Elements
of Physical Chemistry

Peter Atkins & Julio de Paula

Fifth edition

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Fundamental constants

Quantity	Symbol	Value	Power of ten	Units

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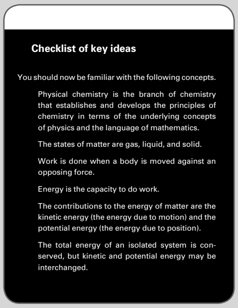
About the book

We pay particular attention to the needs of the student, and provide many pedagogical features to make the learning process more enjoyable and effective. This section reviews these features. Paramount among them, though, is something that pervades the entire text: we try throughout to *interpret* the mathematical expressions, for mathematics is a language, and it is crucially important to be able to recognize what it is seeking to convey. We pay particular attention to the level at which we introduce information, the possibility of progressively deepening one's understanding, and providing background information to support the development in the text. We are also very alert to the demands associated with problem solving, and provide a variety of helpful procedures.

Organizing the information

Checklist of key ideas

We summarize the principal concepts introduced in each chapter as a checklist at the end of the chapter. We suggest checking off the box that precedes each entry when you feel confident about the topic.



Checklist of key ideas

You should now be familiar with the following concepts.

- Physical chemistry is the branch of chemistry that establishes and develops the principles of chemistry in terms of the underlying concepts of physics and the language of mathematics.
- The states of matter are gas, liquid, and solid.
- Work is done when a body is moved against an opposing force.
- Energy is the capacity to do work.
- The contributions to the energy of matter are the kinetic energy (the energy due to motion) and the potential energy (the energy due to position).
- The total energy of an isolated system is conserved, but kinetic and potential energy may be interchanged.

Table of key equations

We summarize the most important equations introduced in each chapter as a checklist that follows the chapter's *Table of key ideas*. When appropriate, we describe the physical conditions under which an equation applies.

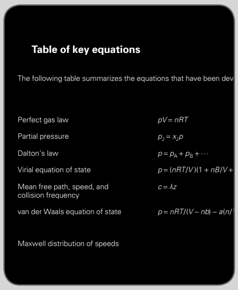


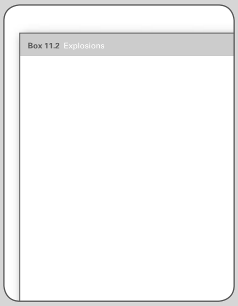
Table of key equations

The following table summarizes the equations that have been dev

Perfect gas law	$pV = nRT$
Partial pressure	$p_J = x_J p$
Dalton's law	$p = p_A + p_B + \cdots$
Virial equation of state	$p = (nRT/V)(1 + nB/V +$
Mean free path, speed, and collision frequency	$c = \lambda z$
van der Waals equation of state	$p = nRT/(V - nb) - a(n/$
Maxwell distribution of speeds	

Boxes

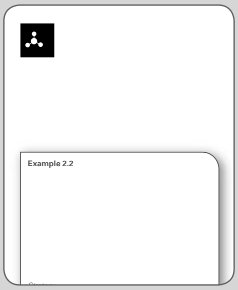
Where appropriate, we separate the principles from their applications: the principles are constant; the applications come and go as the subject progresses. The *Boxes*, about one in each chapter, show how the principles developed in the chapter are currently being applied in a variety of modern contexts, especially biology and materials science.



Box 11.2 Explosions

Molecular Interpretation icons

Although thermo-dynamics is a self-contained subject, it is greatly enriched when its concepts are explained in terms of atoms and molecules.



Example 2.2

This icon indicates where we are introducing a molecular interpretation.

Notes on good practice

Science is a precise activity and its language should be used accurately. We use 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.

A note on good practice

Derivations

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

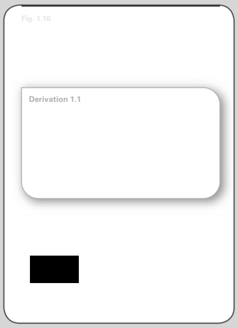


Fig. 1.16

Derivation 1.1

Visualizing the information

Artwork

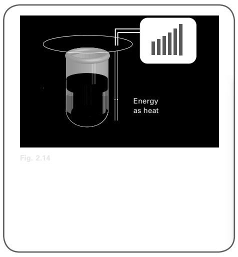
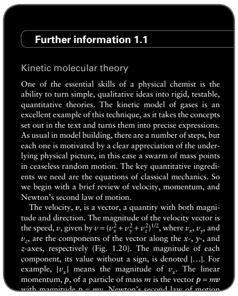


Fig. 2.14

Further information



Further information 1.1

Kinetic molecular theory

One of the essential skills of a physical chemist is the ability to turn simple, qualitative ideas into rigid, testable, quantitative theories. The kinetic model of gases is an excellent example of this technique, as it takes the concepts set out in the text and turns them into precise expressions. As usual in model building, there are a number of steps, but each one is motivated by a clear appreciation of the underlying physical picture, in this case a swarm of mass points in ceaseless random motion. The key quantitative ingredients we need are the equations of classical mechanics. So we begin with a brief review of velocity, momentum, and Newton's second law of motion.

The velocity, $\boldsymbol{v}$, is a vector, a quantity with both magnitude and direction. The magnitude of the velocity vector is the speed, v, given by $v = (v_x^2 + v_y^2 + v_z^2)^{1/2}$, where v_x, v_y, and v_z, are the components of the vector along the x-, y-, and z-axes, respectively (Fig. 1.20). The magnitude of each component, its value without a sign, is denoted |…|. For example, $|v_x|$ means the magnitude of v_x. The linear momentum, $\boldsymbol{p}$, of a particle of mass m is the vector $\boldsymbol{p} = m\boldsymbol{v}$

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Living Graphs

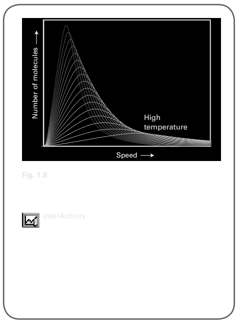

Fig. 1.8

InterActivity

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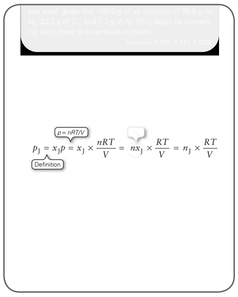
Mathematics support

Bubbles

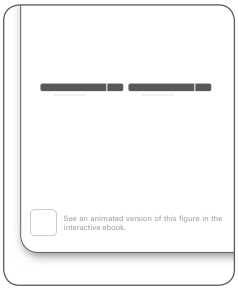


sea level, given that 100.0 g of air consists of 75.5 g of N_2, 23.2 g of O_2, and 1.3 g of Ar. *Hint:* Begin by converting each mass to an amount in moles.

[*Answer:* 0.780, 0.210, 0.009]

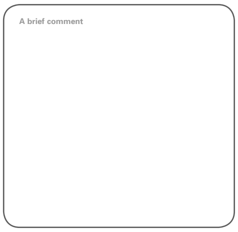
$$p_J = x_J p = x_J \times \frac{nRT}{V} = nx_J \times \frac{RT}{V} = n_J \times \frac{RT}{V}$$

Animations



See an animated version of this figure in the interactive ebook.

A brief comment



A brief comment

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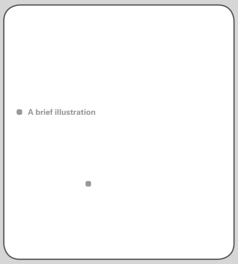
Problem solving

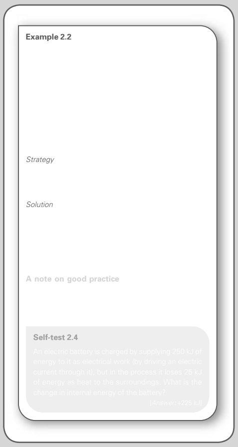
A brief illustration

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

Worked examples



Example 2.2

Strategy

Solution

A note on good practice

Self-test 2.4

An electric battery is charged by supplying 250 kJ of energy to it as electrical work (by driving an electric current through it), but in the process it loses 25 kJ of energy as heat to the surroundings. What is the change in internal energy of the battery?

[*Answer:* +225 kJ]

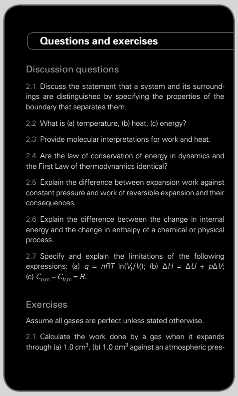
Each *Worked example* has a *Strategy* section to suggest how to set up the problem (another way might seem more natural: setting up problems is a highly personal business) and use or find the necessary data. Then there is the worked-out *Answer*, where we emphasize the importance of using units correctly.

Self-tests

Each *Worked 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.

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.



Questions and exercises

Discussion questions

2.1 Discuss the statement that a system and its surroundings are distinguished by specifying the properties of the boundary that separates them.

2.2 What is (a) temperature, (b) heat, (c) energy?

2.3 Provide molecular interpretations for work and heat.

2.4 Are the law of conservation of energy in dynamics and the First Law of thermodynamics identical?

2.5 Explain the difference between expansion work against constant pressure and work of reversible expansion and their consequences.

2.6 Explain the difference between the change in internal energy and the change in enthalpy of a chemical or physical process.

2.7 Specify and explain the limitations of the following expressions: (a) $q = nRT \ln(V_f/V_i)$; (b) $\Delta H = \Delta U + p\Delta V$; (c) $C_{p,m} - C_{V,m} = R$.

Exercises

Assume all gases are perfect unless stated otherwise.

2.1 Calculate the work done by a gas when it expands through (a) 1.0 cm^3, (b) 1.0 dm^3 against an atmospheric pres-

Exercises

The core of testing understanding is the collection of end-of-chapter *Exercises*. At the end of the *Exercises* you will find a small collection of *Projects* that bring together a lot of the foregoing material, may call for the use of calculus, and are typically based on material introduced in the *Boxes*.

The Book Companion Site

The Book Companion Site provides teaching and learning resources to augment the printed book. It is free of charge, complements the textbook, and offers additional materials which can be downloaded. The resources it provides are fully customizable and can be incorporated into a virtual learning environment.

The Book Companion Site can be accessed by visiting
http://www.whfreeman.com/elements5e

For students

Answers to exercises

The final answers to most end-of-chapter exercises are available for you to check your work.

Web links

Links to a range of useful and relevant physical chemistry web sites.

For lecturers

Artwork

A lecturer may wish to use the illustrations from this text in a lecture. Almost all the illustrations are available in PowerPoint® 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 illustrations.

On-line quizzing

New for this edition, on line quizzing available on the book companion site offers multiple-choice questions for use within a virtual learning environment, with feedback referred back to relevant sections of the book. This feature is a valuable tool for either formative or summative assessment.

Elements of Physical Chemistry eBook

The *eBook*, which is a complete version of the textbook itself, provides a rich learning experience by taking full advantage of the electronic medium integrating all student media resources and adds features unique to the *eBook*. The *eBook* also offers lecturers unparalleled flexibility and customization options. Access to the *eBook* is either provided in the form of an access code packaged with the text or it can be purchased at **http://ebooks.bfwpub.com/elements5e**. Key features of the *eBook* include:

- Living Graphs
- Dynamic figures: animated versions of figures from the book
- Interactive equations: extra annotations, extra interim steps, and explanatory comments
- Hidden answers to self tests and the questions from the end of the chapter
- Full text search, highlighting, and bookmarks
- Quick navigation from key terms to glossary definitions, and from maths and physics comments to fuller explanations

Tailor the book to your own needs:

- Users are able to add, share, and print their own notes
- Registered adopters may add sections to customise the text to match their course

Other resources

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

Explorations in Physical Chemistry consists of interactive Mathcad® worksheets and interactive Excel® workbooks, complete with thought-stimulating exercises. They motivate students to simulate physical, chemical, and biochemical phenomena with their personal computers. Harnessing the computational power of Mathcad® by Mathsoft, Inc. and Excel® by Microsoft Corporation, students can manipulate over 75 graphics, alter simulation parameters, and solve equations to gain deeper insight into physical chemistry. *Explorations in Physical Chemistry* can be purchased at **http://ebooks.bfwpub.com/explorations.php**.

Solutions manual

Charles Trapp and Marshall Cady have produced a solutions manual to accompany the book, which features full worked solutions to all end-of-chapter discussion questions and exercises, and is available free-of-charge to registered adopters of the text. (ISBN 1-4292-2400-2).

Peter Atkins

Julio de Paula

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CHECKLIST OF KEY IDEAS
TABLE OF KEY EQUATIONS
QUESTIONS AND EXERCISES

0.1 The states of matter

A note on good practice

■ **A brief illustration**

■

0.2 Physical state

0.3 Force

A brief illustration

A note on good practice

A brief illustration

0.4 Energy

$$E_p = \frac{Q_1 Q_2}{4\pi\varepsilon_0 r}$$

0.5 Pressure

$$\text{Pressure} = \frac{\text{force}}{\text{area}}, \qquad p = \frac{F}{A}$$

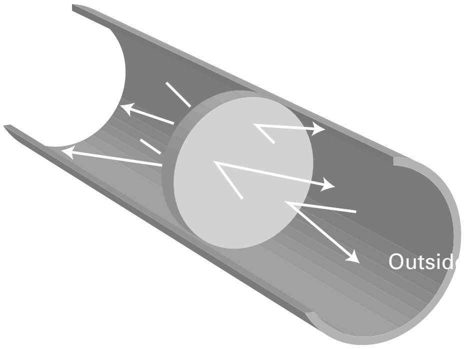

Fig. 0.2

Table 0.1

*Pressure units and conversion factors**

pascal, Pa	1 Pa = 1 N m^{-2}
bar	1 bar = 10^5 Pa
atmosphere, atm	1 atm = **101.325** kPa = **1.013 25** bar
torr, Torr†	**760** Torr = 1 atm
	1 Torr = 133.32 Pa

* Values in bold are exact.

† The name of the unit is torr, its symbol is Torr.

Example 0.1

Strategy

Solution

1 old unit

x new units

1 bar

A note on good practice

Self-test 0.1

The pressure in the eye of a hurricane was recorded as 723 Torr. What is the pressure in kilopascals?

[*Answer:* 96.4 kPa]

$$\rho = \frac{m}{V}$$

$$p = \frac{F}{A} = \frac{\rho h A g}{A} = \rho h g$$

0.6 Temperature

A note on good practice

A note on good practice

$$\text{Number of atoms} = \frac{\text{total mass of sample}}{\text{mass of one atom}} = \frac{12\ \text{g}}{1.992\,65 \times 10^{-23}\ \text{g}} = 6.022 \times 10^{23}$$

A note on good practice

A brief illustration

$$n_{\text{Cu}} = \frac{N}{N_{\text{A}}} = \frac{8.8 \times 10^{22}}{6.022\ 10^{23}\ \text{mol}^{-1}} = 0.15\ \text{mol}$$

A note on good practice

A brief illustration

$$n_C = \frac{m}{M_C} = \frac{21.5\ \text{g}}{12.01\ \text{g mol}^{-1}} = 1.79\ \text{mol}$$

A note on good practice

0.9 Measures of concentration

A note on good practice

$$n_{\text{water}} = \frac{10^3\ \text{g}}{18.02\ \text{g mol}^{-1}} = \frac{10^3}{18.02}\ \text{mol}$$

$$n = 0.140\ \text{mol} + \frac{10^3}{18.02}\ \text{mol}$$

$$x_G = \frac{0.140\ \text{mol}}{0.140 + (10^3/18.02)\ \text{mol}} = 2.52 \times 10^{-3}$$

Self-test 0.5

Calculate the mole fraction of sucrose molecules, $C_{12}H_{22}O_{11}$, in 1.22 m $C_{12}H_{22}O_{11}$(aq).

[*Answer:* 2.15×10^{-2}]

0.10 Reaction stoichiometry

● **A brief illustration**

●

☐ **1**

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☐ **3**

☐ **4**

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☐ **6**

☐ **7**

☐ **8**

☐ **9**

☐ **10**

Description	Equation	Comment

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0.1

0.2

0.3

0.4

0.5

Exercises

0.1

0.2

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0.4

0.5

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0.7

0.8 Calculate the minimum energy that a bird of mass 25 g must expend in order to reach a height of 50 m.

0.9 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. Express 1 eV in (a) joules, (b) kilojoules per mole.

0.10 Calculate the work done by (a) one electron, (b) 1 mol e^- [illegible] they move between the electrodes of a commercial cell [illegible] 1.5 V.

0.11 [illegible] need to assess the fuel needed to send the robot explo[illegible] which has a mass of 185 kg, to Mars. (a) What was the [illegible] needed to raise the vehicle itself from the surface of [illegible] to a distant point where the Earth's gravitational field [illegible] effectively zero? The mean radius of the Earth is 6371 km [illegible] average mass density is 5.517 g cm^{-3}. *Hint:* Use the full ex[illegible] for gravitational potential energy in Exercise 0.35.

0.12 Express (a) 108 kPa [illegible] (b) 0.975 bar in atmospheres, (c) 22.5 kPa in atmosp[illegible] 770 Torr in pascals.

0.13 Calculate the pressure in the [illegible] trench, near the Philippines, the deepest region of the o[illegible] the depth there as 11.5 km and for the average m[illegible] of sea water use 1.10 g cm^{-3}.

0.14 The atmospheric pressure on the surface [illegible], where $g = 3.7$ m s^{-2}, is only 0.0060 atm. To what e[illegible] that low pressure due to the low gravitational attraction [illegible] not to the thinness of the atmosphere? What pressure would the same atmosphere exert on Earth, where $g = 9.81$ m s^{-2}?

0.15 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 mass density 1.0 g cm^{-3} (a) on Earth, (b) on Mars. For data, see Example 0.14.

0.16 The unit '1 millimetre of mercury' (1 mmHg) has been replaced by the unit 1 torr (1 Torr): 1 mmHg is defined as the pressure at the base of a column of mercury exactly 1 mm high when its density is 13.5951 g cm^{-3} and the acceleration of free fall is 9.806 65 m s^{-2}. What is the relation between the two units?

0.17 Suppose that the pressure unit '1 millimetre of water' (1 mmH_2O) is defined as the pressure at the base of a column of water of mass density 1000 kg m^{-3} in a standard gravitational field. Express 1 mmH_2O in (a) pascals, (b) torr.

0.18 Given that the Celsius and Fahrenheit temperature scales are related by $\theta_{\text{Celsius}}/°\text{C} = \frac{5}{9}(\theta_{\text{Fahrenheit}}/°\text{F} - 32)$, what is the temperature of absolute zero ($T = 0$) on the Fahrenheit scale?

0.19 In his original formulation, Anders Celsius identified 0 with the boiling point of water and 100 with its freezing point. Find a relation (expressed like eqn 0.8) between this original scale (denote it $\theta'/°\text{C}'$) and (a) the current Celsius scale ($\theta/°\text{C}$), (b) the Fahrenheit scale.

0.20 Imagine that Pluto is inhabited and that its scientists use a temperature scale in which the freezing point of liquid nitrogen is 0°P (degrees Plutonium) and its boiling point is 100°P. The inhabitants of Earth report these temperatures as −209.9°C and −195.8°C, respectively. What is the relation between temperatures on (a) the Plutonium and Kelvin scales, (b) the Plutonium and Fahrenheit scales?

0.21 The *Rankine scale* is used in some engineering applications. On it, the absolute zero of temperature is set at zero but the size of the Rankine degree (°R) is the same as that of the Fahrenheit degree (°F). What is the boiling point of water on the Rankine scale?

0.22 Calculate the amount of $C_6H_{12}O_6$ molecules in 10.0 g of glucose.

0.23 The density of octane (which we take to model gasoline) is 0.703 g cm^{-3}; what amount (in moles) of octane molecules do you get when you buy 1.00 dm^3 (1.00 litre) of gasoline?

0.24 The molar mass of the oxygen-storage protein myoglobin is 16.1 kg mol^{-1}. How many myoglobin molecules are present in 1.0 g of the compound?

0.25 The mass of a red blood cell is about 33 pg (where 1 pg = 10^{-12} g), and it contains typically 3×10^8 haemoglobin molecules. Each haemoglobin molecule is a tetramer of myoglobin (see preceding exercise). What fraction of the mass of the cell is due to haemoglobin?

0.26 Express the mass density of a compound, which is defined as $\rho = m/V$, in terms of its molar mass and its molar volume.

0.27 [illegible] sugar (sucrose, $C_{12}H_{22}O_{11}$) cube has a mass of 5.0 g. [illegible] molar concentration of sucrose when one sugar cu[illegible] dissolved in a cup of coffee of volume 200 cm^3?

0.28 W[illegible] of sodium chloride should be dissolved in enough wa[illegible] 300 cm^3 of 1.00 M NaCl(aq)?

0.29 Use the fo[illegible] data to calculate (a) the molar concentration of B in (i) [illegible] benzene, (b) the molality of B in (i) water, (ii) benzene.

Mass of B used to make [illegible] cm^3 of solution: 2.11 g
Molar mass of B: 234.01 g [illegible]
Density of solution in water: 1.[illegible]
Density of solution in benzene: 0.[illegible]

0.30 Calculate the mole fractions of [illegible] molecules of a mixture that contains 56 g of benzene and [illegible] methylbenzene (toluene).

0.31 A simple model of dry air at sea level is that it [illegible] of 75.53 per cent (by mass) of nitrogen, 23.14 per cent o[illegible] gen, and 1.33 per cent of other substances (principally argon and carbon dioxide). Calculate the mole fractions of the three principal substances. Treat 'other substances' as argon.

0.32 Treat air (see the preceding exercise) as a solution of oxygen in nitrogen. What is the molality of oxygen in air?

0.33 Calculate the mass of carbon dioxide produced by the combustion of 1.00 dm^3 of gasoline treated as octane of mass density 0.703 g cm^{-3}.

0.34 What mass of carbon monoxide is needed to reduce 1.0 t of iron(III) oxide to the metal?

Projects

0.35 The gravitational potential energy of a body of mass m at a distance r from the centre of the Earth is $-Gmm_E/r$, where m_E is the mass of the Earth and G is the gravitational constant (see inside front cover). Consider the difference in potential energy of the body when it is moved from the surface of the Earth (radius r_E) to a height h above the surface, with $h \ll r_E$, and find an expression for the acceleration of free fall, g, in terms of the mass and radius of the Earth. *Hint*: Use the approximation $(1 + h/r_E)^{-1} = 1 - h/r_E + \cdots$. See Appendix 2 for more information on series expansions.

0.37 Use the same approach as in the preceding exercise to find an approximate expression for moving an electric charge Q_1 through a distance h from a point r_0 from another charge Q_2, with $h \ll r_0$.

Equations of state

Box 1.1 The gas laws and the weather

The kinetic model of gases

Real gases

CHECKLIST OF KEY IDEAS
TABLE OF KEY EQUATIONS
FURTHER INFORMATION 1.1
QUESTIONS AND EXERCISES

Equations of state

1.1 The perfect gas equation of state

A note on good practice

$$p \propto \frac{1}{V}$$

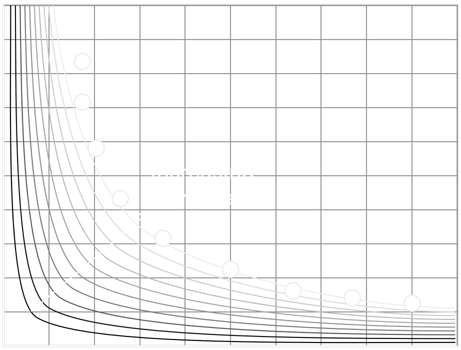


Fig. 1.1

interActivity

Hint

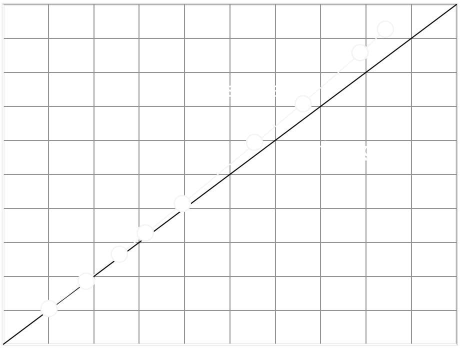


Fig. 1.2

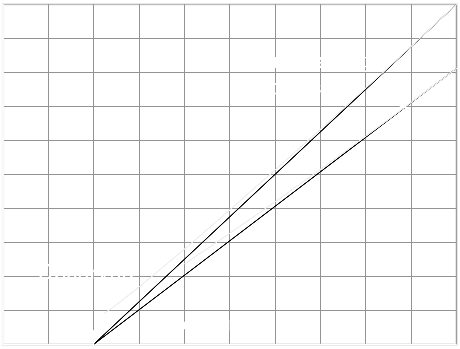


Fig. 1.3

A note on good practice

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

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

$$n_{\mathrm{N_2}} = \frac{m}{M_{\mathrm{N_2}}} = \frac{1.25\ \mathrm{g}}{28.02\ \mathrm{g\ mol^{-1}}} = \frac{1.25}{28.02}\ \mathrm{mol}$$

Self-test 1.1

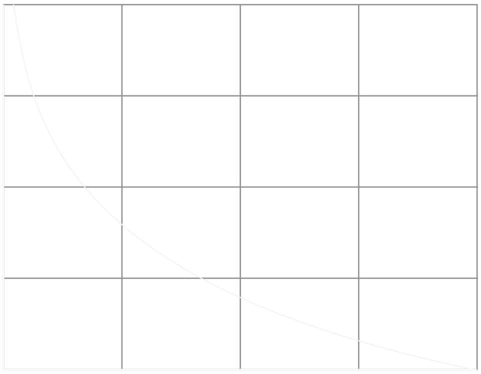
Calculate the pressure exerted by 1.22 g of carbon dioxide confined to a flask of volume 500 cm^3 at 37°C.

[*Answer*: 143 kPa]

$$\frac{p_1V_1}{T_1} = nR$$

$$\frac{p_2V_2}{T_2} = nR$$

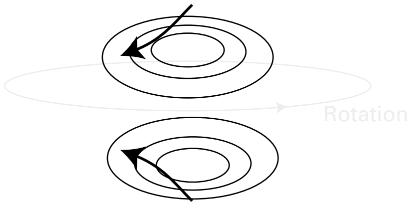
Box 1.1 The gas laws and the weather



interActivity

The composition of the Earth's atmosphere

Substance	Percentage	
	By volume	By mass
Nitrogen, N_2	78.08	75.53
Oxygen, O_2	20.95	23.14
Argon, Ar	0.93	1.28
Carbon dioxide, CO_2	0.031	0.047
Hydrogen, H_2	5.0×10^{-3}	2.0×10^{-4}
Neon, Ne	1.8×10^{-3}	1.3×10^{-3}
Helium, He	5.2×10^{-4}	7.2×10^{-5}
Methane, CH_4	2.0×10^{-4}	1.1×10^{-4}
Krypton, Kr	1.1×10^{-4}	3.2×10^{-4}
Nitric oxide, NO	5.0×10^{-5}	1.7×10^{-6}
Xenon, Xe	8.7×10^{-6}	3.9×10^{-5}
Ozone, O_3 Summer:	7.0×10^{-6}	1.2×10^{-5}
Winter:	2.0×10^{-6}	3.3×10^{-6}



1.3 Mixtures of gases: partial pressures

A brief illustration

$$x_{\mathrm{A}} = \frac{n_{\mathrm{A}}}{n_{\mathrm{A}} + n_{\mathrm{B}}} \qquad x_{\mathrm{B}} = \frac{n_{\mathrm{B}}}{n_{\mathrm{A}} + n_{\mathrm{B}}} \qquad x_{\mathrm{A}} + x_{\mathrm{B}} = 1$$

■ **A brief illustration**

■

1.4 The pressure of a gas according to the kinetic model

$$p = \frac{nMc^2}{3V}$$

$$c = \langle v^2 \rangle^{1/2} = \left(\frac{v_1^2 + v_2^2 + \cdots + v_N^2}{N} \right)^{1/2}$$

$$c = \left(\frac{2\langle E_\mathrm{k} \rangle}{m} \right)^{1/2}$$

$$\bar{c} = \frac{v_1 + v_2 + \cdots + v_N}{N}$$

$$\bar{c} = \left(\frac{8}{3\pi} \right)^{1/2} c \approx 0.921c$$

$$c = \left(\frac{3RT}{M} \right)^{1/2}$$

A brief illustration

$$\left(\frac{273\ \mathrm{K}}{298\ \mathrm{K}} \right)^{1/2} = \left(\frac{273}{298} \right)^{1/2} = 0.957$$

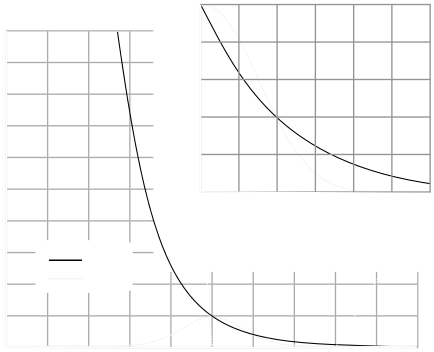


Fig. 1.7

$$f = F(s)\Delta s \quad \text{with} \quad F(s) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} s^2\, \mathrm{e}^{-Ms^2/2RT}$$

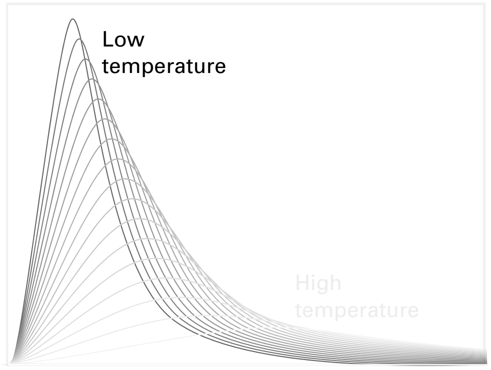


Fig. 1.8

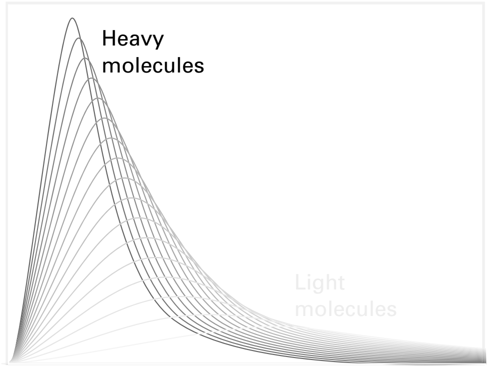


Fig. 1.9

interActivity

interActivity

s^2

3/2

1.7 Diffusion and effusion

$$\text{Rate of effusion} \propto \frac{1}{M^{1/2}}$$

A brief illustration

$$\frac{\text{Rate of effusion of H}_2}{\text{Rate of effusion of CO}_2} = \left(\frac{M_{\text{CO}_2}}{M_{\text{H}_2}}\right)^{1/2} = \left(\frac{44.01\ \text{g mol}^{-1}}{2.016\ \text{g mol}^{-1}}\right)^{1/2}$$

$$= \left(\frac{44.01}{2.016}\right)^{1/2} = 4.672$$

Note of good practice

Fig. 1.11

1.8 Molecular collisions

Use $z = c/\lambda$

$$\lambda = \frac{RT}{2^{1/2}N_A\sigma p} \qquad \overset{\text{Use } z = c/\lambda}{z = \frac{2^{1/2}N_A\sigma c p}{RT}}$$

Table 1.3

Collision cross-sections of atoms and molecules

Species	σ/nm^2
Argon, Ar	0.36
Benzene, C_6H_6	0.88
Carbon dioxide, CO_2	0.52
Chlorine, Cl_2	0.93
Ethene, C_2H_4	0.64
Helium, He	0.21
Hydrogen, H_2	0.27
Methane, CH_4	0.46
Nitrogen, N_2	0.43
Oxygen, O_2	0.40
Sulfur dioxide, SO_2	0.58

$1\ \mathrm{nm}^2 = 10^{-18}\ \mathrm{m}^2$.

$$c = \frac{\text{mean free path}}{\text{time of flight}} = \frac{\lambda}{1/z} = \lambda z$$

A brief illustration

R T

N_A σ p

Real gases

10^{-9} m = 1 nm

1.9 Molecular interactions

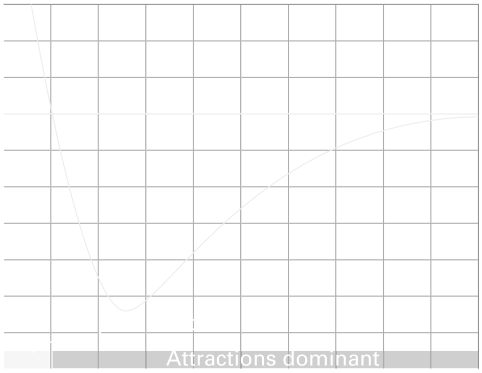


Fig. 1.12

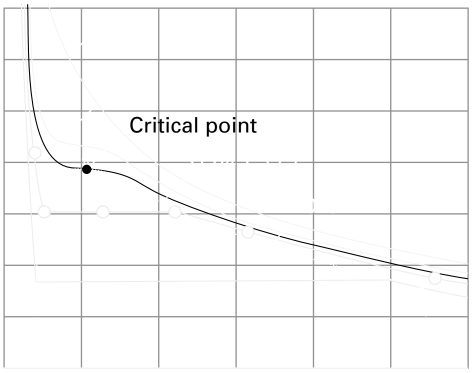


Fig. 1.13

1.10 The critical temperature

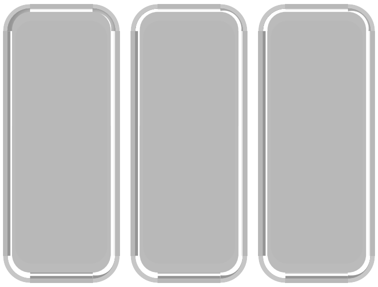


Fig. 1.14

Table 1.4

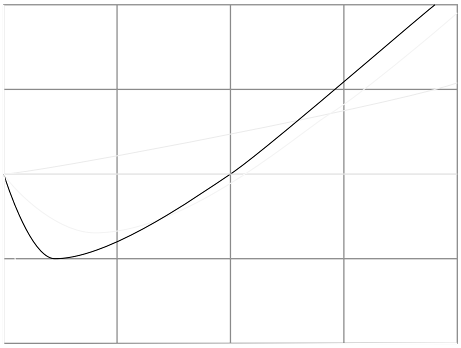
The critical temperatures of gases

	Critical temperature/°C
Noble gases	
Helium, He	–268 (5.2 K)
Neon, Ne	–229
Argon, Ar	–123
Krypton, Kr	–64
Xenon, Xe	17
Halogens	
Chlorine, Cl_2	144
Bromine, Br_2	311
Small inorganic molecules	
Ammonia, NH_3	132
Carbon dioxide, CO_2	31
Hydrogen, H_2	–240
Nitrogen, N_2	–147
Oxygen, O_2	–118
Water, H_2O	374
Organic compounds	
Benzene, C_6H_6	289
Methane, CH_4	–83
Tetrachloromethane, CCl_4	283

Definition

$V_m^{\circ} = RT/p$

$$Z = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} +$$



$$\frac{pV_\mathrm{m}}{RT} = 1 + \frac{B}{V_\mathrm{m}} + \frac{C}{V_\mathrm{m}^2} + \cdots$$

$$p = \frac{RT}{V_\mathrm{m}}\left(1 + \frac{B}{V_\mathrm{m}} + \frac{C}{V_\mathrm{m}^2} + \cdots\right)$$

$$p = \frac{nRT}{V}\left(1 + \frac{nB}{V} + \frac{n^2C}{V^2} + \cdots\right)$$

1.13 The van der Waals equation of state

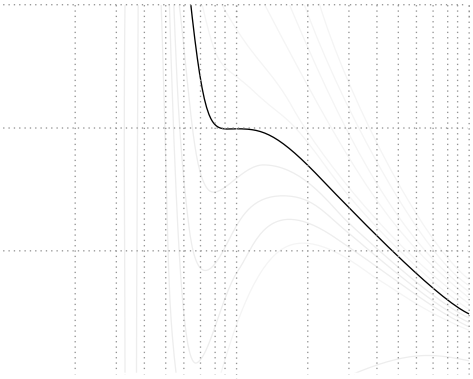
$$p = \frac{nRT}{V - nb}$$

$$\text{Reduction in pressure} = a \times \left(\frac{n}{V}\right)^2$$

$$p = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2$$

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

– – –



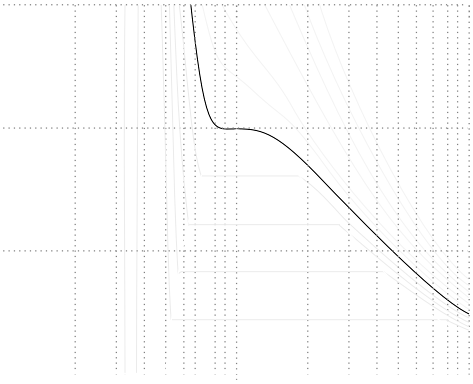
$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

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

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

$$-\frac{RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3} = 0$$

$$\frac{2RT_c}{(V_c - b)^3} - \frac{6a}{V_c^4} = 0$$



1.14 The liquefaction of gases

$$T_c = \frac{8a}{27Rb} \qquad p_c = \frac{a}{27b^2}$$

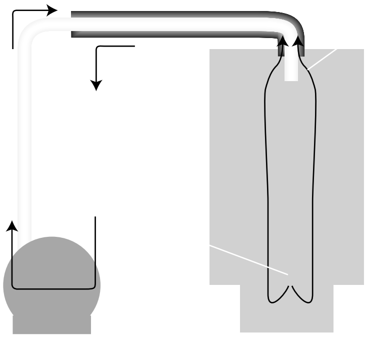


Fig. 1.19

☐ 1

☐ 2

☐ 3

☐ 4

☐ 5

☐ 6

☐ 7

☐ 8

☐ 9

☐ 10

Property	Equation	Comment
	$F(s) = 4\pi\left(\dfrac{M}{2\pi RT}\right)^{3/2} s^2 \mathrm{e}^{-Ms^2/2RT}$	

Kinetic molecular theory

Fig. 1.20

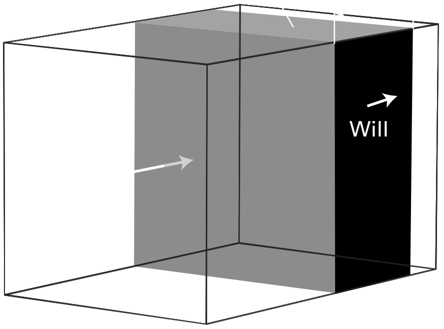


Fig. 1.21

Number of impacts in the interval Δt

Momentum change on each impact

$M = mN_A$

$$\text{Pressure} = \frac{nMAv_x^2/V}{A} = \frac{nMv_x^2}{V}$$

$$p = \frac{nM\langle v_x^2\rangle}{V}$$

Discussion questions

1.1

1.2

1.3

1.4

1.5

1.6

1.7

1.8

Exercises

1.1

1.2

1.3

1.4 A domestic water-carbonating kit uses steel cylinders of carbon dioxide of volume 250 cm^3. They weigh 1.04 kg when full and 0.74 kg when empty. What is the pressure of gas in the cylinder at 20°C?

1.5 The effect of high pressure on organisms, including humans, is studied to gain information about deep-sea diving and anaesthesia. A sample of air occupies 1.00 dm^3 at 25°C and 1.00 atm. What pressure is needed to compress it to 100 [illegible] this temperature?

1.6 [illegible] warned not to dispose of pressurized cans by throwing [illegible] on to a fire. The gas in an aerosol container exerts a [illegible] of 125 kPa at 18°C. The container is thrown on a fire, and [illegible] temperature rises to 700°C. What is the pressure at this temperature?

1.7 Until we find [illegible] [illegible]mical way of extracting oxygen from sea-water or lun[illegible] we have to carry it with us to inhospitable places, and [illegible] compressed form in tanks. A sample of oxygen at 101 [illegible] compressed at constant temperature from 7.20 dm^3 to [illegible] Calculate the final pressure of the gas.

1.8 To what temperature must a sa[illegible]lium gas be cooled from 22.2°C to reduce its volume [illegible]0 dm^3 to 100 cm^3?

1.9 Hot-air balloons gain their lift from the lowe[illegible] sity of air that occurs when the air in the envelope [illegible] To what temperature should you heat a sample of [illegible] at 315 K, to increase its volume by 25 per cent?

1.10 At sea level, where the pressure was 104 kPa and the temperature 21.1°C, a certain mass of air occupied 2.0 m^3. To what volume will the region expand when it has risen to an altitude where the pressure and temperature are (a) 52 kPa, –5.0°C, (b) 880 Pa, –52.0°C?

1.11 A diving bell has an air space of 3.0 m^3 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^{-3} and assume that the temperature is the same as on the surface.

1.12 Balloons were used to obtain much of the early information about the atmosphere and continue to be used today to obtain weather information. In 1782, Jacques Charles used a hydrogen-filled balloon to fly from Paris 25 km into the French countryside. What is the mass density of hydrogen relative to air at the same temperature and pressure? What mass of payload can be lifted by 10 kg of hydrogen, neglecting the mass of the balloon?

1.13 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 SO_2 per day. If this gas is emitted at 800°C and 1.0 atm, what volume of gas is emitted?

1.14 A meteorological balloon had a radius of 1.5 m when released at sea level at 20°C and expanded to a radius of 3.5 m when it had risen to its maximum altitude where the temperature was –25°C. What is the pressure inside the balloon at that altitude?

1.15 A gas mixture being used to simulate the atmosphere of another planet consists of 320 mg of methane, 175 mg of argon, and 225 mg of nitrogen. The partial pressure of nitrogen at 300 K is 15.2 kPa. Calculate (a) the volume and (b) the total pressure of the mixture.

1.16 The vapour pressure of water at blood temperature is 47 Torr. What is the partial pressure of dry air in our lungs when the total pressure is 760 Torr?

1.17 A determination of the density of a gas or vapour can provide a quick estimate of its molar mass even though for practical work mass spectrometry is far more precise. The density of a gaseous compound was found to be 1.23 g dm^{-3} at 330 K and 25.5 kPa. What is the molar mass of the compound?

1.18 In an experiment to measure the molar mass of a gas, 250 cm^3 of the gas was confined in a glass vessel. The pressure was 152 Torr at 298 K and the mass of the gas was 33.5 mg. What is the molar mass of the gas?

1.19 A vessel of volume 22.4 dm^3 contains 2.0 mol H_2 and 1.0 mol N_2 at 273.15 K. Calculate (a) their partial pressures and (b) the total pressure.

1.20 Calculate the mean speed of (a) He atoms, (b) CH_4 molecules at (i) 79 K, (ii) 315 K, (iii) 1500 K.

1.21 A 1.0 dm^3 glass bulb contains 1.0×10^{23} H_2 molecules. If the pressure exerted by the gas is 100 kPa, what is (a) the temperature of the gas, (b) the root-mean-square speeds of the molecules. (c) Would the temperature be different if they [illegible] O_2 molecules?

1.22 [illegible] what pressure does the mean free path of argon at 25 [illegible] comparable to the diameter of a spherical vessel of [illegible]0 dm^3 that contains it? Take $\sigma = 0.36$ nm^2.

1.23 A[illegible] [illegible]re does the mean free path of argon at 25°C become [illegible]ble to 10 times the diameters of the atoms themselve[illegible] $= 0.36$ nm^2.

1.24 When we are [illegible] the photochemical processes that can occur in the uppe[illegible]ere we need to know how often atoms and molecules [illegible] an altitude of 20 km the temperature is 217 K and the [illegible] 0.050 atm. What is the mean free path of N_2 molecul[illegible] $= 0.43$ nm^2.

1.25 How many collisions does a sing[illegible] make in 1.0 s when the temperature is 25°C and the [illegible] is (a) 10 bar, (b) 100 kPa, (c) 1.0 Pa?

1.26 Calculate the total number of collisions pe[illegible] in 1.0 dm^3 of argon under the same conditions as in Exer[illegible]

1.27 How many collisions per second does an N_2 mole[illegible] make at an altitude of 20 km? (See Exercise 1.24 for data.)

1.28 The spread of pollutants through the atmosphere is governed partly by the effects of winds but also by the natural tendency of molecules to diffuse. The latter depends on how far a molecule can travel before colliding with another molecule. Calculate the mean free path of diatomic molecules in air using $\sigma = 0.43$ nm^2 at 25°C and (a) 10 bar, (b) 103 kPa, (c) 1.0 Pa.

1.29 How does the mean free path in a sample of a gas vary with temperature in a constant-volume container?

1.30 Calculate the pressure exerted by 1.0 mol C_2H_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 K in 22.414 dm^3, (ii) at 1000 K in 100 cm^3. Use the data in Table 1.5.

1.31 How reliable is the perfect gas law in comparison with the van der Waals equation? Calculate the difference in pressure of 10.00 g of carbon dioxide confined to a container of volume 100 cm^3 at 25.0°C between treating it as a perfect gas and a van der Waals gas.

1.32 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. *Hint*. The expansion you will need is $(1-x)^{-1} = 1 + x + x^2 + \cdots$. Series expansions are discussed in Appendix 2.

1.33 A certain gas obeys the van der Waals equation with $a = 0.50\ m^6\ Pa\ mol^{-2}$. Its volume is found to be $5.00 \times 10^{-4}\ m^3\ mol^{-1}$ at 273 K and 3.0 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?

1.34 Measurements on argon gave $B = -21.7\ cm^3\ mol^{-1}$ and $C = 1200\ cm^6\ mol^{-2}$ for the virial coefficients at 273 K. What are the values of a and b in the corresponding van der Waals equation of state?

1.35 Show that there is a temperature at which the second virial coefficient, B, is zero for a van der Waals gas, and calculate its value for carbon dioxide. *Hint*. Use the expression for B derived in Exercise 1.32.

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

Projects

The symbol ‡ indicates that calculus is required.

1.37‡ In the following exercises you will explore the Maxwell distribution of speeds in more detail.

(a) Confirm that the mean speed of molecules of molar mass M at a temperature T is equal to $(8RT/\pi M)^{1/2}$. *Hint*: You will need an integral of the form $\int_0^\infty x^3 e^{-ax^2}\, dx = n!/2a^2$.

(b) Confirm that the root-mean-square speed of molecules of molar mass M at a temperature T is equal to $(3RT/M)^{1/2}$ and hence confirm eqn 1.13. *Hint*: You will need an integral of the form $\int_0^\infty x^4 e^{-ax^2}\, dx = (3/8a^2)(\pi/a)^{1/2}$.

(c) Find an expression for the most probable speed of molecules of molar mass M at a temperature T. *Hint*: Look for a maximum in the Maxwell distribution (the maximum occurs as $dF/ds = 0$).

(d) Estimate the fraction of N_2 molecules at 500 K that have speeds in the range 290 to 300 $m\ s^{-1}$.

1.38‡ Here we explore the van der Waals equation of state. Using the language of calculus, the critical point of a van der Waals gas occurs where the isotherm has a flat inflexion, which is where $dp/dV_m = 0$ (zero slope) and $d^2p/dV_m^2 = 0$ (zero curvature).

(a) Evaluate these two expressions using eqn 1.23b, and find expressions for the critical constants in terms of the van der Waals parameters.

(b) Show that the value of the compression factor at the critical point is $\frac{3}{8}$.

1.39 The kinetic model of gases is valid when the size of the particles is negligible compared with their mean free path. It may seem absurd, therefore, to expect the kinetic theory and, as a consequence, the perfect gas law, to be applicable to the dense matter of stellar interiors. In the Sun, for instance, the density is 150 times that of liquid water at its centre and comparable to that of water about half-way to its surface. However, we have to realize that the state of matter is that of a *plasma*, in which the electrons have been stripped from the atoms of hydrogen and helium that make up the bulk of the matter of stars. As a result, the particles making up the plasma have diameters comparable to those of nuclei, or about 10 fm. Therefore, a mean free path of only 0.1 pm satisfies the criterion for the validity of the kinetic model and the perfect gas law. We can therefore use $pV = nRT$ as the equation of state for the stellar interior.

(a) Calculate the pressure half-way to the centre of the Sun, assuming that the interior consists of ionized hydrogen atoms, the temperature is 3.6 MK, and the mass density is 1.20 $g\ cm^{-3}$ (slightly higher than the density of water).

(b) Combine the result from part (a) with the expression for the pressure from kinetic model to show that the pressure of the plasma is related to its *kinetic energy density*, $\rho_k = E_k/V$, the kinetic energy of the molecules in a region divided by the volume of the region, by

$$p = \tfrac{2}{3}\rho_k$$

(c) What is the kinetic energy density half-way to the centre of the Sun? Compare your result with the (translational) kinetic energy density of the Earth's atmosphere on a warm day (25°C): $1.5 \times 10^5\ J\ m^{-3}$ (corresponding to 0.15 $J\ cm^{-3}$).

(d) A star eventually depletes some of the hydrogen in its core, which contracts and results in higher temperatures. The increased temperature results in an increase in the rates of nuclear reactions, some of which result in the formation of heavier nuclei, such as carbon. The outer part of the star expands and cools to produce a red giant. Assume that half-way to the centre a red giant has a temperature of 3500 K, is composed primarily of fully ionized carbon atoms and electrons, and has a mass density of 1200 $kg\ m^{-3}$. What is the pressure at this point?

(e) If the red giant in part (d) consisted of neutral carbon atoms, what would be the pressure at the same point under the same conditions?

The conservation of energy

Internal energy and enthalpy

Box 2.1 Differential scanning calorimetry

CHECKLIST OF KEY IDEAS
TABLE OF KEY EQUATIONS
QUESTIONS AND EXERCISES

The conservation of energy

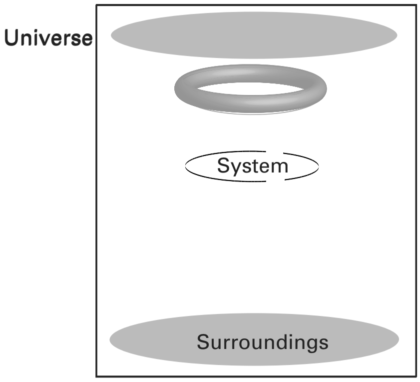


Fig. 2.1

2.1 Systems and surroundings

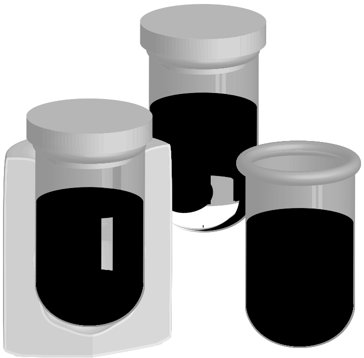


Fig. 2.2

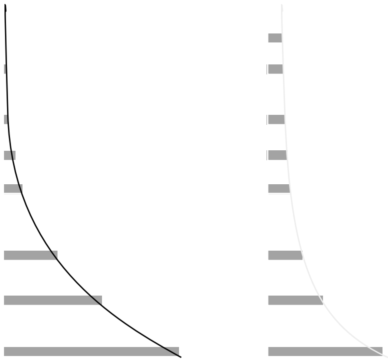


Fig. 2.3

2.2 Work and heat

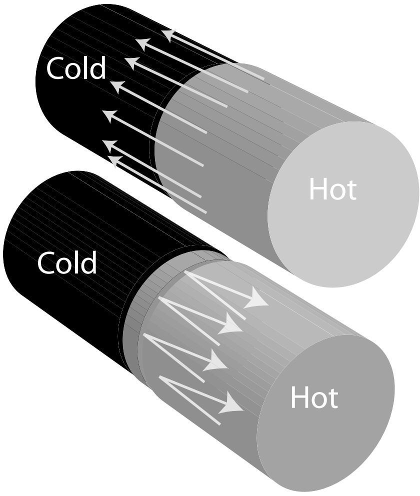


Fig. 2.4

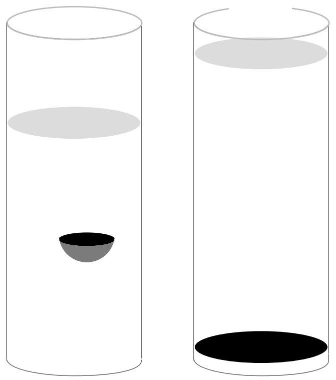


Fig. 2.5

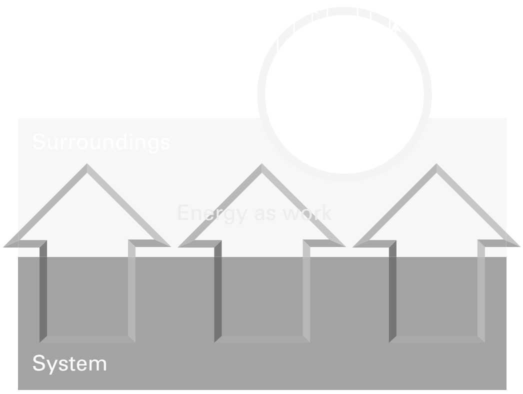


Fig. 2.6

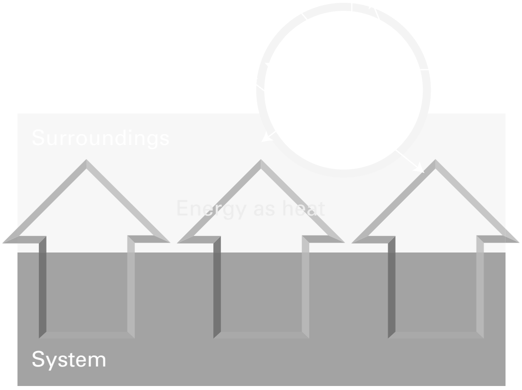


Fig. 2.7

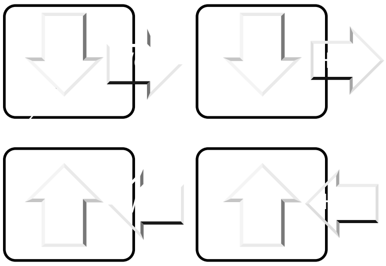


Fig. 2.8

2.3 The measurement of work

A brief illustration

Derivation 2.1

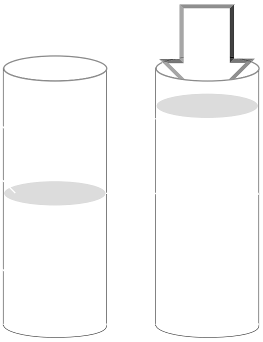


Fig. 2.9

Opposing force

Distance moved

Volume change

A note on good practice

Self-test 2.1

Calculate the work done by a system in which a reaction results in the formation of 1.0 mol $CO_2(g)$ at 25°C and 100 kPa. *Hint.* The increase in volume will be 25 dm^3 under these conditions if the gas is treated as perfect; use the relations 1 $dm^3 = 10^{-3}$ m^3 and 1 Pa m^3 = 1 J.

