 1.00 atm, the temperature fell by 22 K. Calculate the Joule–Thomson coefficient,  $\mu$ , at 0°C, assuming it remains constant over this temperature range.

**2.30(b)** A vapour at 22 atm and 5°C was allowed to expand adiabatically to a final pressure of 1.00 atm; the temperature fell by 10 K. Calculate the Joule–Thomson coefficient,  $\mu$ , at 5°C, assuming it remains constant over this temperature range.

**2.31(a)** For a van der Waals gas,  $\pi_T = a/V_m^2$ . Calculate  $\Delta U_m$  for the isothermal expansion of nitrogen gas from an initial volume of  $1.00 \text{ dm}^3$  to  $24.8 \text{ dm}^3$  at 298 K. What are the values of  $q$  and  $w$ ?

**2.31(b)** Repeat Exercise 2.31(a) for argon, from an initial volume of  $1.00 \text{ dm}^3$  to  $22.1 \text{ dm}^3$  at 298 K.

**2.32(a)** The volume of a certain liquid varies with temperature as

$$V = V' \{0.75 + 3.9 \times 10^{-4}(T/\text{K}) + 1.48 \times 10^{-6}(T/\text{K})^2\}$$

where  $V'$  is its volume at 300 K. Calculate its expansion coefficient,  $\alpha$ , at 320 K.

**2.32(b)** The volume of a certain liquid varies with temperature as

$$V = V' \{0.77 + 3.7 \times 10^{-4}(T/\text{K}) + 1.52 \times 10^{-6}(T/\text{K})^2\}$$

where  $V'$  is its volume at 298 K. Calculate its expansion coefficient,  $\alpha$ , at 310 K.

**2.33(a)** The isothermal compressibility of copper at 293 K is  $7.35 \times 10^{-7} \text{ atm}^{-1}$ . Calculate the pressure that must be applied in order to increase its density by 0.08 per cent.

**2.33(b)** The isothermal compressibility of lead at 293 K is  $2.21 \times 10^{-6} \text{ atm}^{-1}$ . Calculate the pressure that must be applied in order to increase its density by 0.08 per cent.

**2.34(a)** Given that  $\mu = 0.25 \text{ K atm}^{-1}$  for nitrogen, calculate the value of its isothermal Joule–Thomson coefficient. Calculate the energy that must be supplied as heat to maintain constant temperature when  $15.0 \text{ mol N}_2$  flows through a throttle in an isothermal Joule–Thomson experiment and the pressure drop is 75 atm.

**2.34(b)** Given that  $\mu = 1.11 \text{ K atm}^{-1}$  for carbon dioxide, calculate the value of its isothermal Joule–Thomson coefficient. Calculate the energy that must be supplied as heat to maintain constant temperature when  $12.0 \text{ mol CO}_2$  flows through a throttle in an isothermal Joule–Thomson experiment and the pressure drop is 55 atm.

## Problems\*

Assume all gases are perfect unless stated otherwise. Note that 1 atm = 1.013 25 bar. Unless otherwise stated, thermochemical data are for 298.15 K.

### Numerical problems

- 2.1** A sample consisting of 1 mol of perfect gas atoms (for which  $C_{V,m} = \frac{3}{2}R$ ) is taken through the cycle shown in Fig. 2.33. (a) Determine the temperature at the points 1, 2, and 3. (b) Calculate  $q$ ,  $w$ ,  $\Delta U$ , and  $\Delta H$  for each step and for the overall cycle. If a numerical answer cannot be obtained from the information given, then write +, -, 0, or ? as appropriate.

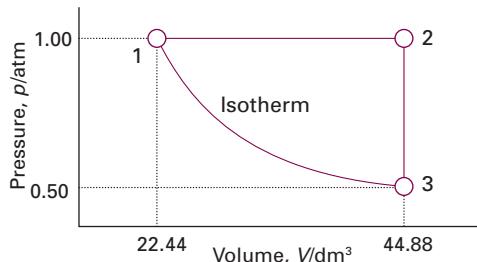


Fig. 2.33

- 2.2** A sample consisting of 1.0 mol  $\text{CaCO}_3(s)$  was heated to 800°C, when it decomposed. The heating was carried out in a container fitted with a piston that was initially resting on the solid. Calculate the work done during complete decomposition at 1.0 atm. What work would be done if instead of having a piston the container was open to the atmosphere?

- 2.3** A sample consisting of 2.0 mol  $\text{CO}_2$  occupies a fixed volume of 15.0  $\text{dm}^3$  at 300 K. When it is supplied with 2.35 kJ of energy as heat its temperature increases to 341 K. Assume that  $\text{CO}_2$  is described by the van der Waals equation of state, and calculate  $w$ ,  $\Delta U$ , and  $\Delta H$ .

- 2.4** A sample of 70 mmol  $\text{Kr(g)}$  expands reversibly and isothermally at 373 K from 5.25  $\text{cm}^3$  to 6.29  $\text{cm}^3$ , and the internal energy of the sample is known to increase by 83.5 J. Use the virial equation of state up to the second coefficient  $B = -28.7 \text{ cm}^3 \text{ mol}^{-1}$  to calculate  $w$ ,  $q$ , and  $\Delta H$  for this change of state.

- 2.5** A sample of 1.00 mol perfect gas molecules with  $C_{p,m} = \frac{7}{2}R$  is put through the following cycle: (a) constant-volume heating to twice its initial pressure, (b) reversible, adiabatic expansion back to its initial temperature, (c) reversible isothermal compression back to 1.00 atm. Calculate  $q$ ,  $w$ ,  $\Delta U$ , and  $\Delta H$  for each step and overall.

- 2.6** Calculate the work done during the isothermal reversible expansion of a van der Waals gas. Account physically for the way in which the coefficients  $a$  and  $b$  appear in the final expression. Plot on the same graph the indicator diagrams for the isothermal reversible expansion of (a) a perfect gas, (b) a van der Waals gas in which  $a = 0$  and  $b = 5.11 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$ , and (c)  $a = 4.2 \text{ dm}^6 \text{ atm mol}^{-2}$  and  $b = 0$ . The values selected exaggerate the imperfections but give rise to significant effects on the indicator diagrams. Take  $V_i = 1.0 \text{ dm}^3$ ,  $n = 1.0 \text{ mol}$ , and  $T = 298 \text{ K}$ .

- 2.7** The molar heat capacity of ethane is represented in the temperature range 298 K to 400 K by the empirical expression  $C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1}) = 14.73 + 0.1272(T/\text{K})$ . The corresponding expressions for  $C(s)$  and  $H_2(g)$  are given in

Table 2.2. Calculate the standard enthalpy of formation of ethane at 350 K from its value at 298 K.

- 2.8** A sample of the sugar d-ribose ( $\text{C}_5\text{H}_{10}\text{O}_5$ ) of mass 0.727 g was placed in a constant-volume calorimeter and then ignited in the presence of excess oxygen. The temperature rose by 0.910 K. In a separate experiment in the same calorimeter, the combustion of 0.825 g of benzoic acid, for which the internal energy of combustion is  $-3251 \text{ kJ mol}^{-1}$ , gave a temperature rise of 1.940 K. Calculate the internal energy of combustion of d-ribose and its enthalpy of formation.

- 2.9** The standard enthalpy of formation of the metallocene bis(benzene)chromium was measured in a calorimeter. It was found for the reaction  $\text{Cr}(\text{C}_6\text{H}_6)_2(s) \rightarrow \text{Cr}(s) + 2 \text{C}_6\text{H}_6(g)$  that  $\Delta_c U^\circ(583 \text{ K}) = +8.0 \text{ kJ mol}^{-1}$ . Find the corresponding reaction enthalpy and estimate the standard enthalpy of formation of the compound at 583 K. The constant-pressure molar heat capacity of benzene is  $136.1 \text{ J K}^{-1} \text{ mol}^{-1}$  in its liquid range and  $81.67 \text{ J K}^{-1} \text{ mol}^{-1}$  as a gas.

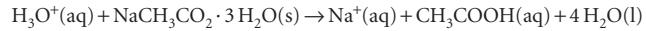
- 2.10‡** From the enthalpy of combustion data in Table 2.6 for the alkanes methane through octane, test the extent to which the relation  $\Delta_c H^\circ = k\{M/(g \text{ mol}^{-1})\}^n$  holds and find the numerical values for  $k$  and  $n$ . Predict  $\Delta_c H^\circ$  for decane and compare to the known value.

- 2.11** An average human produces about 10 MJ of heat each day through metabolic activity. If a human body were an isolated system of mass 65 kg with the heat capacity of water, what temperature rise would the body experience? Human bodies are actually open systems, and the main mechanism of heat loss is through the evaporation of water. What mass of water should be evaporated each day to maintain constant temperature?

- 2.12** Glucose and fructose are simple sugars with the molecular formula  $\text{C}_6\text{H}_{12}\text{O}_6$ . Sucrose, or table sugar, is a complex sugar with molecular formula  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  that consists of a glucose unit covalently bound to a fructose unit (a water molecule is given off as a result of the reaction between glucose and fructose to form sucrose). (a) Calculate the energy released as heat when a typical table sugar cube of mass 1.5 g is burned in air. (b) To what height could you climb on the energy a table sugar cube provides assuming 25 per cent of the energy is available for work? (c) The mass of a typical glucose tablet is 2.5 g. Calculate the energy released as heat when a glucose tablet is burned in air. (d) To what height could you climb on the energy a cube provides assuming 25 per cent of the energy is available for work?

- 2.13** It is possible to investigate the thermochemical properties of hydrocarbons with molecular modelling methods. (a) Use electronic structure software to predict  $\Delta_c H^\circ$  values for the alkanes methane through pentane. To calculate  $\Delta_c H^\circ$  values, estimate the standard enthalpy of formation of  $\text{C}_n\text{H}_{2(n+1)}(g)$  by performing semi-empirical calculations (for example, AM1 or PM3 methods) and use experimental standard enthalpy of formation values for  $\text{CO}_2(g)$  and  $\text{H}_2\text{O(l)}$ . (b) Compare your estimated values with the experimental values of  $\Delta_c H^\circ$  (Table 2.6) and comment on the reliability of the molecular modelling method. (c) Test the extent to which the relation  $\Delta_c H^\circ = k\{M/(g \text{ mol}^{-1})\}^n$  holds and find the numerical values for  $k$  and  $n$ .

- 2.14‡** When 1.3584 g of sodium acetate trihydrate was mixed into 100.0  $\text{cm}^3$  of 0.2000 M  $\text{HCl(aq)}$  at 25°C in a solution calorimeter, its temperature fell by 0.397°C on account of the reaction:



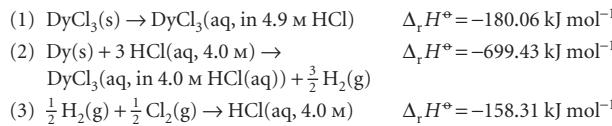
The heat capacity of the calorimeter is  $91.0 \text{ J K}^{-1}$  and the heat capacity density of the acid solution is  $4.144 \text{ J K}^{-1} \text{ cm}^{-3}$ . Determine the standard enthalpy of

\* Problems denoted with the symbol ‡ were supplied by Charles Trapp, Carmen Giunta, and Marshall Cady.

formation of the aqueous sodium cation. The standard enthalpy of formation of sodium acetate trihydrate is  $-1604 \text{ kJ mol}^{-1}$ .

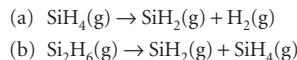
**2.15†** Since their discovery in 1985, fullerenes have received the attention of many chemical researchers. Kolesov *et al.* (*J. Chem. Thermodynamics* **28**, 1121 (1996)) reported the standard enthalpy of combustion and of formation of crystalline  $\text{C}_{60}$  based on calorimetric measurements. In one of their runs, they found the standard specific internal energy of combustion to be  $-36.0334 \text{ kJ g}^{-1}$  at 298.15 K. Compute  $\Delta_c H^\circ$  and  $\Delta_f H^\circ$  of  $\text{C}_{60}$ .

**2.16†** A thermodynamic study of  $\text{DyCl}_3$  by Cordfunke *et al.* (*J. Chem. Thermodynamics* **28**, 1387 (1996)) determined its standard enthalpy of formation from the following information

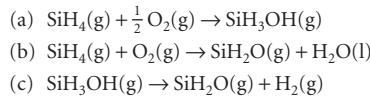


Determine  $\Delta_f H^\circ(\text{DyCl}_3, \text{s})$  from these data.

**2.17†** Silylene ( $\text{SiH}_2$ ) is a key intermediate in the thermal decomposition of silicon hydrides such as silane ( $\text{SiH}_4$ ) and disilane ( $\text{Si}_2\text{H}_6$ ). Moffat *et al.* (*J. Phys. Chem.* **95**, 145 (1991)) report  $\Delta_f H^\circ(\text{SiH}_2) = +274 \text{ kJ mol}^{-1}$ . If  $\Delta_f H^\circ(\text{SiH}_4) = +34.3 \text{ kJ mol}^{-1}$  and  $\Delta_f H^\circ(\text{Si}_2\text{H}_6) = +80.3 \text{ kJ mol}^{-1}$  (*CRC Handbook* (2008)), compute the standard enthalpies of the following reactions:



**2.18†** Silanone ( $\text{SiH}_2\text{O}$ ) and silanol ( $\text{SiH}_3\text{OH}$ ) are species believed to be important in the oxidation of silane ( $\text{SiH}_4$ ). These species are much more elusive than their carbon counterparts. C.L. Darling and H.B. Schlegel (*J. Phys. Chem.* **97**, 8207 (1993)) report the following values (converted from calories) from a computational study:  $\Delta_f H^\circ(\text{SiH}_2\text{O}) = -98.3 \text{ kJ mol}^{-1}$  and  $\Delta_f H^\circ(\text{SiH}_3\text{OH}) = -282 \text{ kJ mol}^{-1}$ . Compute the standard enthalpies of the following reactions:



Note that  $\Delta_f H^\circ(\text{SiH}_4, \text{g}) = +34.3 \text{ kJ mol}^{-1}$  (*CRC Handbook* (2008)).

**2.19** The constant-volume heat capacity of a gas can be measured by observing the decrease in temperature when it expands adiabatically and reversibly. If the decrease in pressure is also measured, we can use it to infer the value of  $\gamma = C_p/C_V$  and hence, by combining the two values, deduce the constant-pressure heat capacity. A fluorocarbon gas was allowed to expand reversibly and adiabatically to twice its volume; as a result, the temperature fell from 298.15 K to 248.44 K and its pressure fell from 202.94 kPa to 81.840 kPa. Evaluate  $C_p$ .

**2.20** A sample consisting of 1.00 mol of a van der Waals gas is compressed from  $20.0 \text{ dm}^3$  to  $10.0 \text{ dm}^3$  at 300 K. In the process, 20.2 kJ of work is done on the gas. Given that  $\mu = \{(2a/RT) - b\}/C_{p,m}$ , with  $C_{p,m} = 38.4 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $a = 3.60 \text{ dm}^6 \text{ atm mol}^{-2}$ , and  $b = 0.044 \text{ dm}^3 \text{ mol}^{-1}$ , calculate  $\Delta H$  for the process.

**2.21** Take nitrogen to be a van der Waals gas with  $a = 1.352 \text{ dm}^6 \text{ atm mol}^{-2}$  and  $b = 0.0387 \text{ dm}^3 \text{ mol}^{-1}$ , and calculate  $\Delta H_m$  when the pressure on the gas is decreased from 500 atm to 1.00 atm at 300 K. For a van der Waals gas,  $\mu = \{(2a/RT) - b\}/C_{p,m}$ . Assume  $C_{p,m} = \frac{7}{2}R$ .

### Theoretical problems

**2.22** Show that the following functions have exact differentials: (a)  $x^2y + 3y^2$ , (b)  $x \cos xy$ , (c)  $x^3y^2$ , (d)  $t(t + e^s) + s$ .

**2.23** (a) What is the total differential of  $z = x^2 + 2y^2 - 2xy + 2x - 4y - 8$ ? (b) Show that  $\partial^2 z/\partial y \partial x = \partial^2 z/\partial x \partial y$  for this function. (c) Let  $z = xy - y \ln x + 2$ . Find  $dz$  and show that it is exact.

**2.24** (a) Express  $(\partial C_V/\partial V)_T$  as a second derivative of  $U$  and find its relation to  $(\partial U/\partial V)_T$  and  $(\partial C_p/\partial p)_T$  as a second derivative of  $H$  and find its relation to  $(\partial H/\partial p)_T$ . (b) From these relations show that  $(\partial C_V/\partial V)_T = 0$  and  $(\partial C_p/\partial p)_T = 0$  for a perfect gas.

**2.25** (a) Derive the relation  $C_V = -(\partial U/\partial V)_T (\partial V/\partial T)_U$  from the expression for the total differential of  $U(T, V)$  and (b) starting from the expression for the total differential of  $H(T, p)$ , express  $(\partial H/\partial p)_T$  in terms of  $C_p$  and the Joule–Thomson coefficient,  $\mu$ .

**2.26** Starting from the expression  $C_p - C_V = T(\partial p/\partial T)_V (\partial V/\partial T)_p$ , use the appropriate relations between partial derivatives to show that

$$C_p - C_V = -\frac{T(\partial V/\partial T)_p^2}{(\partial V/\partial p)_T}$$

Evaluate  $C_p - C_V$  for a perfect gas.

**2.27** (a) By direct differentiation of  $H = U + pV$ , obtain a relation between  $(\partial H/\partial U)_p$  and  $(\partial U/\partial V)_p$ . (b) Confirm that  $(\partial H/\partial U)_p = 1 + p(\partial V/\partial U)_p$  by expressing  $(\partial H/\partial U)_p$  as the ratio of two derivatives with respect to volume and then using the definition of enthalpy.

**2.28** Use the chain relation and the reciprocal identity of partial derivatives (*Mathematical background 2*) to derive the relation  $(\partial H/\partial p)_T = -\mu C_p$ .

**2.29** Use the chain relation and the reciprocal identity of partial derivatives (*Mathematical background 2*) to derive the relation  $(\partial p/\partial T)_V = \alpha/\kappa_T$ . Confirm this relation by evaluating all three terms for (a) a perfect gas, (b) a van der Waals gas.

**2.30** (a) Write expressions for  $dV$  and  $dp$  given that  $V$  is a function of  $p$  and  $T$  and  $p$  is a function of  $V$  and  $T$ . (b) Deduce expressions for  $d \ln V$  and  $d \ln p$  in terms of the expansion coefficient and the isothermal compressibility.

**2.31** Calculate the work done during the isothermal reversible expansion of a gas that satisfies the virial equation of state, eqn 1.19. Evaluate (a) the work for 1.0 mol Ar at 273 K (for data, see Table 1.4) and (b) the same amount of a perfect gas. Let the expansion be from  $500 \text{ cm}^3$  to  $1000 \text{ cm}^3$  in each case.

**2.32** Express the work of isothermal reversible expansion of a van der Waals gas in reduced variables and find a definition of reduced work that makes the overall expression independent of the identity of the gas. Calculate the work of isothermal reversible expansion along the critical isotherm from  $V_c$  to  $xV_c$ .

**2.33†** A gas obeying the equation of state  $p(V - nb) = nRT$  is subjected to a Joule–Thomson expansion. Will the temperature increase, decrease, or remain the same?

**2.34** Use the fact that  $(\partial U/\partial V)_T = a/V_m^2$  for a van der Waals gas to show that  $\mu C_{p,m} \approx (2a/RT) - b$  by using the definition of  $\mu$  and appropriate relations between partial derivatives. (*Hint*. Use the approximation  $pV_m \approx RT$  when it is justifiable to do so.)

**2.35** Rearrange the van der Waals equation of state to give an expression for  $T$  as a function of  $p$  and  $V$  (with  $n$  constant). Calculate  $(\partial T/\partial p)_V$  and confirm that  $(\partial T/\partial p)_V = 1/(\partial p/\partial T)_V$ . Go on to confirm Euler's chain relation.

**2.36** Calculate the isothermal compressibility and the expansion coefficient of a van der Waals gas. Show, using Euler's chain relation, that  $\kappa_T R = \alpha(V_m - b)$ .

**2.37** Given that  $\mu C_p = T(\partial V/\partial T)_p - V$ , derive an expression for  $\mu$  in terms of the van der Waals parameters  $a$  and  $b$ , and express it in terms of reduced variables. Evaluate  $\mu$  at 25°C and 1.0 atm, when the molar volume of the gas is  $24.6 \text{ dm}^3 \text{ mol}^{-1}$ . Use the expression obtained to derive a formula for the inversion temperature of a van der Waals gas in terms of reduced variables, and evaluate it for the xenon sample.

**2.38** The thermodynamic equation of state  $(\partial U/\partial V)_T = T(\partial p/\partial T)_V - p$  was quoted in the chapter. Derive its partner

$$\left(\frac{\partial H}{\partial p}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_p + V$$

from it and the general relations between partial differentials.

**2.39** Show that for a van der Waals gas,

$$C_{p,m} - C_{V,m} = \lambda R \quad \frac{1}{\lambda} = 1 - \frac{(3V_r - 1)^2}{4V_r^3 T_r}$$

and evaluate the difference for xenon at 25°C and 10.0 atm.

**2.40** The speed of sound,  $c_s$ , in a gas of molar mass  $M$  is related to the ratio of heat capacities by  $c_s = (\gamma RT/M)^{1/2}$ . Show that  $c_s = (\gamma p/\rho)^{1/2}$ , where  $\rho$  is the mass density of the gas. Calculate the speed of sound in argon at 25°C.

**2.41‡** A gas obeys the equation of state  $V_m = RT/p + aT^2$  and its constant-pressure heat capacity is given by  $C_{p,m} = A + BT + Cp$ , where  $a$ ,  $A$ ,  $B$ , and  $C$  are constants independent of  $T$  and  $p$ . Obtain expressions for (a) the Joule–Thomson coefficient and (b) its constant-volume heat capacity.

### Applications: to biology and the environment

**2.42** In biological cells that have a plentiful supply of O<sub>2</sub>, glucose is oxidized completely to CO<sub>2</sub> and H<sub>2</sub>O by a process called *aerobic oxidation*. Muscle cells may be deprived of O<sub>2</sub> during vigorous exercise and, in that case, one molecule of glucose is converted to two molecules of lactic acid (CH<sub>3</sub>CH(OH)COOH) by a process called *anaerobic glycolysis* (see *Impact* 16.1). (a) When 0.3212 g of glucose was burned in a bomb calorimeter of calorimeter constant 641 J K<sup>-1</sup> the temperature rose by 7.793 K. Calculate (i) the standard molar enthalpy of combustion, (ii) the standard internal energy of combustion, and (iii) the standard enthalpy of formation of glucose. (b) What is the biological advantage (in kilojoules per mole of energy released as heat) of complete aerobic oxidation compared with anaerobic glycolysis to lactic acid?

**2.43‡** Alkyl radicals are important intermediates in the combustion and atmospheric chemistry of hydrocarbons. Seakins *et al.* (*J. Phys. Chem.* 96, 9847 (1992)) report  $\Delta_f H^\circ$  for a variety of alkyl radicals in the gas phase, information that is applicable to studies of pyrolysis and oxidation reactions of hydrocarbons. This information can be combined with thermodynamic data on alkenes to determine the reaction enthalpy for possible fragmentation of a large alkyl radical into smaller radicals and alkenes. Use the following data to compute the standard reaction enthalpies for three possible fates of the *tert*-butyl radical, namely, (a) *tert*-C<sub>4</sub>H<sub>9</sub> → *sec*-C<sub>4</sub>H<sub>9</sub>, (b) *tert*-C<sub>4</sub>H<sub>9</sub> → C<sub>3</sub>H<sub>6</sub> + CH<sub>3</sub>, (c) *tert*-C<sub>4</sub>H<sub>9</sub> → C<sub>2</sub>H<sub>4</sub> + C<sub>2</sub>H<sub>5</sub>.

Species:	C <sub>2</sub> H <sub>5</sub>	<i>sec</i> -C <sub>4</sub> H <sub>9</sub>	<i>tert</i> -C <sub>4</sub> H <sub>9</sub>
$\Delta_f H^\circ/(kJ mol^{-1})$	+121.0	+67.5	+51.3

**2.44‡** In 2007, the Intergovernmental Panel on Climate Change (IPCC) considered a global average temperature rise of 1.0–3.5°C likely by the year 2100 with 2.0°C its best estimate. Predict the average rise in sea level due to

thermal expansion of sea water based on temperature rises of 1.0°C, 2.0°C, and 3.5°C given that the volume of the Earth's oceans is  $1.37 \times 10^9 \text{ km}^3$  and their surface area is  $361 \times 10^6 \text{ km}^2$ , and state the approximations that go into the estimates.

**2.45‡** Concerns over the harmful effects of chlorofluorocarbons on stratospheric ozone have motivated a search for new refrigerants. One such alternative is 2,2-dichloro-1,1,1-trifluoroethane (refrigerant 123). Younglove and McLinden published a compendium of thermophysical properties of this substance (*J. Phys. Chem. Ref. Data* 23, 7 (1994)), from which properties such as the Joule–Thomson coefficient  $\mu$  can be computed. (a) Compute  $\mu$  at 1.00 bar and 50°C given that  $(\partial H/\partial p)_T = -3.29 \times 10^3 \text{ J MPa}^{-1} \text{ mol}^{-1}$  and  $C_{p,m} = 110.0 \text{ J K}^{-1} \text{ mol}^{-1}$ . (b) Compute the temperature change that would accompany adiabatic expansion of 2.0 mol of this refrigerant from 1.5 bar to 0.5 bar at 50°C.

**2.46‡** Another alternative refrigerant (see preceding problem) is 1,1,1,2-tetrafluoroethane (refrigerant HFC-134a). Tillner-Roth and Baehr published a compendium of thermophysical properties of this substance (*J. Phys. Chem. Ref. Data* 23, 657 (1994)), from which properties such as the Joule–Thomson coefficient  $\mu$  can be computed. (a) Compute  $\mu$  at 0.100 MPa and 300 K from the following data (all referring to 300 K):

$p/\text{MPa}$	0.080	0.100	0.12
Specific enthalpy/(kJ kg <sup>-1</sup> )	426.48	426.12	425.76

(The specific constant-pressure heat capacity is  $0.7649 \text{ kJ K}^{-1} \text{ kg}^{-1}$ .)