[*Answer:* 2.5 kJ]

$$w = -nRT\ln\frac{V_\mathrm{f}}{V_\mathrm{i}}$$

Fig. 2.10

Derivation 2.2

A brief comment

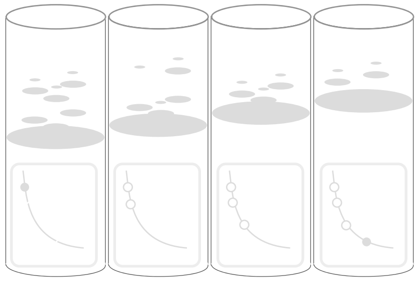
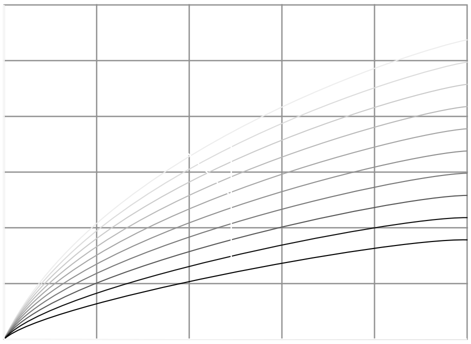


Fig. 2.11

$$\frac{nRT}{V}\,\mathrm{d}V$$

$$\frac{\mathrm{d}V}{V}$$

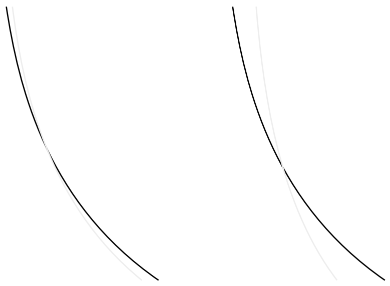
$$\frac{\mathrm{d}x}{x} = \ln x + \text{constant}$$



A brief illustration

$$\Delta T = \frac{q}{C_p} = \frac{q}{nC_{p,\mathrm{m}}}$$

$$= \frac{1.0\times10^5\ \mathrm{J}}{(55.5\ \mathrm{mol})\times(75\ \mathrm{J\,K^{-1}\,mol^{-1}})} = +24\ \mathrm{K}$$



A brief illustration

$$C = \frac{q}{\Delta\theta} = \frac{1.23 \times 12.0 \times 156\ \text{J}}{4.47\,^\circ\text{C}} = \frac{1.23 \times 12.0 \times 156}{4.47}\ \text{J}\ ^\circ\text{C}^{-1}$$

$$q = C\Delta\theta = \left(\frac{1.23 \times 12.0 \times 156}{4.47}\ \text{J}\ ^\circ\text{C}^{-1}\right) \times (3.22\,^\circ\text{C}) = 1.66\ \text{kJ}$$

A brief comment

Self-test 2.3

In an experiment to measure the heat released by the combustion of a sample of fuel, the compound was burned in an oxygen atmosphere inside a calorimeter and the temperature rose by 2.78°C. When a current of 1.12 A from an 11.5 V source flows through a heater in the same calorimeter for 162 s, the temperature rose by 5.11°C. What is the heat released by the combustion reaction?

[*Answer:* 1.1 kJ]

$$q = nRT \ln \frac{V_\mathrm{f}}{V_\mathrm{i}}$$

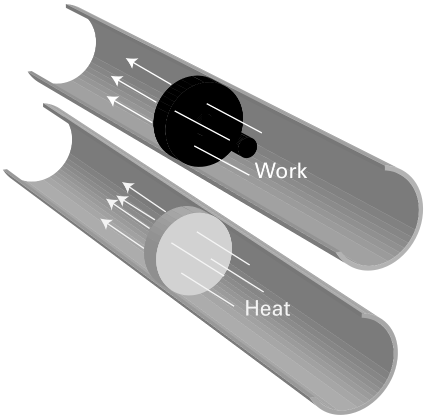


Fig. 2.15

A brief illustration

Another note on good practice

Example 2.2

Strategy

Solution

A note on good practice

Self-test 2.4

An electric battery is charged by supplying 250 kJ of energy to it as electrical work (by driving an electric current through it), but in the process it loses 25 kJ of energy as heat to the surroundings. What is the change in internal energy of the battery?

[*Answer:* +225 kJ]

2.7 Internal energy as a state function

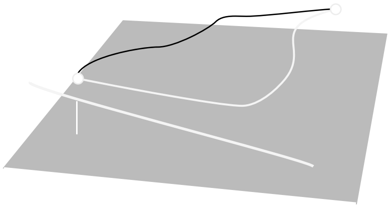


Fig. 2.16

$$C_V = \frac{\Delta U}{\Delta T}$$

A brief comment

$$C_V = \frac{\mathrm{d}U}{\mathrm{d}T}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

2.8 The enthalpy

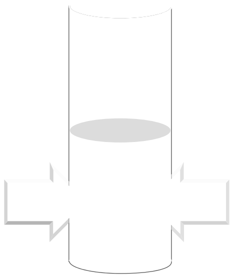
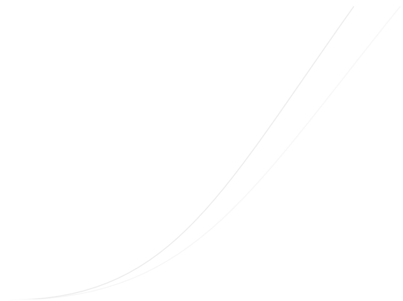


Fig. 2.19

2.9 The temperature variation of the enthalpy

A brief illustration

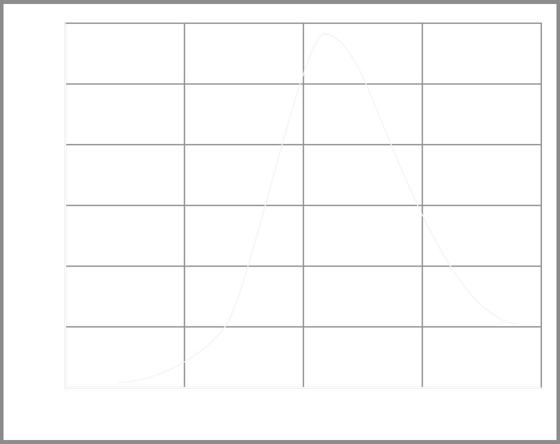
$$C_p = \frac{\Delta H}{\Delta T}$$



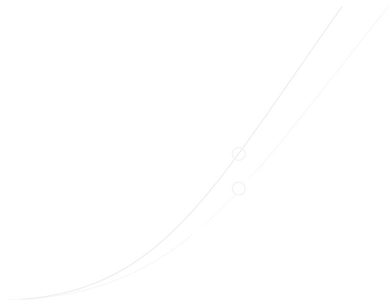
$$C_{\mathrm{ex}} = \frac{\mathrm{d}q_{\mathrm{ex}}}{\mathrm{d}T} = \frac{\mathrm{d}q_{\mathrm{ex}}}{\alpha\mathrm{d}t} = \frac{P_{\mathrm{ex}}}{\alpha}$$

A differential scanning calorimeter. The sample and a reference material are heated in separate but identical compartments. The output is the difference in power needed to maintain the compartments at equal temperatures as the temperature rises.

See an animated version of this figure in the interactive ebook.



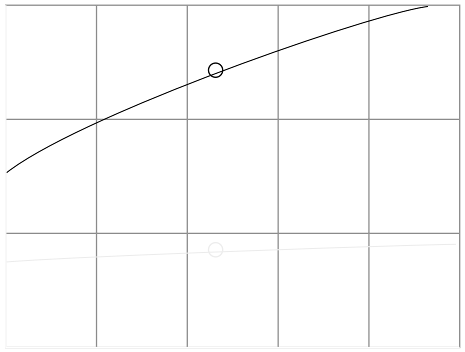
A thermogram for the protein ubiquitin. The protein retains its native structure up to about 45°C and then undergoes an endothermic conformational change. (Adapted from B. Chowdhry and S. LeHarne, *J. Chem. Educ.* **74**, 236 (1997).)



A brief comment

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

$$C_{p,\mathrm{m}} = a + bT + \frac{c}{T^2}$$



A brief illustration

– – – – –

$$\frac{\Delta H_\mathrm{m}}{\Delta T} - \frac{\Delta U_\mathrm{m}}{\Delta T} = R$$

$$\Delta H = \left(a + bT_{\text{a. mean}} + \frac{c}{T^2_{\text{g. mean}}} \right) \Delta T$$

☐ **1**

☐ **2**

☐ **3**

☐ **4**

☐ **5**

☐ **6**

Description	Equation	Comment

Discussion questions

2.1

2.2

2.3

2.4

2.5

2.6

2.7

2.2

2.3

2.4

2.5

2.6

Exercises

2.1

2.7

dioxide and (a) liquid water, (b) water vapour at 20°C when the external pressure is 1.20 atm.

2.8 We are all familiar with the general principles of operation of an internal combustion reaction: the combustion of fuel drives out the piston. It is possible to imagine engines that use reactions other than combustions, and we need to assess the work they can do. A chemical reaction takes place [illegible] container of cross-sectional area 100 cm^2; the container [illegible] piston at one end. As a result of the reaction, the piston is [illegible] out through 10.0 cm against a constant external pressure [illegible]0 kPa. Calculate the work done by the system.

2.9 What [illegible] heat capacity of a sample of liquid that rose in temperature [illegible]°C when supplied with 124 J of energy as heat?

2.10 A cube of iron [illegible] to 70°C and transferred to a beaker containing 100 g [illegible] at 20°C. The final temperature of the water and the iron [illegible]. What is (a) the heat capacity, (b) the specific heat capac[illegible]) the molar heat capacity of the iron cube? Ignore heat [illegible] from the assembly.

2.11 The high heat capacity of water [illegible] benign because it stabilizes the temperatures o[illegible] oceans: a large quantity of energy must be lost or [illegible] there is a significant change in temperature. Conver[illegible] that a lot of heat must be supplied to achieve a [illegible] in temperature. The molar heat capacity of water is 75[illegible] mol^{-1}. What energy is needed to heat 250 g of water [illegible] of coffee, for instance) through 40°C?

2.12 A current of 1.55 A from a 110 V source was passed through a heater for 8.5 min. The heater was immersed in a water bath. What quantity of energy was transferred to the water as heat?

2.13 When 229 J of energy is supplied as heat to 3.00 mol Ar(g), the temperature of the sample increases by 2.55 K. Calculate the molar heat capacities at constant volume and constant pressure of the gas.

2.14 The heat capacity of air is much smaller than that of water, and relatively modest amounts of heat are needed to change its temperature. This is one of the reasons why desert regions, though very hot during the day, are bitterly cold at night. The heat capacity of air at room temperature and pressure is approximately 21 J K^{-1} mol^{-1}. How much energy is required to raise the temperature of a room of dimensions 5.5 m × 6.5 m × 3.0 m by 10°C? If losses are neglected, how long will it take a heater rated at 1.5 kW to achieve that increase given that 1 W = 1 J s^{-1}?

2.15 The transfer of energy from one region of the atmosphere to another is of great importance in meteorology for it affects the weather. Calculate the heat needed to be supplied to a parcel of air containing 1.00 mol air molecules to maintain its temperature at 300 K when it expands reversibly and isothermally from 22 dm^3 to 30.0 dm^3 as it ascends.

2.16 The temperature of a block of iron ($C_{V,\mathrm{m}}$ = 25.1 J K^{-1} mol^{-1}) of mass 1.4 kg fell by 65°C as it cooled to room temperature. What is its change in internal energy?

2.17 In an experiment to determine the calorific value of a food, a sample of the food was burned in an oxygen atmosphere and the temperature rose by 2.89°C. When a current of 1.27 A from a 12.5 V source flowed through the same calorimeter for 157 s, the temperature rose by 3.88°C. What energy is released as heat by the combustion?

2.18 A laboratory animal exercised on a treadmill that, through pulleys, raised a 250 g mass through 1.85 m. At the same time, the animal lost 10.0 J of energy as heat. Disregarding all other losses, and regarding the animal as a closed system, what is its change in internal energy?

2.19 In preparation for a study of the metabolism of an organism, a small, sealed calorimeter was prepared. In the initial phase of the experiment, a current of 22.22 mA from a 11.8 V source was passed for 162 s through a heater inside the calorimeter. What is the change in internal energy of the calorimeter?

2.20 In a computer model of the atmosphere, 20 kJ of energy was transferred as heat to a parcel of air of initial volume 1.0 m^3. What is the change in enthalpy of the parcel of air?

2.21 The internal energy of a perfect gas does not change when the gas undergoes isothermal expansion. What is the change in enthalpy?

2.22 Carbon dioxide, although only a minor component of the atmosphere, plays an important role in determining the weather and the composition and temperature of the atmosphere. Calculate the difference between the molar enthalpy [illegible] molar internal energy of carbon dioxide regarded as a [illegible] 298.15 K. For this calculation treat carbon dioxide as a [illegible] Waals gas and use the data in Table 1.5.

2.23 A s[illegible] serum of mass 25 g is cooled from 290 K to 275 K at [illegible] pressure by the extraction of 1.2 kJ of energy as heat. [illegible] q and ΔH and estimate the heat capacity of the [illegible]

2.24 When 3.0 mol O_2 [illegible] at a constant pressure of 3.25 atm, its temperature [illegible] from 260 K to 285 K. Given that the molar heat cap[illegible] at constant pressure is 29.4 J K^{-1} mol^{-1}, calculate [illegible]

2.25 The molar heat capacity at cons[illegible] of carbon dioxide is 29.14 J K^{-1} mol^{-1}. What is [illegible] its molar heat capacity at constant volume?

2.26 Use the information in Exercise 2.25 to [illegible] the change in (a) molar enthalpy, (b) molar internal [illegible] carbon dioxide is heated from 15°C (the temperature [illegible] air is inhaled) to 37°C (blood temperature, the temperature [illegible] our lungs).

Projects

The sign ‡ indicates that calculus is required.

2.27‡ Here we explore the van der Waals equation of state in more detail. (a) Repeat Derivation 2.2 for a gas that obeys the equation of state $p = nRT/(V - nb)$, which is appropriate when molecular repulsions are important. Does the gas do more or less work than a perfect gas for the same change of volume? (b) Now repeat the preceding exercise for a gas that obeys the equation of state $p = nRT/V - n^2a/V^2$, which is appropriate when molecular attractions are important. Does the gas do more or less work than a perfect gas for the same change of volume?

2.28‡ Derivation 2.2 showed how to calculate the work of reversible, isothermal expansion of a perfect gas. Suppose [illegible] expansion is reversible but not isothermal and that the temperature decreases as the expansion proceeds. (a) Find [illegible] expression for the work when $T = T_i - c(V - V_i)$, with c a positive constant. (b) Is the work greater or smaller than for isothermal expansion?

2.29‡ We now [illegible] the effect of the temperature dependence of the heat capacity [illegible] the internal energy. (a) The heat capacity of a nonmetallic [illegible] at very low temperatures (close to $T = 0$) typically varies [illegible] T^3, where a is a constant. How does its internal energy [illegible] (b) Suppose that the molar internal energy of a substance [illegible] a limited temperature range can be expressed as a polynomial in T as $U_m(T) = a + bT + cT^2$. Find an expression for [illegible] constant-volume molar heat capacity at a temperature T.

2.30‡ Now we explore the implications of the temperature dependence of the heat capacity for the enthalpy. [illegible] The heat capacity of a substance is often reported in the form $C_{p,m} = a + bT + c/T^2$. Use this expression to make a more accurate estimate of the change in molar enthalpy of carbon dioxide when it is heated from 15°C to 37°C (as in the preceding exercise), given $a = 44.22\ \mathrm{J\ K^{-1}\ mol^{-1}}$, $b = 8.79 \times 10^{-3}\ \mathrm{J\ K^{-2}\ mol^{-1}}$, and $c = -8.62 \times 10^5\ \mathrm{J\ K\ mol^{-1}}$. *Hint.* You will need to integrate $dH = C_p dT$. (b) Use the expression from part (a) to determine how the molar enthalpy of the substance changes over that limited temperature range. Plot the molar enthalpy as a function of temperature.

2.31‡ The exact expression for the relation between the heat capacities at constant volume and constant pressure is $C_p - C_V = \alpha^2 TV/\kappa$, where α is the expansion coefficient, $\alpha = (dV/dT)/V$ at constant pressure and κ (kappa) is the isothermal compressibility, $\kappa = -(dV/dp)/V$. Confirm that this general expression reduces to that in eqn 2.19 for a perfect gas.

2.32 This exercise explores differential scanning calorimetry in more detail (a) In many experimental thermograms, such as that shown in Box 2.1, the baseline below T_1 is at a different level from that above T_2. Explain this observation. (b) You have at your disposal a sample of pure polymer P and a sample of P that has just been synthesized in a large chemical reactor and that might contain impurities. Describe how you would use differential scanning calorimetry to determine the mole percentage composition of P in the allegedly impure sample.

Physical change

Chemical change

Box 3.1 Fuels, food, and energy resources

CHECKLIST OF KEY IDEAS
TABLE OF KEY EQUATIONS
QUESTIONS AND EXERCISES

Physical change

3.1 The enthalpy of phase transition

A note on good practice

$$n = \frac{m}{M} = \frac{4.33\ \text{g}}{46.07\ \text{g mol}^{-1}} = \frac{4.33}{46.07}\ \text{mol}$$

$$\Delta_{\text{vap}}H = \frac{0.682 \times 12.0 \times 500\ \text{J}}{(4.33/46.07)\ \text{mol}} = 4.35 \times 10^{4}\ \text{J mol}^{-1}$$

Fig. 3.2

Fig. 3.1

Fig. 3.3

Self-test 3.2

Calculate the standard enthalpy of sublimation of ice at 0°C from its standard enthalpy of fusion at 0°C (6.01 kJ mol^{-1}) and the standard enthalpy of vaporization of water at 0°C (45.07 kJ mol^{-1}).

[*Answer:* 51.08 kJ mol^{-1}]

3.2 Atomic and molecular change

A brief comment

Example 3.2

Strategy

Solution

Fig. 3.4 The contributions to the enthalpy change treated in Example 3.2.

$$n_{Mg} = \frac{m_{Mg}}{M_{Mg}} = \frac{1.00\ \text{g}}{24.31\ \text{g mol}^{-1}} = \frac{1.00}{24.31}\ \text{mol}$$

Self-test 3.3

The enthalpy of sublimation of aluminium is 326 kJ mol^{-1}. Use this information and the ionization enthalpies in Table 3.2 to calculate the energy that must be supplied as heat (at constant pressure) to convert 1.00 g of solid aluminium metal to a gas of Al^{3+} ions and electrons at 25°C.

[*Answer:* +202 kJ]

Table 3.2

1	2	13	15	15	16	17	18

Table 3.3

1	2	13	14	15	16	17	18

Table 3.4

Selected bond enthalpies, $\Delta H(\mathrm{A{-}B})/(\mathrm{kJ\ mol^{-1}})$

Diatomic molecules							
H—H	436	O═O	497	F—F	155	H—F	565
		N≡N	945	Cl—Cl	242	H—Cl	431
		O—H	428	Br—Br	193	H—Br	366
		C≡O	1074	I—I	151	H—I	299
Polyatomic molecules							
H—CH$_3$	435	H—NH$_2$	460	H—OH	492		
H—C$_6$H$_5$	469	O$_2$N—NO$_2$	54	HO—OH	213		
H$_3$C—CH$_3$	368	O═CO	531	HO—CH$_3$	377		
H$_2$C═CH$_2$	720			Cl—CH$_3$	352		
HC≡CH	962			Br—CH$_3$	293		
				I—CH$_3$	237		

Table 3.5

Mean bond enthalpies, $\Delta H_B/(\mathrm{kJ\ mol^{-1}})$

	H	C	N	O	F	Cl	Br	I	S	P	Si
H	436										
C	412	348(1) 612(2) 838(3) 518 (a)									
N	388	305(1) 613 (2) 890 (3)	163 (1) 409 (2) 945 (3)								
O	463	360 (1) 743 (2)	157	146(1) 497(2)							
F	565	484	270	185	155						
Cl	431	338	200	203	254	242					
Br	366	276				219	193				
I	299	238				210	178	151			
S	338	259			496	250	212		264		
P	322									200	
Si	318		374	466							226

Values are for single bonds except where otherwise stated (in parentheses).

(a) Denotes aromatic.

Example 3.3

Strategy

Solution

Fig. 3.5

Self-test 3.4

Estimate the enthalpy change for the combustion of liquid ethanol to carbon dioxide and liquid water under standard conditions by using the bond enthalpies, mean bond enthalpies, and the appropriate standard enthalpies of vaporization.

[*Answer:* −1348 kJ; the experimental value is −1368 kJ]

Chemical change

3.3 **Enthalpies of combustion**

–

A brief illustration

3.4 The combination of reaction enthalpies

Box 3.1 Fuels, food and energy reserves

Box 3.1

Fuel	Combustion equation	$\Delta_c H^\ominus$/ (kJ mol^{-1})	Specific enthalpy/ (kJ g^{-1})	Enthalpy density*/ (kJ dm^{-3})

Example 3.4

Strategy

Solution

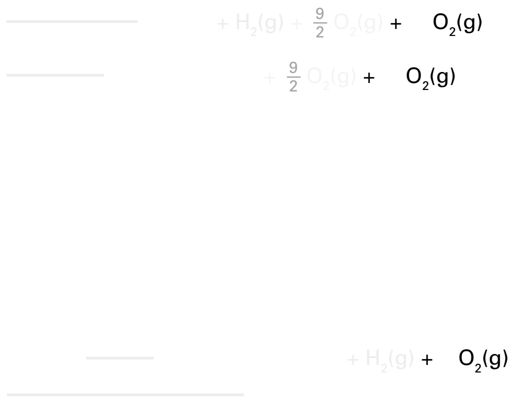


Fig. 3.6

Self-test 3.5

Calculate the standard enthalpy of the reaction $C_6H_6(l) + 3\ H_2(g) \rightarrow C_6H_{12}(l)$ from the standard enthalpies of combustion of benzene (Table 3.6) and cyclohexane (–3930 kJ mol^{-1}).

[*Answer:* –196 kJ]

3.5 Standard enthalpies of formation

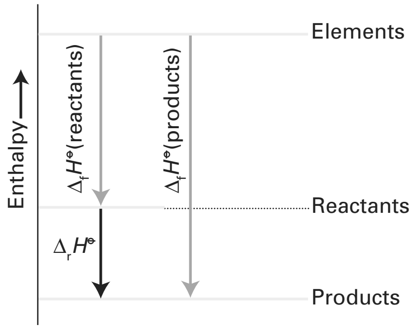


Fig. 3.7

Table 3.7

Element	Reference state

Example 3.5

Strategy

Solution

A note on good practice

Self-test 3.6

Use standard enthalpies of formation to calculate the enthalpy of combustion of propane gas to carbon dioxide and water vapour.

[*Answer:* $-2044\ \text{kJ mol}^{-1}$]

3.6 Enthalpies of formation and molecular modelling

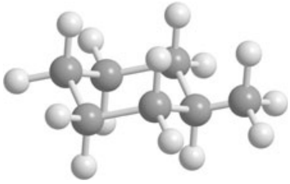
Table 3.8

*Standard enthalpies of formation at 298.15 K**

Substance	$\Delta_f H^\circ/(\text{kJ mol}^{-1})$
Inorganic compounds	
Ammonia, $NH_3(g)$	–46.11
Ammonium nitrate, $NH_4NO_3(s)$	–365.56
Carbon monoxide, $CO(g)$	–110.53
Carbon disulfide, $CS_2(l)$	+89.70
Carbon dioxide, $CO_2(g)$	–393.51
Dinitrogen tetroxide, $N_2O_4(g)$	+9.16
Dinitrogen monoxide, $N_2O(g)$	+82.05
Hydrogen chloride, $HCl(g)$	–92.31
Hydrogen fluoride, $HF(g)$	–271.1
Hydrogen sulfide, $H_2S(g)$	–20.63
Nitric acid, $HNO_3(l)$	–174.10
Nitrogen dioxide, $NO_2(g)$	+33.18
Nitrogen monoxide, $NO(g)$	+90.25
Sodium chloride, $NaCl(s)$	–411.15
Sulfur dioxide, $SO_2(g)$	–296.83
Sulfur trioxide, $SO_3(g)$	–395.72
Sulfuric acid, $H_2SO_4(l)$	–813.99
Water, $H_2O(l)$	–285.83
$H_2O(g)$	–241.82
Organic compounds	
Benzene, $C_6H_6(l)$	+49.0
Ethane, $C_2H_6(g)$	–84.68
Ethanol, $C_2H_5OH(l)$	–277.69
Ethene, $C_2H_4(g)$	+52.26
Ethyne, $C_2H_2(g)$	+226.73
Glucose, $C_6H_{12}O_6(s)$	–1268
Methane, $CH_4(g)$	–74.81
Methanol, $CH_3OH(l)$	–238.86
Sucrose, $C_{12}H_{22}O_{11}(s)$	–2222.86

* A longer list is given in the Data section at the end of the book. The text's website also contains links to additional data.

Fig. 3.8



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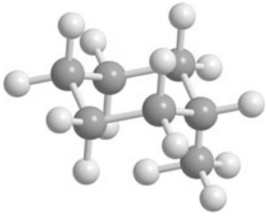

2

3.7 The variation of reaction enthalpy with temperature

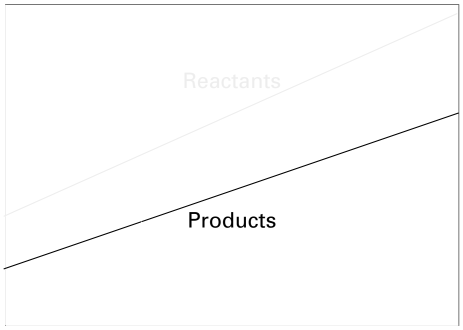

Fig. 3.9

Example 3.6

Strategy

Solution

Self-test 3.7

Estimate the standard enthalpy of formation of NH_3(g) at 400 K from the data in the Data section.

[*Answer:* –48.4 kJ mol^{-1}]

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☐ **7**

Description	Equation	Comment

Discussion questions

3.1

3.2

3.3

3.4

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3.6

3.7

Exercises

3.1

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3.10 How much energy (at constant temperature and pressure) must be supplied as heat to 10.0 g of chlorine gas (as Cl_2) to produce a plasma (a gas of charged particles, in this case ions) composed of Cl^- and Cl^+ ions? The enthalpy of ionization of Cl(g) is +1257.5 kJ mol^{-1} and its electron-gain enthalpy is −354.8 kJ mol^{-1}.

3.11 Use the data in Exercise 3.10 to identify (a) the standard enthalpy of ionization of Cl^-(g) and (b) the accompanying change in molar internal energy.

3.12 The enthalpy changes accompanying the dissociation of successive bonds in NH_3(g) are 460, 390, and 314 kJ mol^{-1}, respectively. (a) What is the mean enthalpy of an N—H bond? (b) Do you expect the mean bond internal energy to be larger or smaller than the mean bond enthalpy?

3.13 Use bond enthalpies and mean bond enthalpies to estimate the (a) the enthalpy of the glycolysis reaction adopted by anaerobic bacteria as a source of energy, $C_6H_{12}O_6(aq) \rightarrow 2\ CH_3CH(OH)COOH(aq)$, lactic acid, which is produced via the formation of pyruvic acid, $CH_3COCOOH$, and the action of lactate dehydrogenase and (b) the enthalpy of combustion of glucose. Ignore the contributions of enthalpies of fusion and vaporization.

3.14 The efficient design of chemical plants depends on the designer's ability to assess and use the heat output of one process to supply another process. The standard enthalpy of reaction for $N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$ is −92.22 kJ mol^{-1}. What is the change in enthalpy when (a) 1.00 t of N_2(g) is consumed, (b) 1.00 t of NH_3(g) is formed?

3.15 Ethane is flamed off in abundance from oil wells, because it is unreactive and difficult to use commercially. But would it make a good fuel? The standard enthalpy of reaction for $2\ C_2H_6(g) + 7\ O_2(g) \rightarrow 4\ CO_2(g) + 6\ H_2O(l)$ is −3120 kJ mol^{-1}. (a) What is the standard enthalpy of combustion of ethane? (b) What is the specific enthalpy of combustion of ethane? (c) Is ethane a more or less efficient fuel than methane?

3.16 Standard enthalpies of formation are widely available, but we might need a standard enthalpy of combustion instead. The standard enthalpy of formation of ethylbenzene is −12.5 kJ mol^{-1}. Calculate its standard enthalpy of combustion.

3.17 Combustion reactions are relatively easy to carry out and study, and their data can be combined to give enthalpies of other types of reaction. As an illustration, calculate the standard enthalpy of hydrogenation of cyclohexene to cyclohexane given that the standard enthalpies of combustion of the two compounds are −3752 kJ mol^{-1} (cyclohexene) and −3953 kJ mol^{-1} (cyclohexane).

3.18 Estimate the standard internal energy of formation of liquid methyl acetate (methyl ethanoate, CH_3COOCH_3) at 298 K from its standard enthalpy of formation, which is −442 kJ mol^{-1}.

3.19 The standard enthalpy of combustion of anthracene is −7163 kJ mol^{-1}. Calculate its standard enthalpy of formation.

3.20 When 320 mg of naphthalene, $C_{10}H_8$(s), was burned in a bomb calorimeter, the temperature rose by 3.05 K. Calculate the heat capacity of the calorimeter. By how much will the temperature rise when 100 mg of phenol, C_6H_5OH(s), is burned in the calorimeter under the same conditions?

3.21 The energy resources of glucose are of major concern for the assessment of metabolic processes. When 0.3212 g of glucose was burned in a bomb calorimeter of heat capacity 641 J K^{-1} the temperature rose by 7.793 K. Calculate (a) the standard molar enthalpy of combustion, (b) the standard internal energy of combustion, and (c) the standard enthalpy of formation of glucose.

3.22 The complete combustion of fumaric acid in a bomb calorimeter released 1333 kJ per mole of $HOOCCH{=}CHCOOH$(s) at 298 K. Calculate (a) the internal energy of combustion, (b) the enthalpy of combustion, (c) the enthalpy of formation of lactic acid.

3.23 The mean bond enthalpies of the C—C, C—H, C═O, and O—H bonds are 348, 412, 743, and 463 kJ mol^{-1}, respectively. The combustion of a fuel such as octane is exothermic because relatively weak bonds break to form relatively strong bonds. Use this information to justify why glucose has a lower specific enthalpy than the lipid decanoic acid ($C_{10}H_{20}O_2$) even though these compounds have similar molar masses.

3.24 Calculate the standard enthalpy of solution of AgI(s) in water from the standard enthalpies of formation of the solid and the aqueous ions.

3.25 The standard enthalpy of decomposition of the yellow complex NH_3SO_2 into NH_3 and SO_2 is +40 kJ mol^{-1}. Calculate the standard enthalpy of formation of NH_3SO_2.

3.26 Given that the standard enthalpy of combustion of graphite is −393.51 kJ mol^{-1} and that of diamond is −395.41 kJ mol^{-1}, calculate the standard enthalpy of the C(s, graphite) → C(s, diamond) transition.

3.27 The pressures deep within the Earth are much greater than those on the surface, and to make use of thermochemical data in geochemical assessments we need to take the differences into account. Use the information in Exercise 3.26 together with the densities of graphite (2.250 g cm^{-3}) and diamond (3.510 g cm^{-3}) to calculate the internal energy of the transition when the sample is under a pressure of 150 kbar.

3.28 A typical human produces about 10 MJ of energy transferred as heat each day through metabolic activity. The main mechanism of heat loss is through the evaporation of water. (a) 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? (b) Human bodies are actually open systems. What mass of water should be evaporated each day to maintain constant temperature?

3.29 Camping gas is typically propane. The standard enthalpy of combustion of propane gas is −2220 kJ mol^{-1} and the standard enthalpy of vaporization of the liquid is +15 kJ mol^{-1}.

Calculate (a) the standard enthalpy and (b) the standard internal energy of combustion of the liquid.

3.30 Classify as endothermic or exothermic: (a) a combustion reaction for which $\Delta_r H^\ominus = -2020$ kJ mol^{-1}; (b) a dissolution for which $\Delta H^\ominus = +4.0$ kJ mol^{-1}; (c) vaporization; (d) fusion; and (e) sublimation.

3.31 Standard enthalpies of formation are of great usefulness, [illegible] they can be used to calculate the standard enthalpies of a [illegible] range of reactions of interest in chemistry, biology, [illegible] and industry. Use information in the Data section to calculate the standard enthalpies of the following reactions:

(a) [illegible] $\rightarrow N_2O_4(g)$

(b) NO_2 [illegible] $O_2(g)$

(c) $3\,NO_2(g)$ [illegible] $\rightarrow 2\,HNO_3(aq) + NO(g)$

(d) Cycloprop[illegible] $\rightarrow$ propene(g)

(e) $HCl(aq) + NaOH$ [illegible] $Cl(aq) + H_2O(l)$

3.32 Calculate the standa[illegible] of formation of N_2O_5 from the following data:

$2\,NO(g) + O_2(g) \rightarrow 2\,NO_2(g)$ Δ_r [illegible] 14.1 kJ mol^{-1}

$4\,NO_2(g) + O_2(g) \rightarrow 2\,N_2O_5(g)$ $\Delta_r H^\ominus$ [illegible] kJ mol^{-1}

$N_2(g) + O_2(g) \rightarrow 2\,NO(g)$ $\Delta_r H^\ominus = +$ [illegible] mol^{-1}

3.33 Heat capacity data can be used to estimate [illegible] reaction enthalpy at one temperature from its value at ano[illegible] the information in the Data section to predict the sta[illegible] reaction enthalpy of $2\,NO_2(g) \rightarrow N_2O_4(g)$ at 100°C from [illegible] value at 25°C.

3.34 Estimate the enthalpy of vaporization of water at 100°C from its value at 25°C (44.01 kJ mol^{-1}) given the constant-pressure heat capacities of 75.29 J K^{-1} mol^{-1} and 33.58 J K^{-1} mol^{-1} for liquid and gas, respectively.

3.35 It is often useful to be able to anticipate, without doing a detailed calculation, whether an increase in temperature will result in a raising or a lowering of a reaction enthalpy. The constant-pressure molar heat capacity of a gas of linear molecules is approximately $\frac{7}{2}R$, whereas that of a gas of nonlinear molecules is approximately $4R$. Decide whether the standard enthalpies of the following reactions will increase or decrease with increasing temperature:

(a) $2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(g)$

(b) $N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g)$

(c) $CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(g)$

3.36 The molar heat capacity of liquid water is approximately $9R$. Decide whether the standard enthalpy of the reactions (a) and (c) in Exercise 3.35 will increase or decrease with a rise in temperature if the water is produced as a liquid.

Projects

The symbol ‡ signifies that calculus is required.

3.37‡ Here we explore Kirchhoff's law (eqn 3.6) in greater detail. (a) Derive a version of Kirchhoff's law for the temperature dependence of the internal energy of reaction. (b) The formulation of Kirchhoff's law given in eqn 3.6 is valid when the difference in heat capacities is independent of temperature over the temperature range of interest. Suppose instead that $\Delta_r C_p^\ominus = a + bT + c/T^2$. Derive a more accurate form of Kirchhoff's law in terms of the parameters a, b, and c. *Hint*: The change in the reaction enthalpy for an infinitesimal change in temperature is $\Delta_r C_p^\ominus dT$. Integrate this expression between the two temperatures of interest.

3.38 Here we explore the thermodynamics of carbohydrates as biological fuels. It is useful to know that glucose and fructose are simple sugars with the molecular formula $C_6H_{12}O_6$. Sucrose (table sugar) is a complex sugar with molecular formula $C_{12}H_{22}O_{11}$ that consists of a glucose unit covalently bound to a fructose unit (a water molecule is eliminated as a result of the reaction between glucose and fructose to form sucrose). There are no dietary recommendations for consumption of carbohydrates. Some nutritionists recommend [illegible] that are largely devoid of carbohydrates, with most of [illegible] energy needs being met by fats. However, the most [illegible] diets are those in which at least 65 per cent of our fo[illegible] come from carbohydrates. (a) A $\frac{3}{4}$-cup serving of pasta [illegible] 40 g of carbohydrates. What percentage of the daily [illegible] requirement for a person on a 2200 Calorie diet (1 Cal [illegible] es this serving represent? (b) The mass of a typical g[illegible] et is 2.5 g. Calculate the energy released as hea[illegible] cose tablet is burned in air. (c) To what height could yo[illegible] the energy a glucose tablet provides assuming 25 [illegible] ergy is available for work? (d) Is the standard enthalp[illegible] ustion of glucose likely to be higher or lower at [illegible] ature than at 25°C? (e) Calculate the energy relea[illegible] en a typical table sugar cube of mass 1.5 g is burned [illegible] To what height could you climb on the energy a table[illegible] provides assuming 25 per cent of the energy is avai[illegible]

Entropy

Box 4.1 Heat engines, refrigerators, and heat pumps

The Gibbs energy

CHECKLIST OF KEY IDEAS
TABLE OF KEY EQUATIONS
QUESTIONS AND EXERCISES

Entropy

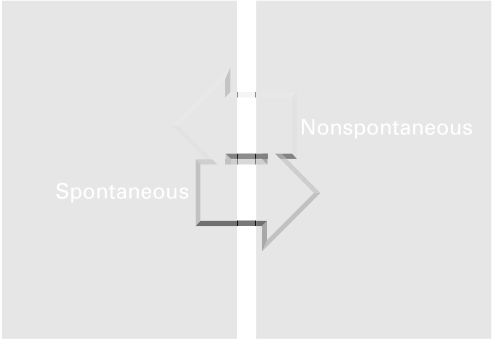


Fig. 4.1

4.1 The direction of spontaneous change

Fig. 4.2

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

A brief illustration

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{100 \times 10^3\ \text{J}}{273\ \text{K}} = +366\ \text{J K}^{-1}$$

$$\Delta S = \frac{100 \times 10^3\ \text{J}}{373\ \text{K}} = +268\ \text{J K}^{-1}$$

A note on good practice

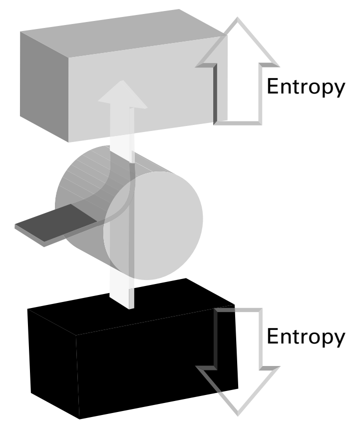
$$\Delta S_{\text{total}} = -\frac{|q|}{T_{\text{hot}}} + \frac{|q'|}{T_{\text{cold}}}$$

$$|q'| = \frac{T_{\text{cold}}}{T_{\text{hot}}} \times |q|$$

$$\eta = \frac{\text{work produced}}{\text{heat absorbed}} = \frac{|q| - |q'|}{|q|} = 1 - \frac{|q'|}{|q|}$$

$$= 1 - \frac{T_{\text{cold}}}{T_{\text{hot}}}$$

$$\eta = 1 - \frac{293\ \text{K}}{473\ \text{K}} = 1 - \frac{293}{473} = 0.381$$



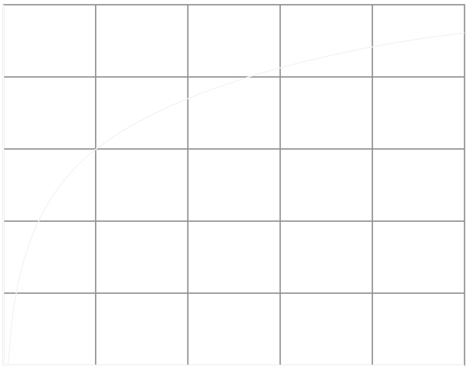
The flow of energy as heat from a cold source to a hot sink becomes feasible if work is provided to add to the energy stream. Then the increase in entropy of the hot sink can be made to cancel the entropy decrease of the hot source.

world at a temperature T_{hot} is $+|q'|/T_{\text{hot}}$. The total change in entropy would be negative if $|q'| = |q|$, and the refrigerator would not work. However, if we increase the flow of energy into the warm exterior by doing work on the refrigerator, then the entropy change of the warm exterior can be increased to the point at which it overcomes the decrease in entropy of the cold interior, and the refrigerator operates. The calculation of the maximum efficiency of this process is left as an exercise (see Project 4.35a).

A heat pump is simply a refrigerator, but in which we are more interested in the supply of heat to the exterior than the cooling achieved in the interior. You are invited to show (see Project 4.35b), that the efficiency of a perfect heat pump, as measured by the heat produced divided by the work done, also depends on the ratio of the two temperatures.

4.3 The entropy change accompanying expansion

$$\Delta S = nR \ln \frac{V_{\text{f}}}{V_{\text{i}}}$$



4.4 The entropy change accompanying heating

$$\Delta S = C \ln \frac{T_f}{T_i}$$

$$q_{rev} = nRT \ \ln \frac{V_f}{V_i}$$

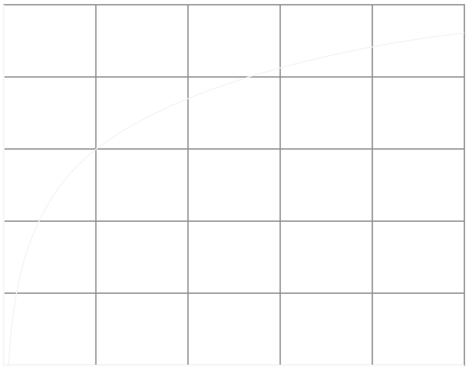


Fig. 4.5

Derivation 4.2

The variation of entropy with temperature

Equation 4.1 refers to the transfer of heat to a system at a temperature T. In general, the temperature changes as we heat a system, so we cannot use eqn 4.1 directly. Suppose, however, that we transfer only an infinitesimal energy, dq, to the system, then there is only an infinitesimal change in temperature and we introduce negligible error if we keep the temperature in the denominator of eqn 4.1 equal to T during that transfer. As a result, the entropy increases by an infinitesimal amount dS given by

$$\mathrm{d}S = \frac{\mathrm{d}q_{\mathrm{rev}}}{T}$$

To calculate dq, we recall from Section 2.4 that the heat capacity C is

$$C = \frac{\overbrace{q}^{\text{The supply of heat}}}{\underbrace{\Delta T}_{\text{The rise in temperature}}}$$

that results in

where ΔT is the macroscopic change in temperature. For the case of an infinitesimal change dT, we write

$$C = \frac{\overbrace{\mathrm{d}q}^{\text{The infinitesimal supply of heat}}}{\underbrace{\mathrm{d}T}_{\text{The infinitesimal rise in temperature}}}$$

that results in

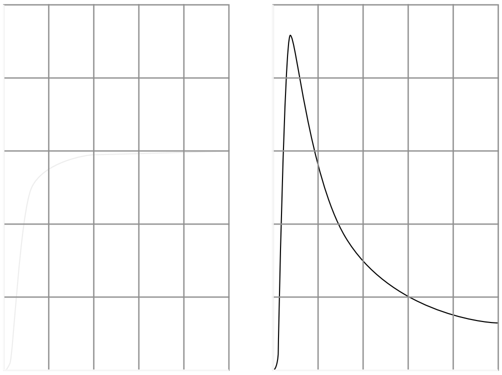
$$\mathrm{d}S = \frac{C\mathrm{d}T}{T}$$

$$\frac{C\mathrm{d}T}{T}$$

Self-test 4.2

Calculate the change in molar entropy when hydrogen gas is heated from 20°C to 30°C at constant volume. ($C_{V,\mathrm{m}} = 22.44\ \mathrm{J\ K^{-1}\ mol^{-1}}$.)

[*Answer:* $+0.75\ \mathrm{J\ K^{-1}\ mol^{-1}}$]



4.5 The entropy change accompanying a phase transition

$$\Delta_{\mathrm{fus}}S = \frac{\Delta_{\mathrm{fus}}H(T_{\mathrm{f}})}{T_{\mathrm{f}}}$$

$$\frac{C\mathrm{d}T}{T}$$

$$\Delta_{\mathrm{vap}}S = \frac{\Delta_{\mathrm{vap}}H(T_{\mathrm{b}})}{T_{\mathrm{b}}}$$

A brief illustration

Then use eqn 4.7 and data from Table 3.1 to calculate the entropy of transition at 100°C. Next, calculate the change in entropy for cooling the vapour from 100°C to 25°C (using eqn 4.3 again, but now with data for the vapour from Table 2.1). Finally, add the three contributions together. The steps may be hypothetical.

Solution From eqn 4.3 with data for the liquid from Table 2.1:

$$\Delta S_1 = C_{p,\mathrm{m}}(\mathrm{H_2O,\ liquid})\ln\frac{T_\mathrm{f}}{T_\mathrm{i}}$$

$$= (75.29\ \mathrm{J\ K^{-1}\ mol^{-1}})\times\ln\frac{373\ \mathrm{K}}{298\ \mathrm{K}}$$

$$= +16.9\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

From eqn 4.7 and data from Table 3.1:

$$\Delta S_2 = \frac{\Delta_\mathrm{vap}H(T_\mathrm{b})}{T_\mathrm{b}} = \frac{4.07\times10^4\ \mathrm{J\ mol^{-1}}}{373\ \mathrm{K}}$$

$$= +109\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

From eqn 4.3 with data for the vapour from Table 2.1:

$$\Delta S_3 = C_{p,\mathrm{m}}(\mathrm{H_2O,\ vapour})\ln\frac{T_\mathrm{f}}{T_\mathrm{i}}$$

$$= (33.58\ \mathrm{J\ K^{-1}\ mol^{-1}})\times\ln\frac{298\ \mathrm{K}}{373\ \mathrm{K}}$$

$$= -7.54\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

The sum of the three entropy changes is the entropy of transition at 25°C:

$$\Delta_\mathrm{vap}S\,(298\ \mathrm{K}) = \Delta S_1 + \Delta S_2 + \Delta S_3 = +118\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

Self-test 4.1

Calculate the entropy of vaporization of benzene at 25°C from the following data: $T_\mathrm{b} = 353.2\ \mathrm{K}$, $\Delta_\mathrm{vap}H^\ominus(T_\mathrm{b}) = 30.8\ \mathrm{kJ\ mol^{-1}}$, $C_{p,\mathrm{m}}(\mathrm{l}) = 136.1\ \mathrm{J\ K^{-1}\ mol^{-1}}$, $C_{p,\mathrm{m}}(\mathrm{g}) = 81.6\ \mathrm{J\ K^{-1}\ mol^{-1}}$.

[*Answer*: $96.4\ \mathrm{J\ K^{-1}\ mol^{-1}}$]

4.6 Entropy changes in the surroundings

$$\Delta S_\mathrm{sur} = \frac{q_\mathrm{sur,rev}}{T}$$

$$\Delta S_\mathrm{sur} = \frac{q_\mathrm{sur}}{T}$$

$$\Delta S_\mathrm{sur} = \frac{q_\mathrm{sur}}{T} = \frac{86\,400\times100\ \mathrm{J}}{293\ \mathrm{K}} = +2.95\times10^4\ \mathrm{J\ K^{-1}}$$

Self-test 4.7

Suppose a small reptile operates at 0.50 W. What entropy does it generate in the course of a day in the water in the lake that it inhabits, where the temperature is 15°C?

[*Answer*: $+150\ \mathrm{J\ K^{-1}}$]

$$\Delta S_{\text{sur}} = -\frac{q}{T}$$

A brief illustration

4.7 Absolute entropies and the Third Law of thermodynamics

A brief comment

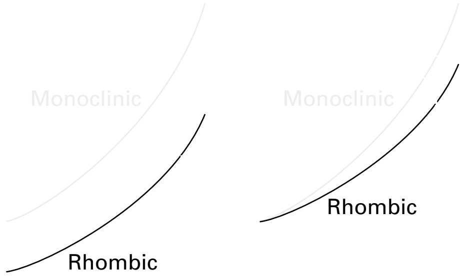


Fig. 4.8

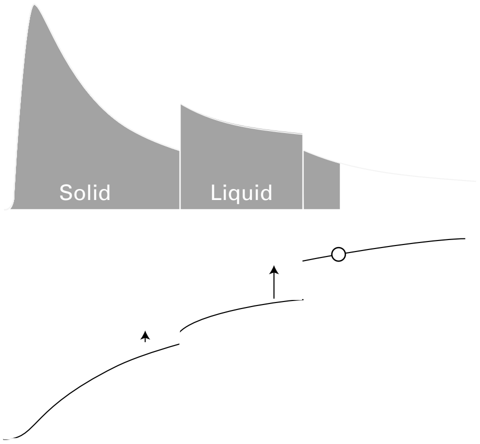


Fig. 4.10

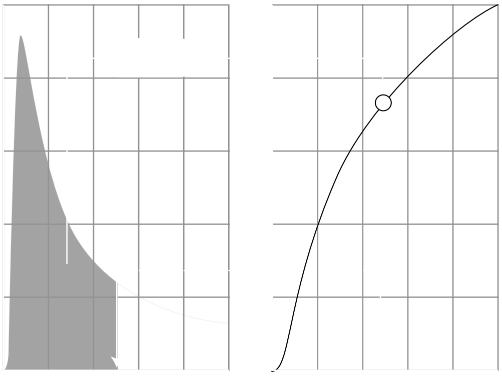


Fig. 4.9

ΔS_m for the change in temperature from T_f to T_i

Eqn 4.4

Set $T_f = T$

Set $T_i = 0$

$C_{p,m}$

Set $S_m(0) = 0$

$\frac{1}{3}$

$\frac{1}{3}$ $\Big|_0^T$

4.8 The statistical entropy

A brief comment

A brief illustration

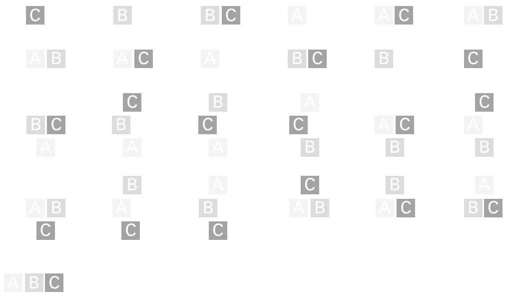


Fig. 4.11

Fig. 4.12

4.9 Residual entropies

Fig. 4.13

Fig. 4.14

Fig. 4.15

A brief illustration

4.10 The standard reaction entropy

A brief illustration

A note on good practice

Use $-572\ \text{kJ mol}^{-1} = -572 \times 10^3\ \text{J mol}^{-1}$

Self-test 4.8

(a) Calculate the standard reaction entropy for $N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g)$ at 25°C. (b) What is the change in entropy when 2 mol H_2 reacts?