(b) Compute  $\mu$  at 1.00 MPa and 350 K from the following data (all referring to 350 K):

$p/\text{MPa}$	0.80	1.00	1.2
Specific enthalpy/(kJ kg <sup>-1</sup> )	461.93	459.12	456.15

(The specific constant-pressure heat capacity is  $1.0392 \text{ kJ K}^{-1} \text{ kg}^{-1}$ .)

**2.47** Differential scanning calorimetry is used to examine the role of solvent–protein interactions in the denaturation process. Figure 2.34 shows the thermogram for ubiquitin in water with the signal observed for ubiquitin in methanol/water mixtures. Suggest an interpretation of the thermograms.

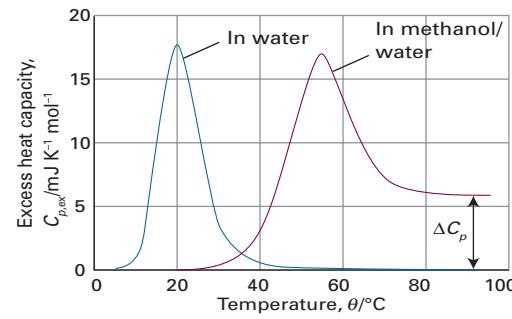


Fig. 2.34

**MATHEMATICAL BACKGROUND 2****Multivariate calculus**

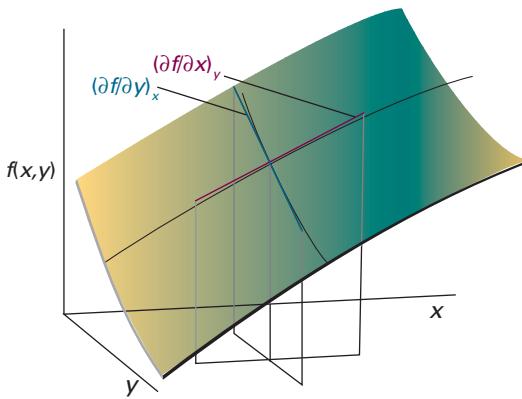
A thermodynamic property of a system typically depends on a number of variables, such as the internal energy depending on the amount, volume, and temperature. To understand how these properties vary with the conditions we need to understand how to manipulate their derivatives. This is the field of **multivariate calculus**, the calculus of several variables.

**MB2.1 Partial derivatives**

A partial derivative of a function of more than one variable, such as  $f(x,y)$ , is the slope of the function with respect to one of the variables, all the other variables being held constant (Fig. MB2.1). Although a partial derivative shows how a function changes when one variable changes, it may be used to determine how the function changes when more than one variable changes by an infinitesimal amount. Thus, if  $f$  is a function of  $x$  and  $y$ , then when  $x$  and  $y$  change by  $dx$  and  $dy$ , respectively,  $f$  changes by

$$df = \left( \frac{\partial f}{\partial x} \right)_y dx + \left( \frac{\partial f}{\partial y} \right)_x dy \quad (\text{MB2.1})$$

where the symbol  $\partial$  is used (instead of  $d$ ) to denote a partial derivative and the subscript on the parentheses indicates which variable is being held constant. The quantity  $df$  is also called the



**Fig. MB2.1** A function of two variables,  $f(x,y)$ , as depicted by the coloured surface, and the two partial derivatives,  $(\partial f / \partial x)_y$  and  $(\partial f / \partial y)_x$ , the slope of the function parallel to the  $x$ - and  $y$ -axes, respectively. The function plotted here is  $f(x,y) = ax^3y + by^2$  with  $a = 1$  and  $b = -2$ .

differential of  $f$ . Successive partial derivatives may be taken in any order:

$$\left( \frac{\partial}{\partial y} \left( \frac{\partial f}{\partial x} \right)_y \right)_x = \left( \frac{\partial}{\partial x} \left( \frac{\partial f}{\partial y} \right)_x \right)_y \quad (\text{MB2.2})$$

- **A brief illustration**

Suppose that  $f(x,y) = ax^3y + by^2$  (the function plotted in Fig. MB2.1) then

$$\left( \frac{\partial f}{\partial x} \right)_y = 3ax^2y \quad \left( \frac{\partial f}{\partial y} \right)_x = ax^3 + 2by$$

Then, when  $x$  and  $y$  undergo infinitesimal changes,  $f$  changes by

$$df = 3ax^2y dx + (ax^3 + 2by) dy$$

To verify that the order of taking the second partial derivative is irrelevant, we form

$$\begin{aligned} \left( \frac{\partial}{\partial y} \left( \frac{\partial f}{\partial x} \right)_y \right)_x &= \left( \frac{\partial(3ax^2y)}{\partial y} \right)_x = 3ax^2 \\ \left( \frac{\partial}{\partial x} \left( \frac{\partial f}{\partial y} \right)_x \right)_y &= \left( \frac{\partial(ax^3 + 2by)}{\partial x} \right)_y = 3ax^2 \bullet \end{aligned}$$

**Self test MB2.1** Evaluate  $df$  for  $f(x,y) = 2x^2 \sin 3y$  and verify that the order of taking the second derivative is irrelevant.

$$[df = 4x \sin 3y dx + 6x^2 \cos 3y dy]$$

In the following,  $z$  is a variable on which  $x$  and  $y$  depend (for example,  $x$ ,  $y$ , and  $z$  might correspond to  $p$ ,  $V$ , and  $T$ ).

**Relation 1** When  $x$  is changed at constant  $z$ :

$$\left( \frac{\partial f}{\partial x} \right)_z = \left( \frac{\partial f}{\partial x} \right)_y + \left( \frac{\partial f}{\partial y} \right)_x \left( \frac{\partial y}{\partial x} \right)_z \quad (\text{MB2.3a})$$

**Relation 2**

$$\left( \frac{\partial y}{\partial x} \right)_z = \frac{1}{(\partial x / \partial y)_z} \quad (\text{MB2.3b})$$

**Relation 3**

$$\left( \frac{\partial x}{\partial y} \right)_z = - \left( \frac{\partial x}{\partial z} \right)_y \left( \frac{\partial z}{\partial y} \right)_x \quad (\text{MB2.3c})$$

By combining this relation and Relation 2 we obtain the Euler chain relation:

$$\left( \frac{\partial y}{\partial x} \right)_z \left( \frac{\partial x}{\partial z} \right)_y \left( \frac{\partial z}{\partial y} \right)_x = -1 \quad \boxed{\text{Euler chain relation}} \quad (\text{MB2.4})$$

## MB2.2 Exact differentials

The relation in eqn MB2.2 is the basis of a test for an **exact differential**, that is, the test of whether

$$df = g(x,y)dx + h(x,y)dy \quad (\text{MB2.5})$$

has the form in eqn MB2.1. If it has that form, then  $g$  can be identified with  $(\partial f / \partial x)_y$  and  $h$  can be identified with  $(\partial f / \partial y)_x$ . Then eqn MB2.2 becomes

$$\left( \frac{\partial g}{\partial y} \right)_x = \left( \frac{\partial h}{\partial x} \right)_y \quad \boxed{\text{Test for exact differential}} \quad (\text{MB2.6})$$

### • A brief illustration

Suppose, instead of the form  $df = 3ax^2ydx + (ax^3 + 2by)dy$  in the previous *brief illustration* we were presented with the expression

$$df = \overbrace{3ax^2ydx}^{g(x,y)} + \overbrace{(ax^2 + 2by)dy}^{h(x,y)}$$

with  $ax^2$  in place of  $ax^3$  inside the second parentheses. To test whether this is an exact differential, we form

$$\left( \frac{\partial g}{\partial y} \right)_x = \left( \frac{\partial (3ax^2y)}{\partial y} \right)_x = 3ax^2$$

$$\left( \frac{\partial h}{\partial x} \right)_y = \left( \frac{\partial (ax^2 + 2by)}{\partial x} \right)_y = 2ax$$

These two expressions are not equal, so this form of  $df$  is not an exact differential and there is not a corresponding integrated function of the form  $f(x,y)$ . ●

**Self-test MB2.2** Determine whether the expression  $df = (2y - x^3)dx + xdy$  is an exact differential. [No]

If  $df$  is exact, then we can do two things: (1) from a knowledge of the functions  $g$  and  $h$  we can reconstruct the function  $f$ ; (2) we can be confident that the integral of  $df$  between specified limits is independent of the path between those limits. The first conclusion is best demonstrated with a specific example.

### • A brief illustration

We consider the differential  $df = 3ax^2ydx + (ax^3 + 2by)dy$ , which we know to be exact. Because  $(\partial f / \partial x)_y = 3ax^2y$ , we can integrate with respect to  $x$  with  $y$  held constant, to obtain

$$f = \int df = \int 3ax^2ydx = 3ay \int x^2 dx = ax^3y + k$$

where the ‘constant’ of integration  $k$  may depend on  $y$  (which has been treated as a constant in the integration), but not on  $x$ . To find  $k(y)$ , we note that  $(\partial f / \partial y)_x = ax^3 + 2by$ , and therefore

$$\left( \frac{\partial f}{\partial y} \right)_x = \left( \frac{\partial (ax^3y + k)}{\partial y} \right)_x = ax^3 + \frac{dk}{dy} = ax^3 + 2by$$

Therefore

$$\frac{dk}{dy} = 2by$$

from which it follows that  $k = by^2 + \text{constant}$ . We have found, therefore, that

$$f(x,y) = ax^3y + by^2 + \text{constant}$$

which, apart from the constant, is the original function in the first *brief illustration*. The value of the constant is pinned down by stating the boundary conditions; thus, if it is known that  $f(0,0) = 0$ , then the constant is zero. ●

**Self-test MB2.3** Confirm that  $df = 3x^2 \cos y dx - x^3 \sin y dy$  is exact and find the function  $f(x,y)$ . [ $f = x^3 \cos y$ ]

To demonstrate that the integral of  $df$  is independent of the path is now straightforward. Because  $df$  is a differential, its integral between the limits  $a$  and  $b$  is

$$\int_a^b df = f(b) - f(a)$$

The value of the integral depends only on the values at the end points and is independent of the path between them. If  $df$  is not an exact differential, the function  $f$  does not exist, and this argument no longer holds. In such cases, the integral of  $df$  does depend on the path.

### • A brief illustration

Consider the inexact differential (the expression with  $ax^2$  in place of  $ax^3$  inside the second parentheses):

$$df = 3ax^2ydx + (ax^2 + 2by)dy$$

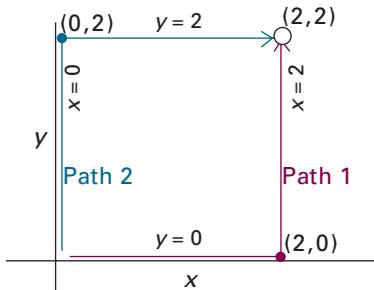
Suppose we integrate  $df$  from  $(0,0)$  to  $(2,2)$  along the two paths shown in Fig. MB2.2. Along Path 1,

$$\begin{aligned} \int_{\text{Path 1}} df &= \int_{0,0}^{2,0} 3ax^2ydx + \int_{2,0}^{2,2} (ax^2 + 2by)dy \\ &= 0 + 4a \int_0^2 dy + 2b \int_0^2 ydy = 8a + 4b \end{aligned}$$

whereas along Path 2,

$$\begin{aligned} \int_{\text{Path 2}} df &= \int_{0,2}^{2,2} 3ax^2ydx + \int_{0,0}^{0,2} (ax^2 + 2by)dy \\ &= 6a \int_0^2 x^2 dx + 0 + 2b \int_0^2 ydy = 16a + 4b \end{aligned}$$

The two integrals are not the same. ●



**Fig. MB2.2** The two integration paths referred to in the *brief illustration*.

**Self-test MB2.4** Confirm that the two paths do give the same value for the exact differential in the first *brief illustration*.

[Both paths:  $16a + 4b$ ]

An inexact differential may sometimes be converted into an exact differential by multiplication by a factor known as an *integrating factor*. A physical example is the integrating factor  $1/T$  that converts the inexact differential  $dq_{\text{rev}}$  into the exact differential  $dS$  in thermodynamics (see Chapter 3).

#### • A brief illustration

We have seen that the differential  $df = 3ax^2ydx + (ax^2 + 2by)dy$  is inexact; the same is true when we set  $b = 0$  and consider

$df = 3ax^2ydx + ax^2 dy$  instead. Suppose we multiply this  $df$  by  $x^m y^n$  and write  $x^m y^n df = df'$ , then we obtain

$$df' = \overbrace{3ax^{m+2}y^{n+1}}^{g(x,y)} dx + \overbrace{ax^{m+2}y^n}^{h(x,y)} dy$$

We evaluate the following two partial derivatives:

$$\left( \frac{\partial g}{\partial y} \right)_x = \left( \frac{\partial (3ax^{m+2}y^{n+1})}{\partial y} \right)_x = 3a(n+1)x^{m+2}y^n$$

$$\left( \frac{\partial h}{\partial x} \right)_y = \left( \frac{\partial (ax^{m+2}y^n)}{\partial x} \right)_y = a(m+2)x^{m+1}y^n$$

For the new differential to be exact, these two partial derivatives must be equal, so we write

$$3a(n+1)x^{m+2}y^n = a(m+2)x^{m+1}y^n$$

which simplifies to

$$3(n+1)x = m+2$$

The only solution that is independent of  $x$  is  $n = -1$  and  $m = -2$ . It follows that

$$df' = 3adx + (a/y)dy$$

is an exact differential. By the procedure already illustrated, its integrated form is  $f'(x,y) = 3ax + a \ln y + \text{constant}$ . •

**Self-test MB2.5** Find an integrating factor of the form  $x^m y^n$  for the inexact differential  $df = (2y - x^3)dx + xdy$  and the integrated form of  $f'$ .

$$[df' = xdf, f' = yx^2 - \frac{1}{5}x^5 + \text{constant}]$$



# 3

# The Second Law

## The direction of spontaneous change

**3.1** The dispersal of energy

**3.2** Entropy

**I3.1** Impact on engineering:  
Refrigeration

**3.3** Entropy changes  
accompanying specific  
processes

**3.4** The Third Law of  
thermodynamics

**I3.2** Impact on materials chemistry:  
Crystal defects

## Concentrating on the system

**3.5** The Helmholtz and Gibbs  
energies

**3.6** Standard molar Gibbs energies

## Combining the First and Second Laws

**3.7** The fundamental equation

**3.8** Properties of the internal  
energy

**3.9** Properties of the Gibbs energy

Checklist of key equations

Further information 3.1: The Born  
equation

Further information 3.2: The fugacity

Discussion questions

Exercises

Problems

The purpose of this chapter is to explain the origin of the spontaneity of physical and chemical change. We examine two simple processes and show how to define, measure, and use a property, the entropy, to discuss spontaneous changes quantitatively. The chapter also introduces a major subsidiary thermodynamic property, the Gibbs energy, which lets us express the spontaneity of a process in terms of the properties of a system. The Gibbs energy also enables us to predict the maximum non-expansion work that a process can do. As we began to see in Chapter 2, one application of thermodynamics is to find relations between properties that might not be thought to be related. Several relations of this kind can be established by making use of the fact that the Gibbs energy is a state function. We also see how to derive expressions for the variation of the Gibbs energy with temperature and pressure and how to formulate expressions that are valid for real gases. These expressions will prove useful later when we discuss the effect of temperature and pressure on equilibrium constants.

Some things happen naturally; some things don't. A gas expands to fill the available volume, a hot body cools to the temperature of its surroundings, and a chemical reaction runs in one direction rather than another. Some aspect of the world determines the **spontaneous** direction of change, the direction of change that does not require work to bring it about. A gas can be confined to a smaller volume, an object can be cooled by using a refrigerator, and some reactions can be driven in reverse (as in the electrolysis of water). However, none of these processes is spontaneous; each one must be brought about by doing work. An important point, though, is that throughout this text 'spontaneous' must be interpreted as a natural *tendency* that may or may not be realized in practice. Thermodynamics is silent on the rate at which a spontaneous change in fact occurs, and some spontaneous processes (such as the conversion of diamond to graphite) may be so slow that the tendency is never realized in practice whereas others (such as the expansion of a gas into a vacuum) are almost instantaneous.

The recognition of two classes of process, spontaneous and non-spontaneous, is summarized by the **Second Law of thermodynamics**. This law may be expressed in a variety of equivalent ways. One statement was formulated by Kelvin:

No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work.

For example, it has proved impossible to construct an engine like that shown in Fig. 3.1, in which heat is drawn from a hot reservoir and completely converted into work. All real heat engines have both a hot source and a cold sink; some energy is always discarded into the cold sink as heat and not converted into work. The Kelvin

statement is a generalization of another everyday observation, that a ball at rest on a surface has never been observed to leap spontaneously upwards. An upward leap of the ball would be equivalent to the conversion of heat from the surface into work.

## The direction of spontaneous change

What determines the direction of spontaneous change? It is not the total energy of the isolated system. The First Law of thermodynamics states that energy is conserved in any process, and we cannot disregard that law now and say that everything tends towards a state of lower energy: the total energy of an isolated system is constant.

Is it perhaps the energy of the *system* that tends towards a minimum? Two arguments show that this cannot be so. First, a perfect gas expands spontaneously into a vacuum, yet its internal energy remains constant as it does so. Secondly, if the energy of a system does happen to decrease during a spontaneous change, the energy of its surroundings must increase by the same amount (by the First Law). The increase in energy of the surroundings is just as spontaneous a process as the decrease in energy of the system.

When a change occurs, the total energy of an isolated system remains constant but it is parcelled out in different ways. Can it be, therefore, that the direction of change is related to the *distribution* of energy? We shall see that this idea is the key, and that spontaneous changes are always accompanied by a dispersal of energy.

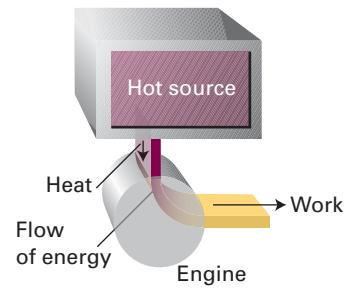
### 3.1 The dispersal of energy

**Key point** During a spontaneous change in an isolated system the total energy is dispersed into random thermal motion of the particles in the system.

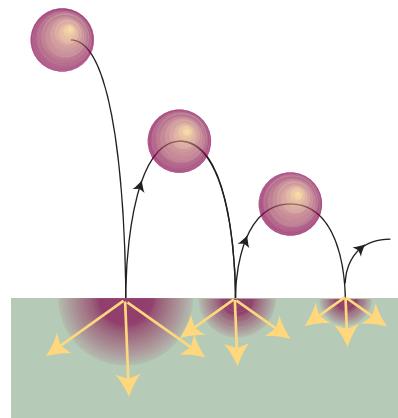
We can begin to understand the role of the distribution of energy by thinking about a ball (the system) bouncing on a floor (the surroundings). The ball does not rise as high after each bounce because there are inelastic losses in the materials of the ball and floor. The kinetic energy of the ball's overall motion is spread out into the energy of thermal motion of its particles and those of the floor that it hits. The direction of spontaneous change is towards a state in which the ball is at rest with all its energy dispersed into disorderly thermal motion of molecules in the air and of the atoms of the virtually infinite floor (Fig. 3.2).

A ball resting on a warm floor has never been observed to start bouncing. For bouncing to begin, something rather special would need to happen. In the first place, some of the thermal motion of the atoms in the floor would have to accumulate in a single, small object, the ball. This accumulation requires a spontaneous localization of energy from the myriad vibrations of the atoms of the floor into the much smaller number of atoms that constitute the ball (Fig. 3.3). Furthermore, whereas the thermal motion is random, for the ball to move upwards its atoms must all move in the same direction. The localization of random, disorderly motion as concerted, ordered motion is so unlikely that we can dismiss it as virtually impossible.<sup>1</sup>

We appear to have found the signpost of spontaneous change: *we look for the direction of change that leads to dispersal of the total energy of the isolated system*. This principle accounts for the direction of change of the bouncing ball, because its energy

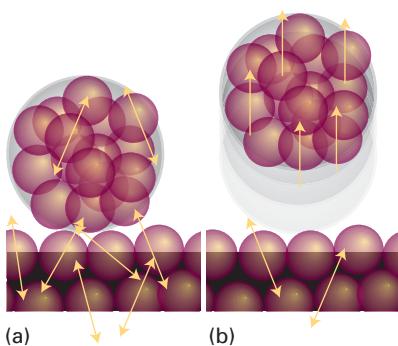


**Fig. 3.1** The Kelvin statement of the Second Law denies the possibility of the process illustrated here, in which heat is changed completely into work, there being no other change. The process is not in conflict with the First Law because energy is conserved.



**Fig. 3.2** The direction of spontaneous change for a ball bouncing on a floor. On each bounce some of its energy is degraded into the thermal motion of the atoms of the floor, and that energy disperses. The reverse has never been observed to take place on a macroscopic scale.

<sup>1</sup> Concerted motion, but on a much smaller scale, is observed as *Brownian motion*, the jittering motion of small particles suspended in a liquid or gas.



**Fig. 3.3** The molecular interpretation of the irreversibility expressed by the Second Law. (a) A ball resting on a warm surface; the atoms are undergoing thermal motion (vibration, in this instance), as indicated by the arrows. (b) For the ball to fly upwards, some of the random vibrational motion would have to change into coordinated, directed motion. Such a conversion is highly improbable.

is spread out as thermal motion of the atoms of the floor. The reverse process is not spontaneous because it is highly improbable that energy will become localized, leading to uniform motion of the ball's atoms. A gas does not contract spontaneously because to do so the random motion of its molecules, which spreads out the distribution of kinetic energy throughout the container, would have to take them all into the same region of the container, thereby localizing the energy. The opposite change, spontaneous expansion, is a natural consequence of energy becoming more dispersed as the gas molecules occupy a larger volume. An object does not spontaneously become warmer than its surroundings because it is highly improbable that the jostling of randomly vibrating atoms in the surroundings will lead to the localization of thermal motion in the object. The opposite change, the spreading of the object's energy into the surroundings as thermal motion, is natural.

It may seem very puzzling that the spreading out of energy and matter can lead to the formation of such ordered structures as crystals or proteins. Nevertheless, in due course, we shall see that dispersal of energy and matter accounts for change in all its forms.

### 3.2 Entropy

**Key points** The entropy acts as a signpost of spontaneous change. (a) Entropy change is defined in terms of heat transactions (the Clausius definition). (b) Absolute entropies are defined in terms of the number of ways of achieving a configuration (the Boltzmann formula). (c) The Carnot cycle is used to prove that entropy is a state function. (d) The efficiency of a heat engine is the basis of the definition of the thermodynamic temperature scale and one realization, the Kelvin scale. (e) The Clausius inequality is used to show that the entropy increases in a spontaneous change and therefore that the Clausius definition is consistent with the Second Law.

The First Law of thermodynamics led to the introduction of the internal energy,  $U$ . The internal energy is a state function that lets us assess whether a change is permissible: only those changes may occur for which the internal energy of an isolated system remains constant. The law that is used to identify the signpost of spontaneous change, the Second Law of thermodynamics, may also be expressed in terms of another state function, the **entropy**,  $S$ . We shall see that the entropy (which we shall define shortly, but is a measure of the energy dispersed in a process) lets us assess whether one state is accessible from another by a spontaneous change. The First Law uses the internal energy to identify *permissible* changes; the Second Law uses the entropy to identify the *spontaneous changes* among those permissible changes.

The Second Law of thermodynamics can be expressed in terms of the entropy:

The entropy of an isolated system increases in the course of a spontaneous change:  

$$\Delta S_{\text{tot}} > 0$$

where  $S_{\text{tot}}$  is the total entropy of the system and its surroundings. Thermodynamically irreversible processes (like cooling to the temperature of the surroundings and the free expansion of gases) are spontaneous processes, and hence must be accompanied by an increase in total entropy.

#### (a) The thermodynamic definition of entropy

The thermodynamic definition of entropy concentrates on the change in entropy,  $dS$ , that occurs as a result of a physical or chemical change (in general, as a result of a 'process'). The definition is motivated by the idea that a change in the extent to which energy is dispersed depends on how much energy is transferred as heat. As we have remarked, heat stimulates random motion in the surroundings. On the other hand,

work stimulates uniform motion of atoms in the surroundings and so does not change their entropy.

The thermodynamic definition of entropy is based on the expression

$$dS = \frac{dq_{rev}}{T} \quad [3.1]$$

where  $q_{rev}$  is the heat supplied reversibly. For a measurable change between two states i and f this expression integrates to

$$\Delta S = \int_i^f \frac{dq_{rev}}{T} \quad (3.2)$$

That is, to calculate the difference in entropy between any two states of a system, we find a *reversible* path between them, and integrate the energy supplied as heat at each stage of the path divided by the temperature at which heating occurs.

### Example 3.1 Calculating the entropy change for the isothermal expansion of a perfect gas

Calculate the entropy change of a sample of perfect gas when it expands isothermally from a volume  $V_i$  to a volume  $V_f$ .

**Method** The definition of entropy instructs us to find the energy supplied as heat for a reversible path between the stated initial and final states regardless of the actual manner in which the process takes place. A simplification is that the expansion is isothermal, so the temperature is a constant and may be taken outside the integral in eqn 3.2. The energy absorbed as heat during a reversible isothermal expansion of a perfect gas can be calculated from  $\Delta U = q + w$  and  $\Delta U = 0$ , which implies that  $q = -w$  in general and therefore that  $q_{rev} = -w_{rev}$  for a reversible change. The work of reversible isothermal expansion was calculated in Section 2.3.

**Answer** Because the temperature is constant, eqn 3.2 becomes

$$\Delta S = \frac{1}{T} \int_i^f dq_{rev} = \frac{q_{rev}}{T}$$

From eqn 2.10, we know that

$$q_{rev} = -w_{rev} = nRT \ln \frac{V_f}{V_i}$$

It follows that

$$\Delta S = nR \ln \frac{V_f}{V_i}$$

#### • A brief illustration

When the volume occupied by 1.00 mol of any perfect gas molecules is doubled at any constant temperature,  $V_f/V_i = 2$  and

$$\Delta S = (1.00 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln 2 = +5.76 \text{ J K}^{-1}$$

**A note on good practice** According to eqn 3.2, when the energy transferred as heat is expressed in joules and the temperature is in kelvins, the units of entropy are joules per kelvin ( $\text{J K}^{-1}$ ). Entropy is an extensive property. Molar entropy, the entropy divided by the amount of substance, is expressed in joules per kelvin per mole ( $\text{J K}^{-1} \text{ mol}^{-1}$ ). The units of entropy are the same as those of the gas constant,  $R$ , and molar heat capacities. Molar entropy is an intensive property.