[*Answer:* (a) (Using values from Table 4.2) $-198.7\ \text{J K}^{-1}\ \text{mol}^{-1}$; (b) $-132.5\ \text{J K}^{-1}$]

From (–)(–) = (+)

4.11 The spontaneity of chemical reactions

The Gibbs energy

4.12 Focusing on the system

Entropy change of system + Entropy change of surroundings

Use eqn 4.10

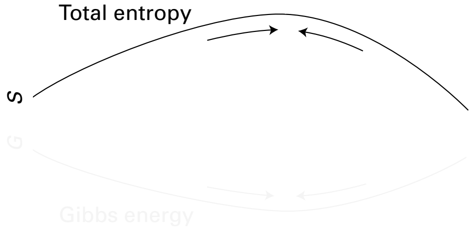


Fig. 4.16

4.13 Properties of the Gibbs energy

Derivation 4.4

Use $\mathrm{d}H = \mathrm{d}U + p\mathrm{d}V$

Use $\mathrm{d}U = \mathrm{d}w + \mathrm{d}q$

Use $\mathrm{d}w = -p_{\mathrm{ex}}\mathrm{d}V + \mathrm{d}w'$

A brief illustration

$$n = \frac{3.0 \times 9.81 \times 1.0 \times 10^{-1}\ \text{J}}{2.828 \times 10^{6}\ \text{J mol}^{-1}} = \frac{3.0 \times 9.81 \times 1.0 \times 10^{-7}}{2.828}\ \text{mol}$$

$$m = nM = \left(\frac{3.0 \times 9.81 \times 1.0 \times 10^{-7}}{2.828}\ \text{mol}\right) \times (180\ \text{g mol}^{-1})$$

☐ **1**

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Description	Equation	Comment

Discussion questions

4.1

4.2

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Exercises

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4.16

4.17

4.18

4.19 Octane is typical of the components of gasoline. Estimate (a) the entropy of vaporization, (b) the enthalpy of vaporization of octane, which boils at 126°C at 1 atm.

4.20 Suppose that the weight of a configuration of N molecules in a gas of volume V is proportional to V^N. Use Boltzmann's formula to deduce the change in entropy when the gas expands isothermally.

4.21 An $FClO_3$ molecule can adopt four orientations in the [illegible] with negligible difference in energy. What is its residual entropy?

4.22 [illegible] performing a calculation, estimate whether the standard [illegible] of the following reactions are positive or negative:

(a) Ala—Ser—[illegible]—Gly—Arg—Ser $\xrightarrow{\text{trypsin}}$ Ala—Ser—Th[illegible]ly—Arg

(b) $N_2(g) + 3\ H_2(g) \rightarrow$ [illegible]

(c) $ATP^{4-}(aq) + 2\ H_2O(l) \rightarrow$ [illegible]$(aq) + HPO_4^{2-}(aq) + H_3O^+(aq)$

4.23 Calculate the standard reaction [illegible] at 298 K of:

(a) $2\ CH_3CHO(g) + O_2(g) \rightarrow 2\ CH_3COO$[illegible]

(b) $2\ AgCl(s) + Br_2(l) \rightarrow 2\ AgBr(s) + Cl_2(g)$

(c) $Hg(l) + Cl_2(g) \rightarrow HgCl_2(s)$

(d) $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

(e) $C_{12}H_{22}O_{11}(s) + 12\ O_2(g) \rightarrow 12\ CO_2(g) + 11\ H_2O(l)$

4.24 Suppose that when you exercise, you consume 100 g of glucose and that all the energy released as heat remains in your body at 37°C. What is the change in entropy of your body?

4.25 Calculate the standard reaction entropy and the change in entropy of the surroundings (at 298 K) of the reaction $N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$.

4.26 The constant-pressure molar heat capacities of linear gaseous molecules are approximately $\frac{7}{2}R$ and those of nonlinear gaseous molecules are approximately $4R$. Estimate the change in standard reaction entropy of the following two reactions when the temperature is increased by 10 K at constant pressure:

(a) $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)$

(b) $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g)$

4.27 Use the information you deduced in Exercise 4.26 to calculate the standard Gibbs energy of reaction of $N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$.

4.28 In a particular biological reaction taking place in the body at 37°C, the change in enthalpy was -135 kJ mol^{-1} and the change in entropy was -136 J K^{-1} mol^{-1}. (a) Calculate the change in Gibbs energy. (b) Is the reaction spontaneous? (c) Calculate the total change in entropy of the system and the surroundings.

4.29 The change in Gibbs energy that accompanies the oxidation of $C_6H_{12}O_6(s)$ to carbon dioxide and water vapour at 25°C is -2828 kJ mol^{-1}. How much glucose does a person of mass 65 kg need to consume to climb through 10 m?

4.30 Fuel cells are being developed that make use of organic fuels; in due course they might be used to power tiny intraveinous machines for carrying out repairs on diseased tissue. What is the maximum nonexpansion work that can be obtained from the metabolism of 1.0 mg of sucrose to carbon dioxide and water?

4.31 The formation of glutamine from glutamate and ammonium ions requires 14.2 kJ mol^{-1} of energy input. It is driven by the hydrolysis of ATP to ADP mediated by the enzyme glutamine synthetase. (a) Given that the change in Gibbs energy for the hydrolysis of ATP corresponds to $\Delta_r G = -31$ kJ mol^{-1} under the conditions prevailing in a typical cell, can the hydrolysis drive the formation of glutamine? (b) How many moles of ATP must be hydrolysed to form 1 mol of glutamine?

4.32 The hydrolysis of acetyl phosphate has $\Delta_r G = -42$ kJ mol^{-1} under typical biological conditions. If acetyl phosphate were to be synthesized by coupling to the hydrolysis of ATP, what is the minimum number of ATP molecules that would need to be involved?

4.33 Suppose that the radius of a typical cell is 10 μm and that inside it 10^6 ATP molecules are hydrolysed each second. What is the power density of the cell in watts per cubic metre ([illegible] = 1 J s^{-1}). A computer battery delivers about 15 W and has a volume of 100 cm^3. Which has the greater power density, the cell or the battery? (For data, see Exercise 4.32.)

Projects

The symbol [illegible] that calculus is required.

4.34‡ Equation 4.3 [illegible] the assumption that the heat capacity is independent of temperature. Suppose, instead, that the heat capacity depends on temperature as $C = a + bT + c/T^2$ (as was explored in Se[illegible]). Find an expression for the change of entropy accompanying heating from T_i to T_f. *Hint:* See Derivation 4.2.

4.35 Here we explore the thermodynamics of refrigerators and heat pumps. (a) Show that the best *coefficient of cooling performance*, c_{cool}, the ratio of the energy extracted as heat at T_{cold} to the energy supplied as work in a perfect refrigerator, is $c_{cool} = T_{cold}/(T_{hot} - T_{cold})$. What is the maximum [illegible] extraction of energy as heat in a domestic refrigerator rated at 200 W operating at 5.0°C in a room at 22°C? (b) Show that the best *coefficient of heating performance*, c_{warm}, the ratio of the energy produced as heat at T_{hot} to the energy supplied as work in a perfect heat pump, is $c_{warm} = T_{hot}/(T_{hot} - T_{cold})$. What is the maximum power rating of a heat pump that consumes power at 2.5 kW operating at 18.0°C and warming a room at 22°C?

The thermodynamics of transition

Phase diagrams

Box 5.1 Supercritical fluids

CHECKLIST OF KEY IDEAS
TABLE OF KEY EQUATIONS
QUESTIONS AND EXERCISES

The thermodynamics of transition

5.1 The condition of stability

Derivation 5.1

G changes to *H* changes to *T* changes to *S* changes to

$dH = dU + pdV + Vdp$

$dU = TdS - pdV$

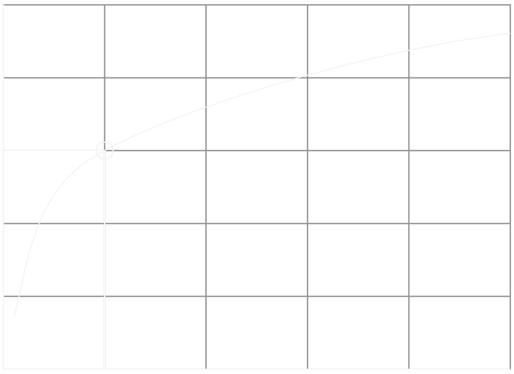
Self-test 5.1

The Gibbs energy of transition from metallic white tin (α-Sn) to nonmetallic grey tin (β-Sn) is +0.13 kJ mol^{-1} at 298 K. Which is the reference state (Section 3.5) of tin at this temperature?

[*Answer:* white tin]

5.2 The variation of Gibbs energy with pressure

$$G_\mathrm{m}(p_\mathrm{f}) = G_\mathrm{m}(p_\mathrm{i}) + RT\ln\frac{p_\mathrm{f}}{p_\mathrm{i}}$$



Perfect gas, $V_\mathrm{m} = RT/p$

Constant temperature

$$\frac{\mathrm{d}x}{x} = \ln x + \text{constant}$$

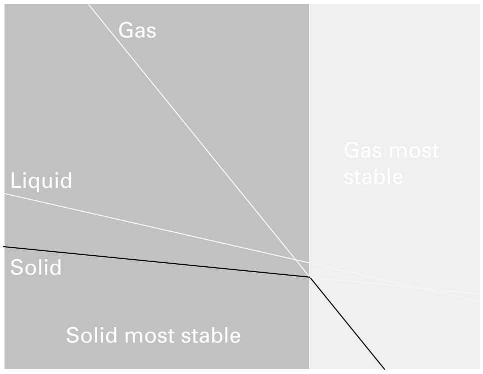


Fig. 5.4

Phase diagrams

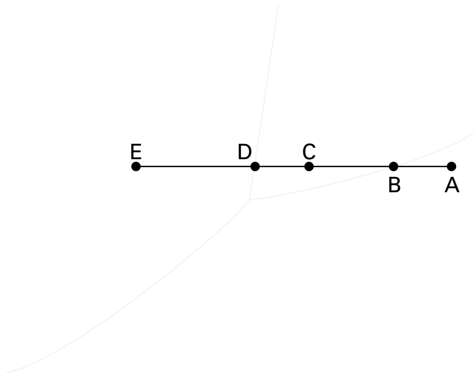


Fig. 5.5

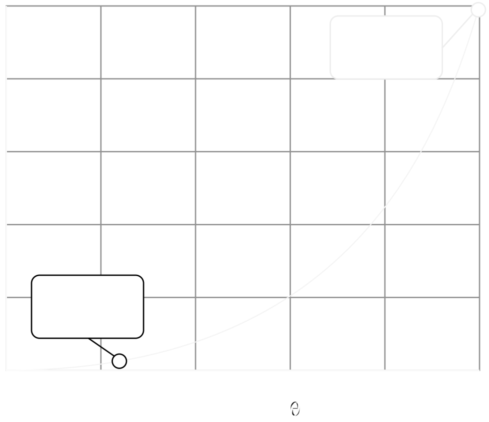


Fig. 5.7

5.4 Phase boundaries

Self-test 5.2

What phase changes would be observed when a pressure of 7.0 kPa is applied to a sample of water in equilibrium with its vapour at 25°C, when its vapour pressure is 3.2 kPa?

[*Answer:* The sample condenses entirely to liquid.]

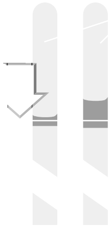


Fig. 5.6

$$\Delta p = \frac{\Delta_{\mathrm{trs}} H}{T\Delta_{\mathrm{trs}} V} \times \Delta T$$

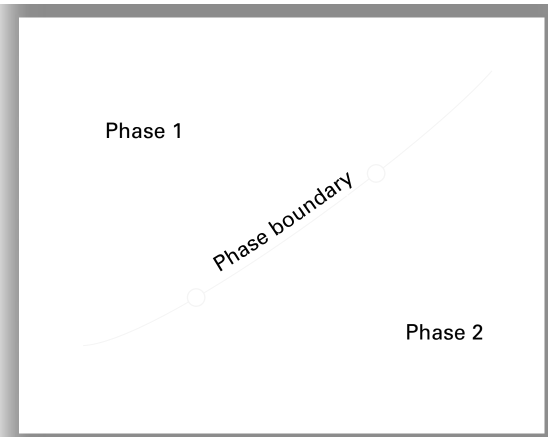
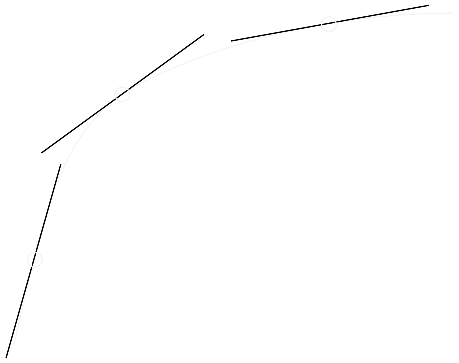


Fig. 5.9 At equilibrium, two phases have the same molar Gibbs energy. When the temperature is changed, for the two phases to remain in equilibrium, the pressure must be changed so that the Gibbs energies of the two phases remain equal.

$$\mathrm{d}p = \frac{\Delta_{\mathrm{trs}}S}{\Delta_{\mathrm{trs}}V}\,\mathrm{d}T$$

$$\mathrm{d}p = \frac{\Delta_{\mathrm{trs}}H}{T\Delta_{\mathrm{trs}}V}\,\mathrm{d}T$$

$$\Delta(\ln p) = \frac{\Delta_{\mathrm{vap}}H}{RT^2} \times \Delta T$$



$$\ln p' = \ln p + \frac{\Delta_{\text{vap}}H}{R}\left(\frac{1}{T} - \frac{1}{T'}\right)$$

Derivation 5.5

The Clausius–Clapeyron equation

For the liquid–vapour boundary the 'trs' label in the exact form of the Clapeyron equation, eqn 5.5b in Derivation 5.4, becomes 'vap' and that equation can be written

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\text{vap}}H}{T\Delta_{\text{vap}}V}$$

Because the molar volume of a gas is much larger than the molar volume of a liquid, the volume of vaporization, $\Delta_{\text{vap}}V = V_m(\text{g}) - V_m(\text{l})$, is approximately equal to the molar volume of the gas itself. Therefore, to a good approximation,

$\Delta_{\text{vap}}V = V_m(\text{g}) - V_m(\text{l})$ $\quad$ $V_m(\text{g}) >> V_m(\text{l})$

To make further progress, we can treat the vapour as a perfect gas and write its molar volume as $V_m = RT/p$. Then

$V_m(\text{g}) = RT/p$

and therefore

$$\frac{1}{p}\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\text{vap}}H}{RT^2}$$

A standard result of calculus is d ln x/dx = 1/x, and therefore (by multiplying both sides by dx), dx/x = d ln x. It follows that we may write the last equation as the Clausius–Clapeyron equation:

$$\frac{\mathrm{d}\ln p}{\mathrm{d}T} = \frac{\Delta_{\text{vap}}H}{RT^2}$$

Provided the range of temperature and pressure is small, the infinitesimal changes d ln p and dT can be replaced by measurable changes, and we obtain eqn 5.6.

To obtain the explicit expression for the vapour pressure at any temperature (eqn 5.7) we rearrange the equation we have just derived into

$$\mathrm{d}\ln p = \frac{\Delta_{\text{vap}}H}{RT^2}\,\mathrm{d}T$$

and integrate both sides. If the vapour pressure is p at a temperature T and p' at a temperature T', this integration takes the form

$$\int_{\ln p}^{\ln p'} \mathrm{d}\ln p = \int_{T}^{T'} \frac{\Delta_{\text{vap}}H}{RT^2}\,\mathrm{d}T$$

A note on good practice When setting up an integration, make sure the limits match on each side of the expression. Here, the lower limits are ln p on the left and T on the right, and the upper limits are ln p' and T', respectively.

The integral on the left evaluates to ln p' – ln p, which simplifies to ln(p'/p). To evaluate the integral on the right, we suppose that the enthalpy of vaporization is constant over the temperature range of interest, so together with R it can be taken outside the integral:

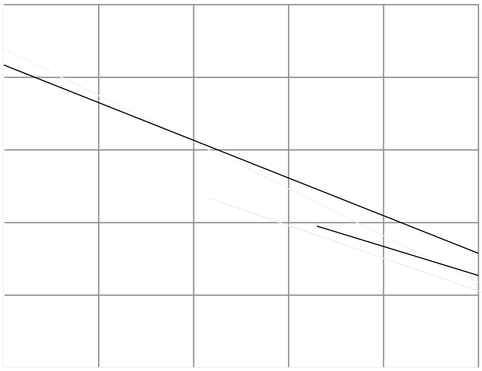
which is eqn 5.7. To obtain this result we have used the standard integral

$$\int \frac{\mathrm{d}x}{x^2} = -\frac{1}{x} + \text{constant}$$

Another note on good practice Keep a note of any approximations made in a derivation. In this lengthy pair of derivations we have made three: (1) the molar volume of a gas is much greater than that of a liquid, (2) the vapour behaves as a perfect gas, (3) the enthalpy of vaporization is independent of temperature in the range of interest. Approximations limit the ways in which an expression may be used to solve problems.

$$\ln p = \ln p' + \frac{\Delta_{\text{vap}}H}{RT'} - \frac{\Delta_{\text{vap}}H}{RT}$$

$$\log p = A - \frac{B}{T}$$



A brief illustration

$$\log(p/\mathrm{kPa}) = 7.0871 - \frac{1785\ \mathrm{K}}{T}$$

A note on good practice

Box 5.1 Supercritical fluids

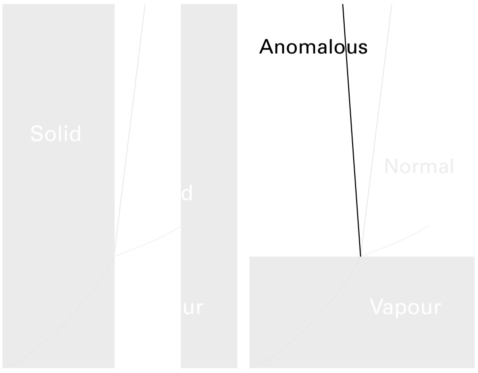


Fig. 5.13

5.7 The phase rule

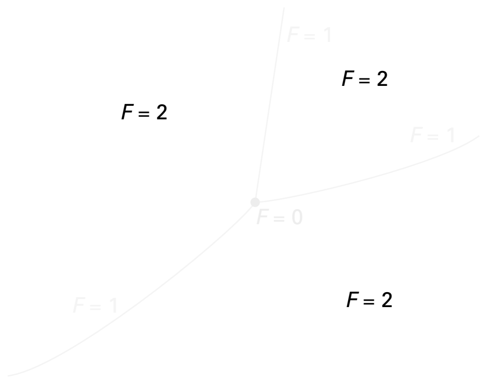


Fig. 5.14

5.8 Phase diagrams of typical materials

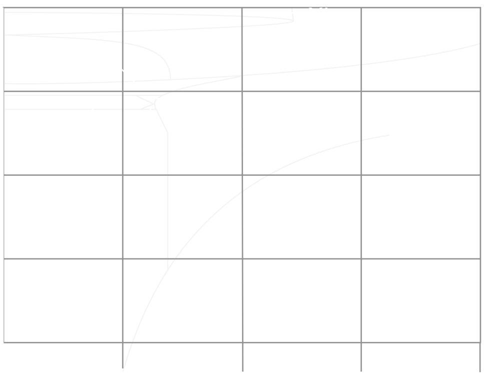


Fig. 5.15

Self-test 5.4

What is the minimum pressure at which liquid is the thermodynamically stable phase of water at 25°C?

[*Answer:* 3.17 kPa (see Fig. 5.7)]

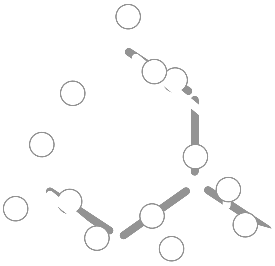


Fig. 5.17

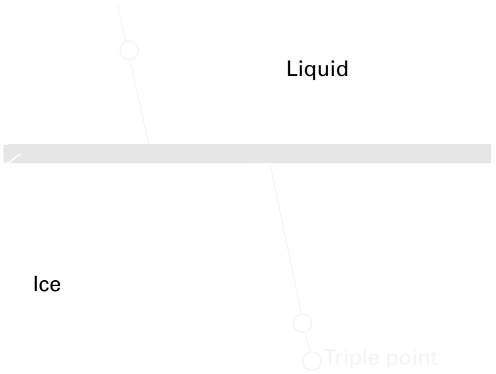


Fig. 5.16

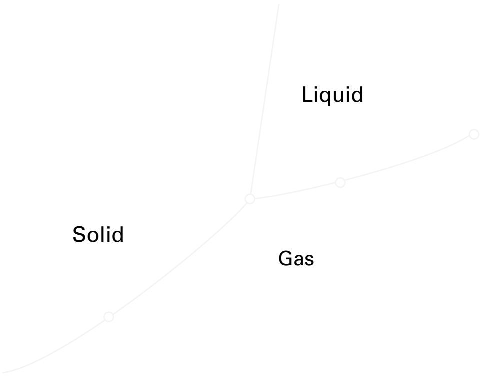


Fig. 5.18

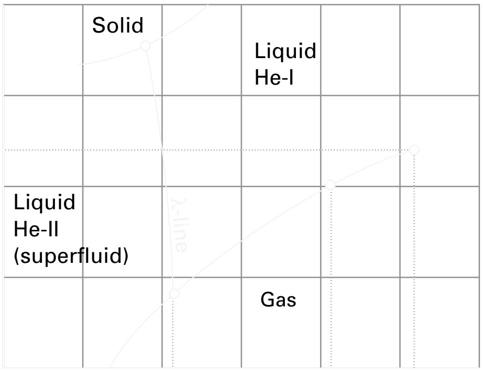


Fig. 5.19

5.9 The molecular structure of liquids

☐ **1**

☐ **2**

☐ **3**

☐ **4**

☐ **5**

☐ **6**

☐ **7**

☐ **8**

☐ **9**

☐ **10**

Property	Equation	Comment

Discussion questions

5.1

5.2

5.3

5.4

5.5

5.6

Exercises

5.1 The standard Gibbs energy of formation of rhombic sulfur is zero and that of monoclinic sulfur is +0.33 kJ mol^{-1} at 25°C. Which polymorph is the more stable at that temperature?

5.2 The density of rhombic sulfur is 2.070 g cm^{-3} and that of monoclinic sulfur is 1.957 g cm^{-3}. Can the application of pressure be expected to make monoclinic sulfur more stable than [illegible] sulfur?

5.3 [illegible] the difference in molar Gibbs energy due to pressure a[illegible] water (density 1.03 g cm^{-3}), at the ocean surface and [illegible] [illegible]danao trench (depth 11.5 km), (b) mercury (density 13.[illegible] at the top and bottom of the column in a barometer. [illegible] the very top, the pressure on the mercury is equal to [illegible] pressure of mercury, which at 20°C is 160 mPa.)

5.4 The density of the fat [illegible] 0.95 g cm^{-3}. Calculate the change in molar Gibbs [illegible] tristearin when a deep-sea creature is brought to the [illegible] p = 1.0 atm) from a depth of 1.5 km. To calculate the hy[illegible] pressure, take the mean density of water to be 1.03 g c[illegible]

5.5 Calculate the change in molar Gibbs en[illegible] carbon dioxide (treated as a perfect gas) at 20°C when [illegible] is changed isothermally from 1.0 bar to (a) 3.0 bar, [illegible] 10^{-4} atm, its partial pressure in dry air at sea level.

5.6 A sample of water vapour at 200°C is compressed isothermally from 350 cm^3 to 120 cm^3. What is the change in its molar Gibbs energy?

5.7 The standard molar entropy of rhombic sulfur is 31.80 J K^{-1} mol^{-1} and that of monoclinic sulfur is 32.6 J K^{-1} mol^{-1}. (a) Can an increase in temperature be expected to make monoclinic sulfur more stable than rhombic sulfur? (b) If so, at what temperature will the transition occur at 1 bar? (See Exercise 5.2 for data.)

5.8 The standard molar entropy of benzene is 173.3 J K^{-1} mol^{-1}. Calculate the change in its standard molar Gibbs energy when benzene is heated from 25°C to 45°C.

5.9 The standard molar entropies of water ice, liquid, and vapour are 37.99, 69.91, and 188.83 J K^{-1} mol^{-1}, respectively. On a single graph, show how the Gibbs energies of each of these phases varies with temperature.

5.10 An open vessel containing (a) water, (b) benzene, (c) mercury stands in a laboratory measuring 5.0 m × 4.3 m × 2.2 m at 25°C. What mass of each substance will be found in the air if there is no ventilation? (The vapour pressures are (a) 2.3 kPa, (b) 10 kPa, (c) 0.30 Pa.)

5.11 (a) Use the Clapeyron equation to estimate the slope of the solid–liquid phase boundary of water given the enthalpy of fusion is 6.008 kJ mol^{-1} and the densities of ice and water at 0°C are 0.916 71 and 0.999 84 g cm^{-3}, respectively. *Hint*: Express the entropy of fusion in terms of the enthalpy of fusion and the melting point of ice. (b) Estimate the pressure required to lower the melting point of ice by 1°C.

5.12 Given the parametrization of the vapour pressure in eqn 5.7 and Table 5.1, what is (a) the enthalpy of vaporization, (b) the normal boiling point of hexane?

5.13 Suppose we wished to express the vapour pressure in eqn 5.7 in torr. What would be the values of A and B for methylbenzene? See Table 5.1 for data.

5.14 The vapour pressure of mercury is at 20°C is 160 mPa; what is its vapour pressure at 40°C given that its enthalpy of vaporization is 59.30 kJ mol^{-1}?

5.15 The vapour pressure of pyridine is 50.0 kPa at 365.7 K and the normal boiling point is 388.4 K. What is the enthalpy of vaporization of pyridine?

5.16 Estimate the boiling point of benzene given that its vapour pressure is 20 kPa at 35°C and 50.0 kPa at 58.8°C.

5.17 A saturated solution of Na_2SO_4, with excess of the solid, is present at equilibrium with its vapour in a closed vessel. (a) How many phases and components are present? (b) What is the number of degrees of freedom of the system? Identify the independent variables.

5.18 Suppose that the solution referred to in Exercise 5.17 is not saturated. (a) How many phases and components are present? (b) What is the number of degrees of freedom of the system? Identify the independent variables.

5.19 [illegible] cold, dry morning after a frost, the temperature was [illegible] the partial pressure of water in the atmosphere fell to [illegible] the frost sublime? What partial pressure of water [illegible] that the frost remained?

5.20 (a) Refer [illegible] 15 and describe the changes that would be observe[illegible] water vapour at 1.0 bar and 400 K is cooled at constan[illegible] to 260 K. (b) Suggest the appearance of a plot [illegible] against time if energy is removed at a constant [illegible] the relative slopes of the cooling curves, you nee[illegible] that the constant-pressure molar heat capacities [illegible] liquid, and solid are approximately $4R$, $9R$, and [illegible] enthalpies of transition are given in Table 3.1.

5.21 Refer to Fig. 5.15 and describe the cha[illegible] would be observed when cooling takes place at the pre[illegible] triple point.

5.22 Use the phase diagram in Fig. 5.18 to state wha[illegible] be observed when a sample of carbon dioxide, initially at 1.0 atm and 298 K is subjected to the following cycle: (a) constant-pressure heating to 320 K, (b) isothermal compression to 100 atm, (c) constant-pressure cooling to 210 K, (d) isothermal decompression to 1.0 atm, constant-pressure heating to 298 K.

5.23 Infer from the phase diagram for helium in Fig. 5.19 whether helium-I is more dense or less dense than helium-II.

Projects

The symbol ‡ indicates that calculus is required .

5.24‡ Suppose that a gas obeys the van der Waals equation of state with the repulsive effects much greater than the attractive effects (that is, neglect the parameter *a*). (a) Find an expression for the change in molar Gibbs energy when the pressure is changed from p_i to p_f. (b) Is the change greater or smaller than for a perfect gas? (c) Estimate the percentage difference between the van der Waals and perfect gas calculations for carbon dioxide undergoing a change from 1.0 atm to [illegible] atm. (*Hint:* For the first part, use calculus as in Derivation [illegible].)

5.25‡ Equation 5.6 has been derived on the assumption that the enthalpy of vaporization is independent of temperature in the range of interest. Derive an improved version of the equation on the basis that the enthalpy of vaporization has the form $\Delta_{\text{vap}}H = a + bT$.

5.26‡ Here we explore supercritical behaviour in more detail. (a) Show that a substance that is described by the equation of state $p = nRT/V - an^2/V^2 + bn^3/V^3$ shows critical behaviour, and express the critical constants in terms of the parameters *a* and *b*. *Hints:* At the critical point, $\mathrm{d}p/\mathrm{d}V = 0$ and $\mathrm{d}^2p/\mathrm{d}V^2 = 0$; use $\mathrm{d}V^n/\mathrm{d}V = nV^{n-1}$. (b) The use of supercritical fluids for the extraction of a component from a complicated mixture is not restricted to the decaffeination of coffee. Consult library and internet resources and prepare a discussion of the principles, advantages, disadvantages, and current uses of supercritical fluid extraction technology.

The thermodynamic description of mixtures

The thermodynamic description of mixtures

Box 6.1 Gas solubility and respiration

Colligative properties

Phase diagrams of mixtures

Box 6.2 Ultrapurity and controlled impurity

CHECKLIST OF KEY IDEAS
TABLE OF KEY EQUATIONS
QUESTIONS AND EXERCISES

6.1 Partial molar properties

A brief illustration

Derivation 6.1

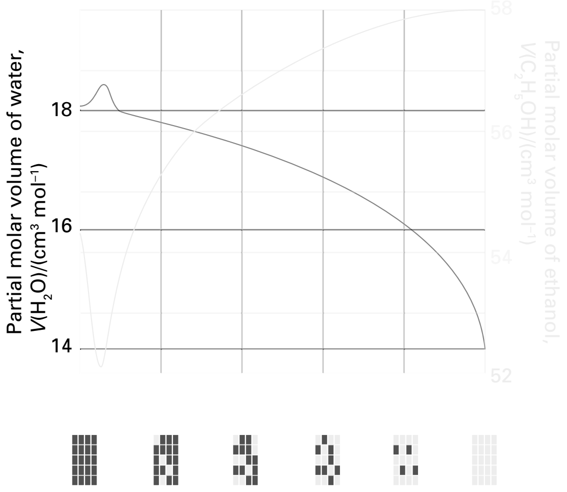


Fig. 6.1

Example 6.2

Strategy

Solution

$$n_{\text{ethanol}} = \frac{50.0\text{ g}}{46.07\text{ g mol}^{-1}} = 1.09\text{ mol}$$

$$n_{\text{water}} = \frac{50.0\text{ g}}{18.02\text{ g mol}^{-1}} = 2.77\text{ mol}$$

Self-test 6.3

Use Fig. 6.1 to calculate the mass density of a mixture of 20 g of water and 100 g of ethanol.

[*Answer:* 0.84 g cm^{-3}]

A brief comment

$$G_{\text{m}}(p_{\text{f}}) = G_{\text{m}}(p_{\text{i}}) + RT\ln\frac{p_{\text{f}}}{p_{\text{i}}}$$

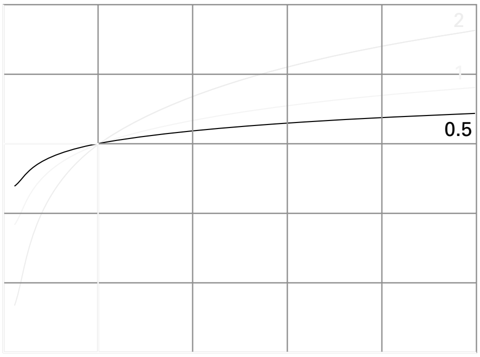


Fig. 6.2

Self-test 6.4

Suppose that the partial pressure of a perfect gas falls from 100 kPa to 50 kPa as it is consumed in a reaction at 25°C. What is the change in chemical potential of the substance?

[*Answer:* -1.7 kJ mol^{-1}]

Derivation 6.2

6.2 Spontaneous mixing

Derivation 6.3

$$\overset{\text{eqn 6.2b}}{G_\mathrm{i}} = n_\mathrm{A}\mu_\mathrm{A} + \overset{\text{eqn 6.4b}}{n_\mathrm{B}\mu_\mathrm{B}}$$

$$= n_\mathrm{A}\{\overset{\text{eqn 6.4b}}{\mu_\mathrm{A}^\ominus} + RT\ln p\} + n_\mathrm{B}\{\mu_\mathrm{B}^\ominus + RT\ln p\}$$

$$\ln x_\mathrm{J}p - \ln p = \overset{\text{Use } \ln a - \ln b = \ln(a/b)}{\ln \frac{x_\mathrm{J}\cancel{p}}{\cancel{p}}} = \ln x_\mathrm{J}$$

$$\Delta G = RT\{\overset{n_\mathrm{A} = nx_\mathrm{A}}{n_\mathrm{A}} \ln x_\mathrm{A} + \overset{n_\mathrm{B} = nx_\mathrm{B}}{n_\mathrm{B}} \ln x_\mathrm{B}\} = nRT\{x_\mathrm{A}\ln x_\mathrm{A} + x_\mathrm{B}\ln x_\mathrm{B}\}$$

Fig. 6.3

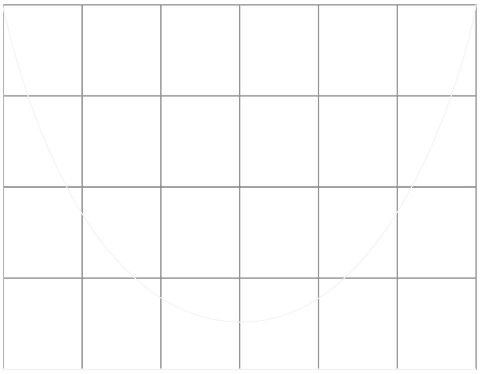


Fig. 6.4

6.3 Ideal solutions

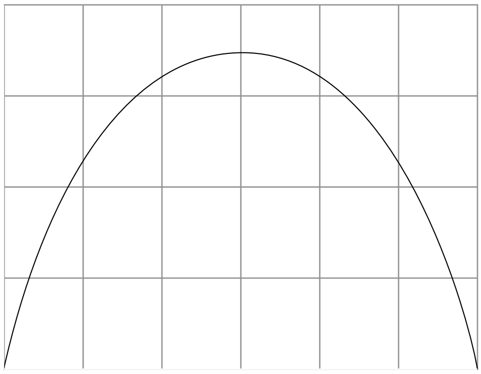


Fig. 6.5

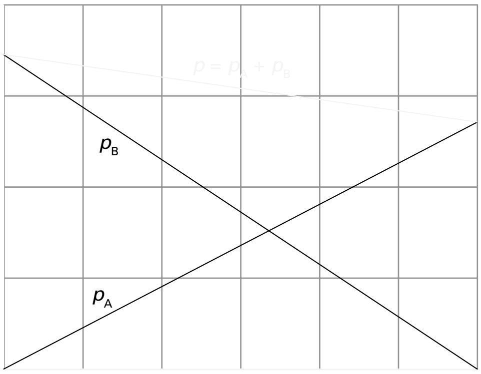


Fig. 6.6

Fig. 6.7

Self-test 6.5

A solution is prepared by dissolving 1.5 mol $C_{10}H_8$ (naphthalene) in 1.00 kg of benzene. The vapour pressure of pure benzene is 12.6 kPa at 25°C. What is the partial vapour pressure of benzene in the solution?

[*Answer:* 11.3 kPa]

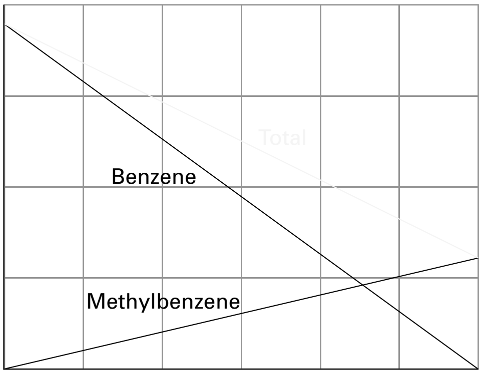


Fig. 6.8

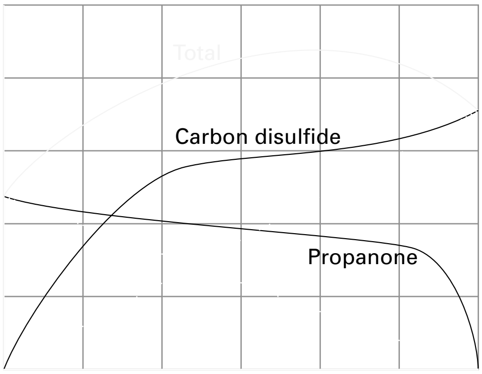


Fig. 6.9

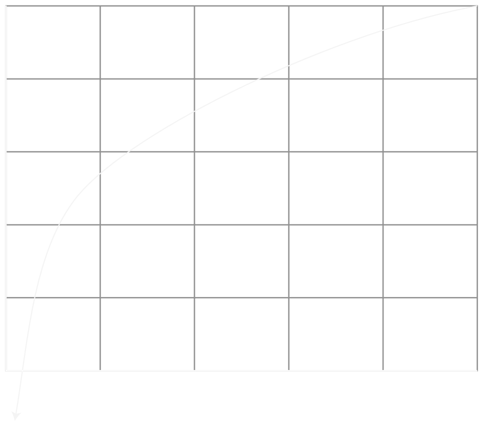


Fig. 6.10

A note on good practice

Derivation 6.4

$p_A = x_A p_A^*$

Use $\ln ab = \ln a + \ln b$

Fig. 6.11

Self-test 6.6

What is the change in chemical potential of benzene at 25°C caused by a solute that is present at a mole fraction of 0.10?

[*Answer:* –0.26 kJ mol^{-1}]

Self-test 6.7

Derive eqn 6.9 by following Derivation 6.3: the initial Gibbs energy of the unmixed components is $G_i = n_A\mu_A^* + n_B\mu_B^*$; after mixing, use the chemical potentials in eqn 6.8.

A note on good practice

6.4 Ideal–dilute solutions

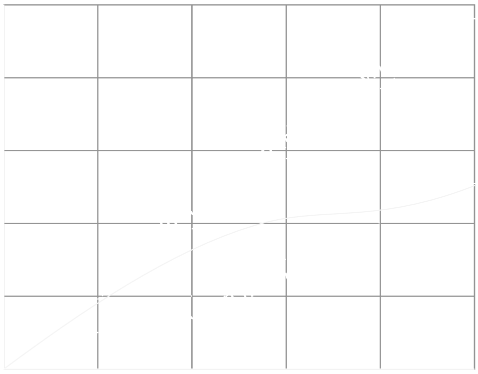


Fig. 6.12

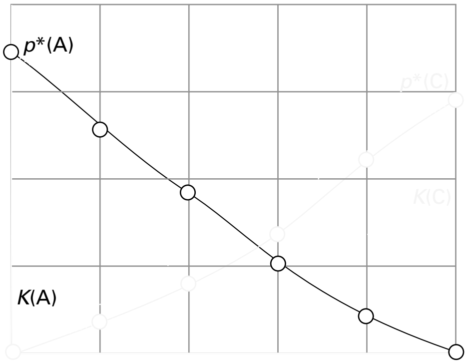


Fig. 6.13

Example 6.3

Strategy

Solution

Self-test 6.8

The vapour pressure of chloromethane at various mole fractions in a mixture at 25°C was found to be as follows:

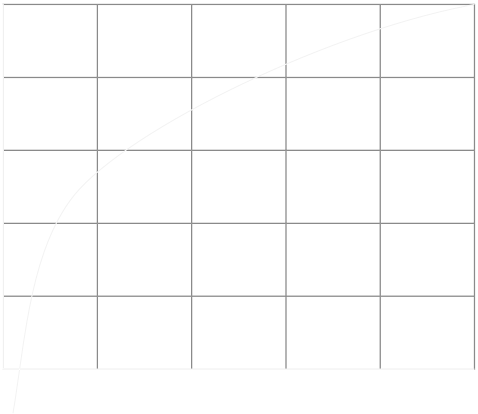
x	0.005	0.009	0.019	0.024
p/Torr	205	363	756	946

Estimate the Henry's law constant.

[*Answer:* 4×10^4 Torr]

A brief illustration

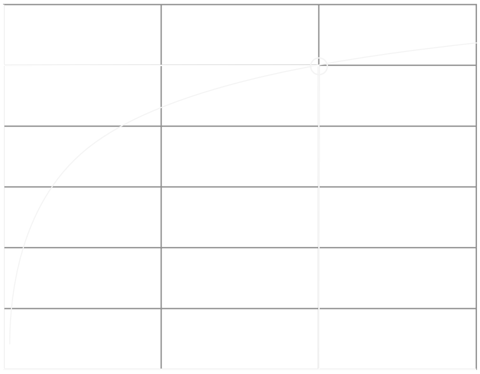
$$[O_2] = \frac{4\times10^{-3}\ \text{g dm}^{-3}}{32\ \text{g mol}^{-1}} = \frac{4\times10^{-3}}{32}\,\text{mol dm}^{-3}$$



$$p_{O_2} = (74.68\ \text{kPa m}^3\ \text{mol}^{-1}) \times \left(\frac{4\times10^{-3}}{32}\ \text{mol dm}^{-3}\right)$$

$$= \frac{74.68\times4\times10^{-3}}{32}\,\frac{\text{kPa m}^3}{\text{dm}^3} = \frac{74.68\times4}{32}\ \text{kPa} = 9\ \text{kPa}$$

A note on good practice



6.5 Real solutions: activities

Table 6.2

*Activities and standard states**

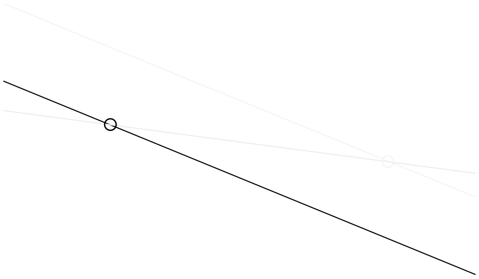
Substance	Standard state	Activity, a
Solid	Pure solid, 1 bar	1
Liquid	Pure liquid, 1 bar	1
Gas	Pure gas, 1 bar	$p/p^{\ominus}$
Solute	Molar concentration of 1 mol dm^{-3}	$[\mathrm{J}]/c^{\ominus}$

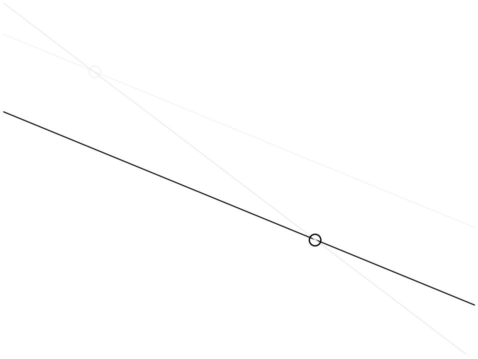
$p^{\ominus} = 1$ bar ($= 10^5$ Pa), $c^{\ominus} = 1$ mol dm^{-3}.

* Activities are for perfect gases and ideal-dilute solutions; all activities are dimensionless.

Colligative properties

6.6 The modification of boiling and freezing points





Vapour remains pure

Solvent mole fraction is now x_A

$$\ln x_A = \frac{\mu_A^*(\mathrm{g}, 1\,\mathrm{atm}, T_b) - \mu_A^*(\mathrm{l}, 1\,\mathrm{atm}, T_b)}{RT_b}$$

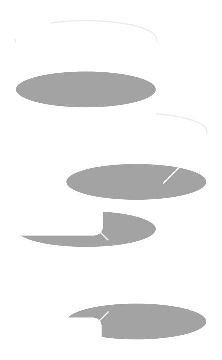


Fig. 6.18 The equilibria between phases and the corresponding relation between chemical potentials of the solvent in solution at (a) the normal boiling point and (b) the normal freezing point.

$$\ln x_A = \frac{G_m(\mathrm{g}, 1\,\mathrm{atm}, T_b) - G_m(\mathrm{l}, 1\,\mathrm{atm}, T_b)}{RT_b}$$

$$= \frac{\Delta_{vap}G(1\ \mathrm{atm},\ T_b)}{RT_b}$$

When $x_A = 1$ (so $\ln x_A = 0$), the pure liquid solvent, the boiling point is T_b^*, and we can write

$$0 = \frac{\Delta_{vap}G(1\ \mathrm{atm},\ T_b^*)}{RT_b^*}$$

The difference between these two equations is

$$\ln x_A = \frac{\Delta_{vap}G(T_b)}{RT_b} - \frac{\Delta_{vap}G(T_b^*)}{RT_b^*}.$$

(For simplicity, we no longer specify the pressure as 1 atm, but remember that that is its value.) Now we use $\Delta G = \Delta H - T\Delta S$ and the approximate temperature independence of ΔH and ΔS to turn this equation into

Use $\Delta_{vap}G(T) = \Delta_{vap}H(T) - T\Delta_{vap}S(T)$ twice

Assume $\Delta_{vap}H$ and $\Delta_{vap}S$ independent of temperature

Now we use $\ln x_A = \ln(1 - x_B) \approx -x_B$ to express this equation as

$$x_B \approx \frac{\Delta_{vap}H}{R}\left(\frac{1}{T_b^*} - \frac{1}{T_b}\right) = \frac{\Delta_{vap}H}{R}\left(\frac{T_b - T_b^*}{T_b^* T_b}\right)$$

A brief comment The series expansion of a natural logarithm is

$$\ln(1 - x) = -x - \tfrac{1}{2}x^2 - \tfrac{1}{3}x^3 \cdots$$

If $x \ll 1$, then the terms involving x raised to a power greater than 1 are much smaller than x, so $\ln(1 - x) \approx -x$. For example, $\ln(1 - 0.050) = \ln 0.950 = -0.051$, which is close to -0.050.

We are almost there. First, we note that the elevation of boiling point is $\Delta T_b = T_b - T_b^*$. Then we note that because the value of T_b is very close to T_b^*, little error is introduced by replacing $T_b^* T_b$ by T_b^{*2}. In this way we arrive at

$$x_B \approx \frac{\Delta_{vap}H}{R} \times \frac{\Delta T_b}{T_b^{*2}}$$

which we can rearrange into

$$\Delta T_b \approx \frac{RT_b^{*2}}{\Delta_{vap}H} \times x_B$$

$$\Delta T_f \approx \frac{RT_f^{*2}}{\Delta_{fus}H} \times x_B$$

6.7 Osmosis

Derivation 6.6

Eqn 6.4b

$n_A V_A = V$ the volume of solvent

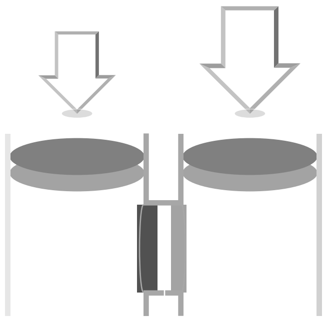
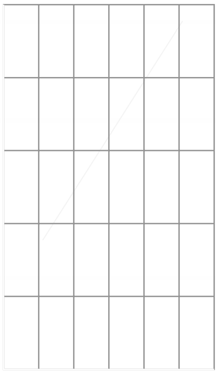
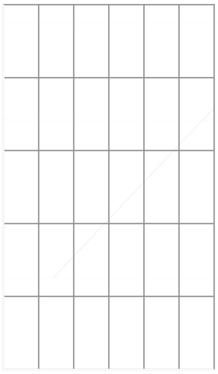


Fig. 6.20

y = intercept + slope × x

$$\frac{\Pi}{[\mathrm{B}]}$$





$$c_B = \frac{m_B}{V} = \frac{m_B}{n_B} \times \frac{n_B}{V} = M \times [B]$$

$$\frac{M\Pi}{c_B} = RT + \frac{BRTc_B}{M} + \cdots$$

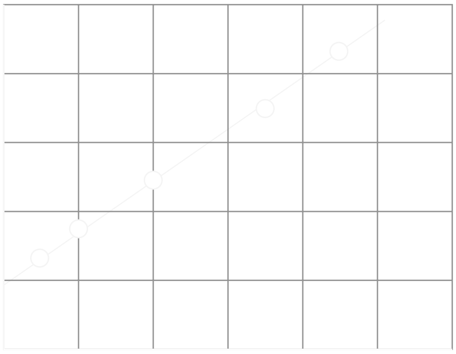


Fig. 6.22

Solution

$$\frac{\Pi\,/\,\mathrm{Pa}}{c_B\,/\,(\mathrm{g\ dm^{-3}})} = 19.6$$

Pa dm^3

g

$$M = \frac{RT}{19.6\ \mathrm{m^2\ s^{-2}}}$$

$\mathrm{J\ mol^{-1}\ m^{-2}\ s^{2}}$
$= \mathrm{(kg\ \cancel{m^{2}}\ \cancel{s^{-2}})\ mol^{-1}\ \cancel{m^{-2}}\ \cancel{s^{2}}}$
$= \mathrm{kg\ mol^{-1}}$

A note on good practice

Self-test 6.11

The osmotic pressure of a solution of poly(vinyl chloride), PVC, in dioxane at 25°C were as follows:

$c/(\mathrm{g\ dm^{-3}})$	0.50	1.00	1.50	2.00	2.50
$\Pi/c\,(\mathrm{Pa\ g^{-1}\ dm^{3}})$	33.6	35.2	36.8	38.4	40.0

Determine the molar mass of the polymer.

[*Answer*: 77 kg mol^{-1}]

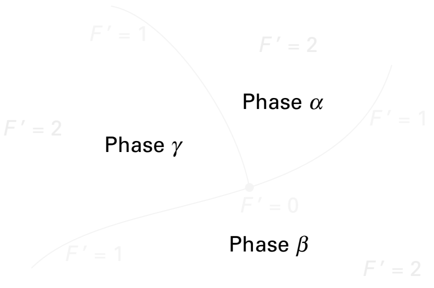


Fig. 6.23

Phase diagrams of mixtures

6.8 Mixtures of volatile liquids

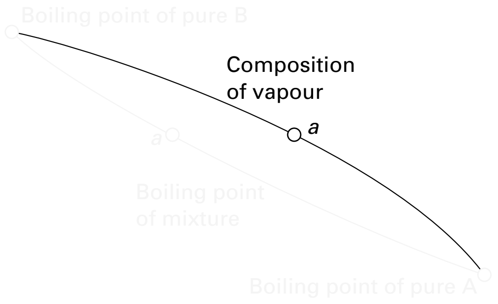


Fig. 6.24

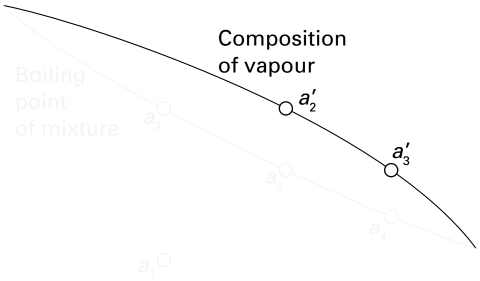


Fig. 6.25

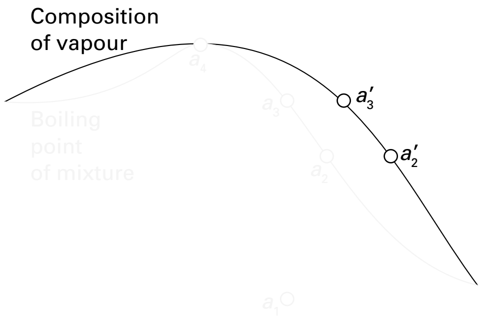
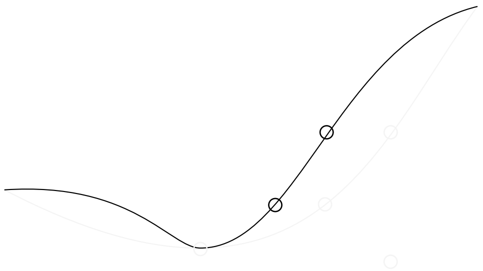
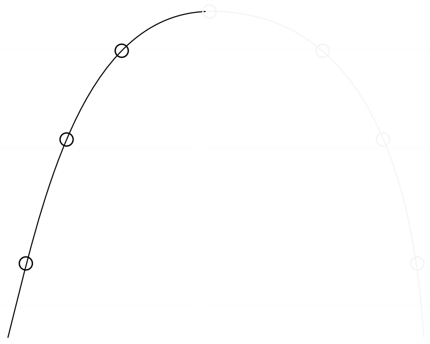


Fig. 6.26



6.9 Liquid–liquid phase diagrams

$$\frac{\text{Amount of phase of composition } a''}{\text{Amount of phase of composition } a'} = \frac{l'}{l''}$$



$$\frac{l'}{l''} = \frac{0.41 - 0.37}{0.83 - 0.41} = \frac{0.04}{0.42} = 0.1$$

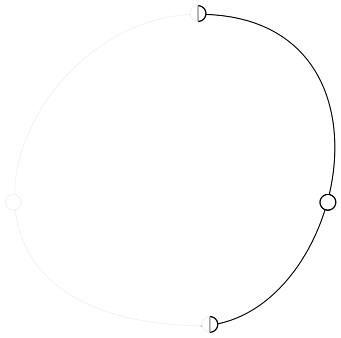


Fig. 6.31

6.10 Liquid–solid phase diagrams

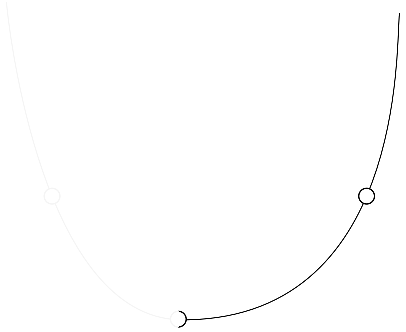


Fig. 6.30

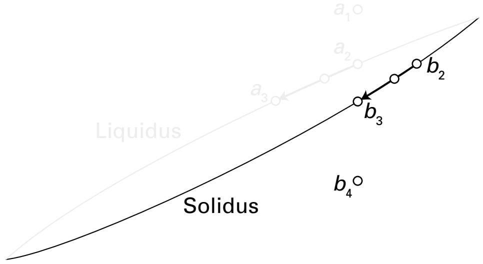


Fig. 6.32

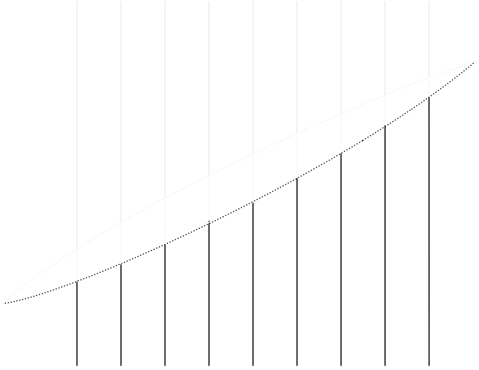


Fig. 6.34

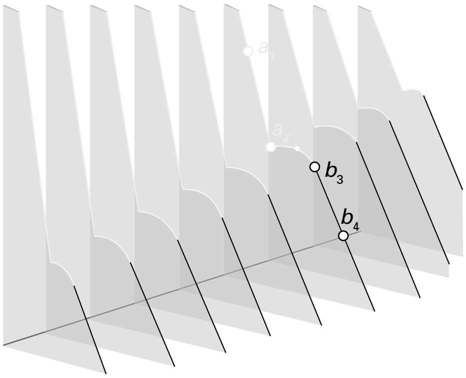


Fig. 6.33

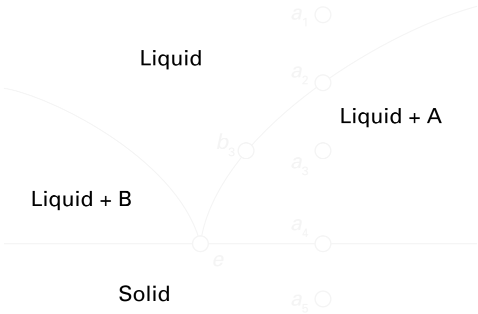


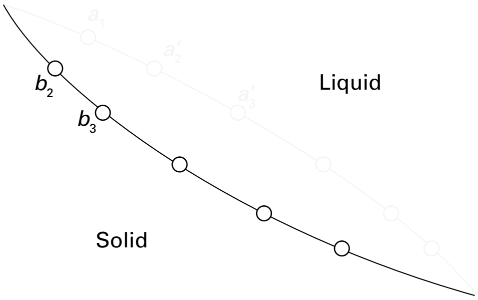
Fig. 6.35

$$\ln \frac{x_\mathrm{C}(2)}{x_\mathrm{C}(1)} = \frac{\mu_\mathrm{C}(1) - \mu_\mathrm{C}(2)}{RT}$$

$$\frac{x_\mathrm{C}(2)}{x_\mathrm{C}(1)} = \text{constant}$$

6.11 The Nernst distribution law

Box 6.2 Ultrapurity and controlled impurity



☐ **1**

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☐ **9**

☐ **10**

Property	Equation	Comment

Discussion questions

6.1

6.2

6.3

6.4

6.5

6.6

6.7

6.8

Exercises

6.1

respectively. What is the volume of a solution of total mass 1.000 kg?

6.2 Use Fig. 6.1 to estimate the total volume of a solution formed by mixing 50.0 cm^3 of ethanol with 50.0 cm^3 of water. The densities of the two liquids are 0.789 and 1.000 g cm^{-3}, respectively.

6.3 By how much does the chemical potential of carbon [illegible] at 310 K and 2.0 bar differ from its standard value at [illegible] temperature?

6.4 [illegible] dard state of a substance used to be defined as 1 atm [illegible] specified temperature. By how much does the current [illegible] of standard chemical potential (at 1 bar) differ from its [illegible] value at 298.15 K?

6.5 Calculate (a) the [illegible] Gibbs energy of mixing, (b) the (molar) entropy of mixing [illegible] the two major components of air (nitrogen and oxygen) [illegible] mixed to form air at 298 K. The mole fractions of N_2 and [illegible] 0.78 and 0.22, respectively. Is the mixing spontaneous?

6.6 Suppose now that argon is [illegible] the mixture in Exercise 6.5 to bring the composition [illegible] real air, with mole fractions 0.780, 0.210, and 0.0096, [illegible] ly. What is the additional change in molar Gibbs energy [illegible] entropy at 298 K? Is the mixing spontaneous?

6.7 A solution is prepared by dissolving 2.33 g of C_{60} ([illegible] minsterfullerene) in 100.0 g of toluene (methylbenzene). Given that the vapour pressure of pure toluene is 5.00 kPa at 30°C, what is the vapour pressure of toluene in the solution?

6.8 Estimate the vapour pressure of sea water at 20°C given that the vapour pressure of pure water is 2.338 kPa at that temperature and the solute is largely Na^+ and Cl^- ions, each present at about 0.50 mol dm^{-3}.

6.9 At 300 K, the vapour pressure of dilute solutions of HCl in liquid $GeCl_4$ are as follows:

x(HCl)	0.005	0.012	0.019
p/kPa	32.0	76.9	121.8

Show that the solution obeys Henry's law in this range of mole fractions and calculate the Henry's law constant at 300 K.

6.10 Calculate the concentration of carbon dioxide in fat given that the Henry's law constant is 8.6 × 10^4 Torr and the partial pressure of carbon dioxide is 55 kPa.

6.11 What partial pressure of hydrogen results in a molar concentration of 1.0 mmol dm^{-3} in water at 25°C?

6.12 The rise in atmospheric carbon dioxide results in higher concentrations of dissolved carbon dioxide in natural waters. Use Henry's law and the data in Table 6.1 to calculate the solubility of CO_2 in water at 25°C when its partial pressure is (a) 3.8 kPa, (b) 50.0 kPa.

6.13 The mole fractions of N_2 and O_2 in air at sea level are approximately 0.78 and 0.21, respectively. Calculate the molalities of the solution formed in an open flask of water at 25°C.

6.14 A water-carbonating plant is available for use in the home and operates by providing carbon dioxide at 1.0 atm. Estimate the molar concentration of the CO_2 in the soda water it produces.

6.15 At 90°C the vapour pressure of toluene (methylbenzene) is 53 kPa and that of *o*-xylene (1,2-dimethylbenzene) is 20 kPa. What is the composition of the liquid mixture that boils at 25°C when the pressure is 0.50 atm? What is the composition of the vapour produced?

6.16 The vapour pressures of the two components A and B of a binary mixture varied as follows:

$$p_A/\text{Torr} = 68x_A - 12x_A^2 + 643x_A^3 - 283x_A^4$$

$$p_B/\text{Torr} = 780 - 440x_A - 401x_A^2 + 92x_A^3$$

Confirm that the mixture conforms to Raoult's law for the component in large excess and to Henry's law for the minor component. Find the Henry's law constants.

6.17 The vapour pressures of the two components A and B of a binary mixture varied as follows:

x_A	0	0.20	0.40	0.60	0.80	1
p_A/Torr	0	127	246	357	457	539
p_B/Torr	701	631	526	394	234	38

Confirm that the mixture conforms to Raoult's law for the component in large excess and to Henry's law for the minor component. Find the Henry's law constants. Hint: proceed as [illegible] Example 6.3.

6.18 [illegible] is the change in chemical potential of glucose when [illegible] concentration in water at 20.0°C is changed from 0.10 mol [illegible] 1.00 mol dm^{-3}?

6.19 The vapo[illegible] re of a sample of benzene is 53.0 kPa at 60.6°C, but it [illegible] 2 kPa when 0.133 g of an organic compound was diss[illegible] 5.00 g of the solvent. Calculate the molar mass of the [illegible]

6.20 Estimate the freezing p[illegible] 0 cm^3 of water sweetened by the addition of 2.5 g o[illegible] Treat the solution as ideal.

6.21 Estimate the freezing point of 2[illegible] water to which 2.5 g of sodium chloride has been [illegible] Treat the solution as ideal.

6.22 The addition of 28.0 g of a compound to 750 [illegible] chloromethane, CCl_4, lowered the freezing point of [illegible] vent by 5.40 K. Calculate the molar mass of the compo[illegible]

6.23 A compound A existed in equilibrium with its dimer, A_2, in propanone solution. Derive an expression for the equilibrium constant $K = [A_2]/[A]^2$ in terms of the depression in vapour pressure caused by a given concentration of compound. (*Hint*. Suppose that a fraction f of the A molecules are present as the dimer. The depression of vapour pressure is proportional to the total concentration of A and A_2 molecules regardless of their chemical identities.)

6.24 The osmotic pressure of an aqueous solution of urea at 300 K is 150 kPa. Calculate the freezing point of the same solution.

6.25 The osmotic pressure of a solution of polystyrene in toluene (methylbenzene) was measured at 25°C with the following results:

$c/(\mathrm{g\,dm^{-3}})$	2.042	6.613	9.521	12.602
Π/Pa	58.3	188.2	270.8	354.6

[illegible] the molar mass of the polymer.

6.26 [illegible] molar mass of an enzyme was determined by dissolving [illegible] water, measuring the osmotic pressure at 20°C and extra[illegible] the data to zero concentration. The following data were [illegible]

$c/(\mathrm{mg\,cm^{-3}})$	[illegible]	4.618	5.112	6.722
h/cm	[illegible]	8.238	9.119	11.990

What is the molar mass [illegible] enzyme? *Hint:* Begin by expressing eqn 6.19 in terms [illegible] height of the solution, by using $\Pi = \rho gh$; take $\rho = 1.000$ g[illegible]

6.27 The following temperature–[illegible] data were obtained for a mixture of octane (O) [illegible] (T) at 760 Torr, where x is the mole fraction in the li[illegible] the mole fraction in the vapour at equilibrium.

$\theta/°\mathrm{C}$	110.9	112.0	114.0	115.8	117.3	119.0	[illegible]	[illegible]
x_T	0.908	0.795	0.615	0.527	0.408	0.300	0.203	[illegible]
y_T	0.923	0.836	0.698	0.624	0.527	0.410	0.297	[illegible]

The boiling points are 110.6°C for toluene and 125.6°C for octane. Plot the temperature–composition diagram of the mixture. What is the composition of the vapour in equilibrium with the liquid of composition (a) $x_T = 0.250$ and (b) $x_O = 0.250$?

6.28 Sketch the phase diagram of the system NH_3/N_2H_4 given that the two substances do not form a compound with each other, that NH_3 freezes at –78°C and N_2H_4 freezes at +2°C, and that a eutectic is formed when the mole fraction of N_2H_4 is 0.07 and that the eutectic melts at –80°C.

6.29 Figure 6.37 shows the phase diagram for two partially miscible liquids, which can be taken to be that for water (A) and 2-methyl-1-propanol (B). Describe what will be observed when a mixture of composition b_3 is heated, at each stage giving the number, composition, and relative amounts of the phases present.

6.30 Figure 6.38 is the phase diagram for silver/tin. Label the regions, and describe what will be observed when liquids of compositions *a* and *b* are cooled to 200°C.

6.31 Sketch the cooling curves for the compositions *a* and *b* in Fig. 6.38.

6.32 Use the phase diagram in Fig. 6.38 to determine (a) the solubility of silver in tin at 800°C, (b) the solubility of Ag_3Sn in silver at 460°C, and (c) the solubility of Ag_3Sn in silver at 300°C.

6.33 Figure 6.39 shows a part of the phase diagram of an alloy of copper and aluminium. Describe what you will

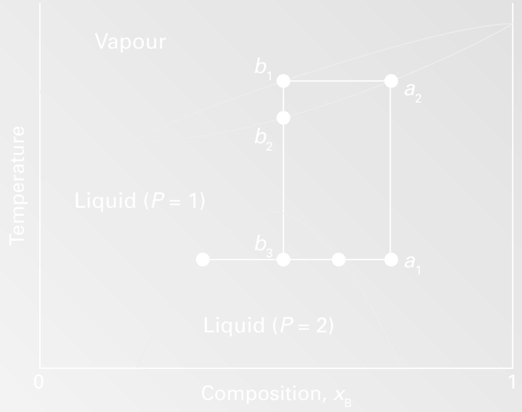


Fig. 6.37 A phase diagram for two partially miscible liquids.

Fig. 6.38 [illegible] diagram for silver/tin.

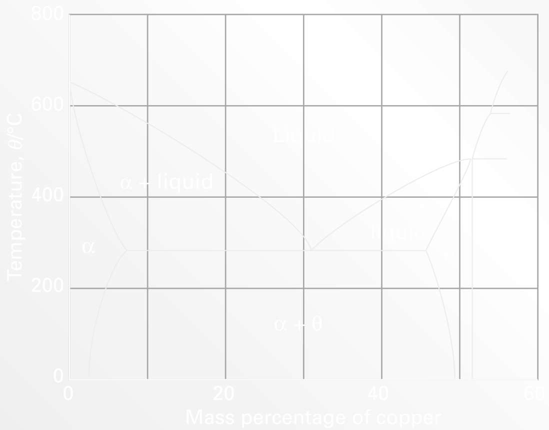


Fig. 6.39 A part of the phase diagram of an alloy of copper and aluminium.

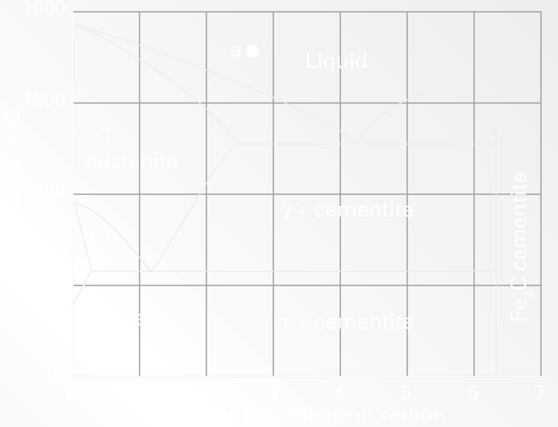


Fig. 6.40 A part of [illegible] diagram typical of a simple steel.

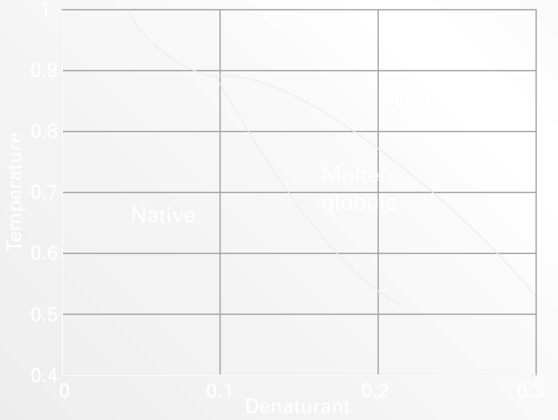


Fig. 6.41 A theoretical phase diagram for a model protein.

Fig. 6.42 The phase diagram for a membrane-forming two-component system.

observe as a melt of composition *a* is cooled. What is the solubility of copper in aluminium at 500°C?

6.34 Figure 6.40 shows a part of the phase diagram typical of a simple steel. Describe what you will observe as the melt at *a* is allowed to cool to room temperature.

6.35 Hexane and perfluorohexane (C_6F_{14}) show partial miscibility below 22.70°C. The critical concentration at the upper critical temperature is $x = 0.355$, where x is the mole fraction of C_6F_{14}. At 22.0°C the two solutions in equilibrium have $x = 0.24$ and $x = 0.48$, respectively, and at 21.5°C the mole fractions are 0.22 and 0.51. Sketch the phase diagram. Describe the phase changes that occur when perfluorohexane is added to a fixed amount of hexane at (a) 23°C, (b) 25°C.

6.36 In a theoretical study of protein-like polymers, the phase diagram shown in Fig. 6.41 was obtained. It shows three structural regions: the native form, the unfolded form, and a 'molten globule' form. (a) Is the molten-globule form ever stable when the denaturant concentration is below 0.1? (b) Describe what happens to the polymer as the native form is heated in the presence of denaturant at concentration 0.15.

6.37 In an experimental study of membrane-like assemblies of synthetic materials, a phase diagram like that shown in Fig. 6.42 was obtained. The two components are dielaidoylphosphatidylcholine (DEL) and dipalmitoylphosphatidylcholine (DPL). Explain what happens as a liquid mixture of composition $x_{\mathrm{DEL}} = 0.5$ is cooled from 45°C.

6.38 When 2.0 g of aspirin was shaken up in a flask containing [illegible] miscible liquids it was found that the mole factions in the [illegible]ds were 0.11 and 0.18. When a further 1.0 g of aspirin [illegible]d it was found that the mole fraction in the first liquid [illegible]d to 0.15. What would you expect the mole fraction [illegible] liquid to become?

Projects

The symbol ‡ indicates that [illegible]ise requires calculus.

6.39‡ (a) The partial molar volu[illegible]hanol in a mixture at 25°C is $V_{\mathrm{ethanol}}/(\mathrm{cm}^3$ mo[illegible] $- 0.727\,88b + 0.084\,768b^2$, where b is the numeric[illegible] the molality of ethanol. Plot this quantity as a function [illegible]ntify the composition at which the partial molar volum[illegible]mum. Express that composition as a mole fraction. (b) [illegible]fer-entiation to identify the minium in part (a).

6.40‡ (a) The total volume of a water/ethanol mixture at [illegible] fits the expression $V/\mathrm{cm}^3 = 1002.93 + 54.6664b - 0.363\,94$[illegible] $+ 0.028\,256b^3$, where b is the numerical value of the molality of ethanol. With the information in Exercise 6.3, find an expression for the partial molar volume of water. Plot the curve. Show that the partial molar volume of water has a maximum value where the partial molar volume of ethanol is a minimum. (b) Use calculus to plot the partial molar volumes of ethanol and water from the data in part (a). *Hint*: Convert b to a mole fraction, then use $V_J = \mathrm{d}V/\mathrm{d}x_J$.

6.41 Haemoglobin, the red blood protein responsible for oxygen transport, binds about 1.34 cm^3 of oxygen per gram. Normal blood has a haemoglobin concentration of 150 g dm^{-3}. Haemoglobin in the lungs is about 97 per cent saturated with oxygen, but in the capillary is only about 75 per cent saturated. (a) What volume of oxygen is given up by 100 cm^3 of blood flowing from the lungs in the capillary? Breathing air at high pressures, such as in scuba diving, results in an increased concentration of dissolved nitrogen. The Henry's law constant in the form $c = Kp$ for the solubility of nitrogen is 0.18 μg/(g H_2O atm). (b) What mass of nitrogen is dissolved in 100 g of water saturated with air at 4.0 atm and 20°C? Compare your answer to that for 100 g of water saturated with air at 1.0 atm. (Air is 78.08 mole per cent N_2.) (c) If nitrogen is four times as soluble in fatty tissues as in water, what is the increase in nitrogen concentration in fatty tissue in going from 1 atm to 4 atm?

Thermodynamic background

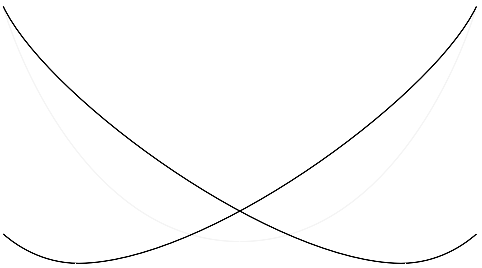
The response of equilibria to the conditions

Box 7.1 Coupled reactions in biochemical processes

Box 7.2 Binding of oxygen to myoglobin and haemoglobin

CHECKLIST OF KEY IDEAS
TABLE OF KEY EQUATIONS
QUESTIONS AND EXERCISES

Thermodynamic background

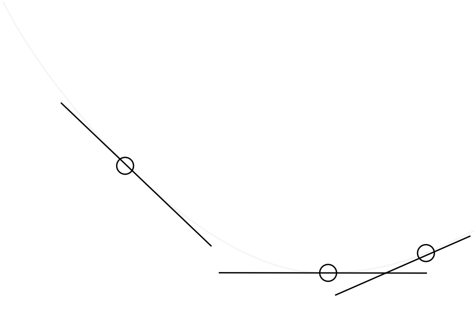


$$\Delta_r G = \frac{\Delta G}{\Delta n} = \mu_{\mathrm{F6P}} - \mu_{\mathrm{G6P}}$$

7.1 The reaction Gibbs energy

7.2 The variation of $\Delta_r G$ with composition

$$\Delta_r G = \frac{\Delta G}{\Delta n} = 2\mu_{NH_3} - (\mu_{N_2} + 3\mu_{H_2})$$



$$c \ln a_{\mathrm{C}} + d \ln a_{\mathrm{D}} - a \ln a_{\mathrm{A}} - b \ln a_{\mathrm{B}}$$

Use $n \ln x = \ln x^n$

$$= \ln a_{\mathrm{C}}^{c} + \ln a_{\mathrm{D}}^{d} - \ln a_{\mathrm{A}}^{a} - \ln a_{\mathrm{B}}^{b}$$

Use $\ln x + \ln y = \ln xy$

$$= \ln a_{\mathrm{C}}^{c} a_{\mathrm{D}}^{d} - \ln a_{\mathrm{A}}^{a} a_{\mathrm{B}}^{b}$$

$$= \ln \frac{a_{\mathrm{C}}^{c} a_{\mathrm{D}}^{d}}{a_{\mathrm{A}}^{a} a_{\mathrm{B}}^{b}}$$

Use $\ln x - \ln y = \ln x/y$

$$\Delta_{\mathrm{r}} G = \Delta_{\mathrm{r}} G^{\circ} + RT \ln \frac{a_{\mathrm{C}}^{c} a_{\mathrm{D}}^{d}}{a_{\mathrm{A}}^{a} a_{\mathrm{B}}^{b}}$$

$$Q = \frac{a_{\mathrm{C}}^{c} a_{\mathrm{D}}^{d}}{a_{\mathrm{A}}^{a} a_{\mathrm{B}}^{b}}$$

A brief illustration

$$Q = \frac{a_{\mathrm{F6P}}}{a_{\mathrm{G6P}}} = \frac{[\mathrm{F6P}]/c^{\ominus}}{[\mathrm{G6P}]/c^{\ominus}}$$

$$Q = \frac{[\mathrm{F6P}]}{[\mathrm{G6P}]}$$

$$Q = \frac{(p_{\mathrm{NH_3}}/p^{\ominus})^2}{(p_{\mathrm{N_2}}/p^{\ominus})(p_{\mathrm{H_2}}/p^{\ominus})^3}$$

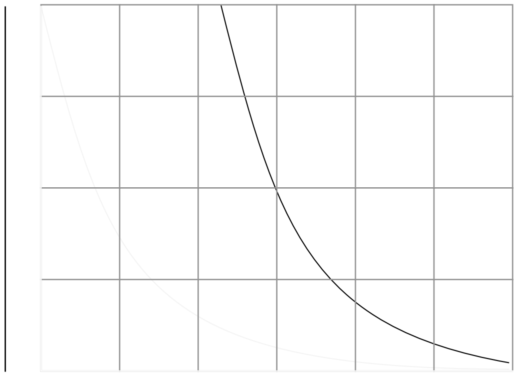
$$Q = \frac{p_{\mathrm{NH_3}}^{2}}{p_{\mathrm{N_2}} p_{\mathrm{H_2}}^{3}}$$

$$K = \left(\frac{a_{\mathrm{C}}^{c} a_{\mathrm{D}}^{d}}{a_{\mathrm{A}}^{a} a_{\mathrm{B}}^{b}} \right)_{\mathrm{equilibrium}}$$

A brief illustration

$$K = \mathrm{e}^{-\frac{3.40\times10^3}{8.314\,47\times298}} = 0.25$$

A note on good practice



$$T = \frac{\Delta_r H}{\Delta_r S}$$

A brief illustration

$$T = \frac{1.78 \times 10^5\ \mathrm{J\,mol^{-1}}}{161\ \mathrm{J\,K^{-1}\,mol^{-1}}} = 1.11 \times 10^3\ \mathrm{K}$$

7.4 The standard reaction Gibbs energy

A brief illustration

	Δ	−

A brief illustration

7.5 The equilibrium composition

$$f = \frac{[\mathrm{F6P}]}{[\mathrm{F6P}] + [\mathrm{G6P}]}$$

$$f = \frac{[\mathrm{F6P}]/[\mathrm{G6P}]}{[\mathrm{F6P}]/[\mathrm{G6P}] + 1} = \frac{K}{K+1}$$

$$\frac{\Delta_r G^\circ}{RT} = \frac{1.7\times10^3\ \mathrm{J\ mol^{-1}}}{(8.3145\ \mathrm{J\,K^{-1}\ mol^{-1}})\times(298\ \mathrm{K})} = \frac{1.7\times10^3}{8.3145\times298}$$

$$K = \mathrm{e}^{-\frac{1.7\times10^3}{8.3145\times298}} = 0.50$$

$$f = \frac{0.50}{1+0.50} = 0.33$$

Self-test 7.6

Estimate the composition of a solution in which two isomers A and B are in equilibrium ($A \rightleftharpoons B$) at 37°C and $\Delta_r G^{\ominus} = -2.2\ \mathrm{kJ\ mol^{-1}}$.

[*Answer:* The fraction of B at equilibrium is $f = 0.70$]

Example 7.3

Strategy

Solution

$$K = \frac{p_{NH_3}^2}{p_{N_2}p_{H_2}^3}$$

Species	N_2	H_2	NH_3

$$K = \frac{(2x)^2}{(1.00 - x) \times (3.00 - 3x)^3}$$

$$977 = \tfrac{4}{27}\left(\frac{x}{(1.00 - x)^2}\right)^2$$

$$\sqrt{\tfrac{27}{4} \times 977} = \frac{x}{(1.00 - x)^2}$$

$$g = \frac{x}{(1.00 - x)^2} = \frac{x}{1.00 - 2.00x + x^2}$$

$$x = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a}$$

$$\frac{p_{NH_3}^2}{p_{N_2}p_{H_2}^3} = \frac{(1.8)^2}{(0.10) \times (0.32)^3} = 9.9 \times 10^2$$

Self-test 7.7

In an experiment to study the formation of nitrogen oxides in jet exhausts, N_2 at 0.100 bar is mixed with O_2 at 0.200 bar and the two gases are allowed to come to equilibrium with the product NO in a reactor of constant volume. Take $K = 3.4 \times 10^{-21}$ at 800 K. What is the equilibrium partial pressure of NO?

[*Answer:* 8.2 pbar]

7.6 The equilibrium constant in terms of concentration

$$K_c = \frac{[\mathrm{NH_3}]^2}{[\mathrm{N_2}][\mathrm{H_2}]^3}$$

$$K = K_c \times \left(\frac{c\ \ RT}{p}\right)^{\Delta\nu_{\text{gas}}}$$

$$K = K_c \times \left(\frac{T}{12.027\ \mathrm{K}}\right)^{\Delta\nu_{\text{gas}}}$$

$$K = \frac{(p_{\mathrm{C}}/p^{\ominus})^c(p_{\mathrm{D}}/p^{\ominus})^d}{(p_{\mathrm{A}}/p^{\ominus})^a(p_{\mathrm{B}}/p^{\ominus})^b} \qquad K_c = \frac{([C]/c^{\ominus})^c([\mathrm{D}]/c^{\ominus})^d}{([\mathrm{A}]/c^{\ominus})^a([\mathrm{B}]/c^{\ominus})^b}$$

$$K = \frac{([\mathrm{C}]RT/p^{\ominus})^c([\mathrm{D}]RT/p^{\ominus})^d}{([\mathrm{A}]RT/p^{\ominus})^a([\mathrm{B}]RT/p^{\ominus})^b} = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b} \times \left(\frac{RT}{p^{\ominus}}\right)^{(c+d)-(a+b)}$$

$$K_c = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b} \times \left(\frac{1}{c^{\ominus}}\right)^{(c+d)-(a+b)}$$

$$K = K_c \times \left(\frac{c^{\ominus}RT}{p^{\ominus}}\right)^{(c+d)-(a+b)}$$

A brief illustration

$$K_c = \frac{K}{(T/12.027\ \mathrm{K})^{-2}} = K \times \left(\frac{T}{12.027\ \mathrm{K}}\right)^2$$

$$K_c = 5.8 \times 10^5 \times \left(\frac{298\ \mathrm{K}}{12.027\ \mathrm{K}}\right)^2 = 3.6 \times 10^8$$

The response of equilibria to the conditions

7.7 The presence of a catalyst

$$\ln K' - \ln K = \frac{\Delta_r H}{R}\left(\frac{1}{T} - \frac{1}{T'}\right)$$

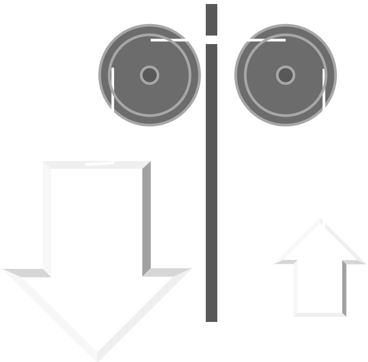
A brief illustration

$$\ln K = \overbrace{-\frac{\Delta_r G^\ominus}{RT}}^{\text{From } \Delta_r G^\ominus = -RT\ln K} = \underbrace{-\frac{\Delta_r H^\ominus}{RT} + \frac{\Delta_r S^\ominus}{R}}_{\text{From } \Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus}$$

$$\ln K' = -\frac{\Delta_r H^\ominus}{RT'} + \frac{\Delta_r S^\ominus}{R}$$

$$\ln K' - \ln K = \frac{\Delta_r H^\ominus}{R}\left(\frac{1}{T} - \frac{1}{T'}\right)$$

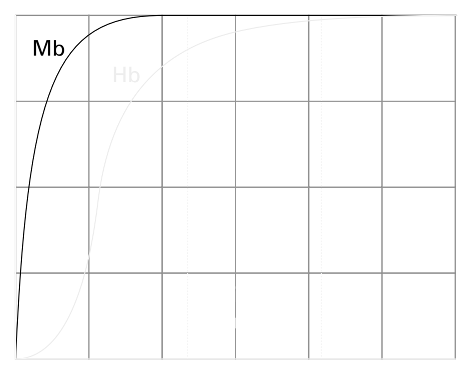
Box 7.1 Coupled reactions in biochemical processes



7.9 The effect of compression

$$K = \frac{[\mathrm{MbO_2}]}{p[\mathrm{Mb}]}$$

$$s = \frac{[\mathrm{MbO_2}]}{[\mathrm{Mb}]_{\mathrm{total}}} = \frac{[\mathrm{MbO_2}]}{[\mathrm{Mb}]+[\mathrm{MbO_2}]} = \frac{Kp}{1+Kp}$$



The variation of the fractional saturation of myoglobin and haemoglobin molecules with the partial pressure of oxygen. The different shapes of the curves account for the different biological functions of the two proteins.

$$K_1 = \frac{[\mathrm{HbO_2}]}{p[\mathrm{Hb}]}$$

$$K_2 = \frac{[\mathrm{Hb(O_2)_2}]}{p[\mathrm{HbO_2}]}$$

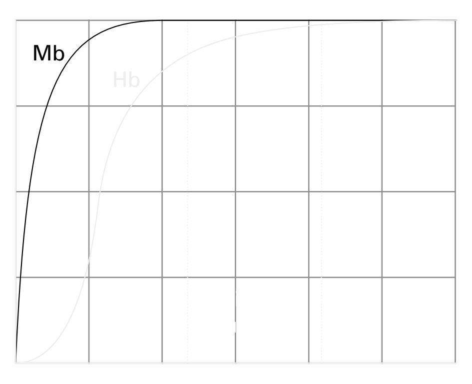
$$K_3 = \frac{[\mathrm{Hb(O_2)_3}]}{p[\mathrm{Hb(O_2)_2}]}$$

$$K_4 = \frac{[\mathrm{Hb(O_2)_4}]}{p[\mathrm{Hb(O_2)_3}]}$$

sharply at intermediate ligand concentrations, and then levels off at high ligand concentrations. Cooperative binding of O_2 by haemoglobin is explained by an *allosteric effect*, in which an adjustment of the conformation of a molecule when one substrate binds affects the ease with which a subsequent substrate molecule binds.

The differing shapes of the saturation curves for myoglobin and haemoglobin have important consequences for the way O_2 is made available in the body: in particular, the greater sharpness of the Hb saturation curve means that Hb can load O_2 more fully in the lungs and unload it more fully in different regions of the organism. In the lungs, where $p \approx 14$ kPa, $s \approx 0.98$, representing almost complete saturation. In resting muscular tissue, p is equivalent to about 5 kPa, corresponding to $s \approx 0.75$, implying that sufficient O_2 is still available should a sudden surge of activity take place. If the local partial pressure falls to 3 kPa, s falls to about 0.1. Note that the steepest part of the curve falls in the range of typical tissue oxygen partial pressure. Myoglobin, on the other hand, begins to release O_2 only when p has fallen below about 3 kPa, so it acts as a reserve to be drawn on only when the Hb oxygen has been used up.

$$s = \frac{[\mathrm{O_2}]_{\mathrm{bound}}}{4[\mathrm{Hb}]_{\mathrm{total}}} = \frac{(1 + 2K_2p + 3K_2K_3p^2 + 4K_2K_3K_4p^3)K_1p}{4(1 + K_1p + K_1K_2p^2 + K_1K_2K_3p^3 + K_1K_2K_3K_4p^4)}$$



The variation of the fractional saturation of myoglobin and haemoglobin molecules with the partial pressure of oxygen. The different shapes of the curves account for the different biological functions of the two proteins.

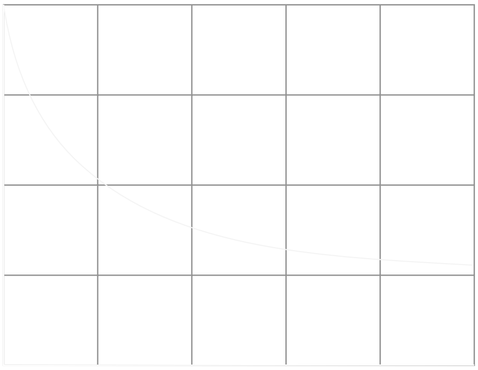


Fig. 7.8

$$K=\frac{p_{\mathrm{HI}}^2}{p_{\mathrm{H_2}}}\ \text{to}\ K'=\frac{(2p_{\mathrm{HI}})^2}{2p_{\mathrm{H_2}}}=2K$$

$$x_{\mathrm{HI}}=\left(\frac{K}{2p}\right)\left\{\left(1+\frac{4p}{K}\right)^{1/2}-1\right\}$$

$$K=\frac{x_{\mathrm{HI}}^2 p}{1-x_{\mathrm{HI}}}$$

$\frac{1}{2}$

$$x_{\mathrm{HI}}=\left(\frac{K}{2p}\right)\left\{\left(1+\frac{2p}{K}+\cdots\right)-1\right\}=\left(\frac{K}{2p}\right)\left\{\frac{2p}{K}+\cdots\right\}=1+\cdots$$

☐ **1**

☐ **2**

☐ **3**

☐ **4**

☐ **5**

☐ **6**

☐ **7**

☐ **8**

Property	Equation	Comment

Discussion questions

7.1

7.2

7.3

7.4

7.5

7.6

7.7

7.8

7.9

7.10

Exercises

7.1

7.2

7.3

7.4

7.5

7.11

7.12

7.13

7.14

7.15

7.16

7.17

7.18 The equilibrium constant for the reaction $I_2(g) \rightarrow 2\ I(g)$ is 0.26 at 1000 K. What is the corresponding value of K_c?

7.19 The second step in glycolysis is the isomerization of glucose-6-phosphate (G6P to fructose-6-phosphate (F6P). Example 7.2 considered the equilibrium between F6P and G6P. Draw a graph to show how the reaction Gibbs energy varies with the fraction *f* of F6P in solution. Label the regions of the graph that correspond to the formation of F6P and G6P being spontaneous, respectively.

7.20 [illegible]ssify the following compounds as endergonic or e[illegible] glucose, (b) methylamine, (c) octane, (d) ethanol.

7.21 C[illegible]e reaction entropies calculated in the following reactio[illegible]he reaction enthalpies and calculate the standard reac[illegible]s energies at 298 K:

(a) $HCl(g) + NH$[illegible]$H_4Cl(s)$

(b) $2\ Al_2O_3(s) + 3\ S$[illegible]$O_2(s) + 4\ Al(s)$

(c) $Fe(s) + H_2S(g) \rightarrow Fe$[illegible]$(g)$

(d) $FeS_2(s) + 2\ H_2(g) \rightarrow Fe$[illegible]$(g)$

(e) $2\ H_2O_2(l) + H_2S(g) \rightarrow H_2SO_4$[illegible]

7.22 Use the Gibbs energies of format[illegible] Data section to decide which of the following reactions [illegible] at 298 K.

(a) $2\ CH_3CHO(g) + O_2(g) \rightleftharpoons 2\ CH_3COOH(l)$

(b) $2\ AgCl(s) + Br_2(l) \rightleftharpoons 2\ AgBr(s) + Cl_2(g)$

(c) $Hg(l) + Cl_2(g) \rightleftharpoons HgCl_2(s)$

(d) $Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$

(e) $C_{12}H_{22}O_{11}(s) + 12\ O_2(g) \rightleftharpoons 12\ CO_2(g) + 11\ H_2O(l)$

7.23 Recall from Chapter 6 that the change in Gibbs energy can be identified with the maximum nonexpansion work that can be extracted from a process. What is the maximum energy that can be extracted as (a) heat, (b) nonexpansion work when 2.0 kg of natural gas (taken to be pure methane) is burned under standard conditions at 25°C? Take the reaction to be $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$.

7.24 In assessing metabolic processes we are usually more interested in the work that may be performed for the consumption of a given mass of compound than the heat it can produce (which merely keeps the body warm). What is the maximum energy that can be extracted as (a) heat, (b) nonexpansion work when 2.0 kg of glucose is burned under standard conditions at 25°C with the production of water vapour? The reaction is $C_6H_{12}O_6(s) + 6\ O_2(g) \rightarrow 6\ CO_2(g) + 6\ H_2O(g)$.

7.25 Is it more energy effective to ingest sucrose or glucose? Calculate the nonexpansion work, the expansion work, and the total work that can be obtained from the combustion of 2.0 kg of sucrose under standard conditions at 25°C when the product includes (a) water vapour, (b) liquid water.

7.26 The standard enthalpy of combustion of solid phenol, C_6H_5OH, is −3054 kJ mol^{-1} at 298 K and its standard molar entropy is 144.0 J K^{-1} mol^{-1}. Calculate the standard Gibbs energy of formation of phenol at 298 K.

7.27 Calculate the maximum nonexpansion work per mole that may be obtained from a fuel cell in which the chemical reaction is the combustion of methane at 298 K.

7.28 Calculate the standard biological Gibbs energy for the reaction

$$\text{Pyruvate}^-(aq) + NADH(aq) + H^+(aq) \rightarrow \text{lactate}^-(aq) + NAD^+(aq)$$

at 310 K given that $\Delta_r G^\ominus = -66.6$ kJ mol^{-1}. (NAD$^+$ is the oxidized form of nicotinamide dinucleotide.) This reaction occurs in muscle cells deprived of oxygen during strenuous exercise and can lead to cramp.

7.29 The standard biological reaction Gibbs energy for the removal of the phosphate group from adenosine monophosphate is −14 kJ mol^{-1} at 298 K. What is the value of the thermodynamic standard reaction Gibbs energy? *Hint*: See Box 7.1.

7.30 Show that if the logarithm of an equilibrium constant is plotted against the reciprocal of the temperature, then the standard reaction enthalpy may be determined.

7.31 Use the following data on the reaction $H_2(g) + Cl_2(g) \rightarrow 2\ HCl(g)$ to determine the standard reaction enthalpy:

T/K	300	500	1000
K	4.0×10^{31}	4.0×10^{18}	5.1×10^{8}

7.32 The equilibrium constant of the reaction $2\ C_3H_6(g) \rightleftharpoons C_2H_4(g) + C_4H_8(g)$ is found to fit the expression

$$\ln K = -1.04 - \frac{1088\ \text{K}}{T} + \frac{1.51 \times 10^5\ \text{K}^2}{T^2}$$

[illegible] 300 K and 600 K. Calculate the standard reaction e[illegible]d standard reaction entropy at 400 K. *Hint*. Begin by ca[illegible] K at 390 K and 410 K; then use eqn 7.14.

7.33 Bor[illegible]ngent compound obtained from the camphorwood tre[illegible]o and Sumatra. The standard reaction Gibbs energy of [illegible]rization of borneol (**5**) to isoborneol (**6**) in the gas phase [illegible] is −9.4 kJ mol^{-1}. Calculate the reaction Gibbs energy [illegible]re consisting of 0.15 mol of borneol and 0.30 mol of is[illegible] when the total pressure is 600 Torr.

5 d-Borneol

6 d-Isoborneol

7.34 The equilibrium constant for the gas-phase isomerization of borneol, $C_{10}H_{17}OH$, to isoborneol (see Exercise 7.33) at 503 K is 0.106. A mixture consisting of 6.70 g of borneol and 12.5 g of isoborneol in a container of volume 5.0 dm^3 is heated to 503 K and allowed to come to equilibrium. Calculate the mole fractions of the two substances at equilibrium.

7.35 Calculate the composition of a system in which nitrogen and hydrogen are mixed at partial pressures of 1.00 bar and 4.00 bar and allowed to reach equilibrium with their product, ammonia, under conditions when $K = 89.8$.

7.36 In a gas-phase equilibrium mixture of $SbCl_5$, $SbCl_3$, and Cl_2 at 500 K, $p_{SbCl_5} = 0.17$ bar and $p_{SbCl_3} = 0.22$ bar. Calculate the equilibrium partial pressure of Cl_2 given that $K = 3.5 \times 10^{-4}$ for the reaction $SbCl_5(g) \rightleftharpoons SbCl_3(g) + Cl_2(g)$.

7.37 [illegible] equilibrium constant $K = 0.36$ for the reaction $PCl_5(g) \rightleftharpoons$ [illegible] $Cl_2(g)$ at 400 K. (a) Given that 1.5 g of PCl_5 was initially [illegible] a reaction vessel of volume 250 cm^3, determine the [illegible] concentrations in the mixture at equilibrium. (b) What is the [illegible]tage of PCl_5 decomposed at 400 K?

7.38 In the Haber [illegible] for ammonia, $K = 0.036$ for the reaction $N_2(g) + 3\,H_2(g) \rightleftharpoons$ [illegible] $NH_3(g)$ at 500 K. If a reactor is charged with partial pressures [illegible] 0.020 bar of N_2 and 0.020 bar of H_2, what will be the [illegible] partial pressure of the components?

7.39 Express the equilibrium constant [illegible]$O_4(g) \rightleftharpoons 2\,NO_2(g)$ in terms of the fraction α of N_2O_4 that [illegible]ated and the total pressure p of the reaction mixture, [illegible] that when the extent of dissociation is small ($\alpha \ll 1$), α [illegible]ly proportional to the square root of the total pressure [illegible]).

7.40 The equilibrium pressure of H_2 over a mixture [illegible] uranium and solid uranium hydride at 500 K is 1.04 [illegible] Calculate the standard Gibbs energy of formation of UH_3 [illegible] at 500 K.

7.41 What is the standard enthalpy of a reaction for which the equilibrium constant is (a) doubled, (b) halved when the temperature is increased by 10 K at 298 K?

7.42 The dissociation vapour pressure (the pressure of gaseous products in equilibrium with the solid reactant) of NH_4Cl at 427°C is 608 kPa but at 459°C it has risen to 1115 kPa. Calculate (a) the equilibrium constant, (b) the standard reaction Gibbs energy, (c) the standard enthalpy, (d) the standard entropy of dissociation, all at 427°C. Assume that the vapour behaves as a perfect gas and that $\Delta H^\ominus$ and $\Delta S^\ominus$ are independent of temperature in the range given.

Projects

The symbol ‡ indicates that calculus is required.

7.43‡ Here we explore the van't Hoff equation in more detail. (a) The bond in molecular iodine is weak, and hot iodine vapour contains a proportion of iodine atoms. When 1.00 g of I_2 is heated to 1000 K in a sealed container of volume 1.00 dm^3, the resulting equilibrium mixture contains 0.830 g of I_2. Calculate K for the dissociation equilibrium $I_2(g) \rightleftharpoons 2\,I(g)$. (b) The thermodynamically exact form of the van 't Hoff equation (eqn 7.15) is $\mathrm{d}(\ln K)/\mathrm{d}T = -\Delta_r H^\ominus/RT^2$. Use the data in part (a) to deduce an expression for the temperature dependence of the standard reaction enthalpy for the reaction treated there, and draw a graph to show the variation. (c) The van 't Hoff equation (eqn 7.15) applies to K, not to K_c. Find the corresponding expression for K_c.

7.44 The saturation curves shown in Box 7.2 may also be modelled mathematically by the equation

$$\log \frac{s}{1-s} = \boldsymbol{\nu} \log p - \boldsymbol{\nu} \log K$$

where s is the saturation, p is the partial pressure of O_2 ([illegible]ecifically, $p/p^\ominus$), K is a constant (not the binding constant for [illegible]e ligand), and ν is the *Hill coefficient*, which varies from [illegible] cooperativity, to N for all-or-none binding of N ligands ([illegible]). The Hill coefficient for myoglobin is 1, and for haem[illegible] is 2.8. (a) Determine the constant K for both Mb and [illegible] the graph of fractional saturation (at $s = 0.5$) and then ca[illegible]e fractional saturation of Mb and Hb for the following [illegible] p/kPa: 1.0, 1.5, 2.5, 4.0, 8.0. (b) Use the information in [illegible] to calculate the value of s at the same p values assum[illegible] has the theoretical maximum value of 4.

Proton transfer equilibria

Salts in water

Box 8.1 Buffer action in blood

Solubility equilibria

CHECKLIST OF KEY IDEAS
TABLE OF KEY EQUATIONS
QUESTIONS AND EXERCISES

Proton transfer equilibria

8.1 Brønsted–Lowry theory

$$K = \frac{a_{H_3O^+} a_{A^-}}{a_{HA} a_{H_2O}}$$

$$K = \frac{a_{BH^+} a_{OH^-}}{a_B a_{H_2O}}$$

$$K_a = \frac{a_{H_3O^+} a_{A^-}}{a_{HA}} \approx \frac{([H_3O^+]/c\ )([A^-]/c\ )}{([HA]/c\ )}$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$K = \frac{a_{H_3O^+} a_{OH^-}}{a^2_{H_2O}}$$

$$K_b = \frac{a_{BH^+}a_{OH^-}}{a_B} \approx \frac{[BH^+][OH^-]}{[B]}$$

$$K_aK_b = \frac{a_{H_3O^+}a_B}{\cancel{a_{BH^+}}} \times \frac{\cancel{a_{BH^+}}a_{OH^-}}{a_B} = a_{H_3O^+}a_{OH} = K_w$$

A brief illustration

$$= \frac{\text{equilibrium molar concentration of conjugate base}}{\text{formal concentration of acid}}$$

$$\alpha = \frac{[A^-]_{\text{equilibrium}}}{F(HA)}$$

$$= \frac{\text{equilibrium molar concentration of conjugate acid}}{\text{formal concentration of base}}$$

$$\alpha = \frac{[BH^+]_{\text{equilibrium}}}{F(B)}$$

Table 8.1

Acidity and basicity constants at 298.15 K

Acid/Base	K_b	pK_b	K_a	pK_a
Strongest weak acids				
Trichloroacetic acid, CCl_3COOH	3.3×10^{-14}	13.48	3.0×10^{-1}	0.52
Benzenesulfonic acid, $C_6H_5SO_3H$	5.0×10^{-14}	13.30	2×10^{-1}	0.70
Iodic acid, HIO_3	5.9×10^{-14}	13.23	1.7×10^{-1}	0.77
Sulfurous acid, H_2SO_3	6.3×10^{-13}	12.19	1.6×10^{-2}	1.81
Chlorous acid, $HClO_2$	1.0×10^{-12}	12.00	1.0×10^{-2}	2.00
Phosphoric acid, H_3PO_4	1.3×10^{-12}	11.88	7.6×10^{-3}	2.12
Chloroacetic acid, $CH_2ClCOOH$	7.1×10^{-12}	11.15	1.4×10^{-3}	2.85
Lactic acid, $CH_3CH(OH)COOH$	1.2×10^{-11}	10.92	8.4×10^{-4}	3.08
Nitrous acid, HNO_2	2.3×10^{-11}	10.63	4.3×10^{-4}	3.37
Hydrofluoric acid, HF	2.9×10^{-11}	10.55	3.5×10^{-4}	3.45
Formic acid, HCOOH	5.6×10^{-11}	10.25	1.8×10^{-4}	3.75
Benzoic acid, C_6H_5COOH	1.5×10^{-10}	9.81	6.5×10^{-5}	4.19
Acetic acid, CH_3COOH	5.6×10^{-10}	9.25	5.6×10^{-5}	4.75
Carbonic acid, H_2CO_3	2.3×10^{-8}	7.63	4.3×10^{-7}	6.37
Hypochlorous acid, HClO	3.3×10^{-7}	6.47	3.0×10^{-8}	7.53
Hypobromous acid, HBrO	5.0×10^{-6}	5.31	2.0×10^{-9}	8.69
Boric acid, $B(OH)_3$†	1.4×10^{-5}	4.86	7.2×10^{-10}	9.14
Hydrocyanic acid, HCN	2.0×10^{-5}	4.69	4.9×10^{-10}	9.31
Phenol, C_6H_5OH	7.7×10^{-5}	4.11	1.3×10^{-10}	9.89
Hypoiodous acid, HIO	4.3×10^{-4}	3.36	2.3×10^{-11}	10.64
Weakest weak acids				
Weakest weak bases				
Urea, $CO(NH_2)_2$	1.3×10^{-14}	13.90	7.7×10^{-1}	0.10
Aniline, $C_6H_5NH_2$	4.3×10^{-10}	9.37	2.3×10^{-5}	4.63
Pyridine, C_5H_5N	1.8×10^{-9}	8.75	5.6×10^{-6}	5.35
Hydroxylamine, NH_2OH	1.1×10^{-8}	7.97	9.1×10^{-7}	6.03
Nicotine, $C_{10}H_{11}N_2$	1.0×10^{-6}	5.98	1.0×10^{-8}	8.02
Morphine, $C_{17}H_{19}O_3N$	1.6×10^{-6}	5.79	6.3×10^{-9}	8.21
Hydrazine, NH_2NH_2	1.7×10^{-6}	5.77	5.9×10^{-9}	8.23
Ammonia, NH_3	1.8×10^{-5}	4.75	5.6×10^{-10}	9.25
Trimethylamine, $(CH_3)_3N$	6.5×10^{-5}	4.19	1.5×10^{-10}	9.81
Methylamine, CH_3NH_2	3.6×10^{-4}	3.44	2.8×10^{-11}	10.56
Dimethylamine, $(CH_3)_2NH$	5.4×10^{-4}	3.27	1.9×10^{-11}	10.73
Ethylamine, $C_2H_5NH_2$	6.5×10^{-4}	3.19	1.5×10^{-11}	10.81
Triethylamine, $(C_2H_5)_3N$	1.0×10^{-3}	2.99	1.0×10^{-11}	11.01
Strongest weak bases				

* Values for polyprotic acids—those capable of donating more than one proton—refer to the first deprotonation.

† The proton-transfer equilibrium is $B(OH)_3(aq) + 2\ H_2O(l) \rightleftharpoons H_3O^+(aq) + B(OH)_4^-(aq)$.