### Self-test 3.1 Calculate the change in entropy when the pressure of a fixed amount of perfect gas is changed isothermally from $p_i$ to $p_f$ . What is this change due to?

[ $\Delta S = nR \ln(p_i/p_f)$ ; the change in volume when the gas is compressed]

We can use the definition in eqn 3.1 to formulate an expression for the change in entropy of the surroundings,  $\Delta S_{\text{sur}}$ . Consider an infinitesimal transfer of heat  $dq_{\text{sur}}$  to the surroundings. The surroundings consist of a reservoir of constant volume, so the energy supplied to them by heating can be identified with the change in the internal energy of the surroundings,  $dU_{\text{sur}}$ <sup>2</sup> The internal energy is a state function, and  $dU_{\text{sur}}$  is an exact differential. As we have seen, these properties imply that  $dU_{\text{sur}}$  is independent of how the change is brought about and in particular is independent of whether the process is reversible or irreversible. The same remarks therefore apply to  $dq_{\text{sur}}$ , to which  $dU_{\text{sur}}$  is equal. Therefore, we can adapt the definition in eqn 3.1, delete the constraint ‘reversible’, and write

$$dS_{\text{sur}} = \frac{dq_{\text{sur,rev}}}{T_{\text{sur}}} = \frac{dq_{\text{sur}}}{T_{\text{sur}}} \quad \boxed{\text{Entropy change of the surroundings}} \quad (3.3a)$$

Furthermore, because the temperature of the surroundings is constant whatever the change, for a measurable change

$$\Delta S_{\text{sur}} = \frac{q_{\text{sur}}}{T_{\text{sur}}} \quad (3.3b)$$

That is, regardless of how the change is brought about in the system, reversibly or irreversibly, we can calculate the change of entropy of the surroundings by dividing the heat transferred by the temperature at which the transfer takes place.

Equation 3.3 makes it very simple to calculate the changes in entropy of the surroundings that accompany any process. For instance, for any adiabatic change,  $q_{\text{sur}} = 0$ , so

$$\text{For an adiabatic change: } \Delta S_{\text{sur}} = 0 \quad (3.4)$$

This expression is true however the change takes place, reversibly or irreversibly, provided no local hot spots are formed in the surroundings. That is, it is true so long as the surroundings remain in internal equilibrium. If hot spots do form, then the localized energy may subsequently disperse spontaneously and hence generate more entropy.

#### • A brief illustration

To calculate the entropy change in the surroundings when 1.00 mol H<sub>2</sub>O(l) is formed from its elements under standard conditions at 298 K, we use  $\Delta H^\circ = -286 \text{ kJ}$  from Table 2.8. The energy released as heat is supplied to the surroundings, now regarded as being at constant pressure, so  $q_{\text{sur}} = +286 \text{ kJ}$ . Therefore,

$$\Delta S_{\text{sur}} = \frac{2.86 \times 10^5 \text{ J}}{298 \text{ K}} = +960 \text{ J K}^{-1}$$

This strongly exothermic reaction results in an increase in the entropy of the surroundings as energy is released as heat into them. •

**Self-test 3.2** Calculate the entropy change in the surroundings when 1.00 mol N<sub>2</sub>O<sub>4</sub>(g) is formed from 2.00 mol NO<sub>2</sub>(g) under standard conditions at 298 K.

$$[-192 \text{ J K}^{-1}]$$

<sup>2</sup> Alternatively, the surroundings can be regarded as being at constant pressure, in which case we could equate  $dq_{\text{sur}}$  to  $dH_{\text{sur}}$ .

### (b) The statistical view of entropy

The entry point into the molecular interpretation of the Second Law of thermodynamics is Boltzmann's insight, first explored in Section F.5a, that an atom or molecule can possess only certain values of the energy, called its 'energy levels'. The continuous thermal agitation that molecules experience in a sample at  $T > 0$  ensures that they are distributed over the available energy levels. Boltzmann also made the link between the distribution of molecules over energy levels and the entropy. He proposed that the entropy of a system is given by

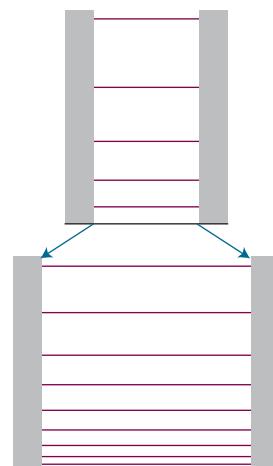
$$S = k \ln W$$

Boltzmann formula  
for the entropy (3.5)

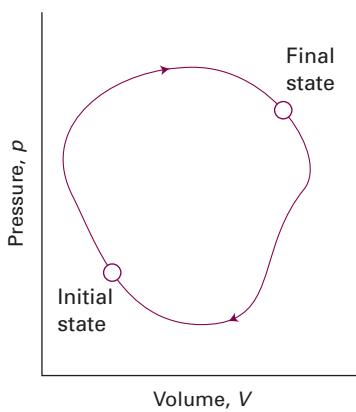
where  $k = 1.381 \times 10^{-23} \text{ J K}^{-1}$  and  $W$  is the number of *microstates*, the ways in which the molecules of a system can be arranged while keeping the total energy constant. Each microstate lasts only for an instant and corresponds to a certain distribution of molecules over the available energy levels. When we measure the properties of a system, we are measuring an average taken over the many microstates the system can occupy under the conditions of the experiment. The concept of the number of microstates makes quantitative the ill-defined qualitative concepts of 'disorder' and 'the dispersal of matter and energy' that are used widely to introduce the concept of entropy: a more 'disorderly' distribution of energy and matter corresponds to a greater number of microstates associated with the same total energy.

Equation 3.5 is known as the **Boltzmann formula** and the entropy calculated from it is sometimes called the **statistical entropy**. We see that, if  $W = 1$ , which corresponds to one microstate (only one way of achieving a given energy, all molecules in exactly the same state), then  $S = 0$  because  $\ln 1 = 0$ . However, if the system can exist in more than one microstate, then  $W > 1$  and  $S > 0$ . If the molecules in the system have access to a greater number of energy levels, then there may be more ways of achieving a given total energy, that is, there are more microstates for a given total energy,  $W$  is greater, and the entropy is greater than when fewer states are accessible. Therefore, the statistical view of entropy summarized by the Boltzmann formula is consistent with our previous statement that the entropy is related to the dispersal of energy. In particular, for a gas of particles in a container, the energy levels become closer together as the container expands (Fig. 3.4; this is a conclusion from quantum theory that we shall verify in Chapter 8). As a result, more microstates become possible,  $W$  increases, and the entropy increases, exactly as we inferred from the thermodynamic definition of entropy.

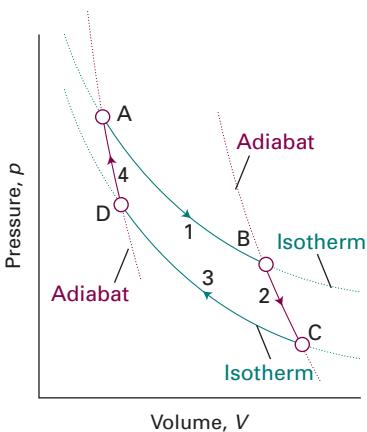
The molecular interpretation of entropy advanced by Boltzmann also suggests the thermodynamic definition given by eqn 3.1. To appreciate this point, consider that molecules in a system at high temperature can occupy a large number of the available energy levels, so a small additional transfer of energy as heat will lead to a relatively small change in the number of accessible energy levels. Consequently, the number of microstates does not increase appreciably and neither does the entropy of the system. In contrast, the molecules in a system at low temperature have access to far fewer energy levels (at  $T = 0$ , only the lowest level is accessible), and the transfer of the same quantity of energy by heating will increase the number of accessible energy levels and the number of microstates significantly. Hence, the change in entropy upon heating will be greater when the energy is transferred to a cold body than when it is transferred to a hot body. This argument suggests that the change in entropy should be inversely proportional to the temperature at which the transfer takes place, as in eqn 3.1.



**Fig. 3.4** When a box expands, the energy levels move closer together and more become accessible to the molecules. As a result the partition function increases and so does the entropy.



**Fig. 3.5** In a thermodynamic cycle, the overall change in a state function (from the initial state to the final state and then back to the initial state again) is zero.



**Fig. 3.6** The basic structure of a Carnot cycle. In Step 1, there is an isothermal reversible expansion at the temperature  $T_h$ . Step 2 is a reversible adiabatic expansion in which the temperature falls from  $T_h$  to  $T_c$ . In Step 3 there is an isothermal reversible compression at  $T_c$ , and that isothermal step is followed by an adiabatic reversible compression, which restores the system to its initial state.

### (c) The entropy as a state function

Entropy is a state function. To prove this assertion, we need to show that the integral of  $dS$  is independent of path. To do so, it is sufficient to prove that the integral of eqn 3.1 around an arbitrary cycle is zero, for that guarantees that the entropy is the same at the initial and final states of the system regardless of the path taken between them (Fig. 3.5). That is, we need to show that

$$\oint \frac{dq_{rev}}{T_{sur}} = 0 \quad (3.6)$$

where the symbol  $\oint$  denotes integration around a closed path. There are three steps in the argument:

1. First, to show that eqn 3.6 is true for a special cycle (a ‘Carnot cycle’) involving a perfect gas.
2. Then to show that the result is true whatever the working substance.
3. Finally, to show that the result is true for any cycle.

A Carnot cycle, which is named after the French engineer Sadi Carnot, consists of four reversible stages (Fig. 3.6):

1. Reversible isothermal expansion from A to B at  $T_h$ ; the entropy change is  $q_h/T_h$ , where  $q_h$  is the energy supplied to the system as heat from the hot source.
2. Reversible adiabatic expansion from B to C. No energy leaves the system as heat, so the change in entropy is zero. In the course of this expansion, the temperature falls from  $T_h$  to  $T_c$ , the temperature of the cold sink.
3. Reversible isothermal compression from C to D at  $T_c$ . Energy is released as heat to the cold sink; the change in entropy of the system is  $q_c/T_c$ ; in this expression  $q_c$  is negative.
4. Reversible adiabatic compression from D to A. No energy enters the system as heat, so the change in entropy is zero. The temperature rises from  $T_c$  to  $T_h$ .

The total change in entropy around the cycle is the sum of the changes in each of these four steps:

$$\oint dS = \frac{q_h}{T_h} + \frac{q_c}{T_c}$$

However, we show in the following *Justification* that for a perfect gas

$$\frac{q_h}{T_h} = -\frac{T_h}{T_c} \quad (3.7)$$

Substitution of this relation into the preceding equation gives zero on the right, which is what we wanted to prove.

---

#### Justification 3.1 Heating accompanying reversible adiabatic expansion

This *Justification* is based on two features of the cycle. One feature is that the two temperatures  $T_h$  and  $T_c$  in eqn 3.7 lie on the same adiabat in Fig. 3.6. The second feature is that the energies transferred as heat during the two isothermal stages are

$$q_h = nRT_h \ln \frac{V_B}{V_A} \quad q_c = nRT_c \ln \frac{V_D}{V_C}$$

We now show that the two volume ratios are related in a very simple way. From the relation between temperature and volume for reversible adiabatic processes ( $VT^c = \text{constant}$ , eqn 2.28):

$$V_A T_h^c = V_D T_c^c \quad V_C T_c^c = V_B T_h^c$$

Multiplication of the first of these expressions by the second gives

$$V_A V_C T_h^c T_c^c = V_D V_B T_h^c T_c^c$$

which, on cancellation of the temperatures, simplifies to

$$\frac{V_A}{V_B} = \frac{V_D}{V_C}$$

With this relation established, we can write

$$q_c = nRT_c \ln \frac{V_D}{V_C} = nRT_c \ln \frac{V_A}{V_B} = -nRT_c \ln \frac{V_B}{V_A}$$

and therefore

$$\frac{q_h}{q_c} = \frac{nRT_h \ln(V_B/V_A)}{-nRT_c \ln(V_B/V_A)} = -\frac{T_h}{T_c}$$

as in eqn 3.7.

In the second step we need to show that eqn 3.6 applies to any material, not just a perfect gas (which is why, in anticipation, we have not labelled it with a  $^\circ$ ). We begin this step of the argument by introducing the efficiency,  $\eta$  (eta), of a heat engine:

$$\eta = \frac{\text{work performed}}{\text{heat absorbed from hot source}} = \frac{|w|}{|q_h|} \quad [3.8]$$

Definition of efficiency

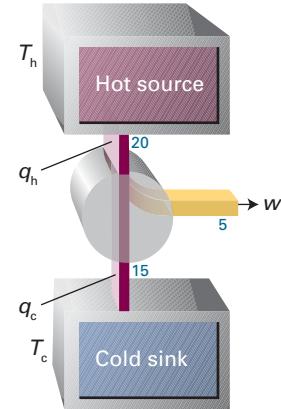
We are using modulus signs to avoid complications with signs: all efficiencies are positive numbers. The definition implies that, the greater the work output for a given supply of heat from the hot reservoir, the greater is the efficiency of the engine. We can express the definition in terms of the heat transactions alone, because (as shown in Fig. 3.7), the energy supplied as work by the engine is the difference between the energy supplied as heat by the hot reservoir and returned to the cold reservoir:

$$\eta = \frac{|q_h| - |q_c|}{|q_h|} = 1 - \frac{|q_c|}{|q_h|} \quad [3.9]$$

It then follows from eqn 3.7 (noting that the modulus signs remove the minus sign) that

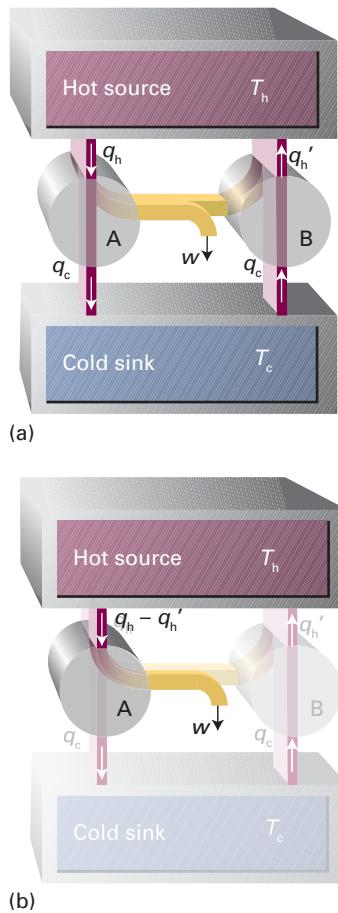
$$\eta = 1 - \frac{T_c}{T_h} \quad [3.10]_{\text{rev}}$$

Carnot efficiency



**Fig. 3.7** Suppose an energy  $q_h$  (for example, 20 kJ) is supplied to the engine and  $q_c$  is lost from the engine (for example,  $q_c = -15$  kJ) and discarded into the cold reservoir. The work done by the engine is equal to  $q_h + q_c$  (for example,  $20 \text{ kJ} + (-15 \text{ kJ}) = 5 \text{ kJ}$ ). The efficiency is the work done divided by the energy supplied as heat from the hot source.

Now we are ready to generalize this conclusion. The Second Law of thermodynamics implies that *all reversible engines have the same efficiency regardless of their construction*. To see the truth of this statement, suppose two reversible engines are coupled together and run between the same two reservoirs (Fig. 3.8). The working substances and details of construction of the two engines are entirely arbitrary. Initially, suppose that engine A is more efficient than engine B, and that we choose a setting of the controls that causes engine B to acquire energy as heat  $q_c$  from the cold reservoir and to release a certain quantity of energy as heat into the hot reservoir. However, because engine A is more efficient than engine B, not all the work that A produces is needed for



**Fig. 3.8** (a) The demonstration of the equivalence of the efficiencies of all reversible engines working between the same thermal reservoirs is based on the flow of energy represented in this diagram. (b) The net effect of the processes is the conversion of heat into work without there being a need for a cold sink: this is contrary to the Kelvin statement of the Second Law.

this process, and the difference can be used to do work. The net result is that the cold reservoir is unchanged, work has been done, and the hot reservoir has lost a certain amount of energy. This outcome is contrary to the Kelvin statement of the Second Law, because some heat has been converted directly into work. In molecular terms, the random thermal motion of the hot reservoir has been converted into ordered motion characteristic of work. Because the conclusion is contrary to experience, the initial assumption that engines A and B can have different efficiencies must be false. It follows that the relation between the heat transfers and the temperatures must also be independent of the working material, and therefore that eqn 3.10 is always true for any substance involved in a Carnot cycle.

For the final step in the argument, we note that any reversible cycle can be approximated as a collection of Carnot cycles and the integral around an arbitrary path is the sum of the integrals around each of the Carnot cycles (Fig. 3.9). This approximation becomes exact as the individual cycles are allowed to become infinitesimal. The entropy change around each individual cycle is zero (as demonstrated above), so the sum of entropy changes for all the cycles is zero. However, in the sum, the entropy change along any individual path is cancelled by the entropy change along the path it shares with the neighbouring cycle. Therefore, all the entropy changes cancel except for those along the perimeter of the overall cycle. That is,

$$\sum_{\text{all}} \frac{q_{\text{rev}}}{T} = \sum_{\text{perimeter}} \frac{q_{\text{rev}}}{T} = 0$$

In the limit of infinitesimal cycles, the non-cancelling edges of the Carnot cycles match the overall cycle exactly, and the sum becomes an integral. Equation 3.6 then follows immediately. This result implies that  $dS$  is an exact differential and therefore that  $S$  is a state function.

#### (d) The thermodynamic temperature

Suppose we have an engine that is working reversibly between a hot source at a temperature  $T_h$  and a cold sink at a temperature  $T$ , then we know from eqn 3.10 that

$$T = (1 - \eta) T_h \quad (3.11)$$

This expression enabled Kelvin to define the **thermodynamic temperature scale** in terms of the efficiency of a heat engine: we construct an engine in which the hot source is at a known temperature and the cold sink is the object of interest. The temperature of the latter can then be inferred from the measured efficiency of the engine. The **Kelvin scale** (which is a special case of the thermodynamic temperature scale) is defined by using water at its triple point as the notional hot source and defining that temperature as 273.16 K exactly. For instance, if it is found that the efficiency of such an engine is 0.20, then the temperature of the cold sink is  $0.80 \times 273.16 \text{ K} = 220 \text{ K}$ . This result is independent of the working substance of the engine.

#### (e) The Clausius inequality

We now show that the definition of entropy is consistent with the Second Law. To begin, we recall that more work is done when a change is reversible than when it is irreversible. That is,  $|dw_{\text{rev}}| \geq |dw|$ . Because  $dw$  and  $dw_{\text{rev}}$  are negative when energy leaves the system as work, this expression is the same as  $-dw_{\text{rev}} \geq -dw$ , and hence  $dw - dw_{\text{rev}} \geq 0$ . Because the internal energy is a state function, its change is the same for irreversible and reversible paths between the same two states, so we can also write:

$$dU = dq + dw = dq_{\text{rev}} + dw_{\text{rev}}$$

It follows that  $dq_{\text{rev}} - dq = dw - dw_{\text{rev}} \geq 0$ , or  $dq_{\text{rev}} \geq dq$ , and therefore that  $dq_{\text{rev}}/T \geq dq/T$ . Now we use the thermodynamic definition of the entropy (eqn 3.1;  $dS = dq_{\text{rev}}/T$ ) to write

$$dS \geq \frac{dq}{T} \quad (3.12)$$

This expression is the **Clausius inequality**. It will prove to be of great importance for the discussion of the spontaneity of chemical reactions, as we shall see in Section 3.5.

#### • A brief illustration

Consider the transfer of energy as heat from one system—the hot source—at a temperature  $T_h$  to another system—the cold sink—at a temperature  $T_c$  (Fig. 3.10). When  $|dq|$  leaves the hot source (so  $dq_h < 0$ ), the Clausius inequality implies that  $dS \geq dq_h/T_h$ . When  $|dq|$  enters the cold sink the Clausius inequality implies that  $dS \geq dq_c/T_c$  (with  $dq_c > 0$ ). Overall, therefore,

$$dS \geq \frac{dq_h}{T_h} + \frac{dq_c}{T_c}$$

However,  $dq_h = -dq_c$ , so

$$dS \geq -\frac{dq_c}{T_h} + \frac{dq_c}{T_c} = \left( \frac{1}{T_c} - \frac{1}{T_h} \right) dq_c$$

which is positive (because  $dq_c > 0$  and  $T_h > T_c$ ). Hence, cooling (the transfer of heat from hot to cold) is spontaneous, as we know from experience. •

We now suppose that the system is isolated from its surroundings, so that  $dq = 0$ . The Clausius inequality implies that

$$dS \geq 0 \quad (3.13)$$

and we conclude that *in an isolated system the entropy cannot decrease when a spontaneous change occurs*. This statement captures the content of the Second Law.

### IMPACT ON ENGINEERING

#### I3.1 Refrigeration

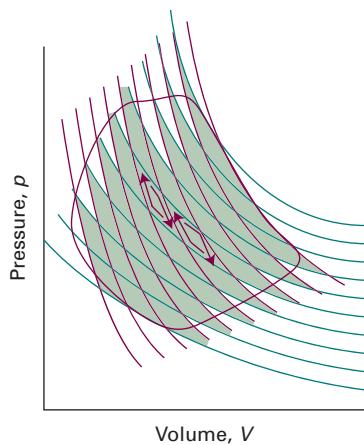
The same argument that we have used to discuss the efficiency of a heat engine can be used to discuss the efficiency of a refrigerator, a device for transferring energy as heat from a cold object (the contents of the refrigerator) to a warm sink (typically, the room in which the refrigerator stands). The less work we have to do to bring this transfer about, the more efficient is the refrigerator.

When an energy  $|q_c|$  migrates from a cool source at a temperature  $T_c$  into a warmer sink at a temperature  $T_h$ , the change in entropy is

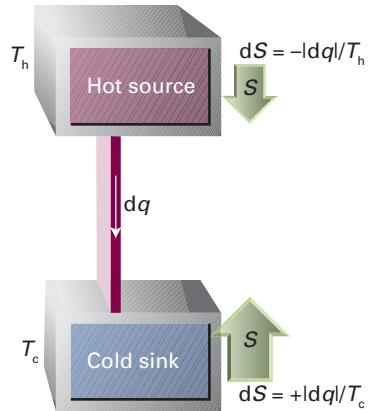
$$\Delta S = -\frac{|q_c|}{T_c} + \frac{|q_c|}{T_h} < 0 \quad (3.14)$$

The process is not spontaneous because not enough entropy is generated in the warm sink to overcome the entropy loss from the cold source (Fig. 3.11). To generate more entropy, energy must be added to the stream that enters the warm sink. Our task is to find the minimum energy that needs to be supplied. The outcome is expressed as the **coefficient of performance**,  $c$ :

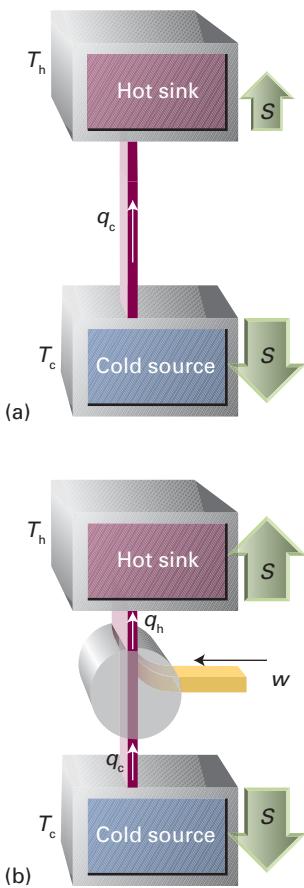
$$c = \frac{\text{energy transferred as heat}}{\text{energy transferred as work}} = \frac{|q_c|}{|w|} \quad \begin{array}{l} \text{Definition of coefficient} \\ \text{of performance} \end{array} \quad [3.15]$$



**Fig. 3.9** A general cycle can be divided into small Carnot cycles. The match is exact in the limit of infinitesimally small cycles. Paths cancel in the interior of the collection, and only the perimeter, an increasingly good approximation to the true cycle as the number of cycles increases, survives. Because the entropy change around every individual cycle is zero, the integral of the entropy around the perimeter is zero too.



**Fig. 3.10** When energy leaves a hot reservoir as heat, the entropy of the reservoir decreases. When the same quantity of energy enters a cooler reservoir, the entropy increases by a larger amount. Hence, overall there is an increase in entropy and the process is spontaneous. Relative changes in entropy are indicated by the sizes of the arrows.



**Fig. 3.11** (a) The flow of energy as heat from a cold source to a hot sink is not spontaneous. As shown here, the entropy increase of the hot sink is smaller than the entropy decrease of the cold source, so there is a net decrease in entropy. (b) The process becomes feasible if work is provided to add to the energy stream. Then the increase in entropy of the hot sink can be made to cancel the entropy decrease of the cold source.

The less the work that is required to achieve a given transfer, the greater the coefficient of performance and the more efficient is the refrigerator. For some of this development it will prove best to work with  $1/c$ .

Because  $|q_c|$  is removed from the cold source, and the work  $|w|$  is added to the energy stream, the energy deposited as heat in the hot sink is  $|q_h| = |q_c| + |w|$ . Therefore,

$$\frac{1}{c} = \frac{|w|}{|q_c|} = \frac{|q_h| - |q_c|}{|q_c|} = \frac{|q_h|}{|q_c|} - 1$$

We can now use eqn 3.7 to express this result in terms of the temperatures alone, which is possible if the transfer is performed reversibly. This substitution leads to

$$\frac{1}{c} = \frac{T_h}{T_c} - 1 = \frac{T_h - T_c}{T_c}$$

and therefore

$$c = \frac{T_c}{T_h - T_c} \quad (3.16)_{\text{rev}}$$

for the thermodynamically optimum coefficient of performance.