+ −

$$K_a = \frac{[H_3O^+][CH_3CO_2^-]}{[CH_3COOH]} = \frac{x \times x}{0.15 - x}$$

$$\alpha = \frac{[CH_3CO_2^-]_{\text{equilibrium}}}{F(CH_3COOH)} = \frac{x}{0.15} = \frac{1.6\times10^{-3}}{0.15} = 0.011$$

Self-test 8.4

Estimate the pH of 0.010 M $CH_3CH(OH)COOH(aq)$ (lactic acid) from the data in Table 8.1. Before carrying out the numerical calculation, decide whether you expect the pH to be higher or lower than that calculated for the same concentration of acetic acid.

[*Answer:* 2.5]

Strategy

Solution

− +

$$K_b = \frac{[OH^-][QH^+]}{[Q]} = \frac{x \times x}{0.010 - x}$$

$$\alpha = \frac{[QH^+]_{\text{equilibrium}}}{F(Q)} = \frac{x}{0.010} = \frac{2.8\times10^{-6}}{0.010} = 2.8\times10^{-4}$$

Self-test 8.5

The pK_a for the first protonation of nicotine (**2**) is 8.02. What is the pH and the fraction of molecules protonated in a 0.015 M aqueous solution of nicotine?

[*Answer:* 10.1; 1/120]

$$K_{a1} = \frac{a_{H_3O^+}a_{HA^-}}{a_{H_2A}}$$

$$K_{a2} = \frac{a_{H_3O^+}a_{A^{2-}}}{a_{HA^-}}$$

Example 8.3

Strategy

Solution

$$K_{a2} = \frac{a_{H_3O^+}a_{CO_3^{2-}}}{a_{HCO_3^-}}$$

$$a_{CO_3^{2-}} = \frac{a_{HCO_3^-}K_{a2}}{a_{H_3O^+}}$$

Self-test 8.6

Calculate the molar concentration of S^{2-} ions in $H_2S(aq)$.

[*Answer:* 7.1×10^{-15} mol dm^{-3}]

$$K_{a1} = \frac{[H_3O^+][HC_2O_4^-]}{[H_2C_2O_4]}$$

$$K_{a2} = \frac{[H_3O^+][C_2O_4^{2-}]}{[HC_2O_4^-]}$$

$$[HC_2O_4^-] = \frac{K_{a1}[H_2C_2O_4]}{[H_3O^+]}$$

$$[C_2O_4^{2-}] = \frac{K_{a2}[HC_2O_4^-]}{[H_3O^+]} = \frac{K_{a1}K_{a2}[H_2C_2O_4]}{[H_3O^+]^2}$$

$$
\begin{aligned}
F(\mathrm{H_2C_2O_4}) &= [\mathrm{H_2C_2O_4}] + \frac{K_{a1}[\mathrm{H_2C_2O_4}]}{[\mathrm{H_3O^+}]} + \frac{K_{a1}K_{a2}[\mathrm{H_2C_2O_4}]}{[\mathrm{H_3O^+}]^2} \\
&= \left\{1 + \frac{K_{a1}}{[\mathrm{H_3O^+}]} + \frac{K_{a1}K_{a2}}{[\mathrm{H_3O^+}]^2}\right\}[\mathrm{H_2C_2O_4}] \\
&= \frac{1}{[\mathrm{H_3O^+}]^2}\{[\mathrm{H_3O^+}]^2 + [\mathrm{H_3O^+}]K_{a1} + K_{a1}K_{a2}\}[\mathrm{H_2C_2O_4}]
\end{aligned}
$$

$$
\alpha(\mathrm{HC_2O_4^-}) = \frac{[\mathrm{HC_2O_4^-}]}{F(\mathrm{H_2C_2O_4})} = \frac{[\mathrm{H_3O^+}]K_{a1}}{[\mathrm{H_3O^+}]^2 + [\mathrm{H_3O^+}]K_{a1} + K_{a1}K_{a2}}
$$

$$
\alpha(\mathrm{C_2O_4^{2-}}) = \frac{[\mathrm{C_2O_4^{2-}}]}{F(\mathrm{H_2C_2O_4})} = \frac{K_{a1}K_{a2}}{[\mathrm{H_3O^+}]^2 + [\mathrm{H_3O^+}]K_{a1} + K_{a1}K_{a2}}
$$

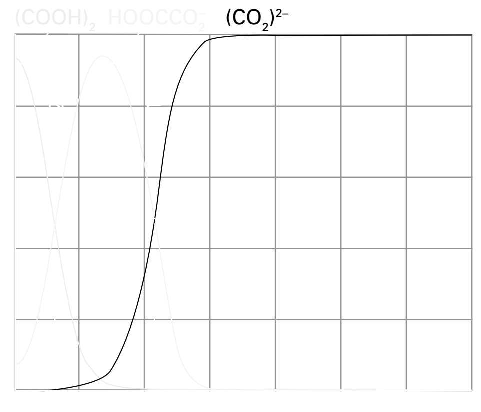


Fig. 8.1 The fractional composition of the protonated and deprotonated forms of oxalic acid in aqueous solution as a function of pH. Note that conjugate pairs are present at equal concentrations when the pH is equal to the pK_a of the acid member of the pair.

Self-test 8.7

Construct the diagram for the fraction of protonated species in an aqueous solution of phosphoric acid.

[*Answer*: Fig. 8.2]

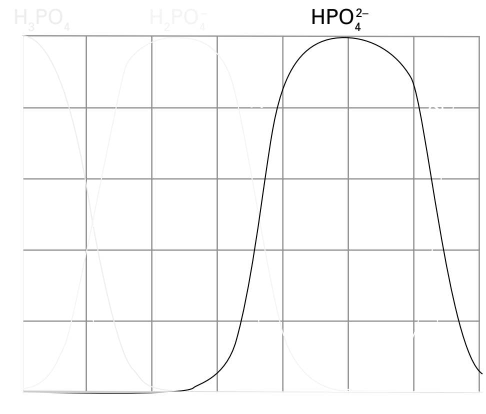


Fig. 8.2 The fractional composition of the protonated and deprotonated forms of phosphoric acid in aqueous solution as a function of pH.

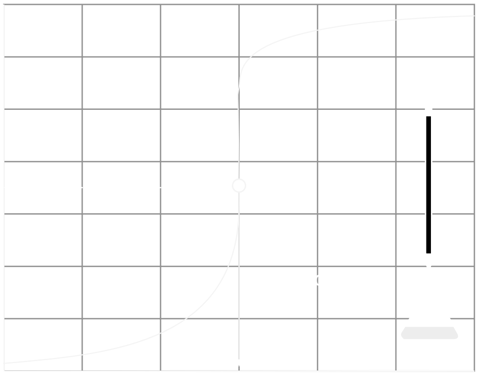
− − +

$$K_{a1} = \frac{[H_3O^+][HA^-]}{[H_2A]} = \frac{(y-x)(F-x-y)}{x}$$

$$K_{a2} = \frac{[H_3O^+][A^{2-}]}{[HA^-]} = \frac{(y-x)y}{F-x-y}$$

$$K_{a1}K_{a2} = \frac{(y-x)^2y}{x} = [H_3O^+]^2 \times \frac{y}{x}$$

Salts in water



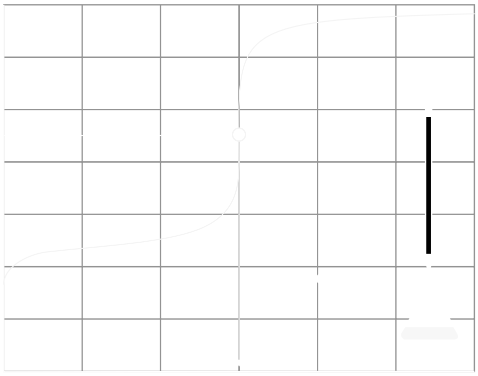
Self-test 8.9

Estimate the pH of 0.0025 M $NH(CH_3)_3Cl(aq)$ at 25°C.

[*Answer:* 6.2]

8.5 Acid–base titrations

Fig. 8.3



A brief comment

Fig. 8.4

$$K_a = \frac{a_{H_3O^+}a_{CH_3CO_2^-}}{a_{CH_3COOH}} \approx \frac{a_{H_3O^+}[\text{base}]}{[\text{acid}]}$$

$$a_{H_3O^+} \approx \frac{K_a[\text{acid}]}{[\text{base}]}$$

Use $\log xy = \log x + \log y$

$$-\log a_{H_3O^+} \approx -\log \frac{K_a[\text{acid}]}{[\text{base}]} = -\log K_a - \log \frac{[\text{acid}]}{[\text{base}]}$$

$$\text{pH} \approx \text{p}K_a - \log \frac{[\text{acid}]}{[\text{base}]}$$

$$\frac{[\text{acid}]}{[\text{base}]} = \frac{n_{\text{acid}}/V}{n_{\text{base}}/V} = \frac{n_{\text{acid}}}{n_{\text{base}}}$$

$$\text{pH} \approx 4.75 - \log \frac{1.50 \times 10^{-3}}{1.00 \times 10^{-3}} = 4.6$$

Self-test 8.10

Calculate the pH after the addition of a further 5.00 cm^3 of titrant.

[*Answer:* 5.4]

A brief illustration

$$V_{\text{base}} = \frac{2.50\times10^{-3}\,\text{mol}}{0.200\ \text{mol dm}^{-3}} = 1.25\times10^{-2}\,\text{dm}^3$$

$$[\text{CH}_3\text{CO}_2^-] = \frac{2.50\times10^{-3}\ \text{mol}}{37.5\times10^{-3}\ \text{dm}^3} = 6.67\times10^{-2}\ \text{mol dm}^{-3}$$

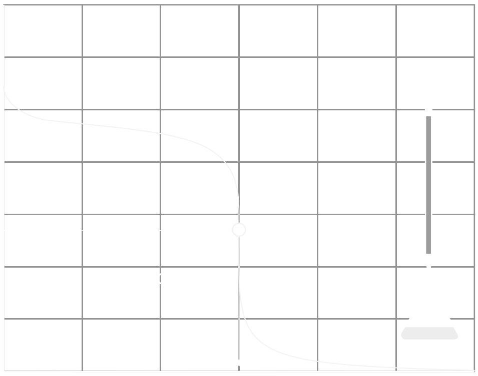


Fig. 8.5

8.6 Buffer action

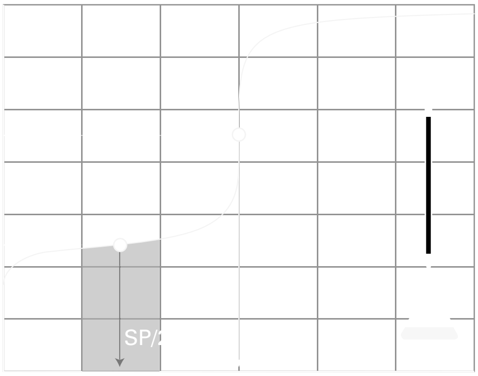


Fig. 8.6

A brief illustration

Self-test 8.11

Calculate the pH of an aqueous buffer solution that contains equal amounts of NH_3 and NH_4Cl.

[*Answer:* 9.25; more realistically: 9]

Box 8.1 Buffer action in blood

Example 8.6

Strategy

Solution

$$\mathrm{pH} = 4.75 - \log\frac{0.080}{0.040} = 4.45$$

$$\mathrm{pH} = 4.75 - \log\frac{0.088}{0.032} = 4.31$$

Self-test 8.12

Estimate the change in pH when 0.20 cm^3 of 1.5 mol dm^{-3} NaOH(aq) is added to 30 cm^3 of (a) pure water and (b) a phosphate buffer that is 0.20 mol dm^{-3} KH_2PO_4(aq) and 0.30 mol dm^{-3} K_2HPO_4(aq).

[*Answer:* (a) 7.00 to 9.00; (b) 7.39 to 4.42]

$$K_{\mathrm{In}} = \frac{a_{\mathrm{H_3O^+}}a_{\mathrm{In^-}}}{a_{\mathrm{HIn}}}$$

$$\frac{[\mathrm{In^-}]}{[\mathrm{HIn}]} \approx \frac{K_{\mathrm{In}}}{a_{\mathrm{H_3O^+}}}$$

$-\mathrm{p}K_{\mathrm{In}}$ $\qquad$ $-\mathrm{pH}$

Use log(*x*/*y*) = log *x* – log *y*

$$\log\frac{[\mathrm{In^-}]}{[\mathrm{HIn}]} \approx \mathrm{pH} - \mathrm{p}K_{\mathrm{In}}$$

Table 8.3
Indicator colour changes

Indicator	Acid colour	pH range of colour change	pK_{In}	Base colour
Thymol blue	Red	1.2 to 2.8	1.7	Yellow
Methyl orange	Red	3.2 to 4.4	3.4	Yellow
Bromophenol blue	Yellow	3.0 to 4.6	3.9	Blue
Bromocresol green	Yellow	4.0 to 5.6	4.7	Blue
Methyl red	Red	4.8 to 6.0	5.0	Yellow
Bromothymol blue	Yellow	6.0 to 7.6	7.1	Blue
Litmus	Red	5.0 to 8.0	6.5	Blue
Phenol red	Yellow	6.6 to 8.0	7.9	Red
Thymol blue	Yellow	9.0 to 9.6	8.9	Blue
Phenolphthalein	Colorless	8.2 to 10.0	9.4	Pink
Alizarin yellow	Yellow	10.1 to 12.0	11.2	Red
Alizarin	Red	11.0 to 12.4	11.7	Purple

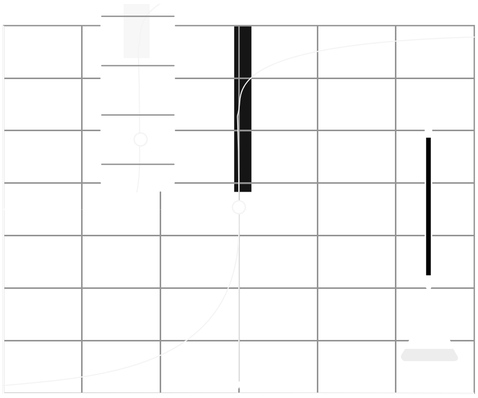


Fig. 8.7

Self-test 8.13

What is the ratio of the yellow and blue forms of bromocresol green in solution of pH (a) 3.7, (b) 4.7, and (c) 5.7?

[*Answer:* (a) 10:1, (b) 1:1, (c) 1:10]

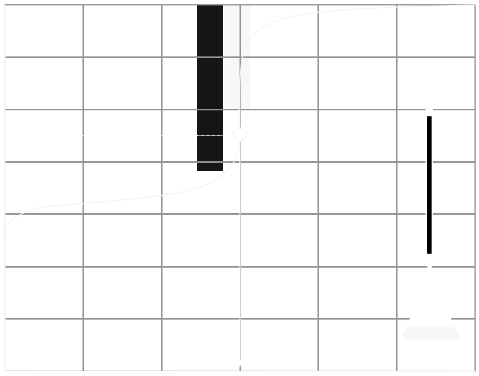


Fig. 8.8

Self-test 8.14

Vitamin C is a weak acid (ascorbic acid), and the amount in a sample may be determined by titration with sodium hydroxide solution. Should you use methyl red or phenolphthalein as the indicator?

[*Answer:* phenolphthalein]

Solubility equilibria

8.8 The solubility constant

Table 8.4

Solubility constants at 298.15 K

Compound	Formula	K_s
Aluminium hydroxide	$Al(OH)_3$	1.0×10^{-33}
Antimony sulfide	Sb_2S_3	1.7×10^{-93}
Barium carbonate	$BaCO_3$	8.1×10^{-9}
fluoride	BaF_2	1.7×10^{-6}
sulfate	$BaSO_4$	1.1×10^{-10}
Bismuth sulfide	Bi_2S_3	1.0×10^{-97}
Calcium carbonate	$CaCO_3$	8.7×10^{-9}
fluoride	CaF_2	4.0×10^{-11}
hydroxide	$Ca(OH)_2$	5.5×10^{-6}
sulfate	$CaSO_4$	2.4×10^{-5}
Copper(I) bromide	CuBr	4.2×10^{-8}
chloride	CuCl	1.0×10^{-6}
iodide	CuI	5.1×10^{-12}
sulfide	Cu_2S	2.0×10^{-47}
Copper(II) iodate	$Cu(IO_3)_2$	1.4×10^{-7}
oxalate	CuC_2O_4	2.9×10^{-8}
sulfide	CuS	8.5×10^{-45}
Iron(II) hydroxide	$Fe(OH)_2$	1.6×10^{-14}
sulfide	FeS	6.3×10^{-18}
Iron(III) hydroxide	$Fe(OH)_3$	2.0×10^{-39}
Lead(II) bromide	$PbBr_2$	7.9×10^{-5}
chloride	$PbCl_2$	1.6×10^{-5}
fluoride	PbF_2	3.7×10^{-8}
iodate	$Pb(IO_3)_2$	2.6×10^{-13}
iodide	PbI_2	1.4×10^{-8}
sulfate	$PbSO_4$	1.6×10^{-8}
sulfide	PbS	3.4×10^{-28}
Magnesium ammonium phosphate	$MgNH_4PO_4$	2.5×10^{-13}
carbonate	$MgCO_3$	1.0×10^{-5}
fluoride	MgF_2	6.4×10^{-9}
hydroxide	$Mg(OH)_2$	1.1×10^{-11}
Mercury(I) chloride	Hg_2Cl_2	1.3×10^{-18}
iodide	Hg_2I_2	1.2×10^{-28}
Mercury(II) sulfide	HgS black:	1.6×10^{-52}
	red:	1.4×10^{-53}
Nickel(II) hydroxide	$Ni(OH)_2$	6.5×10^{-18}
Silver bromide	AgBr	7.7×10^{-13}
carbonate	Ag_2CO_3	6.2×10^{-12}
chloride	AgCl	1.6×10^{-10}
hydroxide	AgOH	1.5×10^{-8}
iodide	AgI	1.5×10^{-16}
sulfide	Ag_2S	6.3×10^{-51}
Zinc hydroxide	$Zn(OH)_2$	2.0×10^{-17}
sulfide	ZnS	1.6×10^{-24}

Self-test 8.15

Copper occurs in many minerals, one of which is chalcocite, Cu_2S. What is the approximate solubility of this compound in water at 25°C? Use the data for Cu_2S in Table 8.4.

[*Answer:* 1.7×10^{-16} mol dm^{-3}]

8.9 The common-ion effect

$$S' \approx \frac{K_s}{C}$$

Self-test 8.16

Estimate the molar solubility of calcium fluoride, CaF_2, in (a) water, (b) 0.010 M NaF(aq).

[*Answer:* (a) 2.2×10^{-4} mol dm^{-3}; (b) 4.0×10^{-7} mol dm^{-3}]

8.10 The effect of added salts on solubility

■ A brief illustration

☐ **1**

☐ **2**

☐ **3**

☐ **4**

☐ **5**

☐ **6**

Property	Equation	Comment

Discussion questions

8.1

8.2

8.3

8.4

8.5

8.6

8.7

Exercises

8.1

8.2

8.3

8.4

8.5

8.6

8.7

8.8 The pK_b of ammonia in water varies with temperature as follows:

θ/°C	10	15	20	25	30	35
pK_b	4.804	4.782	4.767	4.751	4.740	4.733

Deduce as much information as you can from these values.

8.9 The pK_b of the organic base nicotine (denoted Nic) is [illegible]. Write the corresponding protonation reaction, the [illegible]ation reaction of the conjugate acid, and the value of p[illegible] [illegible]ture.

8.10 [illegible] concentration of H_3O^+ ions in the following solutions [illegible] measured at 25°C. Calculate the pH and pOH of the [illegible] (a) 1.5 × 10^{-5} mol dm^{-3} (a sample of rain water), [illegible] mol dm^{-3}, (c) 5.1 × 10^{-14} mol dm^{-3}, (d) 5.01 × $10^{-[illegible]}$ mo[illegible]

8.11 Calculate the mo[illegible]ration of H_3O^+ ions and the pH of the following soluti[illegible]0 cm^3 of 0.144 M HCl(aq) was added to 25.0 cm^3 of [illegible]aOH(aq), (b) 25.0 cm^3 of 0.15 M HCl(aq) was added [illegible] of 0.15 M KOH(aq), (c) 21.2 cm^3 of 0.22 M HNO_3(aq) [illegible] to 10.0 cm^3 of 0.30 M NaOH(aq).

8.12 Determine whether aqueous solution[illegible] [illegible]ollowing salts have a pH equal to, greater than, or less [illegible] [illegible] or pH < 7, write a chemical equation to justify [illegible] (a) NH_4Br, (b) Na_2CO_3, (c) KF, (d) KBr, (e) $AlCl_3$, (f) [illegible]

8.13 Sodium acetate, $NaCH_3CO_2$, of mass 7.4 g is [illegible] prepare 250 cm^3 of aqueous solution. What is the pH of the solution?

8.14 What is the pH of a solution when 2.75 g of ammonium chloride, NH_4Cl, is used to make 100 cm^3 of aqueous solution?

8.15 An aqueous solution of volume 1.0 dm^3 contains 10.0 g of potassium bromide. What is the percentage of Br^- ions that are protonated?

8.16 There are many organic acids and bases in our cells, and their presence modifies the pH of the fluids inside them. It is useful to be able to assess the pH of solutions of acids and bases and to make inferences from measured values of the pH. A solution of equal concentrations of lactic acid and sodium lactate was found to have pH = 3.08. (a) What are the values of pK_a and K_a of lactic acid? (b) What would the pH be if the acid had twice the concentration of the salt?

8.17 Sketch reasonably accurately the pH curve for the titration of 25.0 cm^3 of 0.15 M $Ba(OH)_2$(aq) with 0.22 M HCl(aq). Mark on the curve (a) the initial pH, (b) the pH at the stoichiometric point.

8.18 Determine the fraction of solute deprotonated or protonated in (a) 0.25 M C_6H_5COOH(aq), (b) 0.150 M NH_2NH_2(aq) (hydrazine), (c) 0.112 M $(CH_3)_3N$(aq) (trimethylamine).

8.19 Calculate the pH, pOH, and fraction of solute protonated or deprotonated in the following aqueous solutions: (a) 0.150 M $CH_3CH(OH)COOH$(aq) (lactic acid), (b) 2.4 × 10^{-4} M $CH_3CH(OH)COOH$(aq), (c) 0.25 M $C_6H_5SO_3H$(aq) (benzenesulfonic acid).

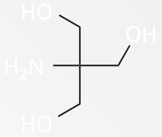
8.20 Show how the composition of an aqueous solution that contains 20 mmol dm^{-3} glycine varies with pH.

8.21 Show how the composition of an aqueous solution that contains 30 mmol dm^{-3} tyrosine varies with pH.

8.22 Estimate the pH of an aqueous solution of sodium hydrogenoxalate. Under what conditions is this estimate reasonably reliable?

8.23 Calculate the pH of the following acid solutions at 25°C; ignore second deprotonations only when that approximation is justified. (a) 1.0 × 10^{-4} M H_3BO_3(aq) (boric acid acts as a monoprotic acid), (b) 0.015 M H_3PO_4(aq), (c) 0.10 M H_2SO_3(aq).

8.24 The weak base colloquially known as Tris, and more precisely as tris(hydroxymethyl)aminomethane (**3**), has pK_a = 8.3 at 20°C and is commonly used to produce a buffer for biochemical applications. At what pH would you expect Tris to act as a buffer in a solution that has equal molar concentrations of Tris and its conjugate acid?



3 tris(hydroxymethyl)aminomethane

8.25 The amino acid tyrosine has pK_a = 2.20 for deprotona[illegible] of its carboxylic acid group. What are the relative con[illegible]tions of tyrosine and its conjugate base at a pH of (a) 7, [illegible] 5?

8.26 [illegible]late the molar concentrations of $(COOH)_2$, $HOOCCO_2^-$, [illegible], H_3O^+, and OH^- in 0.15 M $(COOH)_2$(aq). (b) Calculat[illegible] concentrations of H_2S, HS^-, S^{2-}, H_3O^+, and OH^- in 0.[illegible](aq).

8.27 A sample of [illegible] CH_3COOH(aq) of volume 25.0 cm^3 is titrated with 0.10 [illegible]. The K_a for CH_3COOH is 1.8 × 10^{-5}. (a) What is the [illegible] CH_3COOH(aq)? (b) What is the pH after the addition [illegible] of 0.10 M NaOH(aq)? (c) What volume of 0.10 M NaO[illegible] [illegible]uired to reach halfway to the stoichiometric point? [illegible] the pH at that half-way point. (e) What volume of [illegible] NaOH(aq) is required to reach the stoichiometric poi[illegible] [illegible]culate the pH at the stoichiometric point.

8.28 A buffer solution of volume 100 cm^3 cons[illegible] CH_3COOH(aq) and 0.10 M $Na(CH_3CO_2)$(aq). (a) What [illegible] (b) What is the pH after the addition of 3.3 mmol NaOH [illegible] buffer solution? (c) What is the pH after the addition of [illegible] mmol HNO_3 to the initial buffer solution?

8.29 Predict the pH region in which each of the following buffers will be effective, assuming equal molar concentrations of the acid and its conjugate base: (a) sodium lactate and lactic acid, (b) sodium benzoate and benzoic acid, (c) potassium hydrogenphosphate and potassium phosphate, (d) potassium hydrogenphosphate and potassium dihydrogenphosphate, (e) hydroxylamine and hydroxylammonium chloride.

8.30 At the half-way point in the titration of a weak acid with a strong base the pH was measured as 5.16. What is the acidity constant and the pK_a of the acid? What is the pH of the solution that is 0.025 M in the acid?

8.31 Calculate the pH of (a) 0.10 M $NH_4Cl(aq)$, (b) 0.25 M $NaCH_3CO_2(aq)$, (c) 0.200 M $CH_3COOH(aq)$.

8.32 Calculate the pH at the stoichiometric point of the titration of 25.00 cm^3 of 0.150 M lactic acid with 0.188 M [illegible]H(aq).

8.33 [illegible]ch the pH curve of a solution containing 0.10 M NaC[illegible] and a variable amount of acetic acid.

8.34 Fro[illegible] formation in Tables 8.1 and 8.2, select suitable bu[illegible] pH = 2.2 and (b) pH = 7.0.

8.35 Write the [illegible] for the solubility constants of the following comp[illegible] AgI, (b) Hg_2S, (c) $Fe(OH)_3$, (d) Ag_2CrO_4.

8.36 Use the data in Table [illegible] timate the molar solubilities of (a) $BaSO_4$, (b) Ag_2C[illegible] $(OH)_2$, (d) Hg_2Cl_2 in water.

8.37 Use the data in Table 8.4 to esti[illegible] solubility in water of each sparingly soluble substance [illegible] spective solution: (a) silver bromide in 1.4×10^{-3} M Na[illegible] magnesium carbonate in 1.1×10^{-5} M $Na_2CO_3(aq)$, [illegible](II) sulfate in a 0.10 M $CaSO_4(aq)$, (d) nickel(II) hydroxide [illegible] 10^{-5} M $NiSO_4(aq)$.

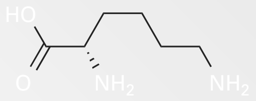
8.38 The solubility of mercury(I) iodide is 5.5 fmol [illegible] (1 fmol = 10^{-15} mol) in water at 25°C. What is the standard Gibbs energy of dissolution of the salt?

8.39 Thermodynamic data can be used to predict the solubilities of compounds that would be very difficult to measure directly. Calculate the solubility of mercury(II) chloride in water at 25°C from standard Gibbs energies of formation.

8.40 (a) Derive an expression for the ratio of solubilities of AgCl at two different temperatures; assume that the standard enthalpy of solution of AgCl is independent of temperature in the range of interest. (b) Do you expect the solubility of AgCl to increase or decrease as the temperature is raised?

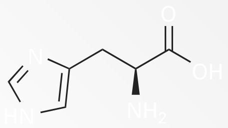
Projects

8.41 Deduce expressions for the fractions of each type of species present in an aqueous solution of lysine (**4**) as a function of pH and plot the appropriate speciation diagram. Use the following values of the acidity constants: p$K_a(H_3Lys^{2+})$ = 2.18, p$K_a(H_2Lys^+)$ = 8.95, pK_a(HLys) = 10.53. *Hint:* Although it is instructive to rework Example 8.4 for a triprotic species, the expressions for the fraction can easily be written down by analogy with those in the example.



4 Lysine (Lys)

8.42 Using the insights gained through your work on Exercise 8.41, and *without doing a calculation*, sketch the speciation diagram for histidine (**5**) in water and label the axes with the significant values of pH. Use p$K_a(H_3His^{2+})$ = 1.77, p$K_a(H_2His^+)$ = 6.10, pK_a(HHis) = 9.18.



5 Histidine (His)

8.43 Here[illegible]lore buffer action in blood more quantitatively. (a) Wh[illegible] values of the ratio $[HCO_3^-]/[H_2CO_3]$ at the onset of ac[illegible] alkalosis? (b) The Bohr effect may be understood in te[illegible] dependence on pH of the degree of cooperativity in the [illegible] O_2 by haemoglobin. Based on the description of the [illegible] given here and the information provided in Exercis[illegible] oes the Hill coefficient of haemoglobin increase or dec[illegible] pH?

Ions in solution

Box 9.1 Ion channels and pumps

Electrochemical cells

Box 9.2 Fuel cells

Applications of standard potentials

CHECKLIST OF KEY IDEAS
TABLE OF KEY EQUATIONS
QUESTIONS AND EXERCISES

Ions in solution

A brief comment

$$E_p = \frac{Q_1 Q_2}{4\pi\varepsilon_0 r}$$

9.1 The Debye–Hückel theory

■ **A brief illustration**

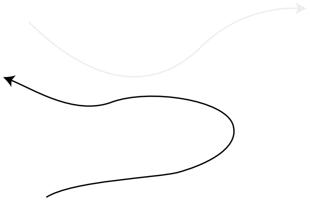
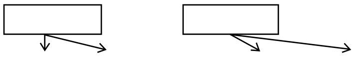
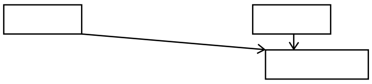
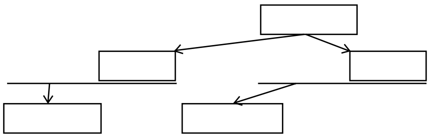


Fig. 9.1

Derivation 9.1







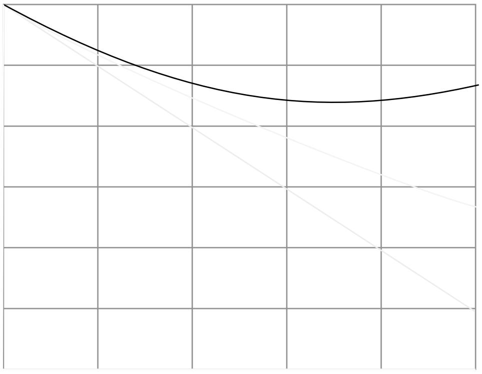


Fig. 9.2

A brief illustration

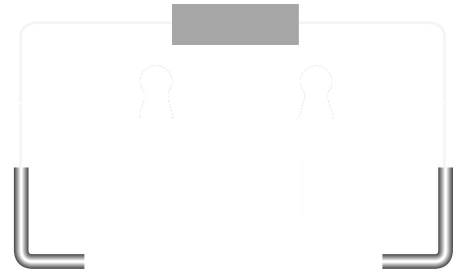


Fig. 9.3

$$I = \tfrac{1}{2}\sum_i z_i^2 b_i / b$$

$$\log \gamma_\pm = -\frac{A\,|z_+ z_-|\,I^{1/2}}{1 + BI^{1/2}} + CI$$

9.2 The migration of ions

……

A brief comment

$$\Lambda_{\mathrm{m}} = \frac{\kappa}{c}$$

Example 9.1

Strategy

Solution

	Species		
	CH_3COOH	H_3O^+	$CH_3CO_2^-$

$$K_a = \frac{[H_3O^+][CH_3CO_2^-]}{[CH_3COOH]} = \frac{x^2}{0.010 - x}$$

Self-test 9.1

The molar conductivity of 0.0250 M HCOOH(aq) is 4.61 mS m^2 mol^{-1}. What is the pK_a of formic acid?

[*Answer:* 3.49]

$$u = \frac{ez}{6\pi\eta a}$$

$$s = \frac{ez\mathcal{E}}{6\pi\eta a}$$

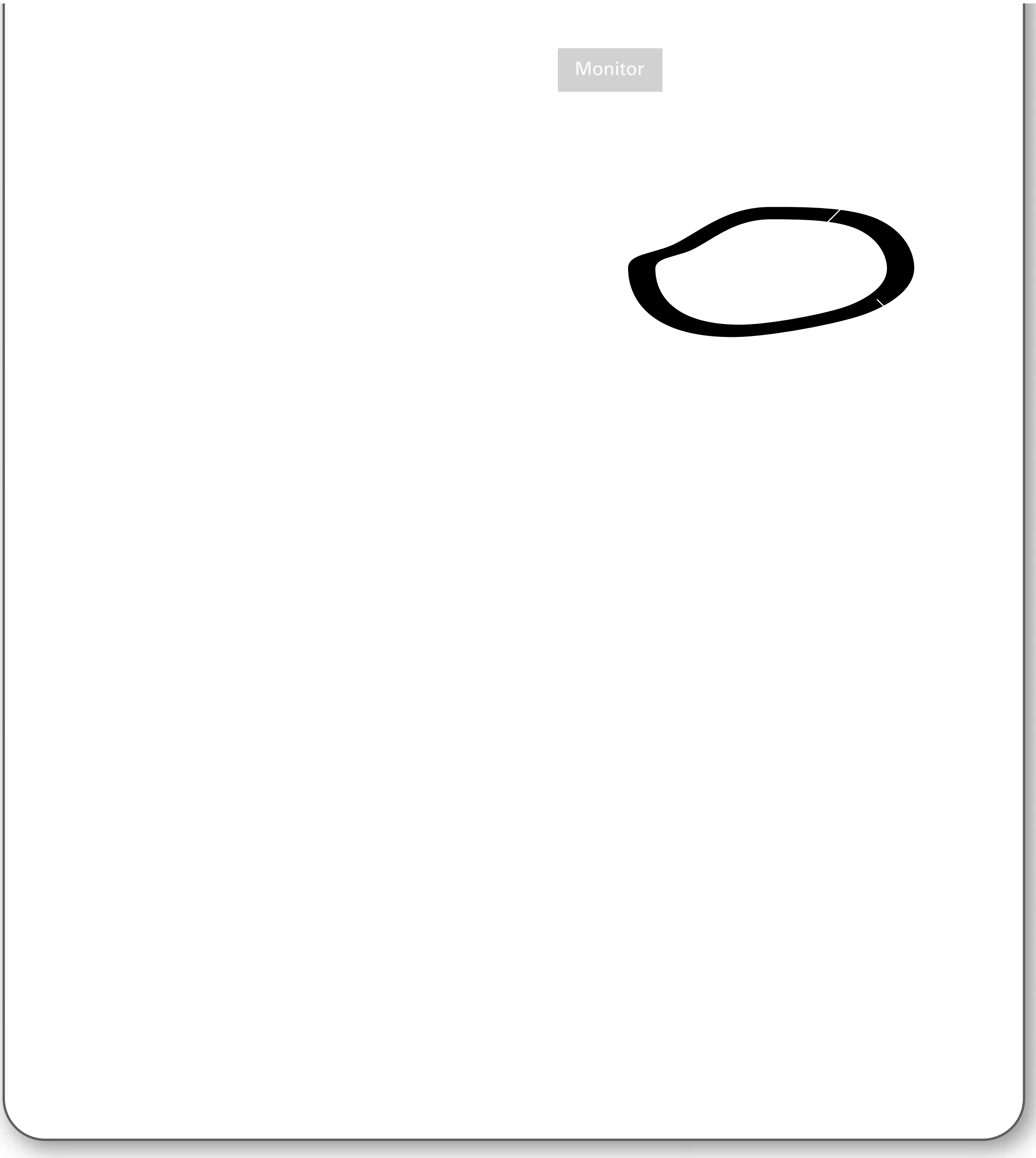
$$\Delta G_{\mathrm{m}} = G_{\mathrm{m,in}} - G_{\mathrm{m,out}} = RT \ln \frac{a_{\mathrm{in}}}{a_{\mathrm{out}}}$$

$[\mathrm{A}]_{\mathrm{out}}$. If A is an ion, there is a second contribution to ΔG_{m} that is due to the different potential energy of the ions on each side of the bilayer, where the difference in electrostatic potential is $\Delta\phi = \phi_{\mathrm{in}} - \phi_{\mathrm{out}}$. The final expression for ΔG is then

$$\Delta G_{\mathrm{m}} = RT \ln \frac{[\mathrm{A}]_{\mathrm{in}}}{[\mathrm{A}]_{\mathrm{out}}} + zF\Delta\phi$$

where z is the ion charge number and F is Faraday's constant. This equation implies that there is a tendency, called *passive transport*, for a species to move down concentration and membrane potential gradients. It is also possible to move a species against these gradients, but now the flow must be driven by an exergonic process, such as the hydrolysis of ATP. This process is called *active transport*.

The transport of ions into or out of a cell needs to be mediated (that is, facilitated by other species) because the hydrophobic environment of the membrane is inhospitable to ions. There are two mechanisms for ion transport:



Electrochemical cells

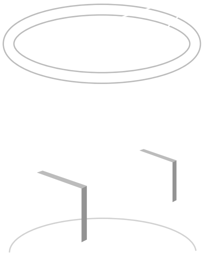


Fig. 9.5

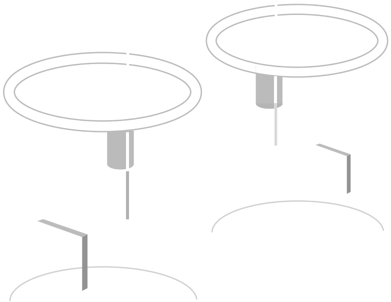


Fig. 9.6

9.3 Half-reactions and electrodes

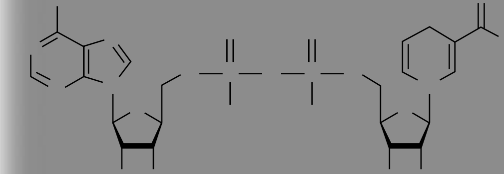
Self-test 9.2

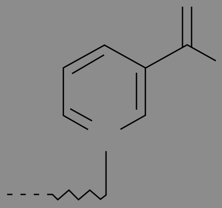
Identify the species that have undergone oxidation and reduction in the reaction $CuS(s) + O_2(g) \rightarrow Cu(s) + SO_2(g)$.

[*Answer*: Cu(+2) reduced to Cu(0), S(−2) oxidized to S(+4), O(0) reduced to O(−2)]

Box 9.2 Fuel cells

Example 9.2





$$Q = \frac{a_{\mathrm{NADH}}}{a_{\mathrm{NAD^+}}\,a_{\mathrm{H^+}}} \approx \frac{[\mathrm{NADH}]}{[\mathrm{NAD^+}][\mathrm{H^+}]}$$

9.4 Reactions at electrodes

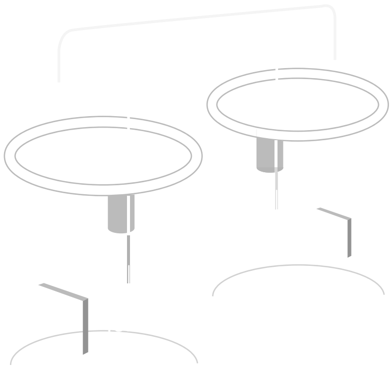


Fig. 9.7

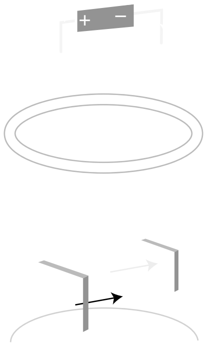


Fig. 9.8

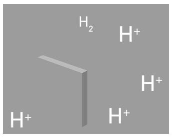


Fig. 9.9

$$Q = \frac{1}{p_{O_2} a_{H^+}^4}$$

Self-test 9.4

Write the half-reaction and the reaction quotient for a chlorine gas electrode.

[*Answer:* $Cl_2(g) + 2\,e^- \rightarrow 2\,Cl^-(aq)$, $Q = a_{Cl^-}^2/p_{Cl_2}$]

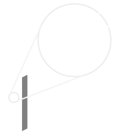


Fig. 9.10

$$Q = \frac{a_{HSO_4^-}}{a_{H^+}}$$

Self-test 9.5

Write the half-reaction and the reaction quotient for the *calomel electrode*, $Hg(l)|Hg_2Cl_2(s)|Cl^-(aq)$, in which mercury(I) chloride (calomel) is reduced to mercury metal in the presence of chloride ions. This electrode is a component of instruments used to measure pH, as explained later.

[*Answer:* $Hg_2Cl_2(s) + 2\,e^- \rightarrow 2\,Hg(l) + 2\,Cl^-(aq)$, $Q = a_{Cl^-}^2$]

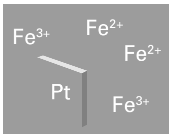


Fig. 9.11

$$Q = \frac{a_{Red}}{a_{Ox}}$$

$$Q = \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}}$$

9.5 Varieties of cell

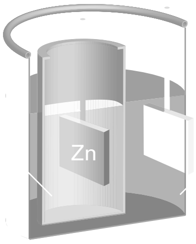


Fig. 9.12

9.6 The cell reaction

Self-test 9.6

Write the chemical equation for the reaction in the cell $Ag(s)|AgBr(s)|NaBr(aq)||NaCl(aq)|Cl_2(g)|Pt(s)$.

[*Answer:* $2\,Ag(s) + 2\,Br^-(aq) + Cl_2(g) \rightarrow 2\,AgBr(s) + 2\,Cl^-(aq)$]

9.7 The cell potential

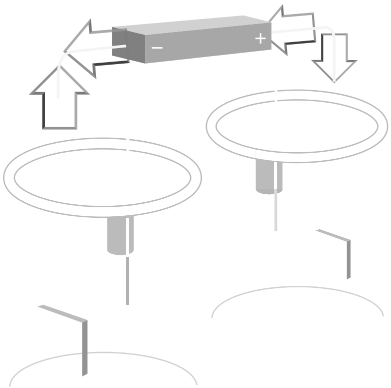


Fig. 9.13

Derivation 9.3

A brief illustration

$$E_{\text{cell}} = -\frac{\Delta_r G}{\nu F} = -\frac{(-1\times 10^5\ \text{J mol}^{-1})}{1\times(9.6485\times 10^4\ \text{C mol}^{-1})} = 1\ \text{V}$$

$$E_{\text{cell}} = E_{\text{cell}} - \frac{RT}{\nu F}\ln Q$$

$$E_{\text{cell}} = -\frac{\Delta_r G}{\nu F}$$

$$\frac{RT}{F} = \frac{(8.314\ 47\ \text{J K}^{-1}\ \text{mol}^{-1})\times(298.15\ \text{K})}{9.6485\times 10^4\ \text{C mol}^{-1}}$$

$$\frac{RT}{F} = 25.693\ \text{mV}$$

9.8 Cells at equilibrium

$$0 = E_{\text{cell}} - \frac{RT}{\nu F}\ln K$$

$$\ln K = \frac{\nu F E_{\text{cell}}}{RT}$$

A brief illustration

$$\ln K = \frac{2\times(9.6485\times 10^4\ \text{C mol}^{-1})\times(1.10\ \text{V})}{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\times(298.15\ \text{K})}$$

$$= \frac{2\times 9.6485\times 1.10\times 10^4}{8.3145\times 298.15}$$

A brief comment

Table 9.3

Standard potentials at 25°C

Reduction half-reaction				$E^{\ominus}$/V
Oxidizing agent			Reducing agent	
Strongly oxidizing				
F_2	+ 2 e^-	→	2 F^-	+2.87
$S_2O_8^{2-}$	+ 2 e^-	→	2 SO_4^{2-}	+2.05
Au^+	+ e^-	→	Au	+1.69
Pb^{4+}	+ 2 e^-	→	Pb^{2+}	+1.67
Ce^{4+}	+ e^-	→	Ce^{3+}	+1.61
$MnO_4^- + 8\,H^+$	+ 5 e^-	→	$Mn^{2+} + 4\,H_2O$	+1.51
Cl_2	+ 2 e^-	→	2 Cl^-	+1.36
$Cr_2O_7^{2-} + 14\,H^+$	+ 6 e^-	→	$2\,Cr^{3+} + 7\,H_2O$	+1.33
$O_2 + 4\,H^+$	+ 4 e^-	→	2 H_2O	+1.23, +0.81 at pH = 7
Br_2	+ 2 e^-	→	2 Br^-	+1.09
Ag^+	+ e^-	→	Ag	+0.80
Hg_2^{2+}	+ 2 e^-	→	2 Hg	+0.79
Fe^{3+}	+ e^-	→	Fe^{2+}	+0.77
I_2	+ e^-	→	2 I^-	+0.54
$O_2 + 2\,H_2O$	+ 4 e^-	→	4 OH^-	+0.40, +0.81 at pH = 7
Cu^{2+}	+ 2 e^-	→	Cu	+0.34
AgCl	+ e^-	→	$Ag + Cl^-$	+0.22
2 H^+	+ 2 e^-	→	H_2	0, by definition
Fe^{3+}	+ 3 e^-	→	Fe	–0.04
$O_2 + H_2O$	+ 2 e^-	→	$HO_2^- + OH^-$	–0.08
Pb^{2+}	+ 2 e^-	→	Pb	–0.13
Sn^{2+}	+ 2 e^-	→	Sn	–0.14
Fe^{2+}	+ 2 e^-	→	Fe	–0.44
Zn^{2+}	+ 2 e^-	→	Zn	–0.76
2 H_2O	+ 2 e^-	→	$H_2 + 2\,OH^-$	–0.83, –0.42 at pH = 7
Al^{3+}	+ 3 e^-	→	Al	–1.66
Mg^{2+}	+ 2 e^-	→	Mg	–2.36
Na^+	+ e^-	→	Na	–2.71
Ca^{2+}	+ 2 e^-	→	Ca	–2.87
K^+	+ e^-	→	K	–2.93
Li^+	+ e^-	→	Li	–3.05
			Strongly reducing	

For a more extensive table, see the Data section.

$$\ln K = \frac{0.37\ \mathrm{V}}{2.569 \times 10^{-2}\ \mathrm{V}} = \frac{37}{2.569}$$

$$E = E' - \frac{RT \ln 10}{F} \times \mathrm{pH}$$

Fig. 9.14

$$E = E^\ominus - \frac{RT}{2F}\ln\frac{\overset{1}{\boxed{a_{\mathrm{NADH}}}}}{a_{\mathrm{H^+}}\underset{1}{\boxed{a_{\mathrm{NAD^+}}}}} \overset{\ln 1/x = -\ln x}{=} E^\ominus + \frac{RT}{2F}\ln a_{\mathrm{H^+}}$$

$$E = E^\ominus + \frac{RT}{2F}\ln a_{\mathrm{H^+}} = E^\ominus - \frac{RT\ \ln 10}{2F}\times \mathrm{pH}$$

9.11 The determination of pH

Applications of standard potentials

9.12 The electrochemical series

Self-test 9.10

Does acidified dichromate ($Cr_2O_7^{2-}$) have a thermodynamic tendency to oxidize mercury metal to mercury(I)?

[*Answer:* yes]

9.13 The determination of thermodynamic functions

Example 9.7

Strategy

Solution

A note on good practice

Self-test 9.11

Given the standard potentials $E^{\ominus}(Fe^{3+},Fe) = -0.04$ V and $E^{\ominus}(Fe^{2+},Fe) = -0.44$ V, calculate $E^{\ominus}(Fe^{3+},Fe^{2+})$.

[*Answer:* +0.76 V]

$$\Delta_r S = \frac{\nu F(E_{\text{cell}} - E'_{\text{cell}})}{T - T'}$$

Derivation 9.4

The reaction entropy from the cell potential

The definition of the Gibbs energy is $G = H - TS$. This formula applies to all substances involved in a reaction, so at a given temperature $\Delta_r G^\ominus(T) = \Delta_r H^\ominus - T\Delta_r S^\ominus$. If we can ignore the weak temperature dependence of $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$, at a temperature T' we can write $\Delta_r G^\ominus(T') = \Delta_r H^\ominus - T'\Delta_r S^\ominus$. Therefore,

$$\Delta_r G^\ominus(T') - \Delta_r G^\ominus(T) = -(T' - T)\Delta_r S^\ominus$$

Substitution of $\Delta_r G^\ominus = -\nu F E^\ominus_{\text{cell}}$ then gives

$$-\nu F E^{\ominus\prime}_{\text{cell}} + \nu F E^\ominus_{\text{cell}} = -(T' - T)\Delta_r S^\ominus$$

which is easily rearranged into eqn 9.18.

$$\times\left(\frac{0.2699\text{ V} - 0.2669\text{ V}}{293\text{ K} - 303\text{ K}}\right)$$

Self-test 9.12

Predict the standard potential of the *Harned cell*

$$\text{Pt(s)}|\text{H}_2\text{(g)}|\text{HCl(aq)}|\text{AgCl(s)}|\text{Ag(s)}$$

at 303 K from tables of thermodynamic data for 298 K.

[*Answer:* +0.2168 V]

Fig. 9.15

☐ **1**

☐ **2**

☐ **3**

☐ **4**

☐ **5**

☐ **6**

☐ **7**

☐ **8**

☐ **9**

☐ **10**

☐ **11**

☐ **12**

☐ **13**

☐ **14**

☐ **15**

Property	Equation	Comment

Discussion questions

9.1

9.2

9.3

9.4

9.5

Exercises

9.1

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9.13

9.14

9.15

9.16

9.17

(a) $Ag(s)|AgNO_3(aq,b_L)||AgNO_3(aq,b_R)|Ag(s)$

(b) $Pt(s)|H_2(g,p_L)|HCl(aq)|H_2(g,p_R)|Pt(s)$

(c) $Pt(s)|K_3[Fe(CN)_6](aq),K_4[Fe(CN)_6](aq)||Mn^{2+}(aq),H^+(aq)|MnO_2(s)|Pt(s)$

(d) $Pt(s)|Cl_2(g)|HCl(aq)||HBr(aq)|Br_2(l)|Pt(s)$

(e) $Pt(s)|Fe^{3+}(aq),Fe^{2+}(aq)||Sn^{4+}(aq),Sn^{2+}(aq)|Pt(s)$

(f) $Fe(s)|Fe^{2+}(aq)||Mn^{2+}(aq),H^+(aq)|MnO_2(s)|Pt(s)$

9.18 Write the Nernst equations for the cells in the preced[illegible]ise.

9.19 [illegible] cells in which the following are the reactions. In each [illegible] the value for *ν* to use in the Nernst equation.

(a) Fe(s) + [illegible](aq) → $FeSO_4$(aq) + Pb(s)

(b) Hg_2Cl_2(s) [illegible] → 2 HCl(aq) + 2 Hg(l)

(c) 2 H_2(g) + O_2[illegible]O(l)

(d) H_2(g) + O_2(g) → [illegible]

(e) H_2(g) + I_2(g) → 2 HI(a[illegible]

(f) 2 CuCl(aq) → Cu(s) + Cu[illegible]

9.20 Use the standard potentials of [illegible]odes to calculate the standard potentials of the cells [illegible]e 9.17.

9.21 Use the standard potentials of the electro[illegible]lculate the standard potentials of the cells devised in E[illegible]19.

9.22 A fuel cell develops an electric potential from th[illegible]ical reaction between reagents supplied from an ou[illegible] source. What is the potential of a cell fuelled by (a) hydroge[illegible] and oxygen, (b) the complete oxidation of benzene at 1.0 bar and 298 K?

9.23 A fuel cell is constructed in which both electrodes make use of the oxidation of methane. The left-hand electrode makes use of the complete oxidation of methane to carbon dioxide and water; the right-hand electrode makes use of the partial oxidation of methane to carbon monoxide and water. (a) Which electrode is the cathode? (b) What is the cell potential at 25°C when all gases are at 1 bar?

9.24 The permanganate ion is a common oxidizing agent. What is the standard potential of the $MnO_4^-,H^+/Mn^{2+}$ couple at (a) pH = 6.00, (b) general pH?

9.25 State what you would expect to happen to the cell potential when the following changes are made to the corresponding cells in Exercise 9.17. Confirm your prediction by using the Nernst equation in each case.

(a) The molar concentration of silver nitrate in the left-hand compartment is increased.

(b) The pressure of hydrogen in the left-hand compartment is increased.

(c) The pH of the right-hand compartment is decreased.

(d) The concentration of HCl is increased.

(e) Some iron(III) chloride is added to both compartments.

(f) Acid is added to both compartments.

9.26 State what you would expect to happen to the cell potential when the following changes are made to the corresponding cells devised in Exercise 9.19. Confirm your prediction by using the Nernst equation in each case.