#### • A brief illustration

For a refrigerator withdrawing heat from ice-cold water ( $T_c = 273$  K) in a typical environment ( $T_h = 293$  K),  $c = 14$ , so, to remove 10 kJ (enough to freeze 30 g of water), requires transfer of at least 0.71 kJ as work. Practical refrigerators, of course, have a lower coefficient of performance. •

### 3.3 Entropy changes accompanying specific processes

**Key points** (a) The entropy of a perfect gas increases when it expands isothermally. (b) The change in entropy of a substance accompanying a change of state at its transition temperature is calculated from its enthalpy of transition. (c) The increase in entropy when a substance is heated is expressed in terms of its heat capacity. (d) The entropy of a substance at a given temperature is determined from measurements of its heat capacity from  $T=0$  up to the temperature of interest, allowing for phase transitions in that range.

We now see how to calculate the entropy changes that accompany a variety of basic processes.

#### (a) Expansion

We established in Example 3.1 that the change in entropy of a perfect gas that expands isothermally from  $V_i$  to  $V_f$  is

$$\Delta S = nR \ln \frac{V_f}{V_i} \quad \boxed{\begin{array}{l} \text{Entropy change for the isothermal} \\ \text{expansion of a perfect gas} \end{array}} \quad (3.17)^{\circ}$$

Because  $S$  is a state function, the value of  $\Delta S$  of the system is independent of the path between the initial and final states, so this expression applies whether the change of state occurs reversibly or irreversibly. The logarithmic dependence of entropy on volume is illustrated in Fig. 3.12.

The total change in entropy, however, does depend on how the expansion takes place. For any process the energy lost as heat from the system is acquired by the

surroundings, so  $dq_{\text{sur}} = -dq$ . For a reversible change we use the expression in Example 3.1 ( $q_{\text{rev}} = nRT \ln(V_f/V_i)$ ); consequently, from eqn 3.3b

$$\Delta S_{\text{sur}} = \frac{q_{\text{sur}}}{T} = -\frac{q_{\text{rev}}}{T} = -nR \ln \frac{V_f}{V_i} \quad (3.18)^{\circ}_{\text{rev}}$$

This change is the negative of the change in the system, so we can conclude that  $\Delta S_{\text{tot}} = 0$ , which is what we should expect for a reversible process. If, on the other hand, the isothermal expansion occurs freely ( $w = 0$ ), then  $q = 0$  (because  $\Delta U = 0$ ). Consequently,  $\Delta S_{\text{sur}} = 0$ , and the total entropy change is given by eqn 3.17 itself:

$$\Delta S_{\text{tot}} = nR \ln \frac{V_f}{V_i} \quad (3.19)^{\circ}$$

In this case,  $\Delta S_{\text{tot}} > 0$ , as we expect for an irreversible process.

### (b) Phase transition

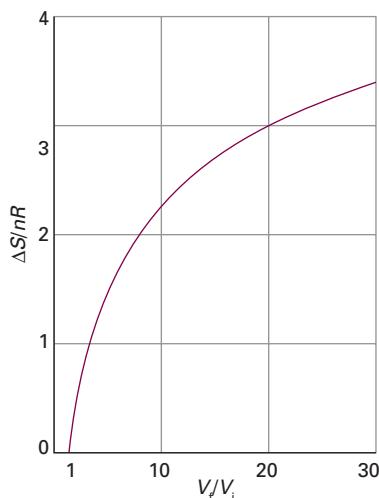
The degree of dispersal of matter and energy changes when a substance freezes or boils as a result of changes in the order with which the molecules pack together and the extent to which the energy is localized or dispersed. Therefore, we should expect the transition to be accompanied by a change in entropy. For example, when a substance vaporizes, a compact condensed phase changes into a widely dispersed gas and we can expect the entropy of the substance to increase considerably. The entropy of a solid also increases when it melts to a liquid and when that liquid turns into a gas.

Consider a system and its surroundings at the **normal transition temperature**,  $T_{\text{trs}}$ , the temperature at which two phases are in equilibrium at 1 atm. This temperature is 0°C (273 K) for ice in equilibrium with liquid water at 1 atm, and 100°C (373 K) for liquid water in equilibrium with its vapour at 1 atm. At the transition temperature, any transfer of energy as heat between the system and its surroundings is reversible because the two phases in the system are in equilibrium. Because at constant pressure  $q = \Delta_{\text{trs}} H$ , the change in molar entropy of the system is<sup>3</sup>

$$\Delta_{\text{trs}} S = \frac{\Delta_{\text{trs}} H}{T_{\text{trs}}} \quad \boxed{\begin{array}{l} \text{Entropy of} \\ \text{phase transition} \end{array}} \quad (3.20)$$

If the phase transition is exothermic ( $\Delta_{\text{trs}} H < 0$ , as in freezing or condensing), then the entropy change of the system is negative. This decrease in entropy is consistent with the increased order of a solid compared with a liquid and with the increased order of a liquid compared with a gas. The change in entropy of the surroundings, however, is positive because energy is released as heat into them, and at the transition temperature the total change in entropy is zero. If the transition is endothermic ( $\Delta_{\text{trs}} H > 0$ , as in melting and vaporization), then the entropy change of the system is positive, which is consistent with dispersal of matter in the system. The entropy of the surroundings decreases by the same amount, and overall the total change in entropy is zero.

Table 3.1 lists some experimental entropies of transition. Table 3.2 lists in more detail the standard entropies of vaporization of several liquids at their boiling points. An interesting feature of the data is that a wide range of liquids give approximately the same standard entropy of vaporization (about  $85 \text{ J K}^{-1} \text{ mol}^{-1}$ ): this empirical observation is called **Trouton's rule**. The explanation of Trouton's rule is that a comparable change in volume occurs when any liquid evaporates and becomes a gas. Hence, all



**Fig. 3.12** The logarithmic increase in entropy of a perfect gas as it expands isothermally.

 **interActivity** Evaluate the change in expansion of 1.00 mol  $\text{CO}_2$  (g) from  $0.001 \text{ m}^3$  to  $0.010 \text{ m}^3$  at 298 K, treated as a van der Waals gas.

<sup>3</sup> Recall from Section 2.6 that  $\Delta_{\text{trs}} H$  is an enthalpy change per mole of substance; so  $\Delta_{\text{trs}} S$  is also a molar quantity.

**Table 3.1\*** Standard entropies (and temperatures) of phase transitions,  $\Delta_{\text{trs}}S^{\circ}/(\text{J K}^{-1} \text{ mol}^{-1})$ 

	Fusion (at $T_f$ )	Vaporization (at $T_b$ )
Argon, Ar	14.17 (at 83.8 K)	74.53 (at 87.3 K)
Benzene, $C_6H_6$	38.00 (at 279 K)	87.19 (at 353 K)
Water, $H_2O$	22.00 (at 273.15 K)	109.0 (at 373.15 K)
Helium, He	4.8 (at 1.8 K and 30 bar)	19.9 (at 4.22 K)

\* More values are given in the *Data section*.

**Table 3.2\*** The standard entropies of vaporization of liquids

	$\Delta_{\text{vap}}H^{\circ}/(\text{kJ mol}^{-1})$	$\theta_b/^\circ\text{C}$	$\Delta_{\text{vap}}S^{\circ}/(\text{J K}^{-1} \text{ mol}^{-1})$
Benzene	30.8	80.1	87.2
Carbon tetrachloride	30	76.7	85.8
Cyclohexane	30.1	80.7	85.1
Hydrogen sulfide	18.7	-60.4	87.9
Methane	8.18	-161.5	73.2
Water	40.7	100.0	109.1

\* More values are given in the *Data section*.

liquids can be expected to have similar standard entropies of vaporization. Liquids that show significant deviations from Trouton's rule do so on account of strong molecular interactions that result in a partial ordering of their molecules. As a result, there is a greater change in disorder when the liquid turns into a vapour than for a fully disordered liquid. An example is water, where the large entropy of vaporization reflects the presence of structure arising from hydrogen-bonding in the liquid. Hydrogen bonds tend to organize the molecules in the liquid so that they are less random than, for example, the molecules in liquid hydrogen sulfide (in which there is no hydrogen bonding). Methane has an unusually low entropy of vaporization. A part of the reason is that the entropy of the gas itself is slightly low ( $186 \text{ J K}^{-1} \text{ mol}^{-1}$  at 298 K); the entropy of  $N_2$  under the same conditions is  $192 \text{ J K}^{-1} \text{ mol}^{-1}$ . As we shall see in Chapter 12, fewer rotational states are accessible at room temperature for light molecules than for heavy molecules.

#### • A brief illustration

There is no hydrogen bonding in liquid bromine and  $Br_2$  is a heavy molecule that is unlikely to display unusual behaviour in the gas phase, so it is safe to use Trouton's rule. To predict the standard molar enthalpy of vaporization of bromine given that it boils at  $59.2^\circ\text{C}$ , we use the rule in the form

$$\Delta_{\text{vap}}H^{\circ} = T_b \times (85 \text{ J K}^{-1} \text{ mol}^{-1})$$

Substitution of the data then gives

$$\Delta_{\text{vap}}H^{\circ} = (332.4 \text{ K}) \times (85 \text{ J K}^{-1} \text{ mol}^{-1}) = +2.8 \times 10^3 \text{ J mol}^{-1} = +28 \text{ kJ mol}^{-1}$$

The experimental value is  $+29.45 \text{ kJ mol}^{-1}$ . ■

**Self-test 3.3** Predict the enthalpy of vaporization of ethane from its boiling point,  $-88.6^\circ\text{C}$ .  
 [16 kJ mol $^{-1}$ ]

### (c) Heating

We can use eqn 3.2 to calculate the entropy of a system at a temperature  $T_f$  from a knowledge of its entropy at another temperature  $T_i$  and the heat supplied to change its temperature from one value to the other:

$$S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{dq_{\text{rev}}}{T} \quad (3.21)$$

We shall be particularly interested in the entropy change when the system is subjected to constant pressure (such as from the atmosphere) during the heating. Then, from the definition of constant-pressure heat capacity (eqn 2.22, written as  $dq_{\text{rev}} = C_p dT$ ). Consequently, at constant pressure:

$$S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{C_p dT}{T} \quad \boxed{\text{Entropy variation with temperature}} \quad (3.22)$$

The same expression applies at constant volume, but with  $C_p$  replaced by  $C_V$ . When  $C_p$  is independent of temperature in the temperature range of interest, it can be taken outside the integral and we obtain

$$S(T_f) = S(T_i) + C_p \int_{T_i}^{T_f} \frac{dT}{T} = S(T_i) + C_p \ln \frac{T_f}{T_i} \quad (3.23)$$

with a similar expression for heating at constant volume. The logarithmic dependence of entropy on temperature is illustrated in Fig. 3.13.

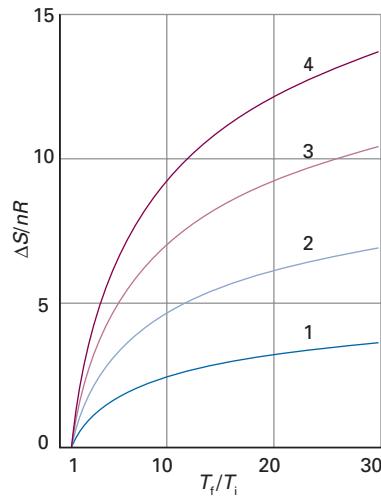
#### Example 3.2 Calculating the entropy change

Calculate the entropy change when argon at  $25^\circ\text{C}$  and 1.00 bar in a container of volume  $0.500 \text{ dm}^3$  is allowed to expand to  $1.000 \text{ dm}^3$  and is simultaneously heated to  $100^\circ\text{C}$ .

**Method** Because  $S$  is a state function, we are free to choose the most convenient path from the initial state. One such path is reversible isothermal expansion to the final volume, followed by reversible heating at constant volume to the final temperature. The entropy change in the first step is given by eqn 3.17 and that of the second step, provided  $C_V$  is independent of temperature, by eqn 3.23 (with  $C_V$  in place of  $C_p$ ). In each case we need to know  $n$ , the amount of gas molecules, and can calculate it from the perfect gas equation and the data for the initial state from  $n = p_i V_i / RT_i$ . The molar heat capacity at constant volume is given by the equipartition theorem as  $\frac{3}{2}R$ . (The equipartition theorem is reliable for monatomic gases; for others and, in general, use experimental data like those in Table 2.8, converting to the value at constant volume by using the relation  $C_{p,m} - C_{V,m} = R$ .)

**Answer** From eqn 3.17 the entropy change of the isothermal expansion from  $V_i$  to  $V_f$  is

$$\Delta S(\text{Step 1}) = nR \ln \frac{V_f}{V_i}$$



**Fig. 3.13** The logarithmic increase in entropy of a substance as it is heated at constant volume. Different curves correspond to different values of the constant-volume heat capacity (which is assumed constant over the temperature range) expressed as  $C_{V,m}/R$ .

**interActivity** Plot the change in entropy of a perfect gas of (a) atoms, (b) linear rotors, (c) nonlinear rotors as the sample is heated over the same range under conditions of (i) constant volume, (ii) constant pressure.

From eqn 3.23, the entropy change in the second step, from  $T_i$  to  $T_f$  at constant volume, is

$$\Delta S(\text{Step 2}) = nC_{V,m} \ln \frac{T_f}{T_i} = \frac{3}{2} nR \ln \frac{T_f}{T_i} = nR \ln \left( \frac{T_f}{T_i} \right)^{3/2}$$

The overall entropy change of the system, the sum of these two changes, is

$$\Delta S = nR \ln \frac{V_f}{V_i} + nR \ln \left( \frac{T_f}{T_i} \right)^{3/2} = nR \ln \left\{ \frac{V_f}{V_i} \left( \frac{T_f}{T_i} \right)^{3/2} \right\}$$

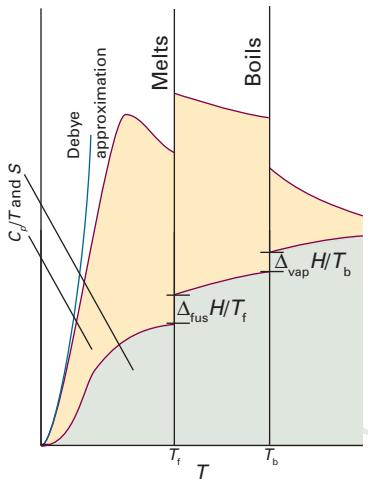
(We have used  $\ln x + \ln y = \ln xy$ .) Now we substitute  $n = p_i V_i / RT_i$  and obtain

$$\Delta S = \frac{p_i V_i}{T_i} \ln \left\{ \frac{V_f}{V_i} \left( \frac{T_f}{T_i} \right)^{3/2} \right\}$$

At this point we substitute the data:

$$\begin{aligned} \Delta S &= \frac{(1.00 \times 10^5 \text{ Pa}) \times (0.500 \times 10^{-3} \text{ m}^3)}{298 \text{ K}} \times \ln \left\{ \frac{1.000}{0.500} \left( \frac{373}{298} \right)^{3/2} \right\} \\ &= +0.173 \text{ J K}^{-1} \end{aligned}$$

**Self-test 3.4** Calculate the entropy change when the same initial sample is compressed to  $0.0500 \text{ dm}^3$  and cooled to  $-25^\circ\text{C}$ .  $[-0.43 \text{ J K}^{-1}]$



**Fig. 3.14** The variation of  $C_p/T$  with the temperature for a sample is used to evaluate the entropy, which is equal to the area beneath the upper curve up to the corresponding temperature, plus the entropy of each phase transition passed.

 **interActivity** Allow for the temperature dependence of the heat capacity by writing  $C = a + bT + c/T^2$ , and plot the change in entropy for different values of the three coefficients (including negative values of  $c$ ).

#### (d) The measurement of entropy

The entropy of a system at a temperature  $T$  is related to its entropy at  $T = 0$  by measuring its heat capacity  $C_p$  at different temperatures and evaluating the integral in eqn 3.22, taking care to add the entropy of transition ( $\Delta_{\text{trs}}H/T_{\text{trs}}$ ) for each phase transition between  $T = 0$  and the temperature of interest. For example, if a substance melts at  $T_f$  and boils at  $T_b$ , then its molar entropy above its boiling temperature is given by

$$\begin{aligned} S_m(T) &= S_m(0) + \int_0^{T_f} \frac{C_{p,m}(s,T)}{T} dT + \frac{\Delta_{\text{fus}}H}{T_f} + \int_{T_f}^{T_b} \frac{C_{p,m}(1,T)}{T} dT \\ &\quad + \frac{\Delta_{\text{vap}}H}{T_b} + \int_{T_b}^T \frac{C_{p,m}(g,T)}{T} dT \end{aligned} \quad (3.24)$$

All the properties required, except  $S_m(0)$ , can be measured calorimetrically, and the integrals can be evaluated either graphically or, as is now more usual, by fitting a polynomial to the data and integrating the polynomial analytically. The former procedure is illustrated in Fig. 3.14: the area under the curve of  $C_{p,m}/T$  against  $T$  is the integral required. Because  $dT/T = d \ln T$ , an alternative procedure is to evaluate the area under a plot of  $C_{p,m}$  against  $\ln T$ .

One problem with the determination of entropy is the difficulty of measuring heat capacities near  $T = 0$ . There are good theoretical grounds for assuming that the heat capacity is proportional to  $T^3$  when  $T$  is low (see Section 7.1), and this dependence is the basis of the **Debye extrapolation**. In this method,  $C_p$  is measured down to as low a temperature as possible, and a curve of the form  $aT^3$  is fitted to the data. That fit determines the value of  $a$ , and the expression  $C_{p,m} = aT^3$  is assumed valid down to  $T = 0$ .

● **A brief illustration**

The standard molar entropy of nitrogen gas at 25°C has been calculated from the following data:

	$S_m^\ominus / (\text{J K}^{-1} \text{ mol}^{-1})$
Debye extrapolation	1.92
Integration, from 10 K to 35.61 K	25.25
Phase transition at 35.61 K	6.43
Integration, from 35.61 K to 63.14 K	23.38
Fusion at 63.14 K	11.42
Integration, from 63.14 K to 77.32 K	11.41
Vaporization at 77.32 K	72.13
Integration, from 77.32 K to 298.15 K	39.20
Correction for gas imperfection	0.92
Total	192.06

Therefore

$$S_m^\ominus(298.15 \text{ K}) = S_m(0) + 192.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

**Example 3.3** Calculating the entropy at low temperatures

The molar constant-pressure heat capacity of a certain solid at 4.2 K is  $0.43 \text{ J K}^{-1} \text{ mol}^{-1}$ . What is its molar entropy at that temperature?

**Method** Because the temperature is so low, we can assume that the heat capacity varies with temperature as  $aT^3$ , in which case we can use eqn 3.22 to calculate the entropy at a temperature  $T$  in terms of the entropy at  $T = 0$  and the constant  $a$ . When the integration is carried out, it turns out that the result can be expressed in terms of the heat capacity at the temperature  $T$ , so the data can be used directly to calculate the entropy.

**Answer** The integration required is

$$\begin{aligned} S_m(T) &= S_m(0) + \int_0^T \frac{aT^3}{T} dT = S_m(0) + a \int_0^T T^2 dT \\ &= S_m(0) + \frac{1}{3}aT^3 = S_m(0) + \frac{1}{3}C_{p,m}(T) \end{aligned}$$

from which it follows that

$$S_m(4.2 \text{ K}) = S_m(0) + 0.14 \text{ J K}^{-1} \text{ mol}^{-1}$$

**Self-test 3.5** For metals, there is also a contribution to the heat capacity from the electrons that is linearly proportional to  $T$  when the temperature is low. Find its contribution to the entropy at low temperatures.  $[S(T) = S(0) + C_p(T)]$

## 3.4 The Third Law of thermodynamics

**Key points** (a) The Nernst heat theorem implies the Third Law of thermodynamics. (b) The Third Law allows us to define absolute entropies of substances and to define the standard entropy of a reaction.

At  $T = 0$ , all energy of thermal motion has been quenched, and in a perfect crystal all the atoms or ions are in a regular, uniform array. The localization of matter and the absence of thermal motion suggest that such materials also have zero entropy. This conclusion is consistent with the molecular interpretation of entropy, because  $S = 0$  if there is only one way of arranging the molecules and only one microstate is accessible (all molecules occupy the ground state).

### (a) The Nernst heat theorem

The experimental observation that turns out to be consistent with the view that the entropy of a regular array of molecules is zero at  $T = 0$  is summarized by the **Nernst heat theorem**:

The entropy change accompanying any physical or chemical transformation approaches zero as the temperature approaches zero:  
 $\Delta S \rightarrow 0$  as  $T \rightarrow 0$  provided all the substances involved are perfectly ordered.

Nernst  
heat  
theorem

#### • A brief illustration

Consider the entropy of the transition between orthorhombic sulfur,  $S(\alpha)$ , and monoclinic sulfur,  $S(\beta)$ , which can be calculated from the transition enthalpy ( $-402 \text{ J mol}^{-1}$ ) at the transition temperature (369 K):

$$\Delta_{\text{trs}} S = S_m(\beta) - S_m(\alpha) = \frac{(-402 \text{ J mol}^{-1})}{369 \text{ K}} = -1.09 \text{ J K}^{-1} \text{ mol}^{-1}$$

The two individual entropies can also be determined by measuring the heat capacities from  $T = 0$  up to  $T = 369 \text{ K}$ . It is found that  $S_m(\alpha) = S_m(\alpha, 0) + 37 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $S_m(\beta) = S_m(\beta, 0) + 38 \text{ J K}^{-1} \text{ mol}^{-1}$ . These two values imply that at the transition temperature

$$\Delta_{\text{trs}} S = S_m(\alpha, 0) - S_m(\beta, 0) = -1 \text{ J K}^{-1} \text{ mol}^{-1}$$

On comparing this value with the one above, we conclude that  $S_m(\alpha, 0) - S_m(\beta, 0) \approx 0$ , in accord with the theorem. •

It follows from the Nernst theorem that, if we arbitrarily ascribe the value zero to the entropies of elements in their perfect crystalline form at  $T = 0$ , then all perfect crystalline compounds also have zero entropy at  $T = 0$  (because the change in entropy that accompanies the formation of the compounds, like the entropy of all transformations at that temperature, is zero). This conclusion is summarized by the **Third Law of thermodynamics**:

The entropy of all perfect crystalline substances is zero at  $T = 0$ .

Third Law of  
thermodynamics

As far as thermodynamics is concerned, choosing this common value as zero is a matter of convenience. The molecular interpretation of entropy, however, justifies the value  $S = 0$  at  $T = 0$ . We saw in Section 3.2b that, according to the Boltzmann formula, the entropy is zero if there is only one accessible microstate ( $W = 1$ ). In most cases,  $W = 1$  at  $T = 0$  because there is only one way of achieving the lowest total energy: put all the molecules into the same, lowest state. Therefore,  $S = 0$  at  $T = 0$ , in accord with the Third Law of thermodynamics. In certain cases, though,  $W$  may differ from 1 at  $T = 0$ . This is the case if there is no energy advantage in adopting a particular orientation even at absolute zero. For instance, for a diatomic molecule AB there may

be almost no energy difference between the arrangements . . . AB AB AB . . . and . . . BA AB BA . . . , so  $W > 1$  even at  $T = 0$ . If  $S > 0$  at  $T = 0$  we say that the substance has a **residual entropy**. Ice has a residual entropy of  $3.4 \text{ J K}^{-1} \text{ mol}^{-1}$ . It stems from the arrangement of the hydrogen bonds between neighbouring water molecules: a given O atom has two short O–H bonds and two long O···H bonds to its neighbours, but there is a degree of randomness in which two bonds are short and which two are long.

### (b) Third-Law entropies

Entropies reported on the basis that  $S(0) = 0$  are called **Third-Law entropies** (and often just ‘entropies’). When the substance is in its standard state at the temperature  $T$ , the **standard (Third-Law) entropy** is denoted  $S^\ominus(T)$ . A list of values at 298 K is given in Table 3.3.

The **standard reaction entropy**,  $\Delta_r S^\ominus(T)$ , is defined, like the standard reaction enthalpy, as the difference between the molar entropies of the pure, separated products and the pure, separated reactants, all substances being in their standard states at the specified temperature:

$$\Delta_r S^\ominus = \sum_{\text{Products}} vS_m^\ominus - \sum_{\text{Reactants}} vS_m^\ominus \quad (3.25a)$$

Definition of standard reaction entropy

In this expression, each term is weighted by the appropriate stoichiometric coefficient. A more sophisticated approach is to adopt the notation introduced in Section 2.8 and to write

$$\Delta_r S^\ominus = \sum_j v_j S_m^\ominus(J) \quad (3.25b)$$

Standard reaction entropies are likely to be positive if there is a net formation of gas in a reaction, and are likely to be negative if there is a net consumption of gas.

#### • A brief illustration

To calculate the standard reaction entropy of  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$  at 25°C, we use the data in Table 2.8 of the *Data section* to write

$$\begin{aligned} \Delta_r S^\ominus &= S_m^\ominus(\text{H}_2\text{O},\text{l}) - \{S_m^\ominus(\text{H}_2,\text{g}) + \frac{1}{2}S_m^\ominus(\text{O}_2,\text{g})\} \\ &= 69.9 \text{ J K}^{-1} \text{ mol}^{-1} - \{130.7 + \frac{1}{2}(205.0)\} \text{ J K}^{-1} \text{ mol}^{-1} \\ &= -163.4 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

The negative value is consistent with the conversion of two gases to a compact liquid. •

**Table 3.3\*** Standard Third-Law entropies at 298 K

	$S_m^\ominus / (\text{J K}^{-1} \text{ mol}^{-1})$
<i>Solids</i>	
Graphite, C(s)	5.7
Diamond, C(s)	2.4
Sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s})$	360.2
Iodine, $\text{I}_2(\text{s})$	116.1
<i>Liquids</i>	
Benzene, $\text{C}_6\text{H}_6(\text{l})$	173.3
Water, $\text{H}_2\text{O}(\text{l})$	69.9
Mercury, $\text{Hg}(\text{l})$	76.0
<i>Gases</i>	
Methane, $\text{CH}_4(\text{g})$	186.3
Carbon dioxide, $\text{CO}_2(\text{g})$	213.7
Hydrogen, $\text{H}_2(\text{g})$	130.7
Helium, He	126.2
Ammonia, $\text{NH}_3(\text{g})$	192.4

\* More values are given in the *Data section*.

**A note on good practice** Do not make the mistake of setting the standard molar entropies of elements equal to zero: they have non-zero values (provided  $T > 0$ ), as we have already discussed.