(a) The molar concentration of $FeSO_4$ is increased.

(b) Some nitric acid is added to both cell compartments.

(c) The pressure of oxygen is increased.

(d) The pressure of hydrogen is increased.

(e) Some (i) hydrochloric acid, (ii) hydroiodic acid is added to both compartments.

(f) Hydrochloric acid is added to both compartments.

9.27 (a) Calculate the standard potential of the cell $Hg(l)|HgCl_2(aq)||TlNO_3(aq)|Tl(s)$ at 25°C. (b) Calculate the cell potential when the molar concentration of the Hg^{2+} ion is 0.230 mol dm^{-3} and that of the Tl^+ ion is 0.720 mol dm^{-3}.

9.28 (a) Can mercury produce zinc metal from aqueous zinc sulfate under standard conditions? (b) Can chlorine gas oxidize water to oxygen gas under standard conditions in basic solution?

9.29 Calculate the standard Gibbs energies at 25°C of the following reactions from the standard potential data in the Data section.

(a) Ca(s) + 2 H_2O(l) → $Ca(OH)_2$(aq) + H_2(g)

(b) 2 Ca(s) + 4 H_2O(l) → 2 $Ca(OH)_2$(aq) + 2 H_2(g)

(c) Fe(s) + 2 H_2O(l) → $Fe(OH)_2$(aq) + H_2(g)

(d) $Na_2S_2O_8$(aq) + 2 NaI(aq) → I_2(s) + 2 Na_2SO_4(aq)

(e) [illegible]S_2O_8(aq) + 2 KI(aq) → I_2(s) + Na_2SO_4(aq) + K_2SO_4(aq)

(f) [illegible] Na_2CO_3(aq) → $PbCO_3$(aq) + 2 Na(s)

9.30 Ca[illegible] biological standard Gibbs energies of reactions of th[illegible]ng reactions and half-reactions:

(a) 2 NADH(a[illegible] + 2 H^+(aq) → 2 NAD^+(aq) + 2 H_2O(l) $E^\ominus = +1.14$ V

(b) Malate(aq) + NAD[illegible]xaloacetate(aq) + NADH(aq) + H^+(aq) $E^\ominus = -0.154$ V

(c) O_2(g) + 4H^+(aq) + 4 e^- → [illegible] $E^\ominus = +0.81$ V

9.31 Tabulated thermodynamic da[illegible]sed to predict the standard potential of a cell even [illegible] be measured directly. The standard Gibbs energ[illegible] reaction K_2CrO_4(aq) + 2 Ag(s) + 2 $FeCl_3$(aq) → Ag_2CrO_4[illegible]Cl(aq) + 2 KCl(aq) is −62.5 kJ mol^{-1} at 298 K. (a) Calcula[illegible]ard potential of the corresponding galvanic cell an[illegible] standard potential of the $Ag_2CrO_4/Ag,CrO_4^{2-}$ couple.

9.32 Estimate the potential at 25°C of the cell

$$Ag(s)|AgCl(s)|KCl(aq, 0.025\ mol\ kg^{-1})||AgNO_3(aq, 0.010\ mol\ kg^{-1})|Ag(s)$$

9.33 (a) Use the information in the Data section to calculate the standard potential of the cell $Ag(s)|AgNO_3(aq)||Cu(NO_3)_2(aq)|Cu(s)$ and the standard Gibbs energy and enthalpy of the cell reaction at 25°C. (b) Estimate the value of $\Delta_r G^{\ominus}$ at 35°C.

9.34 (a) Calculate the standard potential of the cell Pt(s)|cystine(aq), cysteine(aq)||H^+(aq)|O_2(g)|Pt(s) and the standard Gibbs energy and enthalpy of the cell reaction at 25°C. (b) Estimate the value of $\Delta_r G^{\ominus}$ at 35°C. Use $E^{\ominus} = -0.34$ V for the cysteine/cystine couple.

9.35 The biological standard potential of the couple pyruvic a[illegible] acid is −0.19 V at 25°C. What is the thermodyn[illegible] [illegible]dard potential of the couple? Pyruvic acid is CH_3CO[illegible]d lactic acid is $CH_3CH(OH)COOH$.

9.36 One e[illegible] important equilibrium is that between carbonate and [illegible]carbonate (bicarbonate) ions in natural water. (a) The [illegible]d Gibbs energies of formation of CO_3^{2-}(aq) and HCO_3^-(a[illegible]7.81 kJ mol^{-1} and −586.77 kJ mol^{-1}, respectively. Wh[illegible] standard potential of the $HCO_3^-/CO_3^{2-},H_2$ couple? (b) C[illegible]e standard potential of a cell in which the cell reac[illegible]CO_3(aq) + H_2O(l) → $NaHCO_3$(aq) + NaOH(aq). (c) Wri[illegible]nst equation for the cell, and (d) predict and calc[illegible]e in potential when the pH is changed to 7.0. (e) Calc[illegible]alue of pK_a for HCO_3^-(aq).

9.37 Calculate the equilibrium constants of the [illegible] reactions at 25°C from standard potential data:

(a) $Sn(s) + Sn^{4+}(aq) \rightleftharpoons 2\,Sn^{2+}(aq)$

(b) $Sn(s) + 2\,AgBr(s) \rightleftharpoons SnBr_2(aq) + 2\,Ag(s)$

(c) $Fe(s) + Hg(NO_3)_2(aq) \rightleftharpoons Hg(l) + Fe(NO_3)_2(aq)$

(d) $Cd(s) + CuSO_4(aq) \rightleftharpoons Cu(s) + CdSO_4(aq)$

(e) $Cu^{2+}(aq) + Cu(s) \rightleftharpoons 2\,Cu^+(aq)$

(f) $3\,Au^{2+}(aq) \rightleftharpoons Au(s) + 2\,Au^{3+}(aq)$

9.38 The dichromate ion in acidic solution is a common oxidizing agent for organic compounds. Derive an expression for the potential of an electrode for which the half-reaction is the reduction of $Cr_2O_7^{2-}$ ions to Cr^{3+} ions in acidic solution.

9.39 The molar solubilities of AgCl and $BaSO_4$ in water are 1.34×10^{-5} mol dm^{-3} and 9.51×10^{-4} mol dm^{-3}, respectively, at 25°C. Calculate their solubility constants from the appropriate standard potentials.

9.40 The potential of the cell Pt(s)|H_2(g)|HCl(aq)|AgCl(s)|Ag(s) is 0.312 V at 25°C. What is the pH of the electrolyte solution?

9.41 The molar solubility of AgBr is 2.6 μmol dm^{-3} at 25°C. What is the potential of the cell Ag(s)|AgBr(aq)|AgBr(s)|Ag(s) at that temperature?

9.42 The standard potential of the cell Ag(s)|AgI(s)|AgI(aq)|Ag(s) is +0.9509 V at 25°C. Calculate (a) the molar solubility of AgI and (b) its solubility constant.

Projects

9.43 Consider the Harned cell Pt(s)|H_2(g, 1 bar)|HCl(aq, b)|AgCl(s)|Ag(s). Show that the standard potential of the silver–silver-chloride electrode may be determined by plotting $E - (RT/F)\ln b$ against $b^{1/2}$. *Hint*: Express the cell potential in terms of activities, and use the Debye–Hückel law to estimate the mean activity coefficient. (b) Use the procedure you devised in part (a) and the following data at 25°C to determine the standard potential of the silver–silver-chloride electrode

$b/(10^{-3}\,b^{\ominus})$	3.215	5.619	9.138	25.63
E/V	0.520 53	0.492 57	0.468 60	0.418 24

9.44 The standard potentials of proteins are not commonly measured by the methods described in this chapter because proteins often lose their native structure and their function when they react on the surfaces of electrodes. In an alternative method, the oxidized protein is allowed to react with an appropriate electron donor in solution. The standard potential of the protein is then determined from the Nernst equation, the equilibrium concentrations of all species in solution, and the known standard potential of the electron donor. We illustrate this method with the protein cytochrome *c*. (a) The one-electron reaction between cytochrome *c*, cyt, and 2,6-dichloroindophenol, D, can be written as

$$\mathrm{cyt_{ox}} + \mathrm{D_{red}} \rightleftharpoons \mathrm{cyt_{red}} + \mathrm{D_{ox}}$$

Consider $E^{\ominus}_{\mathrm{cyt}}$ and $E^{\ominus}_{\mathrm{D}}$ to be the standard potentials of cytochrome *c* and D, respectively. Show that, at equilibrium (eq), a plot of $\ln([\mathrm{D_{ox}}]_{eq}/[\mathrm{D_{red}}]_{eq})$ against $\ln([\mathrm{cyt_{ox}}]_{eq}/[\mathrm{cyt_{red}}]_{eq})$ [illegible] linear with slope of one and *y*-intercept $F(E^{\ominus}_{\mathrm{cyt}} - E^{\ominus}_{\mathrm{D}})/RT$, [illegible] equilibrium activities are replaced by the numerical [illegible]f equilibrium molar concentrations. (b) The following da[illegible] obtained for the reaction between oxidized cytoc[illegible] and reduced D at pH = 6.5 buffer and 298 K. The ratios [illegible]$\mathrm{D_{red}}]_{eq}$ and $[\mathrm{cyt_{ox}}]_{eq}/[\mathrm{cyt_{red}}]_{eq}$ were adjusted by adding k[illegible]mes of a solution of sodium ascorbate, a reducing ag[illegible] solution containing oxidized cytochrome *c* and red[illegible] From the data and the standard potential of D of 0.23[illegible]mine the standard potential of cytochrome *c* at pH = 6.[illegible] K.

$[\mathrm{D_{ox}}]_{eq}/[\mathrm{D_{red}}]_{eq}$	0.002 79	[illegible]	0.0257	0.0497
$[\mathrm{cyt_{ox}}]_{eq}/[\mathrm{cyt_{red}}]_{eq}$	0.0106	[illegible]	0.0894	0.197
$[\mathrm{D_{ox}}]_{eq}/[\mathrm{D_{red}}]_{eq}$	0.0748	[illegible]	[illegible]	
$[\mathrm{cyt_{ox}}]_{eq}/[\mathrm{cyt_{red}}]_{eq}$	0.335	0.809		

9.45 Here we explore ion channels in mor[illegible] detail. (a) Estimate the resting potential, the memb[illegible]tial at equilibrium, of a neuron at 298 K by using the [illegible] the concentration of K^+ inside an inactive nerve cell is a[illegible] 20 times that on the outside. Now repeat the calculation, th[illegible] time using the fact that the concentration of Na^+ outside the inactive cell is about 10 times that on the inside. Are the two values the same or different? How do each of the calculated values compare with the observed resting potential of −62 mV? (b) Your estimates of the resting potential from part (a) did not agree with the experimental value because the cell is never at equilibrium and ions continually cross the membrane, which is more permeable to some ions than others.

To take into account membrane permeability, we use the *Goldman equation* to calculate the resting potential:

$$\Delta\phi = \frac{RT}{F} \ln \frac{P_{\mathrm{M^+}}[\mathrm{M^+}]_{\mathrm{out}} + P_{\mathrm{M'^+}}[\mathrm{M'^+}]_{\mathrm{out}} + P_{\mathrm{X^-}}[\mathrm{X^-}]_{\mathrm{in}} + P_{\mathrm{X'^-}}[\mathrm{X'^-}]_{\mathrm{in}}}{P_{\mathrm{M^+}}[\mathrm{M^+}]_{\mathrm{in}} + P_{\mathrm{M'^+}}[\mathrm{M'^+}]_{\mathrm{in}} + P_{\mathrm{X^-}}[\mathrm{X^-}]_{\mathrm{out}} + P_{\mathrm{X'^-}}[\mathrm{X'^-}]_{\mathrm{out}}}$$

where the salts present on each side of the membrane are MX and M′X′ and the *P*s are the relative permeabilities of the ions. Consider an experiment in which $[\mathrm{Na^+}]_{\mathrm{in}} = 50$ mmol dm^{-3}, $[\mathrm{K^+}]_{\mathrm{in}} = 400$ mmol dm^{-3}, $[\mathrm{Cl^-}]_{\mathrm{in}} = 50$ mmol dm^{-3}, $[\mathrm{Na^+}]_{\mathrm{out}} = 440$ mmol dm^{-3}, $[\mathrm{K^+}]_{\mathrm{out}} = 20$ mmol dm^{-3}, and $[\mathrm{Cl^-}]_{\mathrm{in}} = 560$ mmol dm^{-3}. Use the Goldman equation and the relative permeabilities $P_{\mathrm{K^+}} = 1.0$, $P_{\mathrm{Na^+}} = 0.04$, and $P_{\mathrm{Cl^-}} = 0.45$ to estimate the resting potential at 298 K under the stated conditions. How does your calculated value agree with the experimental value of −62 mV?

Empirical chemical kinetics

Reaction rates

The temperature dependence of reaction rates

Box 10.1 Femtochemistry

CHECKLIST OF KEY IDEAS
TABLE OF KEY EQUATIONS
QUESTIONS AND EXERCISES

Empirical chemical kinetics

10.1 Spectrophotometry

$$\log \frac{I_0}{I} = \varepsilon[\mathrm{J}]L$$

$$T = \frac{I}{I_0}$$

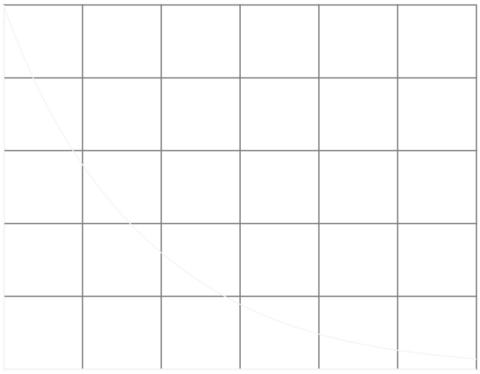


Fig. 10.2

Use log(1/x) = –log x

$$[\mathrm{J}] = \frac{A}{\varepsilon L}$$

10.2 Experimental techniques

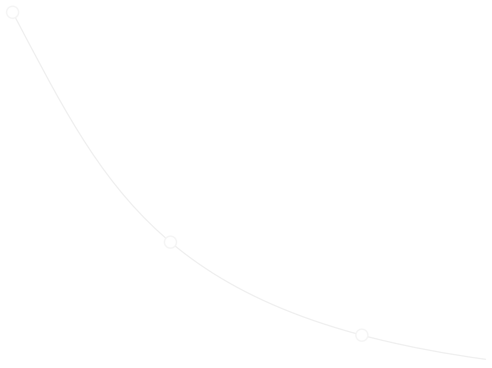


Fig. 10.4

Reaction rates

10.3 The definition of rate

Change in [J]

|. . .| means ignore any negative sign

Time interval of interest

A brief comment

$$v = \frac{|\mathrm{d}[\mathrm{J}]|}{\mathrm{d}t}$$

$$v = \frac{1}{\nu_J}\frac{\mathrm{d}[\mathrm{J}]}{\mathrm{d}t}$$

A brief illustration

$$\frac{1\ \mathrm{dm}}{10}$$

$$1\ \mathrm{molecule} = \frac{1\ \mathrm{mol}}{6.022\times 10^{23}}$$

$$v = \frac{k_{r1}[H_2][Br_2]^{3/2}}{[Br_2] + k_{r2}[HBr]}$$

$$v = \frac{k_r[E][S]}{[S] + K_M}$$

$$v = \frac{k_r}{K_M}[S][E]$$

10.6 The determination of the rate law

Use log $xy = \log x + \log y$

Use log $x^a = a\ \log x$

$$\boxed{y} = \boxed{\text{intercept}} + \boxed{\text{slope}\ x}$$

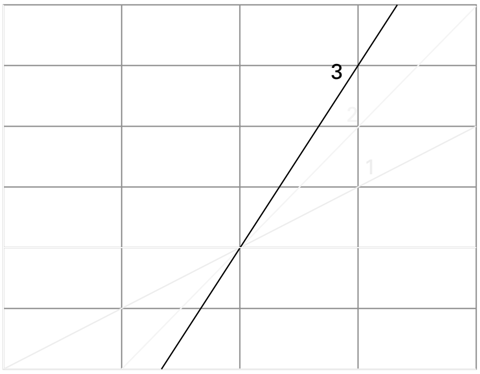


Fig. 10.5

Example 10.1

Strategy

Solution

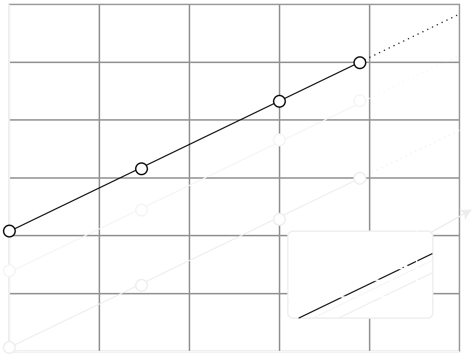


Fig. 10.6

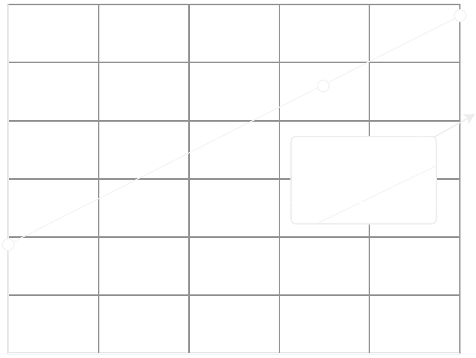


Fig. 10.7

A note on good practice

Self-test 10.3

The initial rate of a certain reaction depended on concentration of a substance J as follows:

$[J]_0/(10^{-3}\ \text{mol dm}^{-3})$	5.0	10.2	17	30
$v_0/(10^{-7}\ \text{mol dm}^{-3}\ \text{s}^{-1})$	3.6	9.6	41	130

Find the order of the reaction with respect to J and the rate constant.

[*Answer:* 2, $1.6 \times 10^{-2}\ \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$]

10.7 Integrated rate laws

$$\ln \frac{[A]_0}{[A]} = k_r t$$

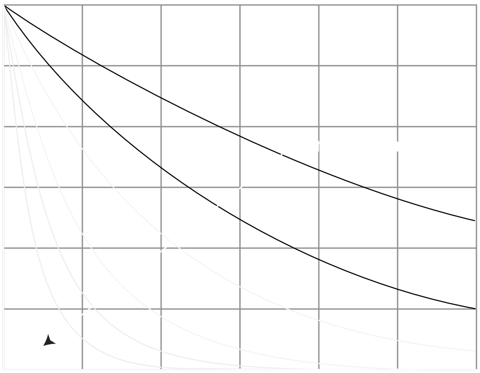


Fig. 10.8

$$-\frac{d[A]}{dt} = k_r[A]$$

$$\frac{d[A]}{[A]} = -k_r dt$$

$$\frac{d[A]}{[A]}$$

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

Table 10.2

Kinetic data for first-order reactions

Reaction	Phase	$\theta/{}^\circ\mathrm{C}$	k_r/s^{-1}	$t_{1/2}$
$2\,N_2O_5 \rightarrow 4\,NO_2 + \mathbf{O_2}$	g	25	3.38×10^{-5}	2.85 h
$2\,N_2O_5 \rightarrow 4\,NO_2 + \mathbf{O_2}$	$Br_2(l)$	25	4.27×10^{-5}	2.25 h
$\mathbf{C_2H_6} \rightarrow 2\,CH_3$	g	700	5.46×10^{-4}	21.2 m
Cyclopropane → propene	g	500	6.17×10^{-4}	17.2 min

The rate constant is for the rate of formation or consumption of the species in bold type. The rate laws for the other species may be obtained from the reaction stoichiometry.

Example 10.2

Strategy

Solution

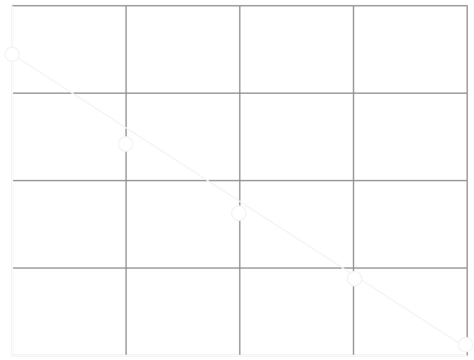


Fig. 10.9

Self-test 10.4

The concentration of N_2O_5 in liquid bromine varied with time as follows:

t/s	0	200	400	600	1000
$[N_2O_5]/(\mathrm{mol\ dm^{-3}})$	0.110	0.073	0.048	0.032	0.014

Confirm that the reaction is first-order in N_2O_5 and determine the rate constant.

[*Answer:* $2.1 \times 10^{-3}\ \mathrm{s}^{-1}$]

$$\frac{1}{[\mathrm{A}]}=\frac{1}{[\mathrm{A}]_0}+k_\mathrm{r}t$$

$$[\mathrm{A}]=\frac{[\mathrm{A}]_0}{1+k_\mathrm{r}t[\mathrm{A}]_0}$$

$$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t}=k_\mathrm{r}[\mathrm{A}]^2$$

$$\frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]^2}=-k_\mathrm{r}\mathrm{d}t$$

$$\frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]^2}$$

$$\frac{\mathrm{d}x}{x^2}=-\frac{1}{x}+\text{constant}$$

$$\begin{aligned}\frac{\mathrm{d}x}{x^2}&=\left\{-\frac{1}{x}+\text{constant}\right\}\bigg|_b-\left\{-\frac{1}{x}+\text{constant}\right\}\bigg|_a\\&=-\frac{1}{b}+\frac{1}{a}\end{aligned}$$

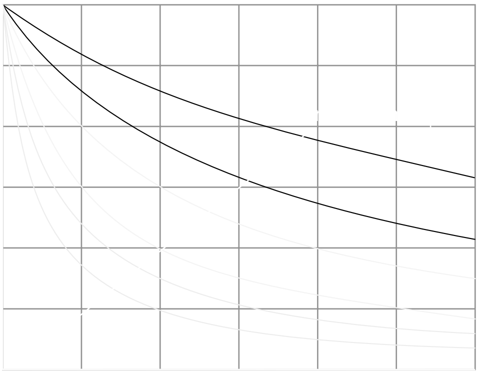


Fig. 10.10

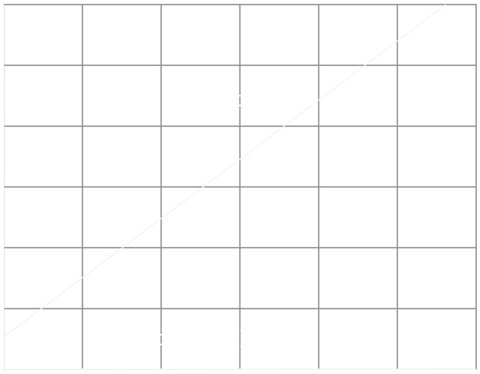
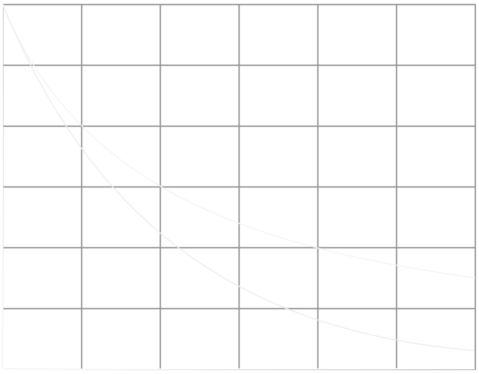


Fig. 11

10.8 Half-lives and time constants



Use ln(1/x) = −ln x

$$t_{1/2} = \frac{\ln 2}{k_\mathrm{r}}$$

A brief illustration

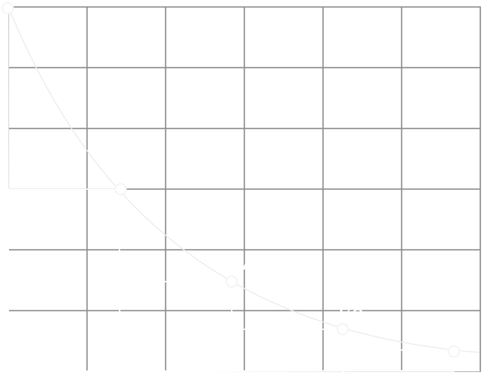


Fig. 10.13

A brief illustration

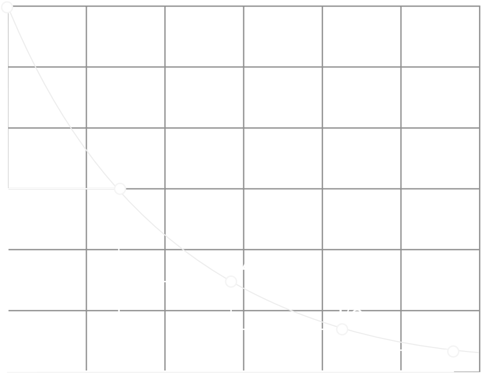
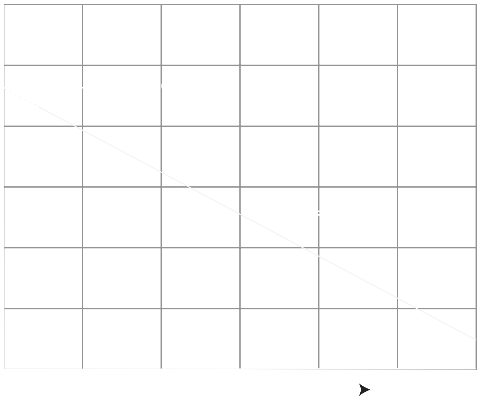


Fig. 10.14

$$\tau = \frac{1}{k_\mathrm{r}}$$

The temperature dependence of reaction rates



10.9 The Arrhenius parameters

Fig. 10.15

Table 10.5

Arrhenius parameters

First-order reactions	$A/\mathrm{s^{-1}}$	$E_a/(\mathrm{kJ\ mol^{-1}})$
Cyclopropene → propane	1.58×10^{15}	272
$CH_3NC \rightarrow CH_3CN$	3.98×10^{13}	160
cis-CHD=CHD → *trans*-CHD=CHD	3.16×10^{12}	256
cyclobutane → 2 C_2H_4	3.98×10^{15}	261
$2\ N_2O_5 \rightarrow 4\ NO_2 + O_2$	4.94×10^{13}	103
$N_2O \rightarrow N_2 + O$	7.94×10^{11}	250
Second-order, gas phase	$A/(\mathrm{dm^3\ mol^{-1}\ s^{-1}})$	$E_a/(\mathrm{kJ\ mol^{-1}})$
$O + N_2 \rightarrow NO + H$	1×10^{11}	315
$OH + H_2 \rightarrow H_2 + H$	8×10^{10}	42
$Cl + H_2 \rightarrow HCl + H$	8×10^{10}	23
$CH_3 + CH_3 \rightarrow C_2H_6$	2×10^{10}	0
$NO + Cl_2 \rightarrow NOCl + Cl$	4×10^{9}	85
Second order, solution	$A/(\mathrm{dm^3\ mol^{-1}\ s^{-1}})$	$E_a/(\mathrm{kJ\ mol^{-1}})$
$NaC_2H_5O + CH_3I$ in ethanol	2.42×10^{11}	81.6
$C_2H_5Br + OH^-$ in water	4.30×10^{11}	89.5
$CH_3I + S_2O_3^{2-}$ in water	2.19×10^{12}	78.7
Sucrose + H_2O in acidic water	1.50×10^{15}	107.9

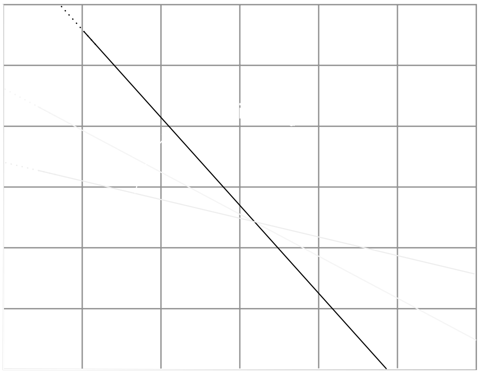


Fig. 10.16

$$\ln k_\mathrm{r} = \text{intercept} + \text{slope} \times \frac{1}{T}$$

$$\ln\, k_\mathrm{r} = \ln\, A - \frac{E_\mathrm{a}}{RT}$$

Example 10.3

Strategy

$$\ln(k_\mathrm{r}/\mathrm{mol^{-1}\ dm^3\ s^{-1}}) = \ln(A/\mathrm{mol^{-1}\ dm^3\ s^{-1}}) - \frac{E_\mathrm{a}}{RT}$$

$$= \ln(A/\mathrm{mol^{-1}\ dm^3\ s^{-1}}) - \frac{E_\mathrm{a}}{R} \times \frac{1}{\mathrm{K}} \times \frac{\mathrm{K}}{T}$$

Solution

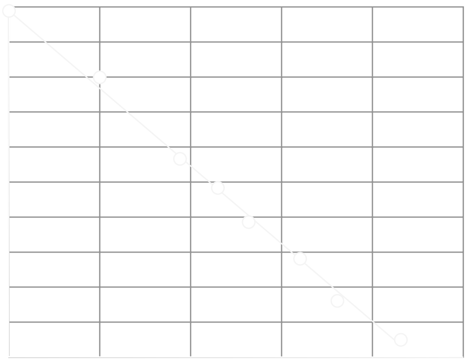


Fig. 10.17

$$\ln k_{\mathrm{r}}(T') = \ln A - \frac{E_{\mathrm{a}}}{RT'} \qquad \ln k_{\mathrm{r}}(T) = \ln A - \frac{E_{\mathrm{a}}}{RT}$$

$$\ln k_{\mathrm{r}}(T') - \ln k_{\mathrm{r}}(T) = -\frac{E_{\mathrm{a}}}{RT'} + \frac{E_{\mathrm{a}}}{RT}$$

$$\ln \frac{k_{\mathrm{r}}(T')}{k_{\mathrm{r}}(T)} = \frac{E_{\mathrm{a}}}{R}\left(\frac{1}{T} - \frac{1}{T'}\right)$$

$$\begin{aligned}\ln \frac{k_{\mathrm{r}}(310\ \mathrm{K})}{k_{\mathrm{r}}(298\ \mathrm{K})} &= \frac{50\times 10^{3}\ \mathrm{J\ mol^{-1}}}{8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}}\left(\frac{1}{298\ \mathrm{K}} - \frac{1}{310\ \mathrm{K}}\right)\\ &= \frac{50\times 10^{3}}{8.3145}\left(\frac{1}{298} - \frac{1}{310}\right)\end{aligned}$$

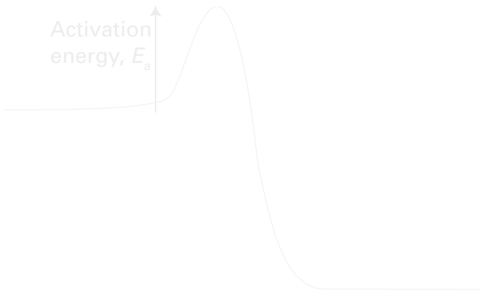


Fig. 10.19

Fig. 10.20

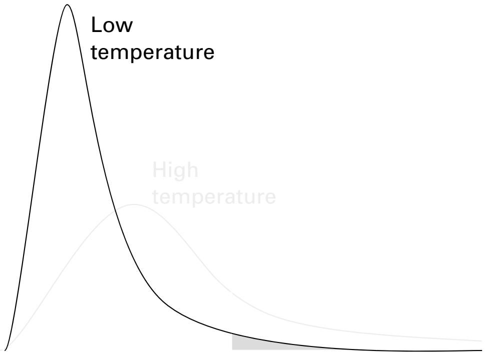


Fig. 10.21

$$A = \sigma\left(\frac{8kT}{\pi\mu}\right)^{1/2} N_{\mathrm{A}}^{2} \qquad \mu = \frac{m_{\mathrm{A}} m_{\mathrm{B}}}{m_{\mathrm{A}} + m_{\mathrm{B}}}$$

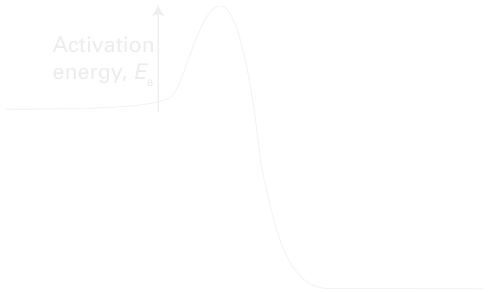


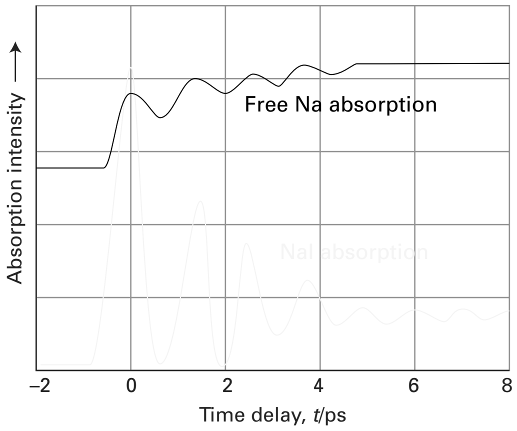
Fig. 10.24

Fig. 10.23

10.11 Transition-state theory

$$K^* = \frac{[C^\ddagger]}{[A][B]}$$

Box 10.1 Femtochemistry



$$k_\mathrm{r} = \kappa \times \frac{kT}{h} \times K^\ddagger$$

$\Delta^\ddagger G$

Use $\mathrm{e}^{x+y} = \mathrm{e}^x\mathrm{e}^y$

A note on good practice

☐ 1

☐ 2

☐ 3

☐ 4

☐ 5

☐ 6

☐ 7

☐ 8

☐ 9

☐ 10

☐ 11

☐ 12

☐ 13

Property	Equation	Comment
	$\frac{1}{[A]} = \frac{1}{[A]_0} + k_r t$	

Discussion questions

10.1

10.2

10.3

10.4

10.5

10.6

10.7

Exercises

10.1

10.2

10.3

10.4

10.5

10.6

10.7

10.8

$$v = \frac{k_{r1}[A][B]^{3/2}}{k_{r2}[A] + k_{r3}[B]^{1/2}}$$

10.9

10.10

10.11

10.12

10.13

10.14

10.15 Carbonic anhydrase is a zinc-based enzyme that catalyses the conversion of carbon dioxide to carbonic acid. In an experiment to study its effect, it was found that the molar concentration of carbon dioxide in solution decreased from 220 mmol dm^{-3} to 56.0 mmol dm^{-3} in 1.22×10^4 s. What is the rate constant of the reaction?

10.16 The formation of NOCl from NO in the presence of a [illegible] excess of chlorine is pseudosecond-order in NO. In [illegible] experiment to study the reaction, the partial pressure of [illegible] increased from zero to 100 Pa in 522 s. What is the rate [illegible] of the reaction?

10.17 [illegible] of reactions that take place on the surfaces of catal[illegible] zero-order in the reactant. One example is the decomposition of ammonia on hot tungsten. In one experiment, [illegible] pressure of ammonia decreased from 21 kPa to 10 kPa [illegible] (a) What is the rate constant for the zero-order reaction [illegible] how long will it take for all the ammonia to disappear?

10.18 The following kinetic [illegible] the initial rate) were obtained for the reaction 2 ICl(g [illegible] $I_2(g)$ + 2 HCl(g):

Experiment	$[ICl]_0$/(mmol dm^{-3})	$[H_2]_0$/(mmol dm^{-3})	v_0/(mol dm^{-3} s^{-1})
1	1.5	1.5	[illegible]
2	3.0	1.5	[illegible]
3	3.0	4.5	22 × 10[illegible]
4	4.7	2.7	?

(a) Write the rate law for the reaction. (b) From the data, determine the value of the rate constant. (c) Use the data to predict the reaction rate for Experiment 4.

10.19 The variation in the partial pressure *p* of mercury dimethyl with time was followed at 800 K, with the results given below. Confirm that the decomposition $Hg(CH_3)_2(g) \rightarrow Hg(g) + 2\ CH_3(g)$ is first-order in $Hg(CH_3)_2$ and find the rate constant at this temperature.

t/s	0	1.0	2.0	3.0	4.0
p/kPa	15.1	11.8	9.21	7.2	5.6

10.20 The following data were collected for the reaction $2\ HI(g) \rightarrow H_2(g) + I_2(g)$ at 580 K:

t/s	0	1000	2000	3000	4000
[HI]/(mol dm^{-3})	1.00	0.112	0.061	0.041	0.031

(a) Plot the data in an appropriate fashion to determine the order of the reaction. (b) From the graph, determine the rate constant.

10.21 The following data were collected for the reaction $H_2(g) + I_2(g) \rightarrow 2\ HI(g)$ at 780 K:

t/s	0	1	2	3	4
[HI]/(mol dm^{-3})	1	0.43	0.27	0.2	0.16

(a) Plot the data in an appropriate fashion to determine the order of the reaction. (b) From the graph, determine the rate constant.

10.22 Laser flash photolysis is often used to measure the binding rate of CO to haem proteins, such as myoglobin (Mb), because CO dissociates from the bound state relatively easily upon absorption of energy from an intense and narrow pulse of light. The reaction is usually run under pseudofirst-order conditions. For a reaction in which $[Mb]_0 = 10$ mmol dm^{-3}, [CO] = 400 mmol dm^{-3}, and the rate constant is 5.8×10^5 dm^3 mol^{-1} s^{-1}, plot a curve of [Mb] against time. The observed reaction is Mb + CO → MbCO.

10.23 The integrated rate law of a second-order reaction of the form 3 A → B is $[A] = [A]_0/(1 + k_r t[A]_0)$. How does the concentration of B change with time?

10.24 The composition of a liquid-phase reaction 2 A → B was followed spectrophotometrically with the following results:

t/min	0	10	20	30	40	∞
[B]/(mol dm^{-3})	0	0.372	0.426	0.448	0.460	0.500

Determine the order of the reaction and its rate constant (written in the form of eqn 10.5c).

10.25 Example 10.2 provided data on a first-order gas-phase reaction. How does the total pressure of the sample change with time?

10.26 The half-life of pyruvic acid in the presence of an [illegible]transferase enzyme (which converts it to alanine) was [illegible] be 221 s. How long will it take for the concentration of [illegible] to fall to $\frac{1}{64}$ of its initial value in this first-order [illegible]

10.27 The [illegible] for the (first-order) radioactive decay of ^{14}C is 5730 a [illegible] unit 1 annum, for 1 year; the nuclide emits β particles, [illegible] electrons, with an energy of 0.16 MeV). An arch[illegible] sample contained wood that had only 69 per cent of [illegible] found in living trees. What is its age?

10.28 One of the hazards of [illegible] explosions is the generation of ^{90}Sr and its subsequent [illegible] in place of calcium in bones. This nuclide emits [illegible] of energy 0.55 MeV, and has a half-life of 28 [illegible] unit annum, for 1 year). Suppose 1.00 μg was [illegible] by a newly born child. How much will remain after [illegible] 75 a, if none is lost metabolically?

10.29 The half-life of a first-order reaction was found [illegible] 439 s; what is the time constant for the reaction?

10.30 The second-order rate constant for the reaction $CH_3COOC_2H_5(aq) + OH^-(aq) \rightarrow CH_3CO_2^-(aq) + CH_3CH_2OH(aq)$ is 0.11 dm^3 mol^{-1} s^{-1}. What is the concentration of ester after (a) 15 s, (b) 15 min, when ethyl acetate is added to sodium hydroxide so that the initial concentrations are [NaOH] = 0.055 mol dm^{-3} and $[CH_3COOC_2H_5]$ = 0.150 mol dm^{-3}?

10.31 A reaction 2 A → P has a second-order rate law with $k_r = 1.44\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$. Calculate the time required for the concentration of A to change from 0.460 mol dm^{-3} to 0.046 mol dm^{-3}.

10.32 The Arrhenius parameters for the reaction $C_4H_8(g) \rightarrow 2\ C_2H_4(g)$, where C_4H_8 is *cyclo*-butane are $\log(A/\mathrm{s^{-1}}) = 15.6$ and $E_a = 261\ \mathrm{kJ\ mol^{-1}}$. What is the half-life of *cyclo*-butane [illegible] 20°C, (b) 500°C?

10.33 [illegible]te constant is $2.78 \times 10^{-4}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ at 19°C and [illegible]$^{-3}$ dm^3 mol^{-1} s^{-1} at 37°C. Evaluate the Arrhenius parame[illegible]e reaction.

10.34 The ac[illegible]ergy for the decomposition of benzene diazonium chlor[illegible]1 kJ mol^{-1}. At what temperature will the rate be 10 per[illegible]er than its rate at 25°C?

10.35 Which reaction [illegible] more strongly to changes of temperature, one with a[illegible] energy of 52 kJ mol^{-1} or one with an activation energ[illegible]J mol^{-1}?

10.36 The rate constant of a reactio[illegible]es by a factor of 1.41 when the temperature is increase[illegible]0°C to 27°C. What is the activation energy of the react[illegible]

10.37 Make an appropriate Arrhenius plot of [illegible] data for the conversion of *cyclo*-propane to pro[illegible] calculate the activation energy for the reaction.

T/K	750	800	850	90[illegible]
$k_r/\mathrm{s^{-1}}$	1.8×10^{-4}	2.7×10^{-3}	3.0×10^{-2}	0.26

10.38 Food rots about 40 times more rapidly at 25°C than when it is stored at 4°C. Estimate the overall activation energy for the processes responsible for its decomposition.

10.39 Suppose that the rate constant of a reaction *de*creases by a factor of 1.23 when the temperature is increased from 20°C to 27°C. How should you report the activation energy of the reaction?

10.40 The enzyme urease catalyses the reaction in which urea is hydrolysed to ammonia and carbon dioxide. The half-life of urea in the pseudofirst-order reaction for a certain amount of urease doubles when the temperature is lowered from 20°C to 10°C and the Michaelis constant is largely unchanged. What is the activation energy of the reaction?

10.41 What proportion of the collisions between NO_2 molecules have enough energy to result in reaction when the temperature is (a) 20°C, (b) 200°C, given that the activation energy for the reaction $2\ NO_2(g) \rightarrow 2\ NO(g) + O_2(g)$ is 111 kJ mol^{-1}?

10.42 Use collision theory to estimate the pre-exponential factor for the reaction in the preceding exercise. The experimental value is $2 \times 10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$. Suggest a reason for any discrepancy.

10.43 Suppose an electronegative reactant needs to come to within 500 pm of a reactant with low ionization energy before an electron can flip across from one to the other (as in the harpoon mechanism). Estimate the reaction cross-section.

10.44 Estimate the activation Gibbs energy for the decomposition of urea in the reaction $CO(NH_2)_2(aq) + 2\ H_2O(l) \rightarrow 2\ NH_4^+(aq) + CO_3^{2-}(aq)$ for which the pseudofirst-order rate constant is $1.2 \times 10^{-7}\ \mathrm{s^{-1}}$ at 60°C and $4.6 \times 10^{-7}\ \mathrm{s^{-1}}$ at 70°C.

10.45 Calculate the entropy of activation of the reaction in Exercise 10.44 at the two temperatures.

Projects

The symbol ‡ indicates that calculus is required.

10.46‡ Here we explore integrated rate laws in more detail. (a) Establish the integrated form of a third-order rate law of the form $\boldsymbol{v} = k_r[A]^3$. What would be appropriate to plot to confirm that a reaction is third-order? (b) Establish the integrated form of a second-order rate law of the form $\boldsymbol{v} = k_r[A][B]$ for a reaction A + B → products (i) with different initial concentrations of A and B, (ii) with the same concentrations of the two reactants. *Hints:* Note that when the concentration of A falls to $[A]_0 - x$, the concentration of B falls to $[B]_0 - x$. Use these relations to show that the rate law may be written as

$$\frac{dx}{dt} = k_r([A]_0 - x)([B]_0 - x)$$

To make progress with integration of the rate law, use the form:

$$\frac{dx}{(a-x)(b-x)} = \frac{1}{b-a}\left(\ln\frac{1}{a-x} - \ln\frac{1}{b-x}\right) + \text{constant}$$

10.47 [illegible]biotic reactions are reactions that might have occ[illegible]er the conditions prevalent on the Earth before the fi[illegible] creatures emerged and that can lead to analogues [illegible]cules necessary for life as we now know it. To qualify, [illegible]n must proceed with a favourable rate and have a reas[illegible]alue for the equilibrium constant. An example of a [illegible] reaction is the formation of 5-hydroxymethyluracil [illegible]m uracil and formaldehyde (HCHO). Amino acid ana[illegible] be formed from HMU under prebiotic conditions [illegible] with various nucleophiles, such as H_2S, HCN, in[illegible]azole, etc. For the synthesis of HMU at pH = 7, the te[illegible] dependence of the rate constant is given by

$$\log k_r/(\mathrm{dm^3\ mol^{-1}\ s^{-1}}) = 11.75 - 5488/(T/\mathrm{K})$$

and the temperature dependence of the equili[illegible]tant is given by

$$\log K = -1.36 + 1794/(T/\mathrm{K})$$

(a) Calculate the rate constants and equilibrium constants over a range of temperatures corresponding to possible prebiotic conditions, such as 0–50°C, and plot them against temperature. (b) Calculate the activation energy and the standard reaction Gibbs energy and enthalpy at 25°C. (c) Prebiotic conditions are not likely to be standard conditions. Speculate about how the actual values of the reaction Gibbs energy and enthalpy might differ from the standard values. Do you expect that the reaction would still be favourable?

Reaction schemes

Box 11.1 Kinetics of protein folding

Reaction mechanisms

Reactions in solution

Catalysis

Chain reactions

Box 11.2 Explosions

CHECKLIST OF KEY IDEAS
TABLE OF KEY EQUATIONS
FURTHER INFORMATION 11.1 FICK'S LAWS OF DIFFUSION
QUESTIONS AND EXERCISES

Reaction schemes

11.1 The approach to equilibrium

A brief comment

$$K=\frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}}=\frac{k_{\mathrm{r}}}{k'_{\mathrm{r}}}$$

$$K=\frac{[\mathrm{C}]_{\mathrm{eq}}/c}{([\mathrm{A}]_{\mathrm{eq}}/c\ \ )([\mathrm{B}]_{\mathrm{eq}}/c\ \ )}=\left(\frac{[\mathrm{C}]}{[\mathrm{A}][\mathrm{B}]}\right)_{\mathrm{eq}}c\ \ =\frac{k_{\mathrm{r}}}{k'_{\mathrm{r}}}\times c$$

A brief illustration

$$K=\frac{8.1\times10^{8}\ \mathrm{dm^{3}\ mol^{-1}\ s^{-1}}}{2.0\times10^{6}\ \mathrm{s^{-1}}}\times1\ \mathrm{mol\ dm^{-3}}=4.0\times10^{2}$$

$$[\mathrm{A}]=\frac{(k'_{\mathrm{r}}+k_{\mathrm{r}}\mathrm{e}^{-(k_{\mathrm{r}}+k'_{\mathrm{r}})t})[\mathrm{A}]_0}{k_{\mathrm{r}}+k'_{\mathrm{r}}}$$

$$[\mathrm{B}]=\frac{k_{\mathrm{r}}(1-\mathrm{e}^{-(k_{\mathrm{r}}+k'_{\mathrm{r}})t})[\mathrm{A}]_0}{k_{\mathrm{r}}+k'_{\mathrm{r}}}$$

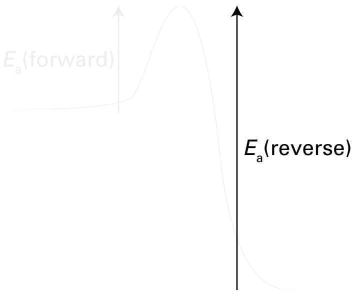


Fig. 11.1

Net rate of formation of A

Rate of loss of A

Rate of formation of A

$$\frac{d[A]}{dt}$$

$$\frac{d}{dx}e^{-ax} = -ae^{-ax}$$

11.2 Relaxation methods

$$[B]_{eq} = \frac{k_r[A]_0}{k_r + k_r'} \qquad [A]_{eq} = \frac{k_r'[A]_0}{k_r + k_r'}$$

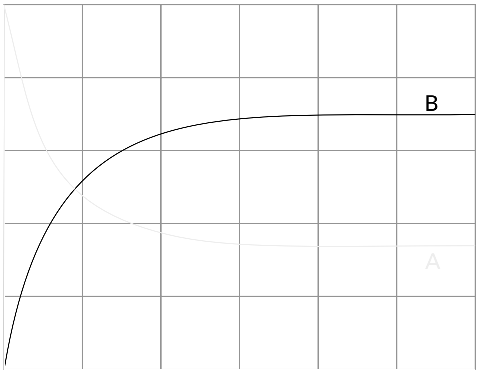


Fig. 11.2

Fig. 11.3

Box 11.1 Kinetics of protein unfolding

$$\frac{1}{\tau}$$

Derivation 11.2

Relaxation to equilibrium

We need to keep track of the fact that rate constants depend on temperature. At the initial temperature, when the rate constants are k_{initial} and k'_{initial}, the net rate of change of [A] is

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_{\mathrm{r,initial}}[\mathrm{A}] + k'_{\mathrm{r,initial}}[\mathrm{B}]$$

At equilibrium under these conditions, we write the concentrations as $[\mathrm{A}]_{\mathrm{eq,initial}}$ and $[\mathrm{B}]_{\mathrm{eq,initial}}$ and because $\mathrm{d}[\mathrm{A}]/\mathrm{d}t$ is then zero,

$$k_{\mathrm{r,initial}}[\mathrm{A}]_{\mathrm{eq,initial}} = k'_{\mathrm{r,initial}}[\mathrm{B}]_{\mathrm{eq,initial}}$$

When the temperature is increased suddenly, the rate constants change to k_{r} and k'_{r}, but the concentrations of A and B remain for an instant at their old equilibrium values. As the system is no longer at equilibrium, it readjusts to the new equilibrium concentrations, which are now given by

$$k_{\mathrm{r}}[\mathrm{A}]_{\mathrm{eq}} = k'_{\mathrm{r}}[\mathrm{B}]_{\mathrm{eq}}$$

and it does so at a rate that depends on the new rate constants.