**Self-test 3.6** Calculate the standard reaction entropy for the combustion of methane to carbon dioxide and liquid water at 25°C.  $[-243 \text{ J K}^{-1} \text{ mol}^{-1}]$

Just as in the discussion of enthalpies in Section 2.8, where we acknowledged that solutions of cations cannot be prepared in the absence of anions, the standard molar entropies of ions in solution are reported on a scale in which the standard entropy of the  $\text{H}^+$  ions in water is taken as zero at all temperatures:

$$S^\ominus(\text{H}^+, \text{aq}) = 0$$

Convention for ions in solution

[3.26]

The values based on this choice are listed in Table 2.8 in the *Data section*.<sup>4</sup> Because the entropies of ions in water are values relative to the hydrogen ion in water, they may be either positive or negative. A positive entropy means that an ion has a higher molar entropy than H<sup>+</sup> in water and a negative entropy means that the ion has a lower molar entropy than H<sup>+</sup> in water. For instance, the standard molar entropy of Cl<sup>-</sup>(aq) is +57 J K<sup>-1</sup> mol<sup>-1</sup> and that of Mg<sup>2+</sup>(aq) is -128 J K<sup>-1</sup> mol<sup>-1</sup>. Ion entropies vary as expected on the basis that they are related to the degree to which the ions order the water molecules around them in the solution. Small, highly charged ions induce local structure in the surrounding water, and the disorder of the solution is decreased more than in the case of large, singly charged ions. The absolute, Third-Law standard molar entropy of the proton in water can be estimated by proposing a model of the structure it induces, and there is some agreement on the value -21 J K<sup>-1</sup> mol<sup>-1</sup>. The negative value indicates that the proton induces order in the solvent.

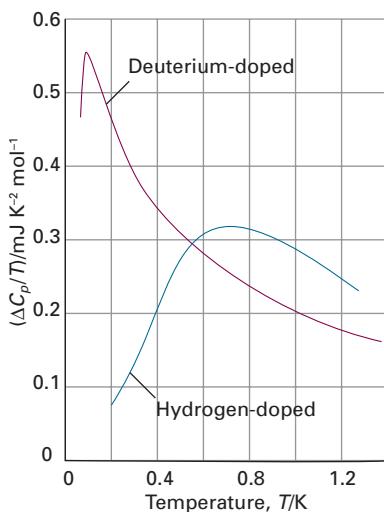
#### IMPACT ON MATERIALS CHEMISTRY

##### I3.2 Crystal defects

The Third Law implies that at  $T = 0$  the entropies of perfect crystalline substances are characterized by long-range, regularly repeating arrangements of atoms, ions, or molecules. This regularity, and the accompanying inter- and intramolecular interactions between the subunits of the crystal, govern the physical, optical, and electronic properties of the solid. In reality, however, all crystalline solids possess one or more defects that affect the physical and chemical properties of the substance. In fact, impurities are often introduced to achieve particular desirable properties, such as the colour of a gemstone or enhanced strength of a metal.

One of the main types of crystalline imperfection is a **point defect**, a location where an atom is missing or irregularly placed in the lattice structure. Other terms used to describe point defects include *voids*, or *lattice vacancies*, *substitutional impurity atoms*, *dopant sites*, and *interstitial impurity atoms*. Many gemstones feature substitutional solids, such as in rubies and blue sapphires where the Al<sup>3+</sup> ions in the corundum structure of alumina are replaced with Cr<sup>3+</sup> and Fe<sup>3+</sup> ions, respectively. Interstitial solids can result from the random diffusion of dopants in interstices (voids) or from self-diffusion, as in ionic crystals, where a lattice ion can migrate into an interstitial position and leave behind a vacancy known as a Frenkel defect.

Figure 3.15 illustrates the impact of impurities on the heat capacity and thus entropy of a pure crystal. Niobium has become the dominant metal in low-temperature superconductor alloys because it can be manufactured economically in a ductile form that is needed for the high critical current of a superconductor. The purity of the metal, however, is essential to yield superconducting properties. Close to 1 K the heat capacity of pure niobium follows the Debye  $T^3$  law. However, when niobium is treated by allowing H<sub>2</sub> or D<sub>2</sub> to diffuse over the sample at 700°C impurities are introduced and the heat capacity diverges from that of the pure metal. To identify the role of the defects the values of  $C_p$  for the pure metal are subtracted from those of the doped samples, divided by  $T$ , and plotted against temperature. The area under the resulting curves then represents the contributions to the entropy from the presence of the impurities.



**Fig. 3.15** Molar heat capacity contributions of the defects in hydrogen- and deuterium doped niobium. The area under each curve is used to calculate the entropy due to the presence of the defects. (Based on G.J. Sellers and A.C. Anderson, *Phys. Rev. B*, **10**, 2771 (1974).)

<sup>4</sup> In terms of the language to be introduced in Section 5.1, the entropies of ions in solution are actually *partial molar entropies*, for their values include the consequences of their presence on the organization of the solvent molecules around them.

## Concentrating on the system

Entropy is the basic concept for discussing the direction of natural change, but to use it we have to analyse changes in both the system and its surroundings. We have seen that it is always very simple to calculate the entropy change in the surroundings, and we shall now see that it is possible to devise a simple method for taking that contribution into account automatically. This approach focuses our attention on the system and simplifies discussions. Moreover, it is the foundation of all the applications of chemical thermodynamics that follow.

### 3.5 The Helmholtz and Gibbs energies

**Key points** (a) The Clausius inequality implies a number of criteria for spontaneous change under a variety of conditions that may be expressed in terms of the properties of the system alone; they are summarized by introducing the Helmholtz and Gibbs energies. (b) A spontaneous process at constant temperature and volume is accompanied by a decrease in the Helmholtz energy. (c) The change in the Helmholtz energy is equal to the maximum work accompanying a process at constant temperature. (d) A spontaneous process at constant temperature and pressure is accompanied by a decrease in the Gibbs energy. (e) The change in the Gibbs energy is equal to the maximum non-expansion work accompanying a process at constant temperature and pressure.

Consider a system in thermal equilibrium with its surroundings at a temperature  $T$ . When a change in the system occurs and there is a transfer of energy as heat between the system and the surroundings, the Clausius inequality ( $dS \geq dq/T$ , eqn 3.12) reads

$$dS - \frac{dq}{T} \geq 0 \quad (3.27)$$

We can develop this inequality in two ways according to the conditions (of constant volume or constant pressure) under which the process occurs.

#### (a) Criteria for spontaneity

First, consider heating at constant volume. Then, in the absence of non-expansion work, we can write  $dq_V = dU$ ; consequently

$$dS - \frac{dU}{T} \geq 0 \quad (3.28)$$

The importance of the inequality in this form is that it expresses the criterion for spontaneous change solely in terms of the state functions of the system. The inequality is easily rearranged into

$$TdS \geq dU \quad (\text{constant } V, \text{ no additional work})^5 \quad (3.29)$$

At either constant internal energy ( $dU = 0$ ) or constant entropy ( $dS = 0$ ), this expression becomes, respectively,

$$dS_{U,V} \geq 0 \quad dU_{S,V} \leq 0 \quad (3.30)$$

where the subscripts indicate the constant conditions.

Equation 3.30 expresses the criteria for spontaneous change in terms of properties relating to the system. The first inequality states that, in a system at constant volume

<sup>5</sup> Recall that ‘additional work’ is work other than expansion work.

and constant internal energy (such as an isolated system), the entropy increases in a spontaneous change. That statement is essentially the content of the Second Law. The second inequality is less obvious, for it says that, if the entropy and volume of the system are constant, then the internal energy must decrease in a spontaneous change. Do not interpret this criterion as a tendency of the system to sink to lower energy. It is a disguised statement about entropy and should be interpreted as implying that, if the entropy of the system is unchanged, then there must be an increase in entropy of the surroundings, which can be achieved only if the energy of the system decreases as energy flows out as heat.

When energy is transferred as heat at constant pressure, and there is no work other than expansion work, we can write  $dq_p = dH$  and obtain

$$TdS \geq dH \quad (\text{constant } p, \text{ no additional work}) \quad (3.31)$$

At either constant enthalpy or constant entropy this inequality becomes, respectively,

$$dS_{H,p} \geq 0 \quad dH_{S,p} \leq 0 \quad (3.32)$$

The interpretations of these inequalities are similar to those of eqn 3.30. The entropy of the system at constant pressure must increase if its enthalpy remains constant (for there can then be no change in entropy of the surroundings). Alternatively, the enthalpy must decrease if the entropy of the system is constant, for then it is essential to have an increase in entropy of the surroundings.

Because eqns 3.29 and 3.31 have the forms  $dU - TdS \leq 0$  and  $dH - TdS \leq 0$ , respectively, they can be expressed more simply by introducing two more thermodynamic quantities. One is the **Helmholtz energy**,  $A$ , which is defined as

$$A = U - TS$$

Definition of  
Helmholtz energy

[3.33]

The other is the **Gibbs energy**,  $G$ :

$$G = H - TS$$

Definition of  
Gibbs energy

[3.34]

All the symbols in these two definitions refer to the system.

When the state of the system changes at constant temperature, the two properties change as follows:

$$(a) dA = dU - TdS \quad (b) dG = dH - TdS \quad (3.35)$$

When we introduce eqns 3.29 and 3.31, respectively, we obtain the criteria of spontaneous change as

$$(a) dA_{T,V} \leq 0 \quad (b) dG_{T,p} \leq 0 \quad (3.36)$$

These inequalities are the most important conclusions from thermodynamics for chemistry. They are developed in subsequent sections and chapters.

### (b) Some remarks on the Helmholtz energy

A change in a system at constant temperature and volume is spontaneous if  $dA_{T,V} \leq 0$ . That is, a change under these conditions is spontaneous if it corresponds to a decrease in the Helmholtz energy. Such systems move spontaneously towards states of lower  $A$  if a path is available. The criterion of equilibrium, when neither the forward nor reverse process has a tendency to occur, is

$$dA_{T,V} = 0 \quad (3.37)$$

The expressions  $dA = dU - TdS$  and  $dA < 0$  are sometimes interpreted as follows. A negative value of  $dA$  is favoured by a negative value of  $dU$  and a positive value of  $TdS$ . This observation suggests that the tendency of a system to move to lower  $A$  is due to its tendency to move towards states of lower internal energy and higher entropy. However, this interpretation is false (even though it is a good rule of thumb for remembering the expression for  $dA$ ) because the tendency to lower  $A$  is solely a tendency towards states of greater overall entropy. Systems change spontaneously if in doing so the total entropy of the system and its surroundings increases, not because they tend to lower internal energy. The form of  $dA$  may give the impression that systems favour lower energy, but that is misleading:  $dS$  is the entropy change of the system,  $-dU/T$  is the entropy change of the surroundings (when the volume of the system is constant), and their total tends to a maximum.

### (c) Maximum work

It turns out, as we show in the following *Justification*, that  $A$  carries a greater significance than being simply a signpost of spontaneous change: *the change in the Helmholtz function is equal to the maximum work accompanying a process at constant temperature*:

$$dw_{\max} = dA \quad (3.38)$$

As a result,  $A$  is sometimes called the ‘maximum work function’, or the ‘work function’.<sup>6</sup>

---

#### Justification 3.2 Maximum work

To demonstrate that maximum work can be expressed in terms of the changes in Helmholtz energy, we combine the Clausius inequality  $dS \geq dq/T$  in the form  $TdS \geq dq$  with the First Law,  $dU = dq + dw$ , and obtain

$$dU \leq TdS + dw$$

( $dU$  is smaller than the term of the right because we are replacing  $dq$  by  $TdS$ , which in general is larger.) This expression rearranges to

$$dw \geq dU - TdS$$

It follows that the most negative value of  $dw$ , and therefore the maximum energy that can be obtained from the system as work, is given by

$$dw_{\max} = dU - TdS$$

and that this work is done only when the path is traversed reversibly (because then the equality applies). Because at constant temperature  $dA = dU - TdS$ , we conclude that  $dw_{\max} = dA$ .

---

When a macroscopic isothermal change takes place in the system, eqn 3.38 becomes

$$w_{\max} = \Delta A$$

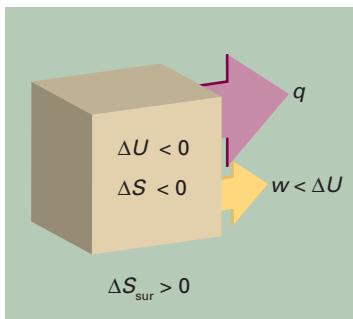
Relation between  $A$   
and maximum work

(3.39)

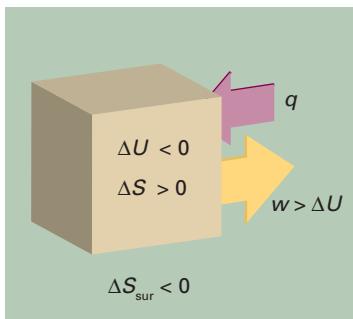
with

$$\Delta A = \Delta U - T\Delta S \quad (3.40)$$

<sup>6</sup> *Arbeit* is the German word for work; hence the symbol  $A$ .



**Fig. 3.16** In a system not isolated from its surroundings, the work done may be different from the change in internal energy. Moreover, the process is spontaneous if overall the entropy of the system and its surroundings increases. In the process depicted here, the entropy of the system decreases, so that of the surroundings must increase in order for the process to be spontaneous, which means that energy must pass from the system to the surroundings as heat. Therefore, less work than  $\Delta U$  can be obtained.



**Fig. 3.17** In this process, the entropy of the system increases; hence we can afford to lose some entropy of the surroundings. That is, some of their energy may be lost as heat to the system. This energy can be returned to them as work. Hence the work done can exceed  $\Delta U$ .

This expression shows that in some cases, depending on the sign of  $T\Delta S$ , not all the change in internal energy may be available for doing work. If the change occurs with a decrease in entropy (of the system), in which case  $T\Delta S < 0$ , then the right-hand side of this equation is not as negative as  $\Delta U$  itself, and consequently the maximum work is less than  $\Delta U$ . For the change to be spontaneous, some of the energy must escape as heat in order to generate enough entropy in the surroundings to overcome the reduction in entropy in the system (Fig. 3.16). In this case, Nature is demanding a tax on the internal energy as it is converted into work. This is the origin of the alternative name ‘Helmholtz free energy’ for  $A$ , because  $\Delta A$  is that part of the change in internal energy that we are free to use to do work.

Further insight into the relation between the work that a system can do and the Helmholtz energy is to recall that work is energy transferred to the surroundings as the uniform motion of atoms. We can interpret the expression  $A = U - TS$  as showing that  $A$  is the total internal energy of the system,  $U$ , less a contribution that is stored as energy of thermal motion (the quantity  $TS$ ). Because energy stored in random thermal motion cannot be used to achieve uniform motion in the surroundings, only the part of  $U$  that is not stored in that way, the quantity  $U - TS$ , is available for conversion into work.

If the change occurs with an increase of entropy of the system (in which case  $T\Delta S > 0$ ), the right-hand side of the equation is more negative than  $\Delta U$ . In this case, the maximum work that can be obtained from the system is greater than  $\Delta U$ . The explanation of this apparent paradox is that the system is not isolated and energy may flow in as heat as work is done. Because the entropy of the system increases, we can afford a reduction of the entropy of the surroundings yet still have, overall, a spontaneous process. Therefore, some energy (no more than the value of  $T\Delta S$ ) may leave the surroundings as heat and contribute to the work the change is generating (Fig. 3.17). Nature is now providing a tax refund.

#### Example 3.4 Calculating the maximum available work

When 1.000 mol  $C_6H_{12}O_6$  (glucose) is oxidized to carbon dioxide and water at 25°C according to the equation  $C_6H_{12}O_6(s) + 6 O_2(g) \rightarrow 6 CO_2(g) + 6 H_2O(l)$ , calorimetric measurements give  $\Delta_r U^\circ = -2808 \text{ kJ mol}^{-1}$  and  $\Delta_r S^\circ = +259.1 \text{ J K}^{-1} \text{ mol}^{-1}$  at 25°C. How much of this energy change can be extracted as (a) heat at constant pressure, (b) work?

**Method** We know that the heat released at constant pressure is equal to the value of  $\Delta H$ , so we need to relate  $\Delta_r H^\circ$  to  $\Delta_r U^\circ$ , which is given. To do so, we suppose that all the gases involved are perfect, and use eqn 2.21 in the form  $\Delta_r H = \Delta_r U + \Delta V_g RT$ . For the maximum work available from the process we use eqn 3.39.

**Answer** (a) Because  $\Delta V_g = 0$ , we know that  $\Delta_r H^\circ = \Delta_r U^\circ = -2808 \text{ kJ mol}^{-1}$ . Therefore, at constant pressure, the energy available as heat is 2808 kJ mol<sup>-1</sup>.  
(b) Because  $T = 298 \text{ K}$ , the value of  $\Delta_r A^\circ$  is

$$\Delta_r A^\circ = \Delta_r U^\circ - T\Delta_r S^\circ = -2808 \text{ kJ mol}^{-1} - 298 \text{ K} \times 259.1 \text{ J K}^{-1} \text{ mol}^{-1} = -2885 \text{ kJ mol}^{-1}$$

Therefore, the combustion of 1.000 mol  $C_6H_{12}O_6$  can be used to produce up to 2885 kJ of work. The maximum work available is greater than the change in internal energy on account of the positive entropy of reaction (which is partly due to the generation of a large number of small molecules from one big one). The system can therefore draw in energy from the surroundings (so reducing their entropy) and make it available for doing work.

**Self-test 3.7** Repeat the calculation for the combustion of 1.000 mol CH<sub>4</sub>(g) under the same conditions, using data from Tables 2.6 and 2.8.

$$[|q_p| = 890 \text{ kJ}, |w_{\max}| = 818 \text{ kJ}]$$

#### (d) Some remarks on the Gibbs energy

The Gibbs energy (the ‘free energy’) is more common in chemistry than the Helmholtz energy because, at least in laboratory chemistry, we are usually more interested in changes occurring at constant pressure than at constant volume. The criterion  $dG_{T,p} \leq 0$  carries over into chemistry as the observation that, *at constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy*. Therefore, if we want to know whether a reaction is spontaneous, the pressure and temperature being constant, we assess the change in the Gibbs energy. If  $G$  decreases as the reaction proceeds, then the reaction has a spontaneous tendency to convert the reactants into products. If  $G$  increases, then the reverse reaction is spontaneous.

The existence of spontaneous endothermic reactions provides an illustration of the role of  $G$ . In such reactions,  $H$  increases, the system rises spontaneously to states of higher enthalpy, and  $dH > 0$ . Because the reaction is spontaneous we know that  $dG < 0$  despite  $dH > 0$ ; it follows that the entropy of the system increases so much that  $TdS$  outweighs  $dH$  in  $dG = dH - TdS$ . Endothermic reactions are therefore driven by the increase of entropy of the system, and this entropy change overcomes the reduction of entropy brought about in the surroundings by the inflow of heat into the system ( $dS_{\text{sur}} = -dH/T$  at constant pressure).

#### (e) Maximum non-expansion work

The analogue of the maximum work interpretation of  $\Delta A$ , and the origin of the name ‘free energy’, can be found for  $\Delta G$ . In the following *Justification*, we show that at constant temperature and pressure, the maximum additional (non-expansion) work,  $w_{\text{add,max}}$ , is given by the change in Gibbs energy:

$$dw_{\text{add,max}} = dG \quad (3.41a)$$

The corresponding expression for a measurable change is

$$w_{\text{add,max}} = \Delta G \quad \boxed{\begin{array}{l} \text{Relation between } G \text{ and} \\ \text{maximum non-expansion work} \end{array}} \quad (3.41b)$$

This expression is particularly useful for assessing the electrical work that may be produced by fuel cells and electrochemical cells, and we shall see many applications of it.

#### Justification 3.3 Maximum non-expansion work

Because  $H = U + pV$ , for a general change in conditions, the change in enthalpy is

$$dH = dq + dw + d(pV)$$

The corresponding change in Gibbs energy ( $G = H - TS$ ) is

$$dG = dH - TdS - SdT = dq + dw + d(pV) - TdS - SdT$$

When the change is isothermal we can set  $dT = 0$ ; then

$$dG = dq + dw + d(pV) - TdS$$

When the change is reversible,  $dw = dw_{\text{rev}}$  and  $dq = dq_{\text{rev}} = TdS$ , so for a reversible, isothermal process

$$dG = TdS + dw_{\text{rev}} + d(pV) - TdS = dw_{\text{rev}} + d(pV)$$

The work consists of expansion work, which for a reversible change is given by  $-pdV$ , and possibly some other kind of work (for instance, the electrical work of pushing electrons through a circuit or of raising a column of liquid); this additional work we denote  $dw_{\text{add}}$ . Therefore, with  $d(pV) = pdV + Vdp$ ,

$$dG = (-pdV + dw_{\text{add,rev}}) + pdV + Vdp = dw_{\text{add,rev}} + Vdp$$

If the change occurs at constant pressure (as well as constant temperature), we can set  $dp = 0$  and obtain  $dG = dw_{\text{add,rev}}$ . Therefore, at constant temperature and pressure,  $dw_{\text{add,rev}} = dG$ . However, because the process is reversible, the work done must now have its maximum value, so eqn 3.41 follows.

### Example 3.5 Calculating the maximum non-expansion work of a reaction

How much energy is available for sustaining muscular and nervous activity from the combustion of 1.00 mol of glucose molecules under standard conditions at 37°C (blood temperature)? The standard entropy of reaction is  $+259.1 \text{ J K}^{-1} \text{ mol}^{-1}$ .

**Method** The non-expansion work available from the reaction is equal to the change in standard Gibbs energy for the reaction ( $\Delta_r G^\ominus$ , a quantity defined more fully below). To calculate this quantity, it is legitimate to ignore the temperature-dependence of the reaction enthalpy, to obtain  $\Delta_r H^\ominus$  from Tables 2.6 and 2.8, and to substitute the data into  $\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$ .

**Answer** Because the standard reaction enthalpy is  $-2808 \text{ kJ mol}^{-1}$ , it follows that the standard reaction Gibbs energy is

$$\Delta_r G^\ominus = -2808 \text{ kJ mol}^{-1} - (310 \text{ K}) \times (259.1 \text{ J K}^{-1} \text{ mol}^{-1}) = -2888 \text{ kJ mol}^{-1}$$

Therefore,  $w_{\text{add,max}} = -2888 \text{ kJ}$  for the combustion of 1 mol glucose molecules, and the reaction can be used to do up to 2888 kJ of non-expansion work. To place this result in perspective, consider that a person of mass 70 kg needs to do 2.1 kJ of work to climb vertically through 3.0 m; therefore, at least 0.13 g of glucose is needed to complete the task (and in practice significantly more).

**Self-test 3.8** How much non-expansion work can be obtained from the combustion of 1.00 mol  $\text{CH}_4(\text{g})$  under standard conditions at 298 K? Use  $\Delta_r S^\ominus = -243 \text{ J K}^{-1} \text{ mol}^{-1}$ . [818 kJ]

### 3.6 Standard molar Gibbs energies

**Key points** Standard Gibbs energies of formation are used to calculate the standard Gibbs energies of reactions. The Gibbs energies of formation of ions may be estimated from a thermodynamic cycle and the Born equation.

Standard entropies and enthalpies of reaction can be combined to obtain the **standard Gibbs energy of reaction** (or ‘standard reaction Gibbs energy’),  $\Delta_r G^\ominus$ :

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$$

Definition of standard Gibbs energy of reaction

[3.42]

The standard Gibbs energy of reaction is the difference in standard molar Gibbs energies of the products and reactants in their standard states at the temperature specified for the reaction as written. As in the case of standard reaction enthalpies, it is convenient to define the **standard Gibbs energies of formation**,  $\Delta_f G^\ominus$ , the standard

reaction Gibbs energy for the formation of a compound from its elements in their reference states.<sup>7</sup> Standard Gibbs energies of formation of the elements in their reference states are zero, because their formation is a ‘null’ reaction. A selection of values for compounds is given in Table 3.4. From the values there, it is a simple matter to obtain the standard Gibbs energy of reaction by taking the appropriate combination:

$$\Delta_r G^\ominus = \sum_{\text{Products}} v \Delta_f G^\ominus - \sum_{\text{Reactants}} v \Delta_f G^\ominus$$

Procedure for calculating  
the standard Gibbs  
energy of reaction

(3.43a)

In the notation introduced in Section 2.8,

$$\Delta_r G^\ominus = \sum_J v_J \Delta_f G^\ominus (J) \quad (3.43b)$$

#### • A brief illustration

To calculate the standard Gibbs energy of the reaction  $\text{CO(g)} + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$  at 25°C, we write

$$\begin{aligned} \Delta_r G^\ominus &= \Delta_f G^\ominus (\text{CO}_2, \text{g}) - \{\Delta_f G^\ominus (\text{CO}, \text{g}) + \frac{1}{2} \Delta_f G^\ominus (\text{O}_2, \text{g})\} \\ &= -394.4 \text{ kJ mol}^{-1} - \{(-137.2) + \frac{1}{2}(0)\} \text{ kJ mol}^{-1} \\ &= -257.2 \text{ kJ mol}^{-1} \bullet \end{aligned}$$

**Self-test 3.9** Calculate the standard reaction Gibbs energy for the combustion of  $\text{CH}_4(\text{g})$  at 298 K. [−818 kJ mol<sup>−1</sup>]

Just as we did in Section 2.8, where we acknowledged that solutions of cations cannot be prepared without their accompanying anions, we define one ion, conventionally the hydrogen ion, to have zero standard Gibbs energy of formation at all temperatures:

$$\Delta_f G^\ominus (\text{H}^+, \text{aq}) = 0$$

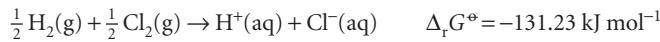
Convention for  
ions in solution

[3.44]

In essence, this definition adjusts the actual values of the Gibbs energies of formation of ions by a fixed amount that is chosen so that the standard value for one of them,  $\text{H}^+(\text{aq})$ , has the value zero.