We write the deviation of [A] from its new equilibrium value as x, so $[\mathrm{A}] = x + [\mathrm{A}]_{\mathrm{eq}}$ and $[\mathrm{B}] = [\mathrm{B}]_{\mathrm{eq}} - x$. The concentration of A then changes as follows:

$$\begin{aligned}\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} &= -k_{\mathrm{r}}[\mathrm{A}] + k'_{\mathrm{r}}[\mathrm{B}]\\ &\overset{[\mathrm{A}] = x+[\mathrm{A}]_{\mathrm{eq}} \text{ and } [\mathrm{B}] = [\mathrm{B}]_{\mathrm{eq}} - x}{=} -k_{\mathrm{r}}(x + [\mathrm{A}]_{\mathrm{eq}}) + k'_{\mathrm{r}}(-x + [\mathrm{B}]_{\mathrm{eq}})\\ \text{Use } k_{\mathrm{r}}[\mathrm{A}]_{\mathrm{eq}} = k'_{\mathrm{r}}[\mathrm{B}]_{\mathrm{eq}} &= -k_{\mathrm{r}}x + k_{\mathrm{r}}[\mathrm{A}]_{\mathrm{eq}} - k'_{\mathrm{r}}x + k'_{\mathrm{r}}[\mathrm{B}]_{\mathrm{eq}}\\ &= -(k_{\mathrm{r}} + k'_{\mathrm{r}})x\end{aligned}$$

From $[\mathrm{A}] = x + [\mathrm{A}]_{\mathrm{eq}}$ it follows that $\mathrm{d}[\mathrm{A}]/\mathrm{d}t = \mathrm{d}x/\mathrm{d}t$ and therefore that

$$\frac{\mathrm{d}x}{\mathrm{d}t} = -(k_{\mathrm{r}} + k'_{\mathrm{r}})x$$

To solve this equation we divide both sides by x and multiply by $\mathrm{d}t$:

$$\frac{\mathrm{d}x}{x} = -(k_{\mathrm{r}} + k'_{\mathrm{r}})\mathrm{d}t$$

$$\ln\frac{x}{x_0} = -(k_{\mathrm{r}} + k'_{\mathrm{r}})t$$

11.3 Consecutive reactions

$${}^{239}\mathrm{U} \xrightarrow{2.35\ \mathrm{min}} {}^{239}\mathrm{Np} \xrightarrow{2.35\ \mathrm{d}} {}^{239}\mathrm{Pu}$$

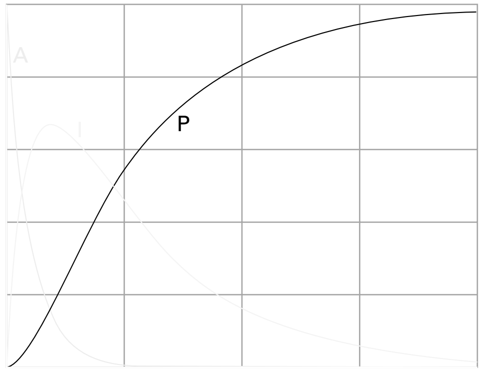


Fig. 11.4

$$[\mathrm{I}] = \frac{k_a}{k_b - k_a}(e^{-k_a t} - e^{-k_b t})[\mathrm{A}]_0$$

$$[\mathrm{P}] = \left(1 + \frac{k_a e^{-k_b t} - k_b e^{-k_a t}}{k_b - k_a}\right)[\mathrm{A}]_0$$

$$t = \frac{1}{k_a - k_b} \ln \frac{k_a}{k_b}$$

$$\frac{d[\mathrm{I}]}{dt} = \frac{k_a}{k_b - k_a}(-k_a e^{-k_a t} + k_b e^{-k_b t})[\mathrm{A}]_0 = 0$$

$$\frac{k_a}{k_b} = e^{(k_a - k_b)t}$$

Reaction mechanisms

11.4 Elementary reactions

Fig. 11.5

Fig. 11.6

11.5 The formulation of rate laws

$$[\mathrm{N_2O_2}] = \frac{k_\mathrm{a}[\mathrm{NO}]^2}{k'_\mathrm{a} + k_\mathrm{b}[\mathrm{O_2}]}$$

From step 3

Substitute the expression for $[N_2O_2]$

$$\text{Rate of formation of NO}_2 = \left(\frac{2k_a k_b}{k'_a}\right)[\text{NO}]^2[\text{O}_2]$$

$$k_r = \frac{2k_a k_b}{k'_a}$$

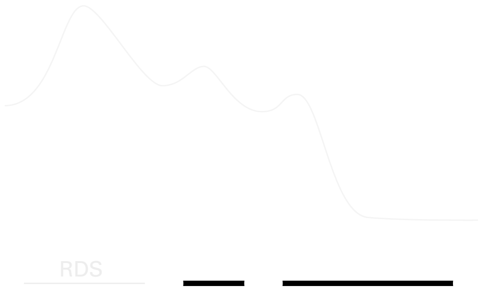


Fig. 11.8

11.8 Kinetic control

$$\frac{[\mathrm{P}_2]}{[\mathrm{P}_1]} = \frac{k_{\mathrm{r},2}}{k_{\mathrm{r},1}}$$

11.9 Unimolecular reactions

$$k_\mathrm{r} = \frac{k_\mathrm{a}k_\mathrm{b}}{k'_\mathrm{a}}$$

Net rate of formation of A*

$$= \overbrace{k_{\mathrm{a}}[\mathrm{A}]^2}^{\text{Formation of A*}} - \overbrace{k'_{\mathrm{a}}[\mathrm{A}^*][\mathrm{A}]}^{\text{Deactivation of A*}} - \overbrace{k_{\mathrm{b}}[\mathrm{A}^*]}^{\text{Decay of A* into P}} \underbrace{= 0}_{\text{Steady-state assumption}}$$

$$[\mathrm{A}^*] = \frac{k_{\mathrm{a}}[\mathrm{A}]^2}{k_{\mathrm{b}} + k'_{\mathrm{a}}[\mathrm{A}]}$$

$$\text{Rate of formation of P} = k_{\mathrm{b}}[\mathrm{A}^*] = \frac{k_{\mathrm{a}}k_{\mathrm{b}}[\mathrm{A}]^2}{k_{\mathrm{b}} + k'_{\mathrm{a}}[\mathrm{A}]}$$

Reactions in solution

11.10 Activation control and diffusion control

$$k_{\mathrm{r}} = \frac{k_{\mathrm{r,a}}k_{\mathrm{r,d}}}{k_{\mathrm{r,a}} + k'_{\mathrm{r,d}}}$$

$$[\mathrm{AB}] = \frac{k_{\mathrm{r,d}}[\mathrm{A}][\mathrm{B}]}{k_{\mathrm{r,a}} + k'_{\mathrm{r,d}}}$$

$$= \frac{k_{\mathrm{r,a}}k_{\mathrm{r,d}}[\mathrm{A}][\mathrm{B}]}{k_{\mathrm{r,a}} + k'_{\mathrm{r,d}}}$$

$$= \frac{k_a k_d}{k'_d}[A][B]$$

$$k_{r,d} = \frac{8RT}{3\eta}$$

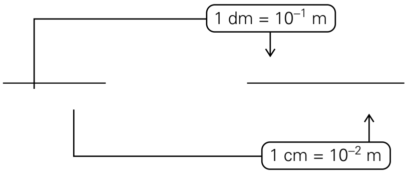
A brief illustration

11.11 Diffusion

$$J = \frac{\text{number of particles passing through window}}{\text{area of window} \times \text{time interval}}$$

A brief comment

$$J = -D\frac{dc}{dx}$$



A brief comment

$$\frac{dc}{dt} = D\frac{d^2c}{dx^2}$$

A brief illustration

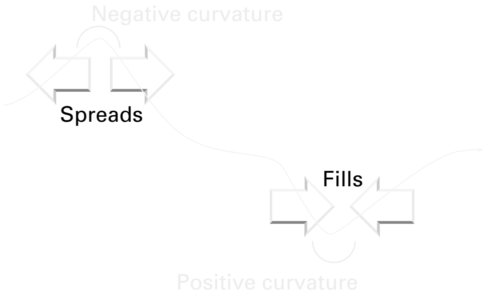


Fig. 11.10

$$D = \frac{\lambda^2}{2\tau}$$

$$D = \frac{kT}{6\pi\eta a}$$

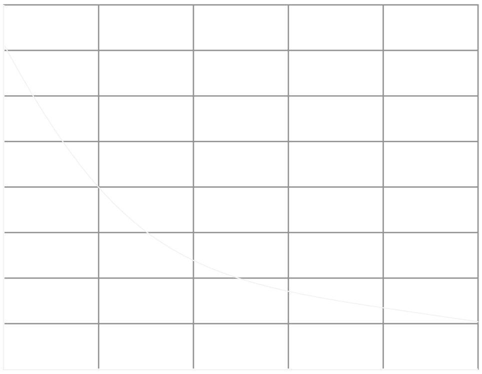


Fig. 11.11

Self-test 11.6

Estimate the activation energy for the viscosity of water from the graph in Fig. 11.11, by using the viscosities at 40°C and 80°C. *Hint:* Use an equation like eqn 11.24 to formulate an expression for the logarithm of the ratio of the two viscosities.

[*Answer:* 13 kJ mol^{-1}]

Catalysis

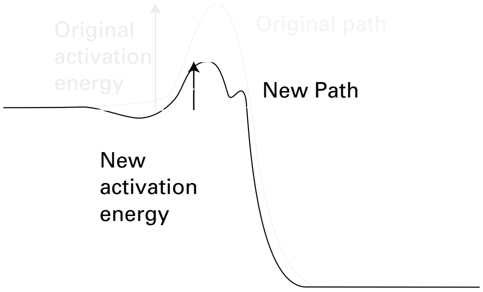


Fig. 11.12

11.12 Homogeneous catalysis

11.13 Enzymes

$$k_r = \frac{k_b[S]}{[S]+K_M}$$

$$K_M = \frac{k'_a + k_b}{k_a}$$

$$[ES] = \frac{k_a[E][S]}{k'_a + k_b}$$

$$[ES] = \frac{k_a([E]_0 - [ES])[S]}{k'_a + k_b}$$

$$\left(\frac{k'_a + k_b}{k_a} + [S]\right)[ES] = [E]_0[S]$$

$$[ES] = \frac{[E]_0[S]}{[S]+K_M}$$

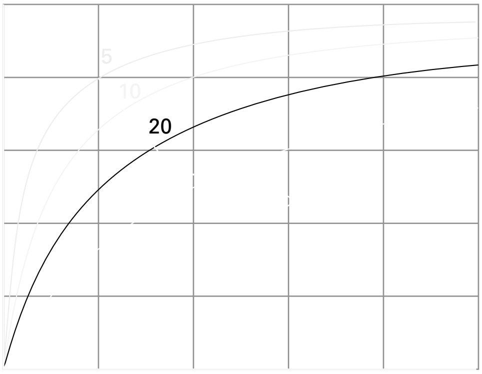


Fig. 11.13

Fig. 11.14

$$v = \frac{[\mathrm{S}]v_{\max}}{[\mathrm{S}] + K_{\mathrm{M}}}$$

$$\frac{1}{v} = \frac{[\mathrm{S}] + K_{\mathrm{M}}}{[\mathrm{S}]v_{\max}} = \frac{1}{v_{\max}} + \left(\frac{K_{\mathrm{M}}}{v_{\max}}\right)\frac{1}{[\mathrm{S}]}$$

y	Intercept	Slope	x

$$k_{\mathrm{cat}} = k_{\mathrm{b}} = \frac{v_{\max}}{[\mathrm{E}]_0}$$

$$\eta = \frac{k_{\mathrm{cat}}}{K_{\mathrm{M}}} = \frac{k_{\mathrm{a}}k_{\mathrm{b}}}{k'_{\mathrm{a}} + k_{\mathrm{b}}}$$

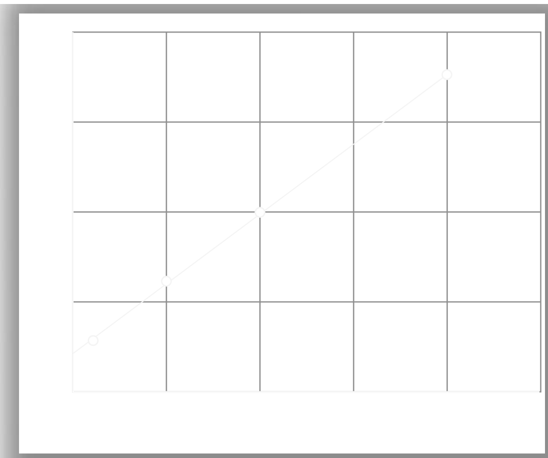


Fig. 11.15 The Lineweaver–Burke plot based on the data in Example 11.1.

Self-test 11.7

[illegible] enzyme α-chymotrypsin is secreted in the pancreas [illegible] mammals and cleaves peptide bonds made between certain amino acids. Several solutions containing the [illegible] peptide *N*-glutaryl-L-phenylalanine-*p*-nitroanilide at different concentrations were prepared and the same small amount of α-chymotrypsin was added to each one. The following data were obtained on the initial rates of the formation of product:

[S]/(mmol dm^{-3})	[illegible]	0.450	0.667
v/(mmol dm^{-3} s^{-1})	[illegible]	0.201	0.269
[S]/(mmol dm^{-3})	1.00	[illegible]	1.67
v/(mmol dm^{-3} s^{-1})	0.417	[illegible]	0.667

Determine the maximum velocity and the Michaelis constant for the reaction.

[*Answer:* $\upsilon_{\max}$ = 2.80 mmol dm [illegible]
K_M = 5.89 mmol dm [illegible]

$$\upsilon_{\max}/(\text{mmol dm}^{-3}\ \text{s}^{-1}) = \frac{1}{\text{intercept}} = \frac{1}{4.00} = 0.250$$

$$K_M/(\text{mmol dm}^{-3}) = \frac{\text{slope}}{\text{intercept}} = \frac{40.0}{4.00} = 10.0$$

$$k_{\text{cat}} = \frac{\upsilon_{\max}}{[\text{E}]_0} = \frac{2.5\times10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1}}{2.3\times10^{-9}\ \text{mol dm}^{-3}} = 1.1\times10^{5}\ \text{s}^{-1}$$

$$\eta = \frac{k_{\text{cat}}}{K_M} = \frac{1.1\times10^{5}\ \text{s}^{-1}}{1.0\times10^{-2}\ \text{mol dm}^{-3}} = 1.1\times10^{7}\ \text{dm}^{3}\ \text{mol}^{-1}\ \text{s}^{-1}$$

Fig. 11.16

A brief comment

Fig. 11.17

Chain reactions

11.14 The structure of chain reactions

11.15 The rate laws of chain reactions

$$\text{Rate of formation of HBr} = \frac{k_{r1}[H_2][Br_2]^{3/2}}{[Br_2]+k_{r2}[HBr]}$$

$$[\mathrm{Br}] = \left(\frac{k_\mathrm{a}[\mathrm{Br_2}]}{k_\mathrm{e}}\right)^{1/2} \qquad [\mathrm{H}] = \frac{k_\mathrm{b}(k_\mathrm{a}/k_\mathrm{e})^{1/2}[\mathrm{H_2}][\mathrm{Br_2}]^{1/2}}{k_\mathrm{c}[\mathrm{Br_2}] + k_\mathrm{d}[\mathrm{HBr}]}$$

$$= \frac{2k_\mathrm{b}(k_\mathrm{a}/k_\mathrm{e})^{1/2}[\mathrm{H_2}][\mathrm{Br_2}]^{3/2}}{[\mathrm{Br_2}] + (k_\mathrm{d}/k_\mathrm{c})[\mathrm{HBr}]}$$

$$k_\mathrm{r1} = 2k_\mathrm{b}\left(\frac{k_\mathrm{a}}{k_\mathrm{e}}\right)^{1/2} \qquad k_\mathrm{r2} = \frac{k_\mathrm{d}}{k_\mathrm{c}}$$

☐ **1**

☐ **2**

☐ **3**

☐ **4**

☐ **5**

☐ **6**

☐ **7**

☐ **8**

☐ **9**

☐ **10**

☐ **11**

☐ **12**

☐ **13**

☐ **14**

Property	Equation	Comment

Fick's laws of diffusion

$$J \propto \frac{c(x-\tfrac{1}{2}l)lA\Delta t - c(x+\tfrac{1}{2}l)lA\Delta t}{A\Delta t}$$

$$= \{c(x-\tfrac{1}{2}l) - c(x+\tfrac{1}{2}l)\}l$$

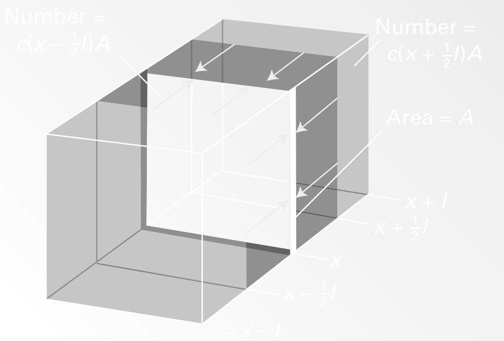


Fig. 11.18 [illegible] calculation of the rate of diffusion considers the net [illegible] molecules through a plane of area *A* as a result of arrivals [illegible] average a distance $\frac{1}{2}l$ in each direction.

We now express the [illegible] concentrations in terms of the concentration at the window itself, $c(x)$, and the concentration gradient, $\Delta c/\Delta x$, as follows:

$$c(x + \tfrac{1}{2}l) = c(x) + \tfrac{1}{2}l \times \frac{\Delta c}{\Delta x} \qquad c(x - \tfrac{1}{2}l) = c(x) - \tfrac{1}{2}l \times \frac{\Delta c}{\Delta x}$$

From which it follows that

$$J \propto \left\{\left(c(x) - \tfrac{1}{2}l\frac{\Delta c}{\Delta x}\right) - \left(c(x) + \tfrac{1}{2}l\frac{\Delta c}{\Delta x}\right)\right\}l$$

$$\propto -l^2\frac{\Delta c}{\Delta x}$$

On writing the constant of proportionality as *D* (and absorbing l^2 into it), we obtain eqn 11.18b.

2. *Fick's second law.* Consider the arrangement in Fig. 11.19. The number of solute particles passing through the window of area *A* located at *x* in an interval Δt is $J(x)A\Delta t$, where $J(x)$ is the flux at the location *x*. The number of particles passing out of the region through a window of area *A* at a short distance away, at $x + \Delta x$, is $J(x + \Delta x)A\Delta t$, where $J(x + \Delta x)$ is the flux at the location of this window. The flux in and the flux out will be different if the concentration gradients are different at the two windows. The net change in the number of solute particles in the region between the two windows is

$$\begin{aligned}\text{Net change in number} &= J(x)A\Delta t - J(x + \Delta x)A\Delta t\\ &= \{J(x) - J(x + \Delta x)\}A\Delta t\end{aligned}$$

Now we express the flux at $x + \Delta x$ in terms of the flux at *x* and the gradient of the flux, $\Delta J/\Delta x$:

$$J(x + \Delta x) = J(x) + \frac{\Delta J}{\Delta x} \times \Delta x$$

It follows that

$$\text{Net change in number} = -\frac{\Delta J}{\Delta x} \times \Delta x \times A\Delta t$$

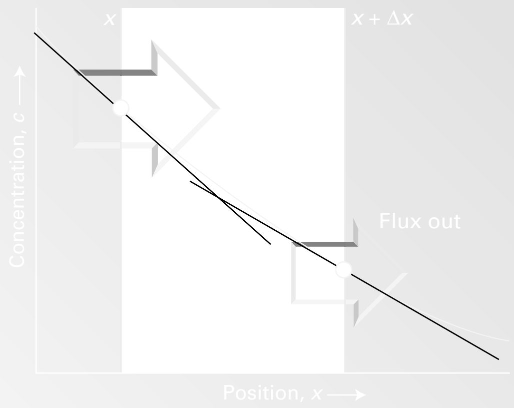


Fig. 11.19 To calculate the change in concentration in the region between the two walls, we need to consider the net effect of the influx or particles from the left and their efflux towards the right. Only if the slope of the concentrations is different at the two walls will there be a net change.

The change in concentration inside the region between the two windows is the net change in number divided by the volume of the region (which is $A\Delta x$), and the net rate of change is obtained by dividing that change in concentration by the time interval Δt. Therefore, on dividing by both $A\delta x$ and Δt we obtain

$$\text{Rate of change of concentration} = -\frac{\Delta J}{\Delta x}$$

[illegible] we express the flux by using Fick's first law:

[illegible] change of concentration

$$= -\frac{\Delta(-D \times (\text{concentration gradient}))}{\Delta x}$$

$$= D\frac{\Delta(\text{concentration gradient})}{\Delta x}$$

The 'gradient of the gr[illegible] the concentration is what we have called the 'curv[illegible] the concentration, and thus we obtain eqn 11.19.

Slightly more formally, on w[illegible] concentration as $\Delta c/\Delta x$ and the rate of change of co[illegible] as $\Delta c/\Delta t$, the last expression becomes

$$\frac{\Delta c}{\Delta t} = D\frac{\Delta(\Delta c/\Delta x)}{\Delta x} = D\frac{\Delta^2 c}{(\Delta x)^2}$$

This expression becomes more exact as the interv[illegible] Δt become smaller, and in the limit of them bec[illegible] infinitesimal it becomes

$$\frac{\mathrm{d}c}{\mathrm{d}t} = D\frac{\mathrm{d}^2 c}{\mathrm{d}x^2}$$

which is the mathematical statement of eqn 11.19.

Discussion questions

11.1

11.2

11.3

11.4

11.5

11.6

11.7

Exercises

11.1

11.2

11.3

$\longrightarrow$ $\longrightarrow$

11.4

11.5

11.6

11.7

11.8

11.9

11.10

11.11 The effective rate constant for a gaseous reaction that has a Lindemann–Hinshelwood mechanism is $2.50 \times 10^{-4}\ \mathrm{s^{-1}}$ at 1.30 kPa and $2.10 \times 10^{-5}\ \mathrm{s^{-1}}$ at 12 Pa. Calculate the rate constant for the activation step in the mechanism.

11.12 Calculate the magnitude of the diffusion-controlled rate constant at 298 K for a species in (a) water, (b) pentane. The viscosities are $1.00 \times 10^{-3}\ \mathrm{kg\ m^{-1}\ s^{-1}}$, and $2.2 \times 10^{-4}\ \mathrm{kg\ m^{-1}\ s^{-1}}$, respectively.

11.13 What is (a) the flux of nutrient molecules down a concentration gradient of $0.10\ \mathrm{mol\ dm^{-3}\ m^{-1}}$, (b) the amount of [illegible]s (in moles) passing through an area of $5.0\ \mathrm{mm^2}$ in 1.[illegible] ake for the diffusion coefficient the value for sucrose [illegible] ($5.22 \times 10^{-10}\ \mathrm{m^2\ s^{-1}}$).

11.14 How [illegible] it take a sucrose molecule in water at 25°C to diffuse [illegible] a single dimension by (a) 10 mm, (b) 10 cm, (d) 10 m [illegible] starting point?

11.15 The mobility of s[illegible]ough fluids is of the greatest importance for nutritional p[illegible] (a) Estimate the diffusion coefficient for a molecule that [illegible]ng a single dimension by 150 pm each 1.8 ps. (b) What w[illegible] the diffusion coefficient if the molecule travelled only [illegible] on each step?

11.16 Is diffusion important in lakes? Ho[illegible]ould it take a small pollutant molecule about the size o[illegible] diffuse across a lake of width 100 m?

11.17 Pollutants spread through the environment by [illegible] tion (winds and currents) and by diffusion. How many [illegible] must a molecule take to be likely to be found 1000 s[illegible] lengths away from its origin if it undergoes a one-dimensional random walk?

11.18 The viscosity of water at 20°C is $1.0019\ \mathrm{mN\ s\ m^{-2}}$ and at 30°C it is $0.7982\ \mathrm{mN\ s\ m^{-2}}$. What is the activation energy for the motion of water molecules?

11.19 Calculate the ratio of rates of catalysed to noncatalysed reactions at 37°C given that the Gibbs energy of activation for a particular reaction is reduced from $150\ \mathrm{kJ\ mol^{-1}}$ to $15\ \mathrm{kJ\ mol^{-1}}$.

11.20 The condensation reaction of acetone, $(CH_3)_2CO$ (propanone), in aqueous solution is catalysed by bases, B, which react reversibly with acetone to form the carbanion $C_3H_5O^-$. The carbanion then reacts with a molecule of acetone to give the product. A simplified version of the mechanism is

(1) $AH + B \rightarrow BH^+ + A^-$

(2) $A^- + BH^+ \rightarrow AH + B$

(3) $A^- + HA \rightarrow$ product

where AH stands for acetone and A^- its carbanion. Use the steady-state approximation to find the concentration of the carbanion and derive the rate equation for the formation of the product.

11.21 Consider the acid-catalysed reaction

$HA + H^+ \rightleftarrows HAH^+$ (fast)

$HAH^+ + B \rightarrow BH^+ + AH$ (slow)

Deduce the rate law and show that it can be made independent of the specific term $[H^+]$.

11.22 As remarked in Derivation 11.6, Michaelis and Menten derived their rate law by assuming a rapid pre-equilibrium of E, S, and ES. Derive the rate law in this manner, and identify the conditions under which it becomes the same as that based on the steady-state approximation (eqn 11.25).

11.23 The enzyme-catalysed conversion of a substrate at 25°C has a Michaelis constant of $0.045\ \mathrm{mol\ dm^{-3}}$. The rate of the reaction is $1.15\ \mathrm{mmol\ dm^{-3}\ s^{-1}}$ when the substrate concentration is $0.110\ \mathrm{mol\ dm^{-3}}$. What is the maximum velocity of this reaction?

11.24 The enzyme-catalysed conversion of a substrate at 25°C has a Michaelis constant of $0.015\ \mathrm{mol\ dm^{-3}}$ and a maximum velocity of $4.25 \times 10^{-4}\ \mathrm{mol\ dm^{-3}\ s^{-1}}$ when the enzyme concentration is $3.60 \times 10^{-9}\ \mathrm{mol\ dm^{-3}}$. Calculate k_{cat} and the catalytic efficiency η. Is the enzyme 'catalytically perfect'?

11.25 The following results were obtained for the action of an ATPase on ATP at 20°C, when the concentration of the ATPase is $20\ \mathrm{nmol\ dm^{-3}}$:

$[ATP]/(\mu\mathrm{mol\ dm^{-3}})$	0.60	0.80	1.4	2.0	3.0
$v/(\mu\mathrm{mol\ dm^{-3}\ s^{-1}})$	0.81	0.97	1.30	1.47	1.69

Determine the Michaelis–Menten constant, the maximum velocity of the reaction, and the maximum turnover number of the enzyme.

11.26 There are different ways to represent and analyse data [illegible] enzyme-catalysed reactions. For example, in the *Eadie–*[illegible] *plot*, $v/[S]_0$ is plotted against v. Alternatively, in the [illegible] $v/[S]_0$ is plotted against $[S]_0$. (a) Use the simple Mich[illegible]nten mechanism to derive relations between $v/[S]_0$ a[illegible] between $v/[S]_0$ and $[S]_0$. (b) Discuss how the values [illegible] d v_{max} are obtained from analysis of the Eadie–Hofste[illegible]es plots. (c) Determine the Michaelis constant and th[illegible]m velocity of the reaction from Problem 11.25 by [illegible]e–Hofstee and Hanes plots to analyse the data.

11.27 Consider the follow[illegible]echanism:

(1) $AH \rightarrow A\cdot + H\cdot$

(2) $A\cdot \rightarrow B\cdot + C$

(3) $AH + B\cdot \rightarrow A\cdot + D$

(4) $A\cdot + B\cdot \rightarrow P$

Identify the initiation, propagation, and termin[illegible] and use the steady-state approximation to deduce [illegible] decomposition of AH is first order in AH.

11.28 Consider the following mechanism for the therm[illegible] decomposition of R_2:

(1) $R_2 \rightarrow R + R$

(2) $R + R_2 \rightarrow P_B + R'$

(3) $R' \rightarrow P_A + R$

(4) $R + R \rightarrow P_A + P_B$

where R_2, P_A, and P_B are stable hydrocarbons and R and R′ are radicals. Find the dependence of the rate of decomposition of R_2 on the concentration of R_2.

11.29 (a) Confirm eqn 11.35 for the rate of formation of HBr. (b) What are the orders of the reaction (with respect to each species) when the concentration of HBr is (i) very low, (ii) very high. Suggest an interpretation in each case.

Projects

The symbol ‡ indicates that calculus is required.

11.30‡ Here we explore more quantitatively the kinetic analysis of a reaction approaching equilibrium. (a) Confirm (by differentiation) that the expressions in eqn 11.2 are the correct solutions of the rate laws for approach to equilibrium. (b) Find the solutions of the same rate laws that led to eqn 11.2, but for some B present initially. [illegible] confirm that the solutions you find reduce to those in eqn 11.2 when $[B]_0 = 0$.

11.31‡ Complete the kinetic analysis of consecutive reactions by confirming that the three expressions in eqn 11.5 are correct solutions of the rate laws for consecutive first-order reactions.

11.32 Consider a mechanism for the helix–coil transition of a polymeric chain in which initiation occurs in the middle of the chain:

hhhh… ⇄ *hchh*…

hchh… ⇄ *cccc*…

We saw in Box 11.1 that this type of initiation is relatively slow, so neither step may be rate-determining. (a) Set up the rate equations for this alternative mechanism. (b) Apply the steady-state approximation and show that, under these circumstances, the mechanism is equivalent to *hhhh*… ⇄ *cccc*… (c) Use your knowledge of experimental techniques and your results from the previous exercise to support or refute the following statement: It is very difficult to obtain experimental evidence for intermediates in protein folding by performing simple rate measurements and one must resort to special time-resolved or trapping techniques to detect intermediates directly.

11.33 Here we explore chain reactions in more detail. (a) Refer to the illustration in Box 11.2 and determine the pressure range for a chain-branching explosion in the hydrogen–oxygen reaction at (i) 700 K and (ii) 900 K. (b) Suppose that a reaction mechanism (such as that for the reaction of hydrogen and oxygen) gives the following expressions for the time dependence of the concentration of H atoms:

Low O_2 concentration:

$$[H] = \frac{v_{\text{initiation}}}{k_{\text{termination}} - k_{\text{branching}}}\{1 - e^{-(k_{\text{termination}} - k_{\text{branching}})t}\}$$

High O_2 concentration:

$$[H] = \frac{v_{\text{initiation}}}{k_{\text{termination}} - k_{\text{branching}}}\{1 - e^{(k_{\text{termination}} - k_{\text{branching}})t}\}$$

where $v_{\text{initiation}}$ is the rate at which H atoms are formed in an initiation step. Plot graphs of these functions and identify the conditions for an explosion.

Three crucial experiments

The dynamics of microscopic systems

Applications of quantum mechanics

CHECKLIST OF KEY IDEAS
TABLE OF KEY EQUATIONS
QUESTIONS AND EXERCISES

Three crucial experiments

12.1 Atomic and molecular spectra: discrete energies

Fig. 12.1

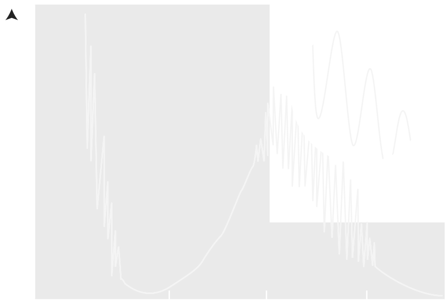


Fig. 12.2

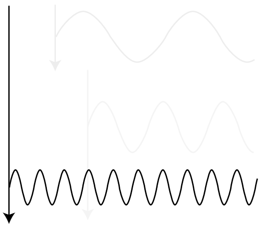


Fig. 12.3

A brief illustration

$$\Delta E = \frac{(6.626\times10^{-34}\ \mathrm{J\,s})\times(2.998\times10^{8}\ \mathrm{m\,s^{-1}})}{5.9\times10^{-7}\ \mathrm{m}}$$

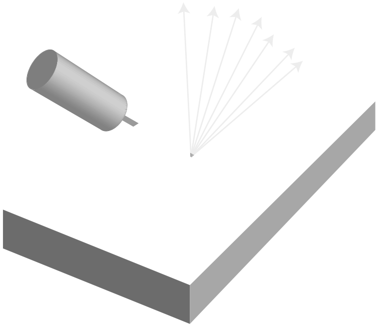


Fig. 12.4

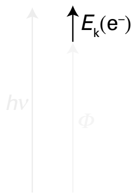


Fig. 12.5

12.2 The photoelectric effect: light as particles

Self-test 12.1

The work function of rubidium is 2.09 eV (1 eV = 1.60 × 10^{-19} J). Can blue (470 nm) light eject electrons from the metal?

[*Answer:* yes]

A brief comment

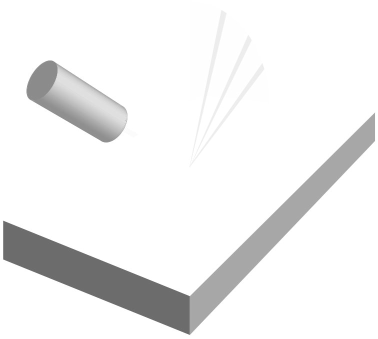


Fig. 12.6

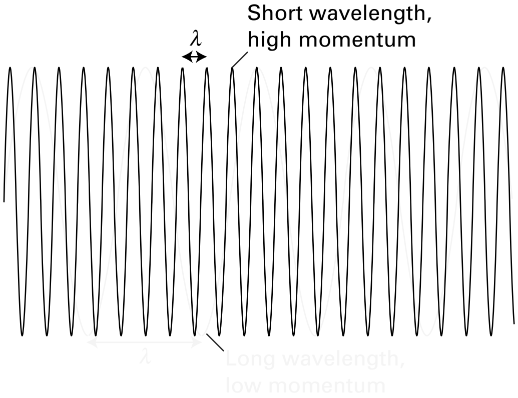


Fig. 12.7

12.3 Electron diffraction: electrons as waves

$$\lambda = \frac{h}{p}$$

$$\lambda = \frac{h}{(2m_e eV)^{1/2}}$$

The dynamics of microscopic systems

12.4 The Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}+V(x)\psi = E\psi$$

$$\hbar = \frac{h}{2\pi} = 1.055\times10^{-34}\ \mathrm{J\ s}$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$$

$$k = \frac{(2mE)^{1/2}}{\hbar}$$

$$\frac{d}{dx}\sin(kx) = k\cos(kx) \qquad \frac{d}{dx}\cos(kx) = -k\sin(kx)$$

$$\frac{d^2}{dx^2}\sin(kx) = -k^2\sin(kx)$$

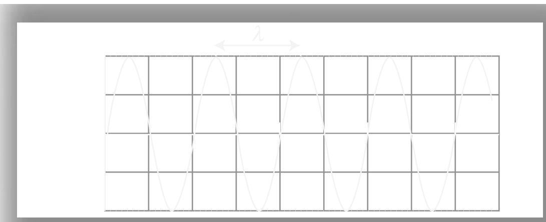


Fig. 12.9 The wavelength of a harmonic wave of the form sin(2πx/λ). The amplitude of the wave is the maximum height above the centre line.

Thus:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = -\frac{\hbar^2}{2m}\frac{d^2\sin(kx)}{dx^2}$$

$$= -\frac{\hbar^2}{2m}(-k^2\sin(kx)) = \frac{k^2\hbar^2}{2m}\psi$$

The final term is equal (according to the Schrödinger equation) to $E\psi$, so we can recognize that $E = k^2\hbar^2/2m$ and therefore that $k = (2mE)^{1/2}/\hbar$.

The function sin(kx) is a wave of wavelength $\lambda = 2\pi/k$, as we can see by comparing sin(kx) with sin(2πx/λ), the standard form of a harmonic wave with wavelength λ (Fig. 12.9). Next, we note that the energy of the particle is entirely kinetic (because $V = 0$ everywhere), so the total energy of the particle is just its kinetic energy:

$$E = E_k = \frac{p^2}{2m}$$

Because E is related to k by $E = k^2\hbar^2/2m$, it follows from a comparison of the two equations that $p = k\hbar$. Therefore, the linear momentum is related to the wavelength of the wavefunction by

$$p = \frac{2\pi}{\lambda}\times\frac{h}{2\pi} = \frac{h}{\lambda}$$

which is the de Broglie relation. We see, in the case of a freely moving particle, that the Schrödinger equation has led to an experimentally verified conclusion.

A note on good practice

A brief comment

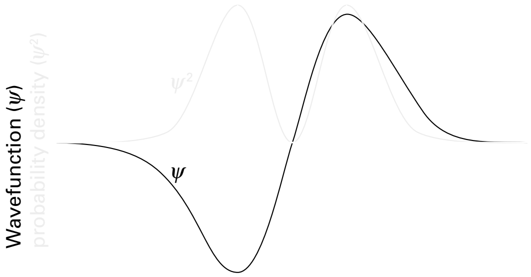


Fig. 12.10

Example 12.2

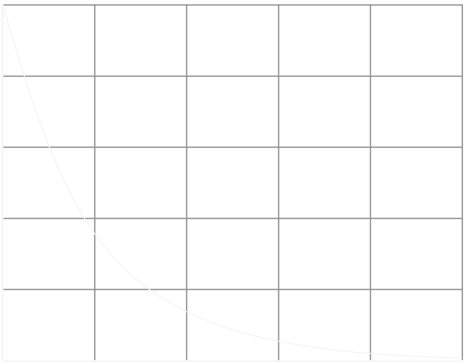


Fig. 12.11

Strategy

Solution

Self-test 12.3

The wavefunction for the lowest energy state in the ion He^+ is proportional to e^{-2r/a_0}. Repeat the calculation for this ion. Any comment?

[*Answer:* 55; a more compact wavefunction on account of the higher nuclear charge]

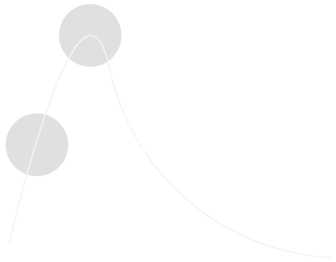


Fig. 12.12

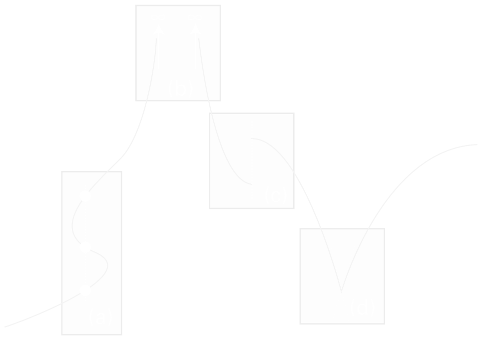


Fig. 12.13

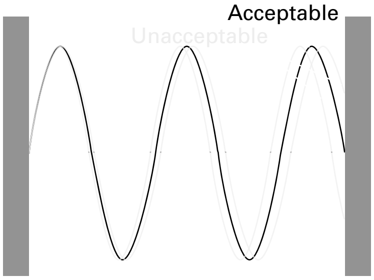


Fig. 12.14

12.6 The uncertainty principle

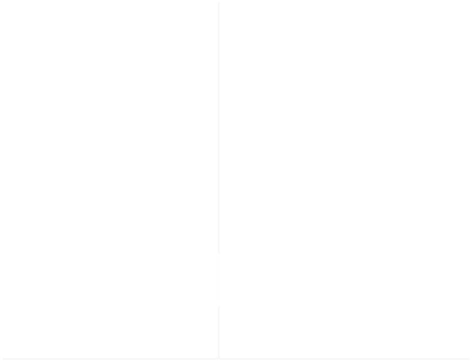


Fig. 12.15

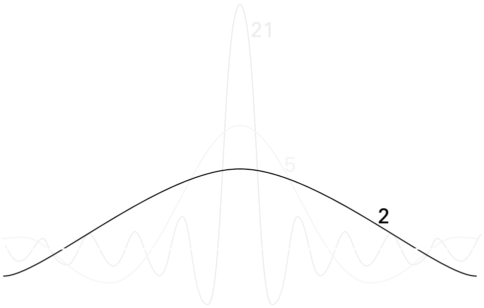


Fig. 12.16

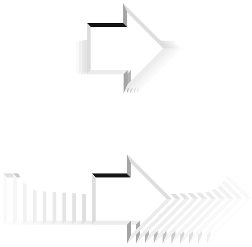


Fig. 12.17

$\frac{1}{2}$

$$\Delta x \geq \frac{\hbar}{2\Delta p} = \frac{1.054\times10^{-34}\ \mathrm{J\ s}}{2\times(1.0\times10^{-3}\ \mathrm{kg})\times(1.0\times10^{-6}\ \mathrm{m\ s^{-1}})}$$

Self-test 12.4

Estimate the minimum uncertainty in the speed of an electron in a hydrogen atom (taking its diameter as 100 pm).

[*Answer:* 580 km $\mathrm{s^{-1}}$]

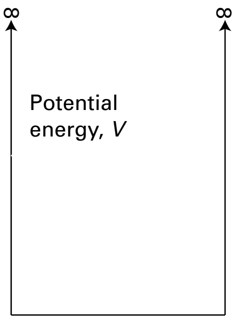


Fig. 12.18

A brief comment

12.7 Translational motion

$$\psi_n = N\sin\left(\frac{n\pi x}{L}\right) \quad n = 1,\ 2,\ \ldots$$

(a) Motion in one dimension

$$\lambda = 2L, L, \tfrac{2}{3}L, \ldots \quad \text{or} \quad \lambda = \frac{2L}{n},\ \text{with } n = 1,2,3,\ldots$$

$$\sin^2\left(\frac{n\pi x}{L}\right)\mathrm{d}x = 1$$

$$\sin^2(ax)\mathrm{d}x = \tfrac{1}{2}x - \frac{\sin(2ax)}{4a} + \text{constant}$$

$$\sin^2\left(\frac{n\pi x}{L}\right)\mathrm{d}x = \tfrac{1}{2}L$$

–

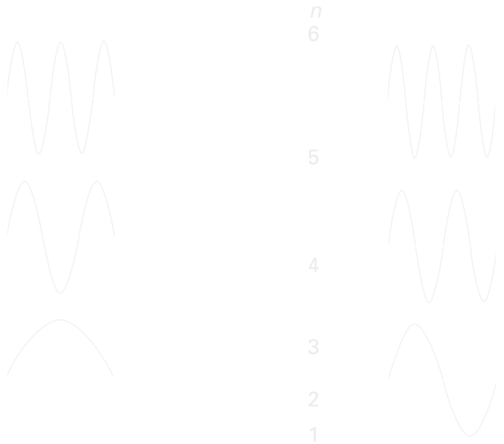


Fig. 12.19

$$p = \frac{h}{\lambda} \overset{\lambda = 2L/n}{=} \frac{nh}{2L},$$

$$E_n = \frac{n^2h^2}{8mL^2}, \quad n = 1, 2, \ldots$$

Fig. 12.20

$$\Delta E = E_{n+1} - E_n = \overset{n^2+2n+1}{(n+1)^2}\,\frac{h^2}{8mL^2} - n^2\,\frac{h^2}{8mL^2}$$

$$= (2n+1)\frac{h^2}{8mL^2}$$

$$\Delta E = E_{n_{\text{final}}} - E_{n_{\text{initial}}} = (n_{\text{final}}^2 - n_{\text{initial}}^2)\frac{h^2}{8mL^2}$$

A brief illustration

$$\begin{aligned}\nu &= (n_{\text{final}}^2 - n_{\text{initial}}^2)\frac{h}{8m_{\text{e}}L^2}\\ &= (12^2 - 11^2) \times \frac{6.626\times10^{-34}\ \text{J s}}{8\times(9.110\times10^{-31}\ \text{kg})\times(2.94\times10^{-9}\ \text{m})^2}\\ &= 2.42\times10^{14}\ \text{s}^{-1}\end{aligned}$$

A note on good practice

(b) Tunnelling

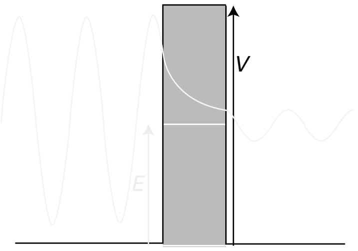


Fig. 12.21

Fig. 12.22

(c) Motion in two dimensions

$$= \left(\frac{4}{L_X L_Y}\right)^{1/2} \sin\left(\frac{n_X \pi x}{L_X}\right) \sin\left(\frac{n_Y \pi y}{L_Y}\right)$$

$$= \frac{n_X^2 h^2}{8mL_X^2} + \frac{n_Y^2 h^2}{8mL_Y^2} = \left(\frac{n_X^2}{L_X^2} + \frac{n_Y^2}{L_Y^2}\right)\frac{h^2}{8m}$$

$$\frac{1}{X(x)}\hat{H}_X X(x) = E_X \qquad \frac{1}{Y(y)}\hat{H}_X Y(y) = E_Y$$

Derivation 12.3

The separation of variables procedure

The Schrödinger equation for the problem is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x,y)}{dx^2} - \frac{\hbar^2}{2m}\frac{d^2\psi(x,y)}{dy^2} = E\psi(x,y)$$

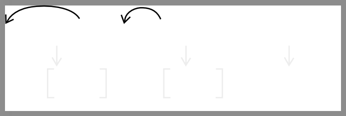
For simplicity, we can write this expression as

$$\hat{H}_X\psi(x,y) + \hat{H}_X\psi(x,y) = E\psi(x,y)$$

where $\hat{H}_X$ affects—mathematicians say 'operates on'—only functions of x and $\hat{H}_Y$ operates only on functions of y. Thus, generalizing slightly from Derivation 12.1, $\hat{H}_X$ just means 'take the second derivative with respect to x' and $\hat{H}_Y$ means the same for y. To see if $\psi(x,y) = X(x)Y(y)$ is indeed a solution, we substitute this product on both sides of the last equation,

$$\hat{H}_X X(x)Y(y) + \hat{H}_X X(x)Y(y) = EX(x)Y(y)$$

and note that $\hat{H}_X$ acts on only $X(x)$, with $Y(y)$ being treated as a constant, and $\hat{H}_Y$ acts on only $Y(y)$, with $X(x)$ being treated as a constant. Therefore, this equation becomes



When we divide both sides by $X(x)Y(y)$, we obtain

$$\frac{1}{X(x)}\hat{H}_X X(x) + \frac{1}{Y(y)}\hat{H}_Y Y(y) = E$$

Now we come to the crucial part of the argument. The first term on the left depends only on x and the second

$$E_{n_X n_Y} = (n_X^2 + n_Y^2)\frac{h^2}{8mL^2}$$

Fig. 12.23

$$\psi_{1,2}(x,y) = \frac{2}{L}\sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{2\pi y}{L}\right)$$

$$\psi_{2,1}(x,y) = \frac{2}{L}\sin\left(\frac{2\pi x}{L}\right)\sin\left(\frac{\pi y}{L}\right)$$

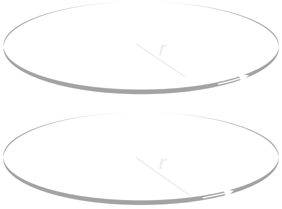


Fig. 12.24

12.8 **Rotational motion**

$$E = \frac{J_z^2}{2mr^2}$$

$$E = \frac{J_z^2}{2I}$$

(a) Rotation in two dimensions

$p = h/\lambda$

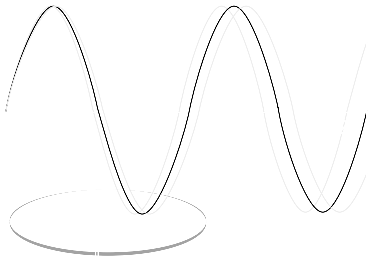


Fig. 12.25

$$\lambda = \frac{2\pi r}{n} \qquad n = 0, 1, \ldots$$

$$\overbrace{E_n =}^{E = J_z^2/2I \text{ and } J_z = hr/\lambda} \frac{(hr/\lambda)^2}{2I} \underbrace{=}_{\lambda = 2\pi r/n} \frac{(nh/2\pi)^2}{2I} \overbrace{=}^{h/2\pi = \hbar} \frac{n^2\hbar^2}{2I}$$

$$E_{m_l} = \frac{m_l^2\hbar^2}{2I} \qquad m_l = 0, \pm1, \ldots$$

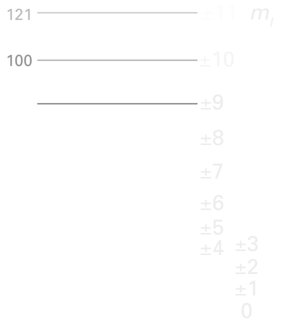


Fig. 12.26

$$J_z = pr = \frac{hr}{\lambda} = \frac{hr}{2\pi r/m_l} = m_l \times \frac{h}{2\pi}$$

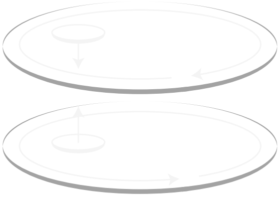


Fig. 12.27

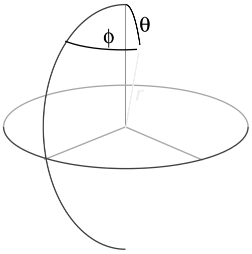


Fig. 12.28

(b) Rotation in three dimensions

$$E_l = l(l+1)\frac{\hbar^2}{2mr^2}$$

$$E = \frac{J^2}{2mr^2} \qquad E_l = \frac{l(l+1)\hbar^2}{2mr^2}$$

Fig. 12.29

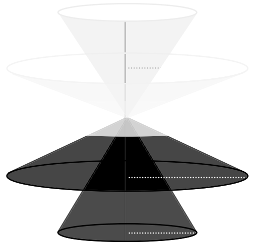


Fig. 12.31

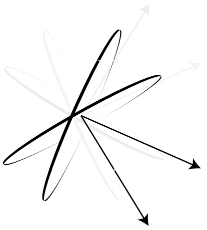


Fig. 12.30

A brief illustration

12.9 Vibrational motion

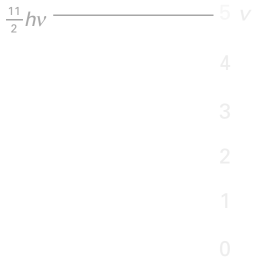


Fig. 12.33

A brief comment

$$\nu = \frac{1}{2\pi}\left(\frac{k}{m}\right)^{1/2}$$

Fig. 12.32

A brief illustration

$$\nu = \frac{1}{2\pi}\left(\frac{k}{m}\right)^{1/2} = \frac{1}{2\pi}\left(\frac{516\ \mathrm{N\ m^{-1}}}{1.67\times10^{-27}\ \mathrm{kg}}\right)^{1/2} = 8.85\times10^{13}\ \mathrm{Hz}$$

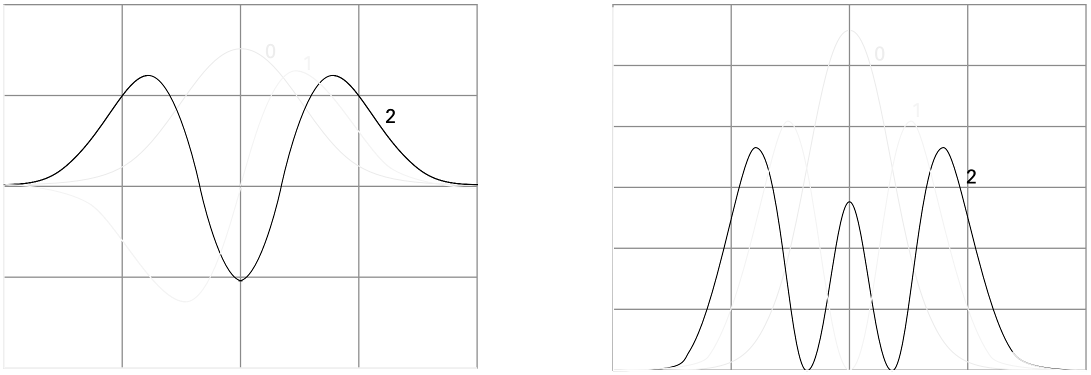


Fig. 12.34

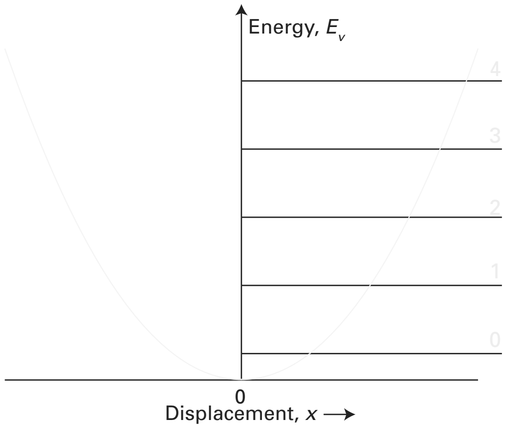


Fig. 12.35

☐ **1**

☐ **2**

☐ **3**

☐ **4**

☐ **5**

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☐ **10**

☐ **11**

☐ **12**

☐ **13**

☐ **14**

☐ **15**

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Property	Equation	Comment

Discussion questions

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Exercises

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12.20

12.21 Suppose a particle has a wavefunction $\psi(x) = Ne^{-ax^2}$. Sketch the form of this wavefunction. Where is the particle most likely to be found? At what values of x is the probability of finding the particle reduced by 50 per cent from its maximum value?

12.22 Calculate the probability that an electron will be found [illegible] between $x = 0.1$ and 0.2 nm, (b) between 4.9 and 5.2 nm [illegible] box of length $L = 10$ nm when its wavefunction is $\psi =$ [illegible]n$(2\pi x/L)$. *Hint*: Treat the wavefunction as a constant in [illegible] region of interest and interpret δV as δx.

12.23 [illegible] of a certain proton is 350 km s^{-1}. If the uncertain[illegible] momentum is 0.0100 per cent, what uncertainty in [illegible]on must be tolerated?

12.24 Calculate [illegible]m uncertainty in the speed of a ball of mass 500 g [illegible]own to be within 5.0 μm of a certain point on a bat.

12.25 What is the minimum [illegible]ty in the position of a bullet of mass 5.0 g that is kno[illegible]ve a speed somewhere between 350.00 000 1 m s[illegible]0 000 0 m s^{-1}?

12.26 An electron is confined to a linear [illegible] a length of the same order as the diameter of an ato[illegible]t to be 100 pm). Calculate the minimum uncertainties [illegible]tion and speed.

12.27 Write the explicit numerical form of the wavefun[illegible] in eqn 12.7 and the corresponding probability density for n [illegible] and $L = 100$ pm at $x =$ (a) 10 pm, (b) 50 pm, and (c) 100 pm.

12.28 A hydrogen atom, treated as a point mass, is confined to a one-dimensional square well of width 1.0 nm. How much energy does it have to give up to fall from the level with $n = 2$ to the lowest energy level?

12.29 The pores in zeolite catalysts are so small that quantum-mechanical effects on the distribution of atoms and molecules within them can be significant. Calculate the location in a box of length L at which the probability of a particle being found is 50 per cent of its maximum probability when $n = 1$.

12.30 The blue solution formed when an alkali metal dissolves in liquid ammonia consists of the metal cations and electrons trapped in a cavity formed by ammonia molecules. (a) Calculate the spacing between the levels with $n = 4$ and $n = 5$ of an electron in a one-dimensional box of length 5.0 nm. (b) What is the wavelength of the radiation emitted when the electron makes a transition between the two levels?