#### • A brief illustration

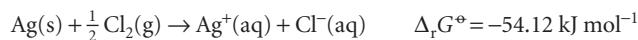
For the reaction



we can write

$$\Delta_r G^\ominus = \Delta_f G^\ominus (\text{H}^+, \text{aq}) + \Delta_f G^\ominus (\text{Cl}^-, \text{aq}) = \Delta_f G^\ominus (\text{Cl}^-, \text{aq})$$

and hence identify  $\Delta_f G^\ominus (\text{Cl}^-, \text{aq})$  as  $-131.23 \text{ kJ mol}^{-1}$ . With the value of  $\Delta_f G^\ominus (\text{Cl}^-, \text{aq})$  established, we can find the value of  $\Delta_f G^\ominus (\text{Ag}^+, \text{aq})$  from



which leads to  $\Delta_f G^\ominus (\text{Ag}^+, \text{aq}) = +77.11 \text{ kJ mol}^{-1}$ . All the Gibbs energies of formation of ions tabulated in the *Data section* were calculated in the same way. •

**Table 3.4\*** Standard Gibbs energies of formation (at 298 K)

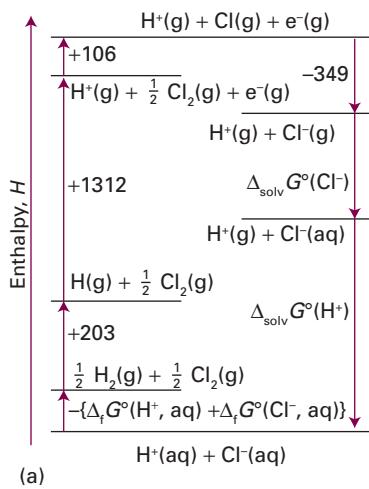
	$\Delta_f G^\ominus / (\text{kJ mol}^{-1})$
Diamond, C(s)	+2.9
Benzene, $\text{C}_6\text{H}_6(\text{l})$	+124.3
Methane, $\text{CH}_4(\text{g})$	−50.7
Carbon dioxide, $\text{CO}_2(\text{g})$	−394.4
Water, $\text{H}_2\text{O(l)}$	−237.1
Ammonia, $\text{NH}_3(\text{g})$	−16.5
Sodium chloride, $\text{NaCl(s)}$	−384.1

\* More values are given in the *Data section*.

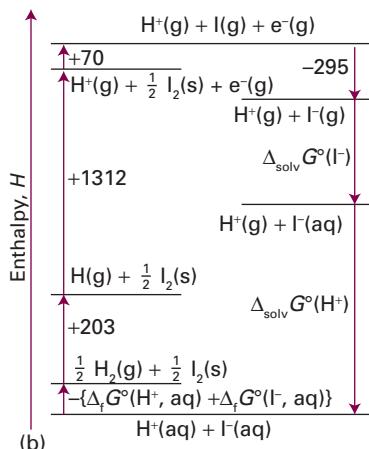
<sup>7</sup> The reference state of an element was defined in Section 2.8.

**A brief comment**

The standard Gibbs energies of formation of the gas-phase ions are unknown. We have therefore used ionization energies and electron affinities and have assumed that any differences from the Gibbs energies arising from conversion to enthalpy and the inclusion of entropies to obtain Gibbs energies in the formation of  $H^+$  are cancelled by the corresponding terms in the electron gain of X. The conclusions from the cycles are therefore only approximate.



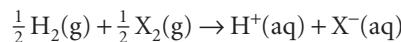
(a)



(b)

**Fig. 3.18** The thermodynamic cycles for the discussion of the Gibbs energies of solvation (hydration) and formation of (a) chloride ions, (b) iodide ions in aqueous solution. The sum of the changes in Gibbs energies around the cycle sum to zero because  $G$  is a state function.

The factors responsible for the magnitude of the Gibbs energy of formation of an ion in solution can be identified by analysing it in terms of a thermodynamic cycle. As an illustration, we consider the standard Gibbs energy of formation of  $Cl^-$  in water, which is  $-131 \text{ kJ mol}^{-1}$ . We do so by treating the formation reaction



as the outcome of the sequence of steps shown in Fig. 3.18 (with values taken from the *Data section*). The sum of the Gibbs energies for all the steps around a closed cycle is zero, so

$$\Delta_f G^\circ(Cl^-, \text{aq}) = 1272 \text{ kJ mol}^{-1} + \Delta_{\text{solv}} G^\circ(H^+) + \Delta_{\text{solv}} G^\circ(Cl^-)$$

An important point to note is that the value of  $\Delta_f G^\circ$  of an ion X is not determined by the properties of X alone but includes contributions from the dissociation, ionization, and hydration of hydrogen.

Gibbs energies of solvation of individual ions may be estimated from an equation derived by Max Born, who identified  $\Delta_{\text{solv}} G^\circ$  with the electrical work of transferring an ion from a vacuum into the solvent treated as a continuous dielectric of relative permittivity  $\epsilon_r$ . The resulting **Born equation**, which is derived in *Further information 3.1*, is

$$\Delta_{\text{solv}} G^\circ = -\frac{z_i^2 e^2 N_A}{8\pi\epsilon_0 r_i} \left(1 - \frac{1}{\epsilon_r}\right) \quad \boxed{\text{Born equation}} \quad (3.45a)$$

where  $z_i$  is the charge number of the ion and  $r_i$  its radius ( $N_A$  is Avogadro's constant). Note that  $\Delta_{\text{solv}} G^\circ < 0$ , and that  $\Delta_{\text{solv}} G^\circ$  is strongly negative for small, highly charged ions in media of high relative permittivity. For water for which  $\epsilon_r = 78.54$  at  $25^\circ\text{C}$ ,

$$\Delta_{\text{solv}} G^\circ = -\frac{z_i^2}{(r_i/\text{pm})} \times (6.86 \times 10^4 \text{ kJ mol}^{-1}) \quad (3.45b)$$

• **A brief illustration**

To see how closely the Born equation reproduces the experimental data, we calculate the difference in the values of  $\Delta_f G^\circ$  for  $Cl^-$  and  $I^-$  in water at  $25^\circ\text{C}$ , given their radii as 181 pm and 220 pm (Table 19.3), respectively, is

$$\begin{aligned} \Delta_{\text{solv}} G^\circ(Cl^-) - \Delta_{\text{solv}} G^\circ(I^-) &= -\left(\frac{1}{181} - \frac{1}{220}\right) \times (6.86 \times 10^4 \text{ kJ mol}^{-1}) \\ &= -67 \text{ kJ mol}^{-1} \end{aligned}$$

This estimated difference is in good agreement with the experimental difference, which is  $-61 \text{ kJ mol}^{-1}$ . •

**Self-test 3.10** Estimate the value of  $\Delta_{\text{solv}} G^\circ(Cl^-) - \Delta_{\text{solv}} G^\circ(Br^-)$  in water from experimental data and from the Born equation.

[ $-26 \text{ kJ mol}^{-1}$  experimental;  $-29 \text{ kJ mol}^{-1}$  calculated]

Calorimetry (for  $\Delta H$  directly, and for  $S$  via heat capacities) is only one of the ways of determining Gibbs energies. They may also be obtained from equilibrium constants and electrochemical measurements (Chapter 6), and for gases they may be calculated using data from spectroscopic observations (Chapter 16).

## Combining the First and Second Laws

The First and Second Laws of thermodynamics are both relevant to the behaviour of matter, and we can bring the whole force of thermodynamics to bear on a problem by setting up a formulation that combines them.

### 3.7 The fundamental equation

**Key point** The fundamental equation, a combination of the First and Second Laws, is an expression for the change in internal energy that accompanies changes in the volume and entropy of a system.

We have seen that the First Law of thermodynamics may be written  $dU = dq + dw$ . For a reversible change in a closed system of constant composition, and in the absence of any additional (non-expansion) work, we may set  $dw_{\text{rev}} = -pdV$  and (from the definition of entropy)  $dq_{\text{rev}} = TdS$ , where  $p$  is the pressure of the system and  $T$  its temperature. Therefore, for a reversible change in a closed system,

$$dU = TdS - pdV \quad \boxed{\text{The fundamental equation}} \quad (3.46)$$

However, because  $dU$  is an exact differential, its value is independent of path. Therefore, the same value of  $dU$  is obtained whether the change is brought about irreversibly or reversibly. Consequently, eqn 3.46 applies to any change—reversible or irreversible—of a closed system that does no additional (non-expansion) work. We shall call this combination of the First and Second Laws the **fundamental equation**.

The fact that the fundamental equation applies to both reversible and irreversible changes may be puzzling at first sight. The reason is that only in the case of a reversible change may  $TdS$  be identified with  $dq$  and  $-pdV$  with  $dw$ . When the change is irreversible,  $TdS > dq$  (the Clausius inequality) and  $-pdV > dw$ . The sum of  $dw$  and  $dq$  remains equal to the sum of  $TdS$  and  $-pdV$ , provided the composition is constant.

### 3.8 Properties of the internal energy

**Key points** Relations between thermodynamic properties are generated by combining thermodynamic and mathematical expressions for changes in their values. (a) The Maxwell relations are a series of relations between derivatives of thermodynamic properties based on criteria for changes in the properties being exact differentials. (b) The Maxwell relations are used to derive the thermodynamic equation of state and to determine how the internal energy of a substance varies with volume.

Equation 3.46 shows that the internal energy of a closed system changes in a simple way when either  $S$  or  $V$  is changed ( $dU \propto dS$  and  $dU \propto dV$ ). These simple proportionalities suggest that  $U$  is best regarded as a function of  $S$  and  $V$ . We could regard  $U$  as a function of other variables, such as  $S$  and  $p$  or  $T$  and  $V$ , because they are all interrelated; but the simplicity of the fundamental equation suggests that  $U(S, V)$  is the best choice.

The *mathematical* consequence of  $U$  being a function of  $S$  and  $V$  is that we can express an infinitesimal change  $dU$  in terms of changes  $dS$  and  $dV$  by

$$dU = \left( \frac{\partial U}{\partial S} \right)_V dS + \left( \frac{\partial U}{\partial V} \right)_S dV \quad (3.47)$$

#### A brief comment

Partial derivatives were introduced in Mathematical background 2. The type of result in eqn 3.47 was first obtained in Section 2.11, where we treated  $U$  as a function of  $T$  and  $V$ .

The two partial derivatives are the slopes of the plots of  $U$  against  $S$  and  $V$ , respectively. When this expression is compared to the *thermodynamic* relation, eqn 3.46, we see that, for systems of constant composition,

$$\left( \frac{\partial U}{\partial S} \right)_V = T \quad \left( \frac{\partial U}{\partial V} \right)_S = -p \quad (3.48)$$

The first of these two equations is a purely thermodynamic definition of temperature (a Zeroth-Law concept) as the ratio of the changes in the internal energy (a First-Law concept) and entropy (a Second-Law concept) of a constant-volume, closed, constant-composition system. We are beginning to generate relations between the properties of a system and to discover the power of thermodynamics for establishing unexpected relations.

### (a) The Maxwell relations

An infinitesimal change in a function  $f(x,y)$  can be written  $df = gdx + hdy$  where  $g$  and  $h$  are functions of  $x$  and  $y$ . The mathematical criterion for  $df$  being an exact differential (in the sense that its integral is independent of path) is that

$$\left( \frac{\partial g}{\partial y} \right)_x = \left( \frac{\partial h}{\partial x} \right)_y \quad (3.49)$$

This criterion is discussed in *Mathematical background 2*. Because the fundamental equation, eqn 3.46, is an expression for an exact differential, the functions multiplying  $dS$  and  $dV$  (namely  $T$  and  $-p$ ) must pass this test. Therefore, it must be the case that

$$\left( \frac{\partial T}{\partial V} \right)_S = - \left( \frac{\partial p}{\partial S} \right)_V \quad \boxed{\text{A Maxwell relation}} \quad (3.50)$$

We have generated a relation between quantities that, at first sight, would not seem to be related.

Equation 3.50 is an example of a **Maxwell relation**. However, apart from being unexpected, it does not look particularly interesting. Nevertheless, it does suggest that there may be other similar relations that are more useful. Indeed, we can use the fact that  $H$ ,  $G$ , and  $A$  are all state functions to derive three more Maxwell relations. The argument to obtain them runs in the same way in each case: because  $H$ ,  $G$ , and  $A$  are state functions, the expressions for  $dH$ ,  $dG$ , and  $dA$  satisfy relations like eqn 3.49. All four relations are listed in Table 3.5 and we put them to work later in the chapter.

**Table 3.5** The Maxwell relations

From $U$ :	$\left( \frac{\partial T}{\partial V} \right)_S = - \left( \frac{\partial p}{\partial S} \right)_V$
From $H$ :	$\left( \frac{\partial T}{\partial p} \right)_S = \left( \frac{\partial V}{\partial S} \right)_p$
From $A$ :	$\left( \frac{\partial p}{\partial T} \right)_V = \left( \frac{\partial S}{\partial V} \right)_T$
From $G$ :	$\left( \frac{\partial V}{\partial T} \right)_p = - \left( \frac{\partial S}{\partial p} \right)_T$

### (b) The variation of internal energy with volume

The quantity  $\pi_T = (\partial U / \partial V)_T$ , which represents how the internal energy changes as the volume of a system is changed isothermally, played a central role in the manipulation of the First Law, and in *Further information 2.2* we used the relation

$$\pi_T = T \left( \frac{\partial p}{\partial T} \right)_V - p \quad \boxed{\text{A thermodynamic equation of state}} \quad (3.51)$$

This relation is called a **thermodynamic equation of state** because it is an expression for pressure in terms of a variety of thermodynamic properties of the system. We are now ready to derive it by using a Maxwell relation.

**Justification 3.4** *The thermodynamic equation of state*

We obtain an expression for the coefficient  $\pi_T$  by dividing both sides of eqn 3.47 by  $dV$ , imposing the constraint of constant temperature, which gives

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_T + \left(\frac{\partial U}{\partial V}\right)_S$$

Next, we introduce the two relations in eqn 3.48 and the definition of  $\pi_T$  to obtain

$$\pi_T = T \left( \frac{\partial S}{\partial V} \right)_T - p$$

The third Maxwell relation in Table 3.5 turns  $(\partial S/\partial V)_T$  into  $(\partial p/\partial T)_V$ , which completes the proof of eqn 3.51.

**Example 3.6** *Deriving a thermodynamic relation*

Show thermodynamically that  $\pi_T = 0$  for a perfect gas, and compute its value for a van der Waals gas.

**Method** Proving a result ‘thermodynamically’ means basing it entirely on general thermodynamic relations and equations of state, without drawing on molecular arguments (such as the existence of intermolecular forces). We know that for a perfect gas,  $p = nRT/V$ , so this relation should be used in eqn 3.51. Similarly, the van der Waals equation is given in Table 1.7, and for the second part of the question it should be used in eqn 3.51.

**Answer** For a perfect gas we write

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial(nRT/V)}{\partial T}\right)_V = \frac{nR}{V}$$

Then, eqn 3.51 becomes

$$\pi_T = \frac{nRT}{V} - p = 0$$

The equation of state of a van der Waals gas is

$$p = \frac{nRT}{V - nb} - a \frac{n^2}{V^2}$$

Because  $a$  and  $b$  are independent of temperature,

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial(nRT/(V - nb))}{\partial T}\right)_V = \frac{nR}{V - nb}$$

Therefore, from eqn 3.51,

$$\pi_T = \frac{nRT}{V - nb} - p = \frac{nRT}{V - nb} - \left( \frac{nRT}{V - nb} - a \frac{n^2}{V^2} \right) = a \frac{n^2}{V^2}$$

This result for  $\pi_T$  implies that the internal energy of a van der Waals gas increases when it expands isothermally (that is,  $(\partial U/\partial V)_T > 0$ ), and that the increase is related to the parameter  $a$ , which models the attractive interactions between the

particles. A larger molar volume, corresponding to a greater average separation between molecules, implies weaker mean intermolecular attractions, so the total energy is greater.

**Self-test 3.11** Calculate  $\pi_T$  for a gas that obeys the virial equation of state (Table 1.7).  

$$[\pi_T = RT^2(\partial B/\partial T)_V/V_m^2 + \dots]$$

### 3.9 Properties of the Gibbs energy

**Key points** (a) The variation of the Gibbs energy of a system suggests that it is best regarded as a function of pressure and temperature. The Gibbs energy of a substance decreases with temperature and increases with pressure. (b) The variation of Gibbs energy with temperature is related to the enthalpy by the Gibbs–Helmholtz equation. (c) The Gibbs energies of solids and liquids are almost independent of pressure; those of gases vary linearly with the logarithm of the pressure.

The same arguments that we have used for  $U$  can be used for the Gibbs energy  $G = H - TS$ . They lead to expressions showing how  $G$  varies with pressure and temperature that are important for discussing phase transitions and chemical reactions.

#### (a) General considerations

When the system undergoes a change of state,  $G$  may change because  $H$ ,  $T$ , and  $S$  all change. As in *Justification 2.1*, we write for infinitesimal changes in each property

$$dG = dH - d(TS) = dH - TdS - SdT$$

Because  $H = U + pV$ , we know that

$$dH = dU + d(pV) = dU + pdV + Vdp$$

and therefore

$$dG = dU + pdV + Vdp - TdS - SdT$$

For a closed system doing no non-expansion work, we can replace  $dU$  by the fundamental equation  $dU = TdS - pdV$  and obtain

$$dG = TdS - pdV + pdV + Vdp - TdS - SdT$$

Four terms now cancel on the right, and we conclude that for a closed system in the absence of non-expansion work and at constant composition

$$dG = Vdp - SdT$$

The fundamental equation of  
chemical thermodynamics

(3.52)

This expression, which shows that a change in  $G$  is proportional to a change in  $p$  or  $T$ , suggests that  $G$  may be best regarded as a function of  $p$  and  $T$ . It may be regarded as the **fundamental equation of chemical thermodynamics** as it is so central to the application of thermodynamics to chemistry: it suggests that  $G$  is an important quantity in chemistry because the pressure and temperature are usually the variables under our control. In other words,  $G$  carries around the combined consequences of the First and Second Laws in a way that makes it particularly suitable for chemical applications.

The same argument that led to eqn 3.48, when applied to the exact differential  $dG = Vdp - SdT$ , now gives

$$\left( \frac{\partial G}{\partial T} \right)_p = -S \quad \left( \frac{\partial G}{\partial p} \right)_T = V$$

The variation of  $G$   
with  $T$  and  $p$

(3.53)

These relations show how the Gibbs energy varies with temperature and pressure (Fig. 3.19). The first implies that:

- Because  $S > 0$  for all substances,  $G$  always *decreases* when the temperature is raised (at constant pressure and composition).
- Because  $(\partial G/\partial T)_p$  becomes more negative as  $S$  increases,  $G$  decreases most sharply when the entropy of the system is large.

Therefore, the Gibbs energy of the gaseous phase of a substance, which has a high molar entropy, is more sensitive to temperature than its liquid and solid phases (Fig. 3.20). Similarly, the second relation implies that:

- Because  $V > 0$  for all substances,  $G$  always *increases* when the pressure of the system is increased (at constant temperature and composition).
- Because  $(\partial G/\partial p)_T$  increases with  $V$ ,  $G$  is more sensitive to pressure when the volume of the system is large.

Because the molar volume of the gaseous phase of a substance is greater than that of its condensed phases, the molar Gibbs energy of a gas is more sensitive to pressure than its liquid and solid phases (Fig. 3.21).

### (b) The variation of the Gibbs energy with temperature

As we remarked in the introduction, because the equilibrium composition of a system depends on the Gibbs energy, to discuss the response of the composition to temperature we need to know how  $G$  varies with temperature.

The first relation in eqn 3.53,  $(\partial G/\partial T)_p = -S$ , is our starting point for this discussion. Although it expresses the variation of  $G$  in terms of the entropy, we can express it in terms of the enthalpy by using the definition of  $G$  to write  $S = (H - G)/T$ . Then

$$\left(\frac{\partial G}{\partial T}\right)_p = \frac{G - H}{T} \quad (3.54)$$

We shall see later that the equilibrium constant of a reaction is related to  $G/T$  rather than to  $G$  itself,<sup>8</sup> and it is easy to deduce from the last equation (see the following *Justification*) that

$$\left(\frac{\partial(G/T)}{\partial T}\right)_p = -\frac{H}{T^2} \quad \boxed{\text{Gibbs-Helmholtz equation}} \quad (3.55)$$

This expression is called the **Gibbs–Helmholtz equation**. It shows that, if we know the enthalpy of the system, then we know how  $G/T$  varies with temperature.

#### Justification 3.5 The Gibbs–Helmholtz equation

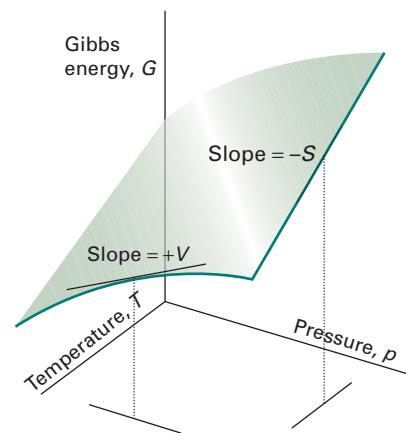
First, we note that

$$\left(\frac{\partial(G/T)}{\partial T}\right)_p = \frac{1}{T} \left(\frac{\partial G}{\partial T}\right)_p + G \frac{d(1/T)}{dT} = \frac{1}{T} \left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T^2} = \frac{1}{T} \left\{ \left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T} \right\}$$

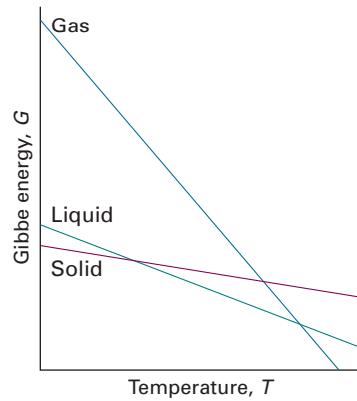
Then we use eqn 3.54 to write

$$\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T} = \frac{G - H}{T} - \frac{G}{T} = -\frac{H}{T}$$

When this expression is substituted in the preceding one, we obtain eqn 3.55.

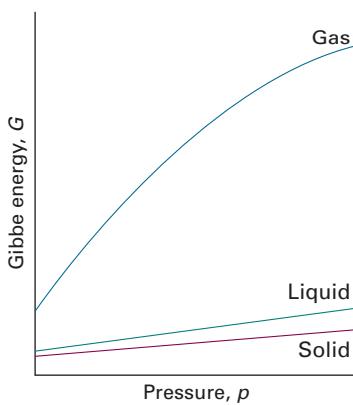


**Fig. 3.19** The variation of the Gibbs energy of a system with (a) temperature at constant pressure and (b) pressure at constant temperature. The slope of the former is equal to the negative of the entropy of the system and that of the latter is equal to the volume.

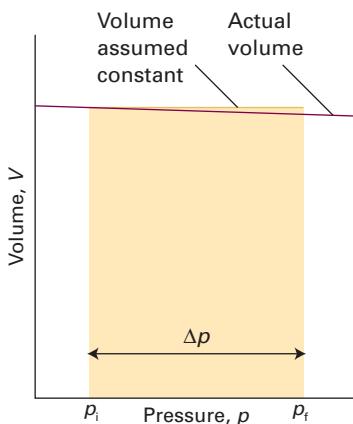


**Fig. 3.20** The variation of the Gibbs energy with the temperature is determined by the entropy. Because the entropy of the gaseous phase of a substance is greater than that of the liquid phase, and the entropy of the solid phase is smallest, the Gibbs energy changes most steeply for the gas phase, followed by the liquid phase, and then the solid phase of the substance.

<sup>8</sup> In Section 6.2b we derive the result that the equilibrium constant for a reaction is related to its standard reaction Gibbs energy by  $\Delta_r G^\circ/T = -R \ln K$ .



**Fig. 3.21** The variation of the Gibbs energy with the pressure is determined by the volume of the sample. Because the volume of the gaseous phase of a substance is greater than that of the same amount of liquid phase, and the entropy of the solid phase is smallest (for most substances), the Gibbs energy changes most steeply for the gas phase, followed by the liquid phase, and then the solid phase of the substance. Because the volumes of the solid and liquid phases of a substance are similar, their molar Gibbs energies vary by similar amounts as the pressure is changed.



**Fig. 3.22** The difference in Gibbs energy of a solid or liquid at two pressures is equal to the rectangular area shown. We have assumed that the variation of volume with pressure is negligible.

The Gibbs–Helmholtz equation is most useful when it is applied to changes, including changes of physical state and chemical reactions at constant pressure. Then, because  $\Delta G = G_f - G_i$  for the change of Gibbs energy between the final and initial states and because the equation applies to both  $G_f$  and  $G_i$ , we can write

$$\left( \frac{\partial(\Delta G/T)}{\partial T} \right)_p = -\frac{\Delta H}{T^2} \quad (3.56)$$

This equation shows that, if we know the change in enthalpy of a system that is undergoing some kind of transformation (such as vaporization or reaction), then we know how the corresponding change in Gibbs energy varies with temperature. As we shall see, this is a crucial piece of information in chemistry.

### (c) The variation of the Gibbs energy with pressure

To find the Gibbs energy at one pressure in terms of its value at another pressure, the temperature being constant, we set  $dT = 0$  in eqn 3.52, which gives  $dG = Vdp$ , and integrate:

$$G(p_f) = G(p_i) + \int_{p_i}^{p_f} V dp \quad (3.57a)$$

For molar quantities,

$$G_m(p_f) = G_m(p_i) + \int_{p_i}^{p_f} V_m dp \quad (3.57b)$$

This expression is applicable to any phase of matter, but to evaluate it we need to know how the molar volume,  $V_m$ , depends on the pressure.

The molar volume of a condensed phase changes only slightly as the pressure changes (Fig. 3.22), so we can treat  $V_m$  as a constant and take it outside the integral:

$$G_m(p_f) = G_m(p_i) + V_m \int_{p_i}^{p_f} dp = G_m(p_i) + (p_f - p_i)V_m \quad (3.58)$$

**Self-test 3.12** Calculate the change in  $G_m$  for ice at  $-10^\circ\text{C}$ , with density  $917 \text{ kg m}^{-3}$ , when the pressure is increased from 1.0 bar to 2.0 bar.  $[+2.0 \text{ J mol}^{-1}]$

Under normal laboratory conditions  $(p_f - p_i)V_m$  is very small and may be neglected. Hence, we may usually suppose that the Gibbs energies of solids and liquids are independent of pressure. However, if we are interested in geophysical problems, then, because pressures in the Earth's interior are huge, their effect on the Gibbs energy cannot be ignored. If the pressures are so great that there are substantial volume changes over the range of integration, then we must use the complete expression, eqn 3.57.

#### • A brief illustration

Suppose that for a certain phase transition of a solid  $\Delta_{\text{trs}}V = +1.0 \text{ cm}^3 \text{ mol}^{-1}$  independent of pressure. Then for an increase in pressure to 3.0 Mbar ( $3.0 \times 10^{11} \text{ Pa}$ ) from 1.0 bar ( $1.0 \times 10^5 \text{ Pa}$ ), the Gibbs energy of the transition changes from  $\Delta_{\text{trs}}G(1 \text{ bar})$  to

$$\begin{aligned} \Delta_{\text{trs}}G(3 \text{ Mbar}) &= \Delta_{\text{trs}}G(1 \text{ bar}) + (1.0 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}) \times (3.0 \times 10^{11} \text{ Pa} - 1.0 \times 10^5 \text{ Pa}) \\ &= \Delta_{\text{trs}}G(1 \text{ bar}) + 3.0 \times 10^2 \text{ kJ mol}^{-1} \end{aligned}$$

where we have used  $1 \text{ Pa m}^3 = 1 \text{ J}$ . •

The molar volumes of gases are large, so the Gibbs energy of a gas depends strongly on the pressure. Furthermore, because the volume also varies markedly with the pressure, we cannot treat it as a constant in the integral in eqn 3.57b (Fig. 3.23). For a perfect gas we substitute  $V_m = RT/p$  into the integral, treat  $RT$  as a constant, and find

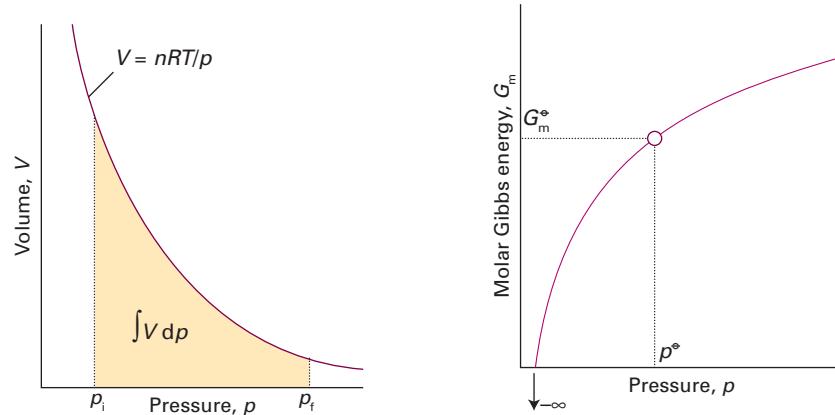
$$G_m(p_f) = G_m(p_i) + RT \int_{p_i}^{p_f} \frac{1}{p} dp = G_m(p_i) + RT \ln \frac{p_f}{p_i} \quad (3.59)^{\circ}$$

This expression shows that, when the pressure is increased tenfold at room temperature, the molar Gibbs energy increases by  $RT \ln 10 \approx 6 \text{ kJ mol}^{-1}$ . It also follows from this equation that, if we set  $p_i = p^*$  (the standard pressure of 1 bar), then the molar Gibbs energy of a perfect gas at a pressure  $p$  (set  $p_f = p$ ) is related to its standard value by

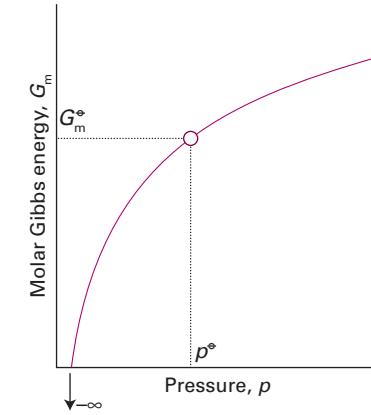
$$G_m(p) = G_m^* + RT \ln \frac{p}{p^*} \quad \boxed{\text{The molar Gibbs energy of a perfect gas}} \quad (3.60)^{\circ}$$

**Self-test 3.13** Calculate the change in the molar Gibbs energy of water vapour (treated as a perfect gas) when the pressure is increased isothermally from 1.0 bar to 2.0 bar at 298 K. Note that, whereas the change in molar Gibbs energy for a condensed phase (Self-test 3.12) is a few joules per mole, the answer you should get for a gas is of the order of kilojoules per mole  
[+1.7 kJ mol<sup>-1</sup>]

The logarithmic dependence of the molar Gibbs energy on the pressure predicted by eqn 3.60 is illustrated in Fig. 3.24. This very important expression, the consequences of which we unfold in the following chapters, applies to perfect gases (which is usually a good enough approximation). *Further information 3.2* describes how to take into account gas imperfections.



**Fig. 3.23** The difference in Gibbs energy for a perfect gas at two pressures is equal to the area shown below the perfect-gas isotherm.



**Fig. 3.24** The molar Gibbs energy of a perfect gas is proportional to  $\ln p$ , and the standard state is reached at  $p^*$ . Note that, as  $p \rightarrow 0$ , the molar Gibbs energy becomes negatively infinite.

 **interActivity** Show how the first derivative of  $G$ ,  $(\partial G/\partial p)_T$ , varies with pressure, and plot the resulting expression over a pressure range. What is the physical significance of  $(\partial G/\partial p)_T$ ?

## Checklist of key equations

Property	Equation	Comment
Thermodynamic entropy	$dS = dq_{rev}/T$	Definition
Boltzmann formula	$S = k \ln W$	Definition
Clausius inequality	$dS \geq dq/T$	
Entropy of isothermal expansion	$\Delta S = nR \ln(V_f/V_i)$	Perfect gas
Entropy of transition	$\Delta_{trs}S = \Delta_{trs}H/T_{trs}$	At the transition temperature
Variation of the entropy with temperature	$S(T_f) = S(T_i) + C \ln(T_f/T_i)$	The heat capacity, $C$ , is independent of temperature and no phase transitions occur
Reaction entropy	$\Delta_rS^\circ = \sum_{\text{Products}} vS_m^\circ - \sum_{\text{Reactants}} vS_m^\circ$	
Helmholtz energy	$A = U - TS$	Definition
Gibbs energy	$G = H - TS$	Definition
Maximum work	$w_{\max} = \Delta A$	
Maximum non-expansion work	$w_{\text{add,max}} = \Delta G$	Constant $p$ and $T$
Criteria of spontaneity	(a) $dS_{U,V} \geq 0$ and $dU_{S,V} \leq 0$ , or (b) $dA_{T,V} \leq 0$ and $dG_{T,p} \leq 0$	
Reaction Gibbs energy	$\Delta_rG^\circ = \sum_{\text{Products}} v\Delta_fG^\circ - \sum_{\text{Reactants}} v\Delta_fG^\circ$	
Fundamental equation	$dU = TdS - pdV$	
Fundamental equation of chemical thermodynamics	$dG = Vdp - SdT$ $(\partial G/\partial p)_T = V$ and $(\partial G/\partial T)_p = -S$ $(\partial(G/T)/\partial T)_p = -H/T^2$	
Gibbs–Helmholtz equation	$G_m(p_f) = G_m(p_i) + V_m\Delta p$ $G(p_f) = G(p_i) + nRT \ln(p_f/p_i)$	Incompressible substance Perfect gas

→ For a chart of the relations between principal equations, see the [Road map section](#) of the Resource section.

## Further information

### Further information 3.1 The Born equation

The strategy of the calculation is to identify the Gibbs energy of solvation with the work of transferring an ion from a vacuum into the solvent. That work is calculated by taking the difference of the work of charging an ion when it is in the solution and the work of charging the same ion when it is in a vacuum.

The Coulomb interaction between two charges  $Q_1$  and  $Q_2$  separated by a distance  $r$  is described by the *Coulombic potential energy*:

$$V = \frac{Q_1 Q_2}{4\pi\epsilon r}$$

where  $\epsilon$  is the medium's permittivity. The permittivity of vacuum is  $\epsilon_0 = 8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$ . The relative permittivity (formerly called the 'dielectric constant') of a substance is defined as  $\epsilon_r = \epsilon/\epsilon_0$ . Ions do not interact as strongly in a solvent of high relative permittivity (such as water, with  $\epsilon_r = 80$  at 293 K) as they do in a solvent of lower relative permittivity (such as ethanol, with  $\epsilon_r = 25$  at 293 K). See Chapter 17 for more details. The potential energy of a

charge  $Q_1$  in the presence of a charge  $Q_2$  can be expressed in terms of the *Coulomb potential*,  $\phi$ :

$$V = Q_1\phi \quad \phi = \frac{Q_2}{4\pi\epsilon r}$$

We model an ion as a sphere of radius  $r_i$  immersed in a medium of permittivity  $\epsilon$ . It turns out that, when the charge of the sphere is  $Q$ , the electric potential,  $\phi$ , at its surface is the same as the potential due to a point charge at its centre, so we can use the last expression and write

$$\phi = \frac{Q}{4\pi\epsilon r_i}$$

The work of bringing up a charge  $dQ$  to the sphere is  $\phi dQ$ . Therefore, the total work of charging the sphere from 0 to  $z_i$  is

$$w = \int_0^{z_i} \phi dQ = \frac{1}{4\pi\epsilon r_i} \int_0^{z_i} Q dQ = \frac{z_i^2 \epsilon}{8\pi\epsilon r_i}$$

This electrical work of charging, when multiplied by Avogadro's constant, is the molar Gibbs energy for charging the ions.

The work of charging an ion in a vacuum is obtained by setting  $\epsilon = \epsilon_0$ , the vacuum permittivity. The corresponding value for charging the ion in a medium is obtained by setting  $\epsilon = \epsilon_r \epsilon_0$ , where  $\epsilon_r$  is the relative permittivity of the medium. It follows that the change in molar Gibbs energy that accompanies the transfer of ions from a vacuum to a solvent is the difference of these two quantities:

$$\Delta_{\text{solv}} G^\ominus = \frac{z_i^2 e^2 N_A}{8\pi \epsilon_r r_i} - \frac{z_i^2 e^2 N_A}{8\pi \epsilon_0 r_i} = \frac{z_i^2 e^2 N_A}{8\pi \epsilon_r \epsilon_0 r_i} - \frac{z_i^2 e^2 N_A}{8\pi \epsilon_0 r_i} = -\frac{z_i^2 e^2 N_A}{8\pi \epsilon_0 r_i} \left(1 - \frac{1}{\epsilon_r}\right)$$

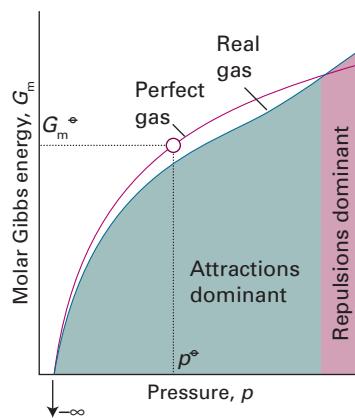
which is eqn 3.45.

### Further information 3.2 The fugacity

At various stages in the development of physical chemistry it is necessary to switch from a consideration of idealized systems to real systems. In many cases it is desirable to preserve the form of the expressions that have been derived for an idealized system. Then deviations from the idealized behaviour can be expressed most simply. For instance, the pressure dependence of the molar Gibbs energy of a real gas might resemble that shown in Fig. 3.25. To adapt eqn 3.60 to this case, we replace the true pressure,  $p$ , by an effective pressure, called the fugacity,<sup>9</sup>  $f$ , and write

$$G_m = G_m^\ominus + RT \ln \frac{f}{p^\ominus} \quad [3.61]$$

The fugacity, a function of the pressure and temperature, is defined so that this relation is exactly true. Although thermodynamic expressions



**Fig. 3.25** The molar Gibbs energy of a real gas. As  $p \rightarrow 0$ , the molar Gibbs energy coincides with the value for a perfect gas (shown by the black line). When attractive forces are dominant (at intermediate pressures), the molar Gibbs energy is less than that of a perfect gas and the molecules have a lower 'escaping tendency'. At high pressures, when repulsive forces are dominant, the molar Gibbs energy of a real gas is greater than that of a perfect gas. Then the 'escaping tendency' is increased.

<sup>9</sup> The name 'fugacity' comes from the Latin for 'fleetness' in the sense of 'escaping tendency'; fugacity has the same dimensions as pressure.

in terms of fugacities derived from this expression are exact, they are useful only if we know how to interpret fugacities in terms of actual pressures. To develop this relation we write the fugacity as

$$f = \phi p \quad [3.62]$$

where  $\phi$  is the dimensionless fugacity coefficient, which in general depends on the temperature, the pressure, and the identity of the gas.

Equation 3.57b is true for all gases whether real or perfect.

Expressing it in terms of the fugacity by using eqn 3.61 turns it into

$$\int_{p'}^p V_m dp = G_m(p) - G_m(p') = \left\{ G_m^\ominus + RT \ln \frac{f}{p^\ominus} \right\} - \left\{ G_m^\ominus + RT \ln \frac{f'}{p^\ominus} \right\}$$

In this expression,  $f$  is the fugacity when the pressure is  $p$  and  $f'$  is the fugacity when the pressure is  $p'$ . If the gas were perfect, we would write

$$\int_{p'}^p V_{\text{perfect},m} dp = RT \int_{p'}^p \frac{1}{p} dp = RT \ln \frac{p}{p'}$$

The difference between the two equations is

$$\int_{p'}^p (V_m - V_{\text{perfect},m}) dp = RT \left( \ln \frac{f}{f'} - \ln \frac{p}{p'} \right) = RT \ln \left( \frac{(f/p')}{(p/p')} \right)$$

which can be rearranged into

$$\ln \left( \frac{f}{p} \times \frac{p'}{f'} \right) = \frac{1}{RT} \int_{p'}^p (V_m - V_{\text{perfect},m}) dp$$

When  $p' \rightarrow 0$ , the gas behaves perfectly and  $f'$  becomes equal to the pressure,  $p'$ . Therefore,  $f'/p' \rightarrow 1$  as  $p' \rightarrow 0$ . If we take this limit, which means setting  $f'/p' = 1$  on the left and  $p' = 0$  on the right, the last equation becomes

$$\ln \frac{f}{p} = \frac{1}{RT} \int_0^p (V_m - V_{\text{perfect},m}) dp$$

Then, with  $\phi = f/p$ ,

$$\ln \phi = \frac{1}{RT} \int_0^p (V_m - V_{\text{perfect},m}) dp$$

For a perfect gas,  $V_{\text{perfect},m} = RT/p$ . For a real gas,  $V_m = RTZ/p$ , where  $Z$  is the compression factor of the gas (Section 1.3a). With these two substitutions, we obtain

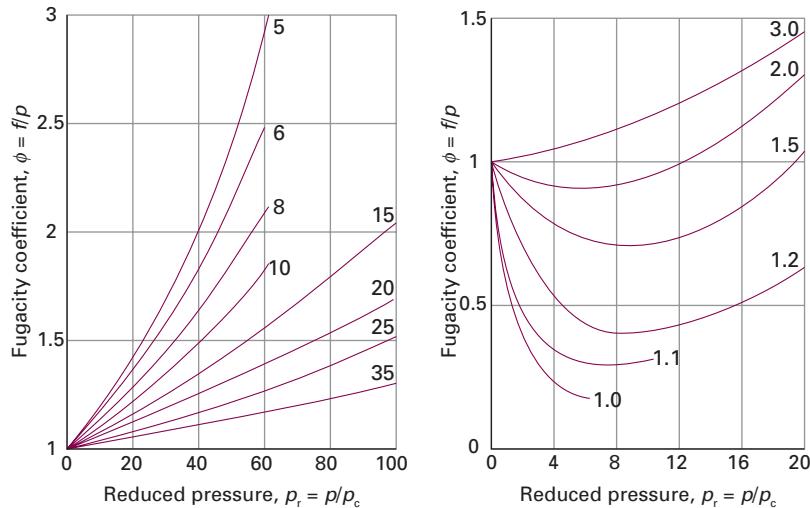
$$\ln \phi = \int_0^p \frac{Z-1}{p} dp \quad (3.63)$$

Provided we know how  $Z$  varies with pressure up to the pressure of interest, this expression enables us to determine the fugacity coefficient and hence, through eqn 3.62, to relate the fugacity to the pressure of the gas.

We see from Fig. 1.14 that for most gases  $Z < 1$  up to moderate pressures, but that  $Z > 1$  at higher pressures. If  $Z < 1$  throughout the range of integration, then the integrand in eqn 3.63 is negative and  $\phi < 1$ . This value implies that  $f < p$  (the molecules tend to stick

**Fig. 3.26** The fugacity coefficient of a van der Waals gas plotted using the reduced variables of the gas. The curves are labelled with the reduced temperature  $T_r = T/T_c$ .

 **interActivity** Evaluate the fugacity coefficient as a function of the reduced volume of a van der Waals gas and plot the outcome for a selection of reduced temperatures over the range  $0.8 \leq V_r \leq 3$ .



together) and that the molar Gibbs energy of the gas is less than that of a perfect gas. At higher pressures, the range over which  $Z > 1$  may dominate the range over which  $Z < 1$ . The integral is then positive,  $\phi > 1$ , and  $f > p$  (the repulsive interactions are dominant and tend to drive the particles apart). Now the molar Gibbs energy of the gas is greater than that of the perfect gas at the same pressure.

Figure 3.26, which has been calculated using the full van der Waals equation of state, shows how the fugacity coefficient depends on the pressure in terms of the reduced variables (Section 1.4). Because critical constants are available in Table 1.5, the graphs can be used for quick estimates of the fugacities of a wide range of gases. Table 3.6 gives some explicit values for nitrogen.

**Table 3.6\*** The fugacity of nitrogen at 273 K

$p/\text{atm}$	$f/\text{atm}$
1	0.999 55
10	9.9560
100	97.03
1000	1839

\* More values are given in the *Data section*.

## Discussion questions

**3.1** The evolution of life requires the organization of a very large number of molecules into biological cells. Does the formation of living organisms violate the Second Law of thermodynamics? State your conclusion clearly and present detailed arguments to support it.

**3.2** You received an unsolicited proposal from a self-declared inventor who is seeking investors for the development of his latest idea: a device that uses heat extracted from the ground by a heat pump to boil water into steam that is used to heat a home and to power a steam engine that drives the heat pump. This procedure is potentially very lucrative because, after an initial extraction of energy from the ground, no fossil fuels would be required to keep the device running indefinitely. Would you invest in this idea? State your conclusion clearly and present detailed arguments to support it.

**3.3** The following expressions have been used to establish criteria for spontaneous change:  $\Delta S_{\text{tot}} > 0$ ,  $dS_{U,V} \geq 0$  and  $dU_{S,V} \leq 0$ ,  $dA_{T,V} \leq 0$ , and  $dG_{T,p} \leq 0$ . Discuss the origin, significance, and applicability of each criterion.

**3.4** The following expressions have been used to establish criteria for spontaneous change:  $dA_{T,V} < 0$  and  $dG_{T,p} < 0$ . Discuss the origin, significance, and applicability of each criterion.

**3.5** Discuss the physical interpretation of any one Maxwell relation.

**3.6** Account for the dependence of  $\pi_T$  of a van der Waals gas in terms of the significance of the parameters  $a$  and  $b$ .

**3.7** Suggest a physical interpretation of the dependence of the Gibbs energy on the pressure.

**3.8** Suggest a physical interpretation of the dependence of the Gibbs energy on the temperature.

## Exercises

Assume that all gases are perfect and that data refer to 298.15 K unless otherwise stated.

**3.1(a)** Calculate the change in entropy when 25 kJ of energy is transferred reversibly and isothermally as heat to a large block of iron at (a) 0°C, (b) 100°C.

**3.1(b)** Calculate the change in entropy when 50 kJ of energy is transferred reversibly and isothermally as heat to a large block of copper at (a) 0°C, (b) 70°C.

**3.2(a)** Calculate the molar entropy of a constant-volume sample of neon at 500 K given that it is 146.22 J K<sup>-1</sup> mol<sup>-1</sup> at 298 K.

**3.2(b)** Calculate the molar entropy of a constant-volume sample of argon at 250 K given that it is 154.84 J K<sup>-1</sup> mol<sup>-1</sup> at 298 K.

**3.3(a)** Calculate  $\Delta S$  (for the system) when the state of 3.00 mol of perfect gas atoms, for which  $C_{p,m} = \frac{5}{2}R$ , is changed from 25°C and 1.00 atm to 125°C and 5.00 atm. How do you rationalize the sign of  $\Delta S$ ?

**3.3(b)** Calculate  $\Delta S$  (for the system) when the state of 2.00 mol diatomic perfect gas molecules, for which  $C_{p,m} = \frac{7}{2}R$ , is changed from 25°C and 1.50 atm to 135°C and 7.00 atm. How do you rationalize the sign of  $\Delta S$ ?

**3.4(a)** A sample consisting of 3.00 mol of diatomic perfect gas molecules at 200 K is compressed reversibly and adiabatically until its temperature reaches 250 K. Given that  $C_{V,m} = 27.5 \text{ J K}^{-1} \text{ mol}^{-1}$ , calculate  $q$ ,  $w$ ,  $\Delta U$ ,  $\Delta H$ , and  $\Delta S$ .

**3.4(b)** A sample consisting of 2.00 mol of diatomic perfect gas molecules at 250 K is compressed reversibly and adiabatically until its temperature reaches 300 K. Given that  $C_{V,m} = 27.5 \text{ J K}^{-1} \text{ mol}^{-1}$ , calculate  $q$ ,  $w$ ,  $\Delta U$ ,  $\Delta H$ , and  $\Delta S$ .

**3.5(a)** Calculate  $\Delta H$  and  $\Delta S_{\text{tot}}$  when two copper blocks, each of mass 10.0 kg, one at 100°C and the other at 0°C, are placed in contact in an isolated container. The specific heat capacity of copper is 0.385 J K<sup>-1</sup> g<sup>-1</sup> and may be assumed constant over the temperature range involved.

**3.5(b)** Calculate  $\Delta H$  and  $\Delta S_{\text{tot}}$  when two iron blocks, each of mass 1.00 kg, one at 200°C and the other at 25°C, are placed in contact in an isolated container. The specific heat capacity of iron is 0.449 J K<sup>-1</sup> g<sup>-1</sup> and may be assumed constant over the temperature range involved.

**3.6(a)** Consider a system consisting of 2.0 mol CO<sub>2</sub>(g), initially at 25°C and 10 atm and confined to a cylinder of cross-section 10.0 cm<sup>2</sup>. It is allowed to expand adiabatically against an external pressure of 1.0 atm until the piston has moved outwards through 20 cm. Assume that carbon dioxide may be considered a perfect gas with  $C_{V,m} = 28.8 \text{ J K}^{-1} \text{ mol}^{-1}$  and calculate (a)  $q$ , (b)  $w$ , (c)  $\Delta U$ , (d)  $\Delta T$ , (e)  $\Delta S$ .

**3.6(b)** Consider a system consisting of 1.5 mol CO<sub>2</sub>(g), initially at 15°C and 9.0 atm and confined to a cylinder of cross-section 100.0 cm<sup>2</sup>. The sample is allowed to expand adiabatically against an external pressure of 1.5 atm until the piston has moved outwards through 15 cm. Assume that carbon dioxide may be considered a perfect gas with  $C_{V,m} = 28.8 \text{ J K}^{-1} \text{ mol}^{-1}$ , and calculate (a)  $q$ , (b)  $w$ , (c)  $\Delta U$ , (d)  $\Delta T$ , (e)  $\Delta S$ .

**3.7(a)** The enthalpy of vaporization of chloroform (CHCl<sub>3</sub>) is 29.4 kJ mol<sup>-1</sup> at its normal boiling point of 334.88 K. Calculate (a) the entropy of vaporization of chloroform at this temperature and (b) the entropy change of the surroundings.

**3.7(b)** The enthalpy of vaporization of methanol is 35.27 kJ mol<sup>-1</sup> at its normal boiling point of 64.1°C. Calculate (a) the entropy of vaporization of methanol at this temperature and (b) the entropy change of the surroundings.

**3.8(a)** Calculate the standard reaction entropy at 298 K of

- (a) 2 CH<sub>3</sub>CHO(g) + O<sub>2</sub>(g) → 2 CH<sub>3</sub>COOH(l)
- (b) 2 AgCl(s) + Br<sub>2</sub>(l) → 2 AgBr(s) + Cl<sub>2</sub>(g)
- (c) Hg(l) + Cl<sub>2</sub>(g) → HgCl<sub>2</sub>(s)

**3.8(b)** Calculate the standard reaction entropy at 298 K of

- (a) Zn(s) + Cu<sup>2+</sup>(aq) → Zn<sup>2+</sup>(aq) + Cu(s)
- (b) C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>(s) + 12 O<sub>2</sub>(g) → 12 CO<sub>2</sub>(g) + 11 H<sub>2</sub>O(l)

**3.9(a)** Combine the reaction entropies calculated in Exercise 3.8a with the reaction enthalpies, and calculate the standard reaction Gibbs energies at 298 K.

**3.9(b)** Combine the reaction entropies calculated in Exercise 3.8b with the reaction enthalpies, and calculate the standard reaction Gibbs energies at 298 K.

**3.10(a)** Use standard Gibbs energies of formation to calculate the standard reaction Gibbs energies at 298 K of the reactions in Exercise 3.8a.

**3.10(b)** Use standard Gibbs energies of formation to calculate the standard reaction Gibbs energies at 298 K of the reactions in Exercise 3.8b.

**3.11(a)** Calculate the standard Gibbs energy of the reaction 4 HCl(g) + O<sub>2</sub>(g) → 2 Cl<sub>2</sub>(g) + 2 H<sub>2</sub>O(l) at 298 K, from the standard entropies and enthalpies of formation given in the *Data section*.

**3.11(b)** Calculate the standard Gibbs energy of the reaction CO(g) + CH<sub>3</sub>OH(l) → CH<sub>3</sub>COOH(l) at 298 K, from the standard entropies and enthalpies of formation given in the *Data section*.

**3.12(a)** The standard enthalpy of combustion of solid phenol (C<sub>6</sub>H<sub>5</sub>OH) is -3054 kJ mol<sup>-1</sup> at 298 K and its standard molar entropy is 144.0 J K<sup>-1</sup> mol<sup>-1</sup>. Calculate the standard Gibbs energy of formation of phenol at 298 K.

**3.12(b)** The standard enthalpy of combustion of solid urea (CO(NH<sub>2</sub>)<sub>2</sub>) is -632 kJ mol<sup>-1</sup> at 298 K and its standard molar entropy is 104.60 J K<sup>-1</sup> mol<sup>-1</sup>. Calculate the standard Gibbs energy of formation of urea at 298 K.

**3.13(a)** Calculate the change in the entropies of the system and the surroundings, and the total change in entropy, when a sample of nitrogen gas of mass 14 g at 298 K and 1.00 bar doubles its volume in (a) an isothermal reversible expansion, (b) an isothermal irreversible expansion against  $p_{\text{ex}} = 0$ , and (c) an adiabatic reversible expansion.

**3.13(b)** Calculate the change in the entropies of the system and the surroundings, and the total change in entropy, when the volume of a sample of argon gas of mass 21 g at 298 K and 1.50 bar increases from 1.20 dm<sup>3</sup> to 4.60 dm<sup>3</sup> in (a) an isothermal reversible expansion, (b) an isothermal irreversible expansion against  $p_{\text{ex}} = 0$ , and (c) an adiabatic reversible expansion.

**3.14(a)** Calculate the maximum non-expansion work per mole that may be obtained from a fuel cell in which the chemical reaction is the combustion of methane at 298 K.

**3.14(b)** Calculate the maximum non-expansion work per mole that may be obtained from a fuel cell in which the chemical reaction is the combustion of propane at 298 K.

**3.15(a)** (a) Calculate the Carnot efficiency of a primitive steam engine operating on steam at 100°C and discharging at 60°C. (b) Repeat the calculation for a modern steam turbine that operates with steam at 300°C and discharges at 80°C.

**3.15(b)** A certain heat engine operates between 1000 K and 500 K. (a) What is the maximum efficiency of the engine? (b) Calculate the maximum work that

can be done by for each 1.0 kJ of heat supplied by the hot source. (c) How much heat is discharged into the cold sink in a reversible process for each 1.0 kJ supplied by the hot source?

**3.16(a)** Suppose that 3.0 mmol N<sub>2</sub>(g) occupies 36 cm<sup>3</sup> at 300 K and expands to 60 cm<sup>3</sup>. Calculate ΔG for the process.

**3.16(b)** Suppose that 2.5 mmol Ar(g) occupies 72 dm<sup>3</sup> at 298 K and expands to 100 dm<sup>3</sup>. Calculate ΔG for the process.

**3.17(a)** The change in the Gibbs energy of a certain constant-pressure process was found to fit the expression ΔG/J = −85.40 + 36.5(T/K). Calculate the value of ΔS for the process.

**3.17(b)** The change in the Gibbs energy of a certain constant-pressure process was found to fit the expression ΔG/J = −73.1 + 42.8(T/K). Calculate the value of ΔS for the process.

**3.18(a)** Calculate the change in Gibbs energy of 35 g of ethanol (mass density 0.789 g cm<sup>−3</sup>) when the pressure is increased isothermally from 1 atm to 3000 atm.

**3.18(b)** Calculate the change in Gibbs energy of 25 g of methanol (mass density 0.791 g cm<sup>−3</sup>) when the pressure is increased isothermally from 100 kPa to 100 MPa. Take  $k_T = 1.26 \times 10^{-9}$  Pa<sup>−1</sup>.

**3.19(a)** Calculate the change in chemical potential of a perfect gas when its pressure is increased isothermally from 1.8 atm to 29.5 atm at 40°C.

**3.19(b)** Calculate the change in chemical potential of a perfect gas that its pressure is increased isothermally from 92.0 kPa to 252.0 kPa at 50°C.

**3.20(a)** The fugacity coefficient of a certain gas at 200 K and 50 bar is 0.72. Calculate the difference of its molar Gibbs energy from that of a perfect gas in the same state.

**3.20(b)** The fugacity coefficient of a certain gas at 290 K and 2.1 MPa is 0.68. Calculate the difference of its molar Gibbs energy from that of a perfect gas in the same state.

**3.21(a)** Estimate the change in the Gibbs energy of 1.0 dm<sup>3</sup> of benzene when the pressure acting on it is increased from 1.0 atm to 100 atm.

**3.21(b)** Estimate the change in the Gibbs energy of 1.0 dm<sup>3</sup> of water when the pressure acting on it is increased from 100 kPa to 300 kPa.

**3.22(a)** Calculate the change in the molar Gibbs energy of hydrogen gas when its pressure is increased isothermally from 1.0 atm to 100.0 atm at 298 K.

**3.22(b)** Calculate the change in the molar Gibbs energy of oxygen when its pressure is increased isothermally from 50.0 kPa to 100.0 kPa at 500 K.

## Problems\*

Assume that all gases are perfect and that data refer to 298 K unless otherwise stated.

### Numerical problems

**3.1** Calculate the difference in molar entropy (a) between liquid water and ice at −5°C, (b) between liquid water and its vapour at 95°C and 1.00 atm. The differences in heat capacities on melting and on vaporization are 37.3 J K<sup>−1</sup> mol<sup>−1</sup> and −41.9 J K<sup>−1</sup> mol<sup>−1</sup>, respectively. Distinguish between the entropy changes of the sample, the surroundings, and the total system, and discuss the spontaneity of the transitions at the two temperatures.

**3.2** The heat capacity of chloroform (trichloromethane, CHCl<sub>3</sub>) in the range 240 K to 330 K is given by  $C_{p,m}/(J\text{ K}^{-1}\text{ mol}^{-1}) = 91.47 + 7.5 \times 10^{-2}$  (T/K). In a particular experiment, 1.00 mol CHCl<sub>3</sub> is heated from 273 K to 300 K. Calculate the change in molar entropy of the sample.

**3.3** A block of copper of mass 2.00 kg ( $C_{p,m} = 24.44\text{ J K}^{-1}\text{ mol}^{-1}$ ) and temperature 0°C is introduced into an insulated container in which there is 1.00 mol H<sub>2</sub>O(g) at 100°C and 1.00 atm. (a) Assuming all the steam is condensed to water, what will be the final temperature of the system, the heat transferred from water to copper, and the entropy change of the water, copper, and the total system? (b) In fact, some water vapour is present at equilibrium. From the vapour pressure of water at the temperature calculated in (a), and assuming that the heat capacities of both gaseous and liquid water are constant and given by their values at that temperature, obtain an improved value of the final temperature, the heat transferred, and the various entropies. (Hint. You will need to make plausible approximations.)

**3.4** Consider a perfect gas contained in a cylinder and separated by a frictionless adiabatic piston into two sections A and B. All changes in B are isothermal, that is, a thermostat surrounds B to keep its temperature constant. There is 2.00 mol of the gas in each section. Initially  $T_A = T_B = 300\text{ K}$ ,  $V_A = V_B$

= 2.00 dm<sup>3</sup>. Energy is supplied as heat to Section A and the piston moves to the right reversibly until the final volume of Section B is 1.00 dm<sup>3</sup>. Calculate (a)  $\Delta S_A$  and  $\Delta S_B$ , (b)  $\Delta A_A$  and  $\Delta A_B$ , (c)  $\Delta G_A$  and  $\Delta G_B$ , (d)  $\Delta S$  of the total system and its surroundings. If numerical values cannot be obtained, indicate whether the values should be positive, negative, or zero or are indeterminate from the information given. (Assume  $C_{V,m} = 20\text{ J K}^{-1}\text{ mol}^{-1}$ .)

**3.5** A Carnot cycle uses 1.00 mol of a monatomic perfect gas as the working substance from an initial state of 10.0 atm and 600 K. It expands isothermally to a pressure of 1.00 atm (Step 1), and then adiabatically to a temperature of 300 K (Step 2). This expansion is followed by an isothermal compression (Step 3), and then an adiabatic compression (Step 4) back to the initial state. Determine the values of  $q$ ,  $w$ ,  $\Delta U$ ,  $\Delta H$ ,  $\Delta S$ ,  $\Delta S_{\text{tot}}$ , and  $\Delta G$  for each stage of the cycle and for the cycle as a whole. Express your answer as a table of values.

**3.6** 1.00 mol of perfect gas molecules at 27°C is expanded isothermally from an initial pressure of 3.00 atm to a final pressure of 1.00 atm in two ways: (a) reversibly, and (b) against a constant external pressure of 1.00 atm. Determine the values of  $q$ ,  $w$ ,  $\Delta U$ ,  $\Delta H$ ,  $\Delta S$ ,  $\Delta S_{\text{sur}}$ ,  $\Delta S_{\text{tot}}$  for each path.

**3.7** The standard molar entropy of NH<sub>3</sub>(g) is 192.45 J K<sup>−1</sup> mol<sup>−1</sup> at 298 K, and its heat capacity is given by eqn 2.25 with the coefficients given in Table 2.2. Calculate the standard molar entropy at (a) 100°C and (b) 500°C.

**3.8** A block of copper of mass 500 g and initially at 293 K is in thermal contact with an electric heater of resistance 1.00 kΩ and negligible mass. A current of 1.00 A is passed for 15.0 s. Calculate the change in entropy of the copper, taking  $C_{p,m} = 24.4\text{ J K}^{-1}\text{ mol}^{-1}$ . The experiment is then repeated with the copper immersed in a stream of water that maintains its temperature at 293 K. Calculate the change in entropy of the copper and the water in this case.

**3.9** Find an expression for the change in entropy when two blocks of the same substance and of equal mass, one at the temperature  $T_h$  and the other at  $T_c$ , are brought into thermal contact and allowed to reach equilibrium. Evaluate the

\* Problems denoted with the symbol ‡ were supplied by Charles Trapp, Carmen Giunta, and Marshall Cady.

change for two blocks of copper, each of mass 500 g, with  $C_{p,m} = 24.4 \text{ J K}^{-1} \text{ mol}^{-1}$ , taking  $T_h = 500 \text{ K}$  and  $T_c = 250 \text{ K}$ .

**3.10** A gaseous sample consisting of 1.00 mol molecules is described by the equation of state  $pV_m = RT(1 + Bp)$ . Initially at 373 K, it undergoes Joule–Thomson expansion from 100 atm to 1.00 atm. Given that  $C_{p,m} = \frac{5}{2}R$ ,  $\mu = 0.21 \text{ K atm}^{-1}$ ,  $B = -0.525(K/T) \text{ atm}^{-1}$ , and that these are constant over the temperature range involved, calculate  $\Delta T$  and  $\Delta S$  for the gas.

**3.11** The molar heat capacity of lead varies with temperature as follows:

$T/\text{K}$	10	15	20	25	30	50
$C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1})$	2.8	7.0	10.8	14.1	16.5	21.4
$T/\text{K}$	70	100	150	200	250	298
$C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1})$	23.3	24.5	25.3	25.8	26.2	26.6

Calculate the standard Third-Law entropy of lead at (a) 0°C and (b) 25°C.

**3.12** From standard enthalpies of formation, standard entropies, and standard heat capacities available from tables in the *Data section*, calculate the standard enthalpies and entropies at 298 K and 398 K for the reaction  $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$ . Assume that the heat capacities are constant over the temperature range involved.

**3.13** The heat capacity of anhydrous potassium hexacyanoferrate(II) varies with temperature as follows:

$T/\text{K}$	$C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1})$	$T/\text{K}$	$C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1})$
10	2.09	100	179.6
20	14.43	110	192.8
30	36.44	150	237.6
40	62.55	160	247.3
50	87.03	170	256.5
60	111.0	180	265.1
70	131.4	190	273.0
80	149.4	200	280.3
90	165.3		

Calculate the molar enthalpy relative to its value at  $T = 0$  and the Third-Law entropy at each of these temperatures.

**3.14** The compound 1,3,5-trichloro-2,4,6-trifluorobenzene is an intermediate in the conversion of hexachlorobenzene to hexafluorobenzene, and its thermodynamic properties have been examined by measuring its heat capacity over a wide temperature range (R.L. Andon and J.F. Martin, *J. Chem. Soc. Faraday Trans. I*, 871 (1973)). Some of the data are as follows:

$T/\text{K}$	14.14	16.33	20.03	31.15	44.08	64.81
$C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1})$	9.492	12.70	18.18	32.54	46.86	66.36
$T/\text{K}$	100.90	140.86	183.59	225.10	262.99	298.06
$C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1})$	95.05	121.3	144.4	163.7	180.2	196.4

Calculate the molar enthalpy relative to its value at  $T = 0$  and the Third-Law molar entropy of the compound at these temperatures.

**3.15†** Given that  $S_m^\circ = 29.79 \text{ JK}^{-1} \text{ mol}^{-1}$  for bismuth at 100 K and the following tabulated heat capacities data (D.G. Archer, *J. Chem. Eng. Data* 40, 1015 (1995)), compute the standard molar entropy of bismuth at 200 K.

$T/\text{K}$	100	120	140	150	160	180	200
$C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1})$	23.00	23.74	24.25	24.44	24.61	24.89	25.11

Compare the value to the value that would be obtained by taking the heat capacity to be constant at  $24.44 \text{ J K}^{-1} \text{ mol}^{-1}$  over this range.

**3.16** Calculate  $\Delta_r G^\circ(375 \text{ K})$  for the reaction  $2 \text{ CO(g)} + \text{O}_2(\text{g}) \rightarrow 2 \text{ CO}_2(\text{g})$  from the value of  $\Delta_f G^\circ(298 \text{ K})$ ,  $\Delta_f H^\circ(298 \text{ K})$ , and the Gibbs–Helmholtz equation.

**3.17** Estimate the standard reaction Gibbs energy of  $\text{N}_2(\text{g}) + 3 \text{ H}_2(\text{g}) \rightarrow 2 \text{ NH}_3(\text{g})$  at (a) 500 K, (b) 1000 K from their values at 298 K.

**3.18** At 200 K, the compression factor of oxygen varies with pressure as shown below. Evaluate the fugacity of oxygen at this temperature and 100 atm.

$p/\text{atm}$	1.0000	4.00000	7.00000	10.0000	40.00	70.00	100.0
$Z$	0.9971	0.98796	0.97880	0.96956	0.8734	0.7764	0.6871

### Theoretical problems

**3.19** Represent the Carnot cycle on a temperature–entropy diagram and show that the area enclosed by the cycle is equal to the work done.

**3.20** Prove that two reversible adiabatic paths can never cross. Assume that the energy of the system under consideration is a function of temperature only. (*Hint*. Suppose that two such paths can intersect, and complete a cycle with the two paths plus one isothermal path. Consider the changes accompanying each stage of the cycle and show that they conflict with the Kelvin statement of the Second Law.)

**3.21** Prove that the perfect gas temperature scale and the thermodynamic temperature scale based on the Second Law of thermodynamics differ from each other by at most a constant numerical factor.

**3.22** The molar Gibbs energy of a certain gas is given by  $G_m = RT \ln p + A + Bp + \frac{1}{2}Cp^2 + \frac{1}{3}Dp^3$ , where  $A$ ,  $B$ ,  $C$ , and  $D$  are constants. Obtain the equation of state of the gas.

**3.23** Evaluate  $(\partial S/\partial V)_T$  for (a) a van der Waals gas, (b) a Dieterici gas (Table 1.7). For an isothermal expansion, for which kind of gas (and a perfect gas) will  $\Delta S$  be greatest? Explain your conclusion.

**3.24** Show that, for a perfect gas,  $(\partial U/\partial S)_V = T$  and  $(\partial U/\partial V)_S = -p$ .

**3.25** Two of the four Maxwell relations were derived in the text, but two were not. Complete their derivation by showing that  $(\partial S/\partial V)_T = (\partial p/\partial T)_V$  and  $(\partial T/\partial p)_S = (\partial V/\partial S)_p$ .

**3.26** Use the Maxwell relations to express the derivatives (a)  $(\partial S/\partial V)_T$  and  $(\partial V/\partial S)_p$  and (b)  $(\partial p/\partial S)_V$  and  $(\partial V/\partial S)_p$  in terms of the heat capacities, the expansion coefficient  $\alpha$ , and the isothermal compressibility,  $\kappa_T$ .

**3.27** Use the Maxwell relations to show that the entropy of a perfect gas depends on the volume as  $S \propto R \ln V$ .

**3.28** Derive the thermodynamic equation of state

$$\left( \frac{\partial H}{\partial p} \right)_T = V - T \left( \frac{\partial V}{\partial T} \right)_p$$

Derive an expression for  $(\partial H/\partial p)_T$  for (a) a perfect gas and (b) a van der Waals gas. In the latter case, estimate its value for 1.0 mol Ar(g) at 298 K and 10 atm. By how much does the enthalpy of the argon change when the pressure is increased isothermally to 11 atm?

**3.29** Show that, if  $B(T)$  is the second virial coefficient of a gas, and  $\Delta B = B(T'') - B(T')$ ,  $\Delta T = T'' - T'$ , and  $T$  is the mean of  $T''$  and  $T'$ , then  $\pi_T \approx RT^2 \Delta B / V_m^2 \Delta T$ . Estimate  $\pi_T$  for argon given that  $B(250 \text{ K}) = -28.0 \text{ cm}^3 \text{ mol}^{-1}$  and  $B(300 \text{ K}) = -15.6 \text{ cm}^3 \text{ mol}^{-1}$  at 275 K at (a) 1.0 atm, (b) 10.0 atm.

**3.30** The Joule coefficient,  $\mu_j$ , is defined as  $\mu_j = (\partial T/\partial V)_U$ . Show that  $\mu_j C_V = p - \alpha T/\kappa_T$ .

**3.31** Evaluate  $\pi_T$  for a Dieterici gas (Table 1.7). Justify physically the form of the expression obtained.

**3.32** The adiabatic compressibility,  $\kappa_S$ , is defined like  $\kappa_T$  (eqn 2.43) but at constant entropy. Show that for a perfect gas  $p\gamma\kappa_S = 1$  (where  $\gamma$  is the ratio of heat capacities).

**3.33** Suppose that  $S$  is regarded as a function of  $p$  and  $T$ . Show that  $TdS = C_p dT - \alpha TVdp$ . Hence, show that the energy transferred as heat when the pressure on an incompressible liquid or solid is increased by  $\Delta p$  is equal to  $-\alpha TV\Delta p$ . Evaluate  $q$  when the pressure acting on 100 cm<sup>3</sup> of mercury at 0°C is increased by 1.0 kbar. ( $\alpha = 1.82 \times 10^{-4}$  K<sup>-1</sup>.)

**3.34** Suppose that (a) the attractive interactions between gas particles can be neglected, (b) the attractive interaction is dominant in a van der Waals gas, and the pressure is low enough to make the approximation  $4ap/(RT)^2 \ll 1$ . Find expressions for the fugacity of a van der Waals gas in terms of the pressure and estimate its value for ammonia at 10.00 atm and 298.15 K in each case.

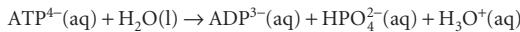
**3.35** Find an expression for the fugacity coefficient of a gas that obeys the equation of state  $pV_m = RT(1 + B/V_m + C/V_m^2)$ . Use the resulting expression to estimate the fugacity of argon at 1.00 atm and 100 K using  $B = -21.13$  cm<sup>3</sup> mol<sup>-1</sup> and  $C = 1054$  cm<sup>6</sup> mol<sup>-2</sup>.

### Applications: to biology, environmental science, polymer science, and engineering

**3.36** The protein lysozyme unfolds at a transition temperature of 75.5°C and the standard enthalpy of transition is 509 kJ mol<sup>-1</sup>. Calculate the entropy of unfolding of lysozyme at 25.0°C, given that the difference in the constant-pressure heat capacities upon unfolding is 6.28 kJ K<sup>-1</sup> mol<sup>-1</sup> and can be assumed to be independent of temperature. Hint. Imagine that the transition at 25.0°C occurs in three steps: (i) heating of the folded protein from 25.0°C to the transition temperature, (ii) unfolding at the transition temperature, and (iii) cooling of the unfolded protein to 25.0°C. Because the entropy is a state function, the entropy change at 25.0°C is equal to the sum of the entropy changes of the steps.

**3.37** At 298 K the standard enthalpy of combustion of sucrose is -5797 kJ mol<sup>-1</sup> and the standard Gibbs energy of the reaction is -6333 kJ mol<sup>-1</sup>. Estimate the additional non-expansion work that may be obtained by raising the temperature to blood temperature, 37°C.

**3.38** In biological cells, the energy released by the oxidation of foods (*Impact* I2.2) is stored in adenosine triphosphate (ATP or ATP<sup>4-</sup>). The essence of ATP's action is its ability to lose its terminal phosphate group by hydrolysis and to form adenosine diphosphate (ADP or ADP<sup>3-</sup>):



At pH = 7.0 and 37°C (310 K, blood temperature) the enthalpy and Gibbs energy of hydrolysis are  $\Delta_r H = -20$  kJ mol<sup>-1</sup> and  $\Delta_r G = -31$  kJ mol<sup>-1</sup>, respectively. Under these conditions, the hydrolysis of 1 mol ATP<sup>4-</sup>(aq) results in the extraction of up to 31 kJ of energy that can be used to do non-expansion work, such as the synthesis of proteins from amino acids, muscular contraction, and the activation of neuronal circuits in our brains. (a) Calculate and account for the sign of the entropy of hydrolysis of ATP at pH = 7.0 and 310 K. (b) Suppose that the radius of a typical biological cell is 10 μm and that inside it 10<sup>9</sup> ATP molecules are hydrolysed each second. What is the power density of the cell in watts per cubic metre (1 W = 1 J s<sup>-1</sup>)? A computer battery delivers about 15 W and has a volume of 100 cm<sup>3</sup>. Which has the greater power density, the cell or the battery? (c) The formation of glutamine from glutamate and ammonium ions requires 14.2 kJ mol<sup>-1</sup> of energy input. It is driven by the hydrolysis of ATP to ADP mediated by the enzyme glutamine synthetase. How many moles of ATP must be hydrolysed to form 1 mol glutamine?

**3.39\*** In 1995, the Intergovernmental Panel on Climate Change (IPCC) considered a global average temperature rise of 1.0–3.5°C likely by the year 2100, with 2.0°C its best estimate. Because water vapour is itself a greenhouse gas, the increase in water vapour content of the atmosphere is of some

concern to climate change experts. Predict the relative increase in water vapour in the atmosphere based on a temperature rises of 2.0 K, assuming that the relative humidity remains constant. (The present global mean temperature is 290 K, and the equilibrium vapour pressure of water at that temperature is 0.0189 bar.)

**3.40†** Nitric acid hydrates have received much attention as possible catalysts for heterogeneous reactions that bring about the Antarctic ozone hole. Worsnop *et al.* investigated the thermodynamic stability of these hydrates under conditions typical of the polar winter stratosphere (*Science* 259, 71 (1993)). They report thermodynamic data for the sublimation of mono-, di-, and trihydrates to nitric acid and water vapours,  $\text{HNO}_3 \cdot n\text{H}_2\text{O}(\text{s}) \rightarrow \text{HNO}_3(\text{g}) + n\text{H}_2\text{O}(\text{g})$ , for  $n = 1, 2$ , and 3. Given  $\Delta_f G^\circ$  and  $\Delta_f H^\circ$  for these reactions at 220 K, use the Gibbs–Helmholtz equation to compute  $\Delta_r G^\circ$  at 190 K.

$n$	1	2	3
$\Delta_f G^\circ/(\text{kJ mol}^{-1})$	46.2	69.4	93.2
$\Delta_f H^\circ/(\text{kJ mol}^{-1})$	127	188	237

**3.41†** J. Gao and J. H. Weiner in their study of the origin of stress on the atomic level in dense polymer systems (*Science* 266, 748 (1994)), observe that the tensile force required to maintain the length,  $l$ , of a long linear chain of  $N$  freely jointed links each of length  $a$ , can be interpreted as arising from an entropic spring. For such a chain,  $S(l) = -3kl^2/2Na^2 + C$ , where  $k$  is the Boltzmann constant and  $C$  is a constant. Using thermodynamic relations of this and previous chapters, show that the tensile force obeys Hooke's law,  $F = -k_f l$ , if we assume that the energy  $U$  is independent of  $l$ .

**3.42** Suppose that an internal combustion engine runs on octane, for which the enthalpy of combustion is -5512 kJ mol<sup>-1</sup> and take the mass of 1 gallon of fuel as 3 kg. What is the maximum height, neglecting all forms of friction, to which a car of mass 1000 kg can be driven on 1.00 gallon of fuel given that the engine cylinder temperature is 2000°C and the exit temperature is 800°C?

**3.43** The cycle involved in the operation of an internal combustion engine is called the *Otto cycle*. Air can be considered to be the working substance and can be assumed to be a perfect gas. The cycle consists of the following steps: (1) reversible adiabatic compression from A to B, (2) reversible constant-volume pressure increase from B to C due to the combustion of a small amount of fuel, (3) reversible adiabatic expansion from C to D, and (4) reversible and constant-volume pressure decrease back to state A. Determine the change in entropy (of the system and of the surroundings) for each step of the cycle and determine an expression for the efficiency of the cycle, assuming that the heat is supplied in Step 2. Evaluate the efficiency for a compression ratio of 10:1. Assume that in state A,  $V = 4.00$  dm<sup>3</sup>,  $p = 1.00$  atm, and  $T = 300$  K, that  $V_A = 10V_B$ ,  $p_C/p_B = 5$ , and that  $C_{p,m} = \frac{7}{2}R$ .

**3.44** To calculate the work required to lower the temperature of an object, we need to consider how the coefficient of performance changes with the temperature of the object. (a) Find an expression for the work of cooling an object from  $T_i$  to  $T_f$  when the refrigerator is in a room at a temperature  $T_h$ . Hint. Write  $dw = dq/c(T)$ , relate  $dq$  to  $dT$  through the heat capacity  $C_p$ , and integrate the resulting expression. Assume that the heat capacity is independent of temperature in the range of interest. (b) Use the result in part (a) to calculate the work needed to freeze 250 g of water in a refrigerator at 293 K. How long will it take when the refrigerator operates at 100 W?

**3.45** The expressions that apply to the treatment of refrigerators also describe the behaviour of heat pumps, where warmth is obtained from the back of a refrigerator while its front is being used to cool the outside world. Heat pumps are popular home heating devices because they are very efficient. Compare heating of a room at 295 K by each of two methods: (a) direct conversion of 1.00 kJ of electrical energy in an electrical heater, and (b) use of 1.00 kJ of electrical energy to run a reversible heat pump with the outside at 260 K. Discuss the origin of the difference in the energy delivered to the interior of the house by the two methods.