12.31 A certain wavefunction is zero everywhere except between $x = 0$ and $x = L$, where it has the constant value A. Normalize the wavefunction.

12.32 As indicated in the text, a particle in a box is a crude model of the distribution and energy of electrons in conjugated polyenes, such as carotene and related molecules. Carotene itself is a molecule in which 22 single and double bonds alternate (11 of each) along a chain of carbon atoms. Take each CC bond length to be about 140 pm and suppose that the first possible upward transition (for reasons related to the Pauli principle, Section 13.9) is from $n = 11$ to $n = 12$. Estimate the wavelength of this transition.

12.33 Suppose a particle has zero potential energy for $x < 0$, a constant value V, for $0 \le x \le L$, and then zero for $x > L$. Sketch the potential. Now suppose that wavefunction is a sine wave on the left of the barrier, declines exponentially inside the barrier, and then becomes a sine wave on the right, being continuous everywhere. Sketch the wavefunction on your sketch of the potential energy.

12.34 Degeneracy is normally associated with symmetry but there are cases where it seems to arise accidentally. Consider a rectangular area of sides L and $2L$. Are there any degenerate states? If there are, identify the two lowest.

12.35 Treat a rotating HI molecule as a stationary I atom around which an H atom circulates in a plane at a distance of 161 pm. Calculate (a) the moment of inertia of the molecule, (b) the greatest wavelength of the radiation that can excite the molecule into rotation.

12.36 The moment of inertia of an H_2O molecule about an axis bisecting the HOH angle is 1.91×10^{-47} kg m^2. Its minimum angular momentum about that axis (other than zero) is $\hbar$. In classical terms, how many revolutions per second do the H atoms make about the axis when in that state?

12.37 What is the minimum energy needed to excite the [illegible]tion of an H_2O molecule about the axis described in the [illegible]ng exercise?

12.38 [illegible]oment of inertia of CH_4 can be calculated from the e[illegible] $I = \frac{8}{3}m_H R^2$ where R is the CH bond length (take $R =$ [illegible] Calculate the minimum rotational energy (other than [illegible]e molecule and the degeneracy of that rotational state.

12.39 A bee of mas[illegible]ds on the end of a horizontal twig, which starts to os[illegible] and down with a period of 1 s. Treat the twig as a [illegible] spring, and estimate its force constant.

12.40 Treat a vibrating HI molecu[illegible]ationary I atom with the H atom oscillating towards an[illegible]m the I atom. Given the force constant of the HI bond [illegible], calculate (a) the vibrational frequency of the [illegible] the wavelength required to excite the molecule into [illegible]

12.41 By what factor will the vibrational frequenc[illegible] change when H is replaced by deuterium?

Projects

The symbol ‡ indicates that calculus is required.

12.42‡ Now we use calculus to carry out more accurate calculations of probabilities. (a) Repeat Exercise 12.22, but allow for the variation of the wavefunction in the region of interest. What are the percentage errors in the procedure used in

Exercise 12.22? What is the probability of finding a particle of mass *m* in (a) the left-hand one-third, (b) the central one-third, (c) the right-hand one-third of a box of length *L* when it is in the state with $n = 1$? *Hint*: You will need to integrate $\psi^2 dx$ between the limits of interest. The indefinite integral you require is given in Derivation 12.2.

12.43‡ Here we explore the quantum-mechanical harmonic oscillator in more quantitative detail. (a) The ground-state wavefunction of an harmonic oscillator is proportional to $e^{-ax^2/2}$, [illegible] a depends on the mass and force constant. (i) Normalize [illegible] function. (ii) At what displacement is the oscillator mo[illegible] be found in its ground state? *Hint:* For (i), you will nee[illegible]egral $\int_{-\infty}^{\infty} e^{-ax^2} dx = (\pi/a)^{1/2}$. For (ii), recall that the maxim[illegible]nimum) of a function $f(x)$ occurs at the value of x for w[illegible]$x = 0$. (b) Repeat part (a) for the first excited state of a[illegible] oscillator, for which the wavefunction is proportio[illegible].

12.44 The solutions of the Schrödinger equation for a harmonic oscillator also apply to diatomic molecules. The only complication is that both atoms joined by the bond move, so the 'mass' of the oscillator has to be interpreted carefully. Detailed calculation shows that for two atoms of masses m_A and m_B joined by a bond of force constant k, the energy levels are given by eqn 12.20 but with m replaced by the 'effective mass' $\mu = m_A m_B/(m_A + m_B)$. Consider the vibration of carbon monoxide, a poison that prevents the transport and storage of O_2. The bond in a $^{12}C^{16}O$ molecule has a force constant of 1860 N m^{-1}. (a) Calculate the vibrational frequency, ν, of the molecule. (b) In infrared spectroscopy it is common to convert the vibrational frequency of a molecule to its vibrational wavenumber, $\tilde{\nu}$, given by $\tilde{\nu} = \nu/c$. What is the vibrational number of a $^{12}C^{16}O$ molecule? (c) Assuming that isotopic substitution does not affect the force constant of the C≡O bond, calculate the vibrational wavenumbers of the following molecules: $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$, $^{13}C^{18}O$.

Hydrogenic atoms

The structures of many-electron atoms

Periodic trends in atomic properties

The spectra of complex atoms

Box 13.1 Spectroscopy of stars

CHECKLIST OF KEY IDEAS
TABLE OF KEY EQUATIONS
FURTHER INFORMATION 13.1: THE PAULI PRINCIPLE
QUESTIONS AND EXERCISES

Hydrogenic atoms

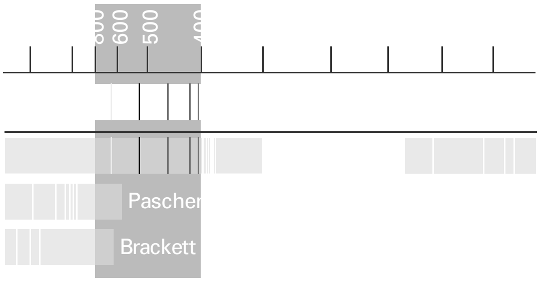


Fig. 13.1

13.1 The spectra of hydrogenic atoms

$$\tilde{\nu} \propto \frac{1}{2^2} - \frac{1}{n^2}$$

$$\tilde{\nu} = R_{\mathrm{H}}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

13.2 The permitted energies of hydrogenic atoms

$$V = \frac{Q_1 Q_2}{4\pi\varepsilon_0 r}$$

$$V = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi - \frac{Ze^2}{4\pi\varepsilon_0 r}\psi = E\psi \qquad \mu = \frac{m_{\mathrm{e}} m_{\mathrm{N}}}{m_{\mathrm{e}} + m_{\mathrm{N}}}$$

A brief comment

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$E_n = -\frac{hcRZ^2}{n^2}$$

$$hcR = \frac{\mu e^4}{32\pi^2 \varepsilon_0^2 \hbar^2} \qquad \mu = \frac{m_e m_N}{m_e + m_N}$$

Fig. 13.2

$$\Delta E = \frac{hcR_H}{n_1^2} - \frac{hcR_H}{n_2^2} = hcR_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Self-test 13.1

The shortest wavelength transition in the Paschen series in hydrogen occurs at 821 nm; at what wavelength does it occur in Li^{2+}? *Hint:* Think about the variation of energies with atomic number Z.

[*Answer:* $\frac{1}{9} \times 821\ \text{nm} = 91.2\ \text{nm}$]

Self-test 13.2

Predict the ionization energy of He^+ given that the ionization energy of H is 13.59 eV. *Hint:* Decide how the energy of the ground state varies with Z.

[*Answer:* $I_{He^+} = 4I_H = 54.36\ \text{eV}$]

13.3 Quantum numbers

Quantum number	Name	Allowed values	Determines
n	principal	1, 2, . . . ,	Energy, through $E_n = -hcRZ^2/n^2$
l	orbital angular momentum	0, 1, . . . $n - 1$	Orbital angular momentum, through $J = \{l(l+1)\}^{1/2}\hbar$
m_l	magnetic	$l, l - 1, l - 2, \ldots, -l$	z-Component of orbital angular momentum, through $J_z = m_l\hbar$

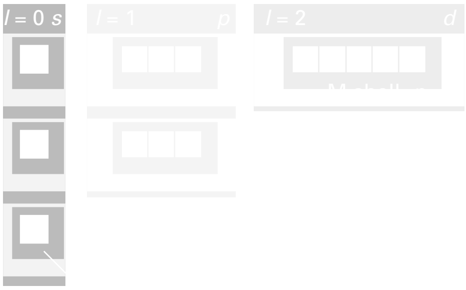


Fig. 13.3

A brief illustration

A note on good practice

Self-test 13.3

How many orbitals are there in a shell with $n = 5$ and what is their designation?

[*Answer:* 25; one s, three p, five d, seven f, nine g]

13.4 The wavefunctions: s orbitals

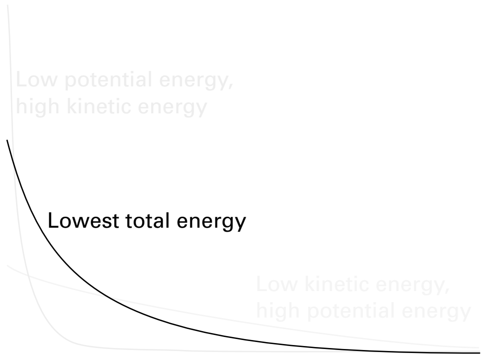


Fig. 13.4

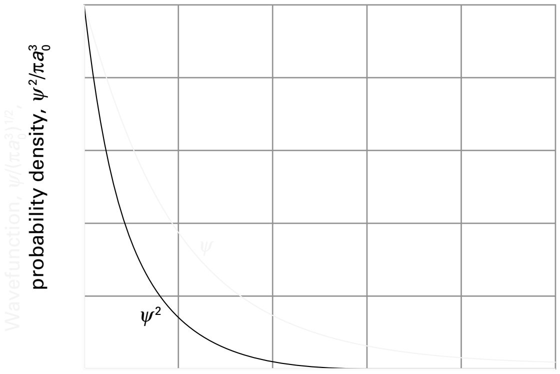


Fig. 13.5

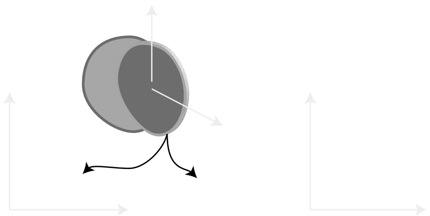


Fig. 13.6

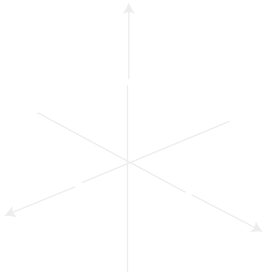


Fig. 13.7

■ **A brief illustration**

$$\text{Probability} = \frac{1}{\pi a_0^3} \times \delta V = \frac{1}{\pi \times (52.9\ \text{pm})^3} \times (1.0\ \text{pm}^3)$$

$$= \frac{(1.0)^3}{\pi \times (52.9)^3} = 2.2 \times 10^{-6}$$

■

■ **A brief illustration**

$$\text{Probability} = \overset{P(r)}{\boxed{4\pi r^2 \psi^2}} \times \delta r = 4\,\pi r^2 \times \overset{\psi^2}{\boxed{\frac{1}{\pi a_0^3} e^{-2r/a_0}}} \times \delta r$$

$$= \frac{4r^2}{a_0^3} e^{-2r/a_0} \times \delta r$$

$$\text{Probability} = \overset{\text{With } r = a_0,\ 4r^2/a_0^3 = 4/a_0}{\frac{4}{a_0}} e^{-2} \times \delta r = \frac{4}{52.9\ \text{pm}} e^{-2} \times (1.0\ \text{pm}) = 0.010$$

■

Derivation 13.1

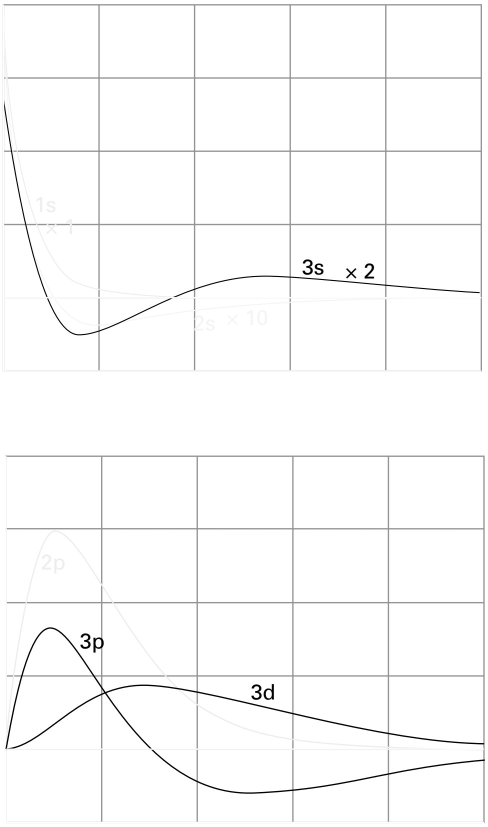


Fig. 13.9

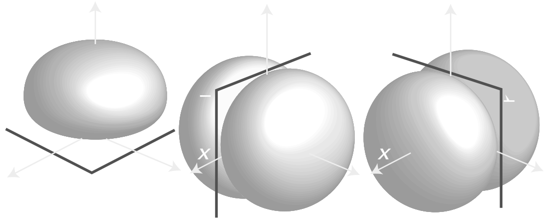


Fig. 13.10

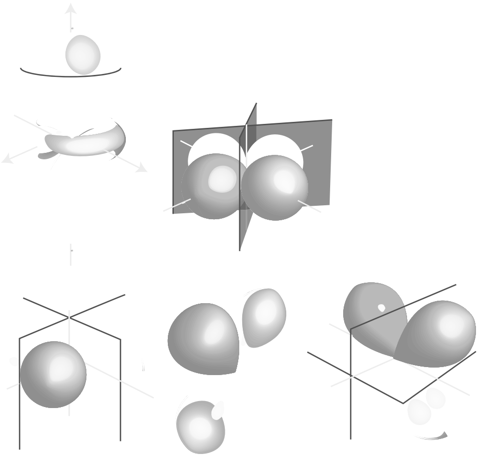


Fig. 13.11

13.5 The wavefunctions: p and d orbitals

$$\psi = \underbrace{\boxed{\tfrac{1}{2}\left(\frac{1}{6a_0^3}\right)^{1/2}\frac{r}{a_0}\mathrm{e}^{-r/2a_0}}}_{}^{R_{2,1}(r)} \times \overset{Y_{1,0}(\theta,\,\phi)}{\boxed{\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta}}$$

$$= \left(\frac{1}{32\pi a_0^5}\right)^{1/2} r\cos\theta\,\mathrm{e}^{-r/2a_0}$$

A brief comment

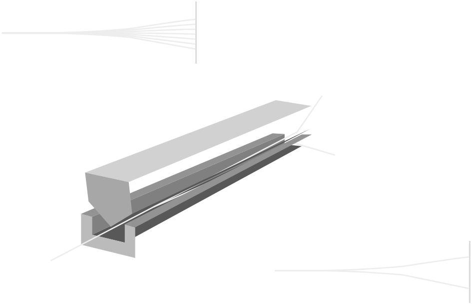


Fig. 13.13

13.6 Electron spin

A note on good practice

Fig. 13.12

Fig. 13.14

13.7 Spectral transitions and selection rules

A brief illustration

Self-test 13.5

To what orbitals may a 4s electron make spectroscopic transitions?

[*Answer: n*p orbitals only]

The structures of many-electron atoms

13.8 The orbital approximation

A brief illustration

Use $e^x e^y = e^{x+y}$

Derivation 13.2

13.9 The Pauli principle

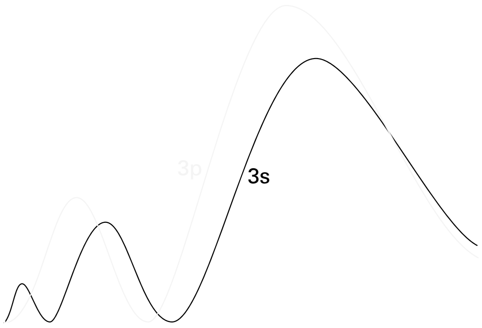


Fig. 13.16

13.10 Penetration and shielding

A note on good practice

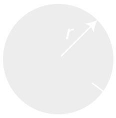


Fig. 13.15

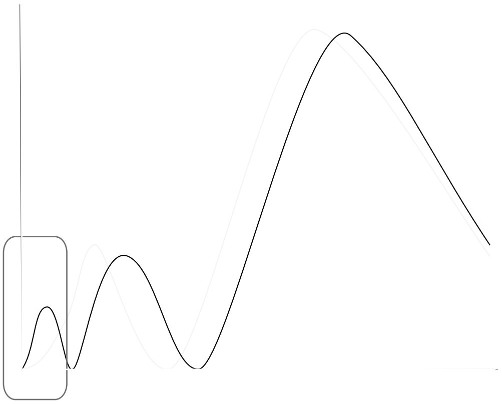


Fig. 13.17

13.11 The building-up principle

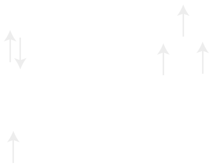


Fig. 13.18

Self-test 13.6

Predict the ground-state electron configuration of sulfur.

[*Answer:* [Ne]$3s^2 3p_x^2 3p_y^1 3p_z^1$]

13.12 The occupation of d orbitals

13.13 The configurations of cations and anions

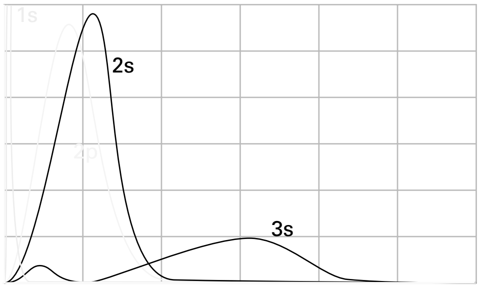


Fig. 13.19

Self-test 13.7

Predict the electron configurations of (a) a Cu^{2+} ion and (b) an S^{2-} ion.

[*Answer:* (a) [Ar]$3d^9$, (b) [Ne]$3s^23p^6$]

13.14 Self-consistent field orbitals

Periodic trends in atomic properties

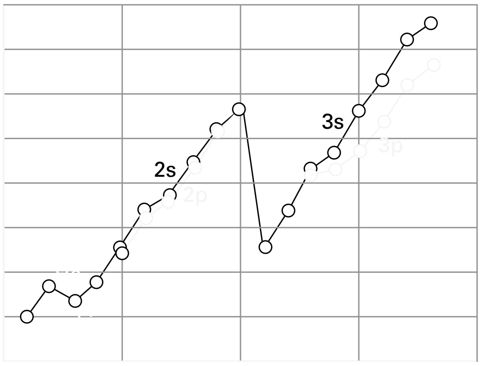


Fig. 13.20

13.15 Atomic radius

Table 13.1

Atomic radii of main-group elements, r/pm

Li	Be	B	C	N	O	F
157	112	88	77	74	66	64
Na	Mg	Al	Si	P	S	Cl
191	160	143	118	110	104	99
K	Ca	Ga	Ge	As	Se	Br
235	197	153	122	121	117	114
Rb	Sr	In	Sn	Sb	Te	I
250	215	167	158	141	137	133
Cs	Ba	Tl	Pb	Bi	Po	
272	224	171	175	182	167	

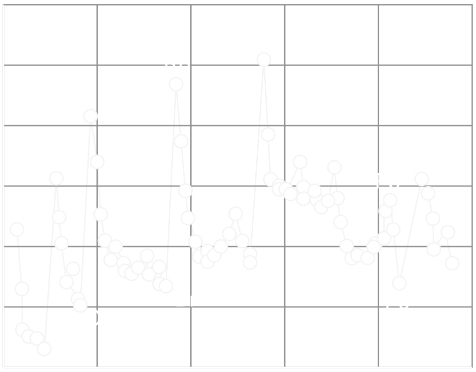


Fig. 13.21

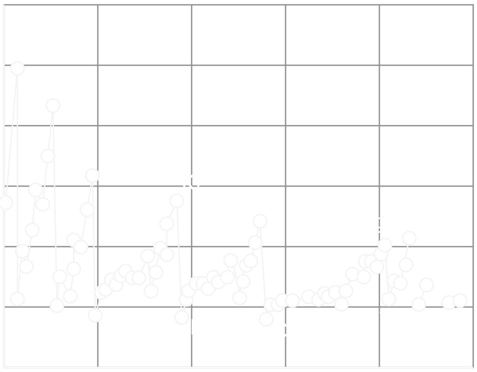


Fig. 13.22

13.16 Ionization energy and electron affinity

Table 13.2

*First ionization energies of main-group elements, I/eV**

H							He
13.60							24.59
Li	Be	B	C	N	O	F	Ne
5.32	9.32	8.30	11.26	14.53	13.62	17.42	21.56
Na	Mg	Al	Si	P	S	Cl	Ar
5.14	7.65	5.98	8.15	10.49	10.36	12.97	15.76
K	Ca	Ga	Ge	As	Se	Br	Kr
4.34	6.11	6.00	7.90	9.81	9.75	11.81	14.00
Rb	Sr	In	Sn	Sb	Te	I	Xe
4.18	5.70	5.79	7.34	8.64	9.01	10.45	12.13
Cs	Ba	Tl	Pb	Bi	Po	At	Rn
3.89	5.21	6.11	7.42	7.29	8.42	9.64	10.78

* 1 eV = 96.485 kJ mol^{-1}. See also Table 3.2.

Table 13.3

Electron affinities of main-group elements, E_{ea}/eV*

H							He
+0.75							<0[†]
Li	Be	B	C	N	O	F	Ne
+0.62	−0.19	+0.28	+1.26	−0.07	+1.46	+3.40	−0.30[†]
Na	Mg	Al	Si	P	S	Cl	Ar
+0.55	−0.22	+0.46	+1.38	+0.46	+2.08	+3.62	−0.36[†]
K	Ca	Ga	Ge	As	Se	Br	Kr
+0.50	−1.99	+0.3	+1.20	+0.81	+2.02	+3.37	−0.40[†]
Rb	Sr	In	Sn	Sb	Te	I	Xe
+0.49	+1.51	+0.3	+1.20	+1.05	+1.97	+3.06	−0.42[†]
Cs	Ba	Tl	Pb	Bi	Po	At	Rn
+0.47	−0.48	+0.2	+0.36	+0.95	+1.90	+2.80	−0.42[†]

* 1 eV = 96.485 kJ mol^{-1}. See also Table 3.3.

† Calculated.

13.17 Term symbols

Box 13.1 Spectroscopy of stars

A brief illustration

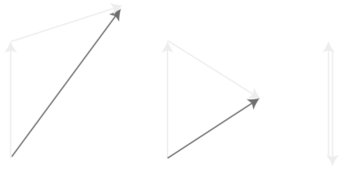


Fig. 13.23

Another brief illustration

A brief illustration

A note on good practice

A brief illustration

A note on good practice

Self-test 13.8

What terms and levels can arise from the configuration …4p^{1}3d^1?

[*Answer:* $^1F_3$, $^1D_2$, $^1P_1$, $^3F_{4,3,2}$, $^3D_{3,2,1}$, $^3P_{2,1,0}$]

13.18 Spin–orbit coupling

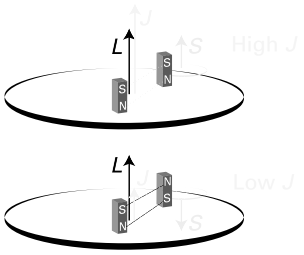


Fig. 13.24

☐ **1**

☐ **2**

☐ **3**

☐ **4**

☐ **5**

☐ **6**

☐ **7**

☐ **8**

☐ **9**

☐ **10**

☐ **11**

☐ **12**

☐ **13**

☐ **14**

☐ **15**

☐ **16**

Property	Equation	Comment
	$\tilde{\nu} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$	

The Pauli principle

Discussion questions

13.1

13.2

13.3

13.4

13.5

13.6

13.7

Exercises

13.1

13.2

13.3

13.4

13.5

13.6

13.7

13.8

13.9

13.10

13.11

13.12

13.13 The Li^{2+} ion is hydrogenic and has a Lyman series of lines at 740 747 cm^{-1}, 877 924 cm^{-1}, 925 933 cm^{-1}, and beyond. (a) Show that the energy levels are of the form $-hcR_{Li}/n^2$ and find the value of R_{Li} for this ion. (b) Go on to predict the wavenumbers of the two longest-wavelength transitions of the Balmer series of the ion and (c) find the ionization energy of the ion.

13.14 At what radius does the probability of finding an elec[illegible] in a small volume located at a point in the ground state of [illegible] fall to 30 per cent of its maximum value?

13.15 [illegible] radius in the H atom does the radial distribution [illegible] the ground state have (a) 30 per cent, (b) 5 per cent of [illegible] value?

13.16 What [illegible] of finding an electron anywhere in one lobe of a p [illegible] that it occupies the orbital?

13.17 What is the [illegible] of finding the electron in a volume of 6.5 pm^3 [illegible] nucleus in (a) a hydrogen atom, (b) a He^+ ion?

13.18 Locate the radial nodes in [illegible] orbital, (b) the 4s orbital of an H atom.

13.19 The wavefunction of one of the [illegible] proportional to sin θ cos θ. At what angles [illegible] nodal planes?

13.20 What is the orbital angular momentum [illegible] of $\hbar$) of an electron in the orbitals (a) 1s, (b) 3s, (c) 3d, [illegible] (e) 3p? Give the numbers of angular and radial nodes [illegible] each case.

13.21 State the orbital degeneracy of the levels in the hydrogen atom that have energy (a) $-hcR_H$, (b) $-\frac{1}{9}hcR_H$, and (c) $-\frac{1}{49}hcR_H$.

13.22 How many electrons can occupy subshells with the following values of l: (a) 0, (b) 3, (c) 5?

13.23 How is the ionization energy of an anion related to the electron affinity of the parent atom?

13.24 When ultraviolet radiation of wavelength 58.4 nm from a helium lamp is directed on to a sample of krypton, electrons are ejected with a speed of 1.59×10^6 m s^{-1}. Calculate the ionization energy of krypton.

13.25 One important function of atomic and ionic radius is in regulating the uptake of oxygen by haemoglobin, for the change in ionic radius that accompanies the conversion of Fe(II) to Fe(III) when O_2 attaches triggers a conformational change in the protein. Which do you expect to be larger: Fe^{2+} or Fe^{3+}? Why?

13.26 What terms (expressed as S, D, etc.) can arise from the [He]$2s^22p^13d^1$ excited configuration of carbon?

13.27 What are the total spin angular momenta (reported as the value of S) that can arise from four electrons? *Hint*: Use the Clebsch–Gordan series successively.

13.28 What levels can the following terms possess: (a) ^1S, (b) ^3F, (c) ^5S, (d) ^5P?

13.29 The ground configuration of a Ti^{2+} ion is [Ar]$3d^2$. (a) What is the term of lowest energy and which level of that term lies lowest? (b) How many states belong to that lowest level?

13.30 Which of the following transitions are allowed in the normal electronic emission spectrum of an atom: (a) 2s → 1s; (b) 2p → 1s; (c) 3d → 2p; (d) 5d → 2s; (e) 5p → 3s; (f) 6f → 4p?

13.31 To what orbitals may a 5f electron make spectroscopic transitions?

13.32 Which of the following transitions between terms are allowed in the normal electronic emission spectrum of a many-electron atom: (a) $^3D_2 \rightarrow {}^3P_1$; (b) $^3P_2 \rightarrow {}^1S_0$; (c) $^3F_4 \rightarrow {}^3D_3$?

Projects

The symbol ‡ indicates that calculus is required.

13.33‡ Here we explore hydrogenic wavefunctions in more quantitative detail. (a) What is the most probable distance of an electron from the nucleus in a hydrogen atom in its ground sate? *Hint*: Look for a maximum in the radial distribution function of a hydrogenic 1s electron). (b) The (normalized) wavefunction for a 2s orbital in hydrogen is

$$\psi = \left(\frac{1}{32\pi a_0^3}\right)^{1/2}\left(2 - \frac{r}{a_0}\right)e^{-r/2a_0}$$

[illegible] the probability of finding an electron that is [illegible] by this wavefunction in a volume of 1.0 pm^3 (i) centred [illegible] nucleus, (ii) at the Bohr radius, (iii) at twice the Bohr [illegible] Construct an expression for the radial distribution [illegible] a hydrogenic 2s electron (see part (b) for the form of [illegible] and plot the function against r. What is the most [illegible] at which the electron will be found? (d) For a [illegible] determination of the most probable radius at [illegible] will be found in an H2s orbital, differentiate the [illegible] function to find where it is a maximum.

13.34 Thallium, a neurotoxin, is [illegible] member of Group 13 of the periodic table and is [illegible] usually in the +1 oxidation state. Aluminium, which [illegible] aemia and dementia, is also a member of the group [illegible] chemical properties are dominated by the +3 oxidation [illegible] this issue by plotting the first, second, and third [illegible] energies for the Group 13 elements against atomic [illegible] Explain the trends you observe. *Hints*: The third ioniz[illegible] energy, I_3, is the minimum energy needed to remove an electron from the doubly charged cation: $E^{2+}(g) \rightarrow E^{3+}(g) + e^-(g)$, $I_3 = E(E^{3+}) - E(E^{2+})$. For data, see the links to databases of atomic properties provided in the text's web site.

13.35 The spectrum of a star is used to measure its *radial velocity* with respect to the Sun, the component of the star's velocity vector that is parallel to a vector connecting the star's centre to the centre of the Sun. The measurement relies on the Doppler effect, in which radiation is shifted in frequency when the source is moving towards or away from the observer. When a star emitting electromagnetic radiation of frequency ν moves with a speed s relative to an observer, the observer detects radiation of frequency $\nu_{\text{receding}} = \nu f$ or $\nu_{\text{approaching}} = \nu/f$, where $f = \{(1 - s/c)/(1 + s/c)\}^{1/2}$ and c is the speed of light. (a) Three Fe I lines of the star HDE 271 182, which belongs to the Large Magellanic Cloud, occur at 438.882 nm, 441.000 nm, and 442.020 nm. The same lines occur at 438.392 nm, 440.510 nm, and 441.510 nm in the spectrum of an Earth-bound iron arc. Determine whether HDE 271 182 is receding from or approaching the Earth and estimate the star's radial speed with respect to the Earth. (b) What additional information would you need to calculate the radial velocity of HDE 271 182 with respect to the Sun?

Introductory concepts

Valence bond theory

Molecular orbitals

Computational chemistry

CHECKLIST OF KEY IDEAS
TABLE OF KEY EQUATIONS
QUESTIONS AND EXERCISES

Introductory concepts

14.1 The classification of bonds

14.2 Potential-energy curves

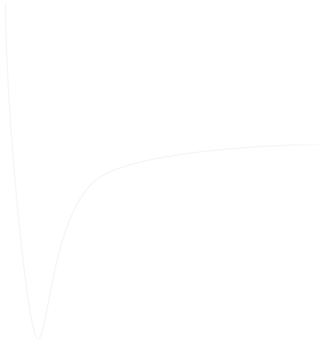


Fig. 14.1

Valence bond theory

Fig. 14.2

Derivation 14.1

14.3 Diatomic molecules

Fig. 14.3

Fig. 14.4

$$V_{\text{nuc,nuc}} = \frac{Z_A Z_B e^2}{4\pi\varepsilon_0 R}$$

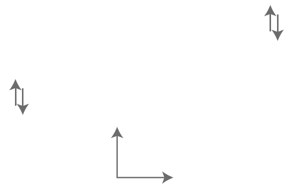


Fig. 14.5

14.4 Polyatomic molecules

A brief illustration

Self-test 14.2

Give a VB description of NH_3, and predict the bond angle of the molecule on the basis of this description.

[*Answer:* three σ(N2p,H1s) bonds, 90°; the experimental bond angle is 107°.]

14.5 Promotion and hybridization

Fig. 14.7

Fig. 14.6

A brief comment

Fig. 14.8

Fig. 14.9

Self-test 14.3

Describe the bonding in a PCl_5 molecule in VB terms.

[*Answer*: Five σ bonds formed from sp^3d hybrids on the central P atom.]

Table 14.1

Hybrid orbitals

Number	Shape	Hybridization*
2	Linear	sp
3	Trigonal planar	sp^2
4	Tetrahedral	sp^3
5	Trigonal bipyramidal	sp^3d
6	Octahedral	sp^3d^2

* Other combinations are possible.

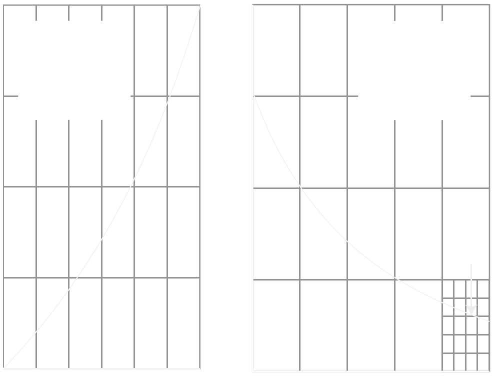
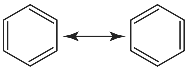


Fig. 14.10

Fig. 14.11

14.6 Resonance



14.7 Linear combinations of atomic orbitals

Molecular orbitals

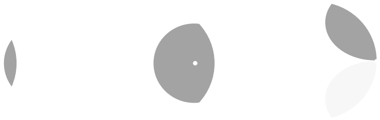


Fig. 14.14

Fig. 14.12

Fig. 14.13

$$S = \left\{1 + \frac{R}{a_0} + \frac{R^2}{3a_0^2}\right\} e^{-R/a_0}$$

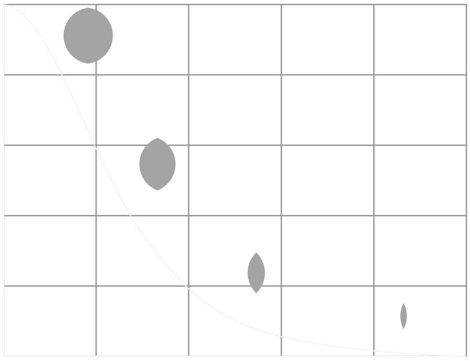


Fig. 14.15

Fig. 14.16

14.8 Bonding and antibonding orbitals

Self-test 14.4

Show that the molecular orbital written above is zero on a plane cutting through the internuclear axis at its midpoint. Take each atomic orbital to be of the form e^{-r/a_0}, with r_A measured from nucleus A and r_B measured from nucleus B.

[*Answer:* The atomic orbitals cancel for values equidistant from the two nuclei.]

Fig. 14.17

14.9 The structures of diatomic molecules

Self-test 14.5

How many molecular orbitals can be built from the valence shell orbitals in O_2?

[*Answer:* 8]

14.10 Hydrogen and helium molecules

Fig. 14.18

Fig. 14.19

Fig. 14.21

Fig. 14.20

Example 14.1

Strategy

Solution

Self-test 14.6

Is LiH likely to exist if the Li atom uses only its 2s orbital for bonding

[*Answer*: Yes, $\sigma(\text{Li2s},\text{H1s})^2$]

Fig. 14.22

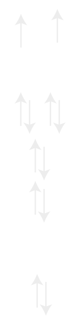


Fig. 14.23

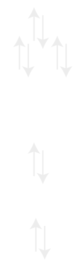


Fig. 14.24

Fig. 14.25

Fig. 14.26

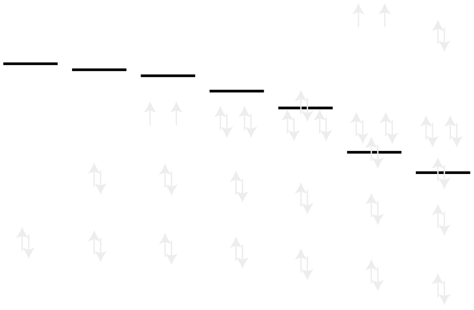


Fig. 14.27

14.12 Symmetry and overlap

Fig. 14.28

A brief illustration

Fig. 14.29

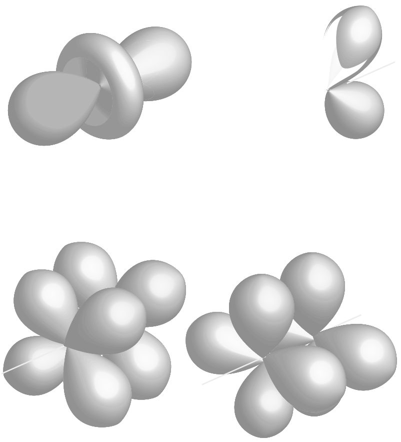


Fig. 14.30

Self-test 14.7

Sketch the 'δ orbitals' (orbitals that resemble four-lobed d orbitals when viewed along the internuclear axis) that may be formed by the remaining two d orbitals (and which contribute to bonding in some d-metal cluster compounds). Give their inversion-symmetry classification.

[*Answer:* see Fig. 14.30: bonding are g, antibonding are u]

14.13 The electronic structures of homonuclear diatomic molecules

Example 14.3

Strategy

Solution

Self-test 14.8

Write the electron configuration of F_2 and deduce its bond order.

[*Answer:* $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 1\pi_g^4$, $b = 1$]

Example 14.4

Strategy

Solution

Self-test 14.9

Which can be expected to have the higher dissociation energy, F_2 or F_2^+?

[*Answer:* F_2^+]

14.14 Heteronuclear diatomic molecules

Table 14.2

Electronegativities of the main-group elements

H						
2.1						
Li	Be	B	C	N	O	F
1.01	1.5	2.0	2.5	3.0	3.5	4.0
Na	Mg	Al	Si	P	S	Cl
0.9	1.2	1.5	1.8	2.1	2.5	3.0
K	Ca	Ga	Ge	As	Se	Br
0.8	1.0	1.6	1.8	2.0	2.4	2.8
Rb	Sr	In	Sn	Sb	Te	I
0.8	1.0	1.7	1.8	1.9	2.1	2.5
Cs	Ba	Tl	Pb	Bi	Po	
0.7	0.9	1.8	1.8	1.9	2.0	

Self-test 14.10

Predict the signs of the charge distribution of a C—H bond.

[*Answer:* $^{\delta-}$C—H$^{\delta+}$]

Fig. 14.31

Fig. 14.32

Fig. 14.33

Self-test 14.11

What is the probability of finding a σ electron in HF in a F2p_z orbital?

[*Answer:* 88 per cent = $(0.94)^2 \times 100$ per cent]

14.15 The structures of polyatomic molecules

Fig. 14.34

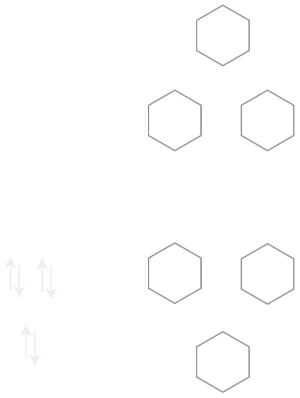


Fig. 14.35

A brief comment

14.16 The Hückel method

Derivation 14.3

H_{AA} H_{AB}

1 S_{AB}

Fig. 14.36

Self-test 14.12

Calculate the π-electron energy of butadiene in its ground state.

[*Answer*: $4\alpha + 4.48\beta$]

A brief illustration

A brief illustration

Computational chemistry

14.17 Techniques

14.18 Graphical output

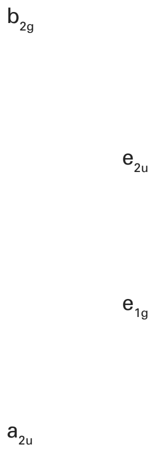


Fig. 14.37

Fig. 14.38

Fig. 14.39

Table 14.3

Summary of ab-initio *calculations and spectroscopic data for four linear polyenes*

	$\Delta E_{\text{HOMO–LUMO}}$/eV	$\lambda_{\text{transition}}$/nm
═	18.1	163
══─══	14.5	217
═─═─═	12.7	252
═─═─═─═	11.6	304

1 eV = 1.602×10^{-19} J

14.19 Applications

☐ 1

☐ 2

☐ 3

☐ 4

☐ 5

☐ 6

☐ 7

☐ 8

☐ 9

☐ 10

☐ 11

Property	Equation	Comment

Discussion questions

14.1

14.2

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14.4

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14.7

14.8

Exercises

14.1

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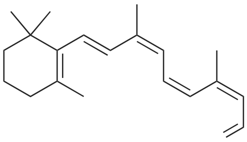
14.6



14.7

14.8

14.9

14.10‡

14.11

14.12

14.13

14.14

14.15

14.16

14.17

14.18

14.19

14.20 Give the (g,u) parities of the first four levels of a particle-in-a-box wavefunction.

14.21 (a) Give the parities of the wavefunctions for the first four levels of a harmonic oscillator. (b) How may the parity be expressed in terms of the quantum number υ?

14.22 State the parities of the six π-orbitals of benzene (see Fig. 14.35).

14.23 Two important diatomic molecules for the welfare of [illegible]nity are NO and N_2: the former is both a pollutant and a [illegible]nsmitter, and the latter is the ultimate source of the ni[illegible] proteins and other biomolecules. Use the electron [illegible]ons of NO and N_2 to predict which is likely to have the [illegible] bond length.

14.24 Put th[illegible]g species in order of increasing bond length: F_2^-, F_2, [illegible]

14.25 Identify the [illegible] of each of the species in the preceding exercise.

14.26 Arrange the species [illegible] O_2^-, O_2^{2-} in order of increasing bond length.

14.27 Identify the bond order of [illegible] species in the preceding exercise.

14.28 Construct the molecular orbital energ[illegible]rams of (a) ethene and (b) ethyne on the basis that the [illegible]s are formed from the appropriately hybridized CH_2 or CH [illegible]

14.29 Try to anticipate the form that the bon[illegible] antibonding 'ϕ orbitals' that could be constructed from neighbouring f orbitals. What are their parities?

14.30 Predict the polarities of the bonds (a) P—H, (b) B—H.

14.31 Predict the electronic configurations of (a) the benzene anion, (b) the benzene cation. Estimate the π-bond energy in each case.

14.32 Many of the colours of vegetation are due to electronic transitions in conjugated π-electron systems. In the *free-electron molecular orbital* (FEMO) theory, the electrons in a conjugated molecule are treated as independent particles in a box of length *L*. Sketch the form of the two occupied orbitals in butadiene predicted by this model and predict the minium excitation energy of the molecule. The tetraene $CH_2{=}CHCH{=}CHCH{=}CHCH{=}CH_2$ can be treated as a box of length 8*R*, where *R* = 140 pm (as in this case, an extra half bond length is often added at each end of the box). Calculate the minimum excitation energy of the molecule and sketch the HOMO and LUMO.

14.33 Suppose that the π-electron molecular orbitals of naphthalene can be represented by the wavefunctions of a particle in a rectangular box. What are the parities of the occupied orbitals?

14.34 How many molecular orbitals can be constructed from a diatomic molecule in which s, p, d, and f orbitals are all important for bonding?

14.35 The FEMO theory (Exercise 14.32) of conjugated molecules is rather crude and better results are obtained with simple Hückel theory. (a) For a linear conjugated polyene with each of *N* carbon atoms contributing an electron in a 2p orbital, the energies E_k of the resulting π molecular orbitals are given by:

$$E_k = \alpha + 2\beta\cos\frac{k\pi}{N+1} \qquad k = 1, 2, 3, \ldots, N$$

Use this expression to determine a reasonable empirical estimate of the resonance integral β for the series consisting of ethene, butadiene, hexatriene, and octatetraene given that π←π ultraviolet absorptions from the HOMO to the LUMO occur at 61 500, 46 080, 39 750, and 32 900 cm^{-1}, respectively. (b) Calculate the π-electron delocalization energy, $E_{deloc} = E_\pi - n(\alpha+\beta)$, of octatetraene, where E_π is the total π-electron binding energy and *n* is the total number of π-electrons.

14.36 For monocyclic conjugated polyenes (such as cyclobutadiene and benzene) with each of *N* carbon atoms contributing an electron in a 2p orbital, simple Hückel theory gives the following expression for the energies E_k of the resulting π molecular orbitals:

$$E_k = \alpha + 2\beta\cos\frac{2k\pi}{N+1} \qquad k = 0, \pm1, \pm2, \ldots, \pm N/2 \ \ (\text{even } N)$$

$$k = 0, \pm1, \pm2, \ldots, \pm(N-1)/2 \ \ (\text{odd } N)$$

(a) Calculate the energies of the π molecular orbitals of benzene and cyclooctaene. Comment on the presence or absence of degenerate energy levels. (b) Calculate and compare the delocalization energies of benzene (using the expression above) and hexatriene (see Exercise 14.35). What do you conclude from your results? (c) Calculate and compare the delocalization energies of cyclooctaene and octatetraene. Are your conclusions for this pair of molecules the [illegible]s for the pair of molecules investigated in part (b)?

Projects

The symbo[illegible]tes that calculus is required.

14.37‡ Here w[illegible] hybrid orbitals in more quantitative detail. (a) Sho[illegible] orbitals $h_1 = s + p_x + p_y + p_z$ and $h_2 = s - p_x - p_y + p_z$ a[illegible]onal. *Hint:* Each atomic orbital individually normalized to [illegible]ote that: (i) s and p orbitals are orthogonal and, (ii) p or[illegible] perpendicular orientations are orthogonal. (b) Show [illegible] sp² hybrid orbital $(s + 2^{1/2}p)/3^{1/2}$ is normalized to [illegible] orbitals are each normalized to 1. (c) Find another [illegible] orbital that is orthogonal to the hybrid orbital in part (b).

14.38‡ Now we explore orbital overlap and [illegible]grals in detail. (a) Without doing a calculation, sketch [illegible]lap between an H1s orbital and a 2p orbital can be [illegible] to depend on their separation. (b) The overlap integ[illegible]tween an H1s orbital and a H2p orbital on nuclei separated [illegible] a distance *R* is $S = (R/a_0)\{1 + (R/a_0) + \frac{1}{3}(R/a_0)^2\}e^{-R/a_0}$. Plot this function, and find the separation for which the overlap is a maximum. (c) Suppose that a molecular orbital has the form $N(0.245A + 0.644B)$. Find a linear combination of the orbitals *A* and *B* that does not overlap with (that is, is orthogonal to) this combination. (d) Normalize the wavefunction $\psi = \psi_{cov} + \lambda\psi_{ion}$ in terms of the parameter λ and the overlap integral *S* between the covalent and ionic wavefunctions.

van der Waals interactions

The total interaction

Box 15.1 Molecular recognition

CHECKLIST OF KEY IDEAS
TABLE OF KEY EQUATIONS
QUESTIONS AND EXERCISES

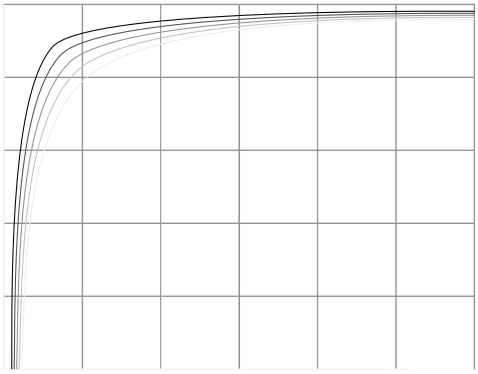
van der Waals interactions

A brief comment

Use $d(1/x^n)/dx = -n(1/x^{n+1})$

15.1 Interactions between partial charges

$$V = \frac{Q_1 Q_2}{4\pi\varepsilon_0 r}$$



$$V = \frac{Q_1 Q_2}{4\pi\varepsilon r}$$

15.2 Electric dipole moments

Table 15.2

Dipole moments and mean polarizability volumes

	μ/D	$\alpha'/(10^{-30}\ \text{m}^3)$
Ar	0	1.85
CCl_4	0	11.7
C_6H_6	0	11.6
H_2	0	0.911
H_2O	1.85	1.65
NH_3	1.47	2.47
HCl	1.08	2.93
HBr	0.80	4.01
HI	0.42	6.06

A brief illustration

$$\mu_x = \sum_J Q_J x_J$$

Example 15.1

Calculating a molecular dipole moment

Estimate the electric dipole moment of the peptide group using the partial charges (as multiples of *e*) in Table 15.1 and the locations of the atoms shown in (**6**).

Strategy We use eqn 15.4b to calculate each of the components of the dipole moment and then eqn 15.4a to assemble the three components into the magnitude of the dipole moment. Note that the partial charges are multiples of the fundamental charge, $e = 1.609 \times 10^{-19}$ C (see inside front cover).

Solution The expression for μ_x is

$$\begin{aligned}\mu_x &= (-0.36e) \times (132\text{ pm}) + (0.45e) \times (0\text{ pm}) + \\ &\quad (0.18e) \times (182\text{ pm}) + (-0.38e) \times (-62\text{ pm}) = 8.8e\text{ pm} \\ &= 8.8 \times (1.609 \times 10^{-19}\text{ C}) \times (10^{-12}\text{ m}) \\ &= 1.4 \times 10^{-30}\text{ C m}\end{aligned}$$

corresponding to $\mu_x = 0.42$ D. The expression for μ_y is:

$$\begin{aligned}\mu_y &= (-0.36e) \times (0\text{ pm}) + (0.45e) \times (0\text{ pm}) + \\ &\quad (0.18e) \times (-87\text{ pm}) + (-0.38e) \times (107\text{ pm}) \\ &= -56e\text{ pm} = -9.1 \times 10^{-30}\text{ C m}\end{aligned}$$

It follows that $\mu_y = -2.7$ D. Therefore, because $\mu_z = 0$,

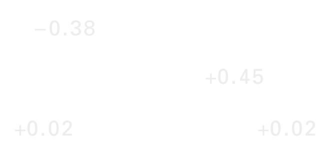
$$\mu = \{(0.42\text{ D})^2 + (-2.7\text{ D})^2\}^{1/2} = 2.7\text{ D}$$

We can find the orientation of the dipole moment by arranging an arrow of length 2.7 units of length to have *x*-, *y*-, and *z*-components of 0.42, −2.7, and 0 units; the orientation is superimposed on (**6**).

Self-test 15.3

Calculate the electric dipole moment of formaldehyde, using the information in (7).

[*Answer:* −2.3 D]



15.3 Interactions between dipoles

$$V = -\frac{Q_2\mu_1}{4\pi\varepsilon_0 r^2}$$

$$\begin{aligned}V &= \overbrace{\frac{Q_1Q_2}{4\pi\varepsilon_0(r+\frac{1}{2}l)}}^{\text{Repulsion between }+Q_1\text{ and }Q_2} - \overbrace{\frac{Q_1Q_2}{4\pi\varepsilon_0(r-\frac{1}{2}l)}}^{\text{Attraction between }-Q_1\text{ and }Q_2} \\ &= \frac{Q_1Q_2}{4\pi\varepsilon_0 r\left(1+\dfrac{l}{2r}\right)} - \frac{Q_1Q_2}{4\pi\varepsilon_0 r\left(1-\dfrac{l}{2r}\right)}\end{aligned}$$

$$\frac{1}{1+x} \approx 1-x \qquad \frac{1}{1-x} \approx 1+x$$

$$V = -\frac{\mu_1 Q_2\cos\theta}{4\pi\varepsilon_0 r^2}$$

$$V = \frac{\mu_1\mu_2(1-3\cos^2\theta)}{4\pi\varepsilon_0 r^3}$$

A brief illustration

$$\begin{aligned} V &= \frac{(9.1\times10^{-30}\ \mathrm{C\ m})^2\times(-2)}{4\pi\times(8.854\times10^{-12}\ \mathrm{J^{-1}\ C^2\ m^{-1}})\times(3.0\times10^{-9}\ \mathrm{m})^3} \\ &= \frac{(9.1\times10^{-30})^2\times(-2)}{4\pi\times(8.854\times10^{-12})\times(3.0\times10^{-9})^3}\,\frac{\mathrm{C^2\ m^2}}{\mathrm{J^{-1}\ C^2\ m^{-1}\ m^3}} \\ &= -5.5\times10^{-23}\ \mathrm{J} \end{aligned}$$

A note on good practice

$$V = -\frac{2\mu_1^2\mu_2^2}{3(4\pi\varepsilon_0)^2 kTr^6}$$

$$\alpha' = \frac{\alpha}{4\pi\varepsilon_0}$$

15.4 Induced dipole moments

$$V = -\frac{\mu_1^2\alpha_2}{\pi\varepsilon_0 r^6}$$

15.5 Dispersion interactions

(a)

$$V = -\tfrac{2}{3} \times \frac{\alpha_1' \alpha_2'}{r^6} \times \frac{I_1 I_2}{I_1 + I_2}$$

(b)

Fig. 15.5

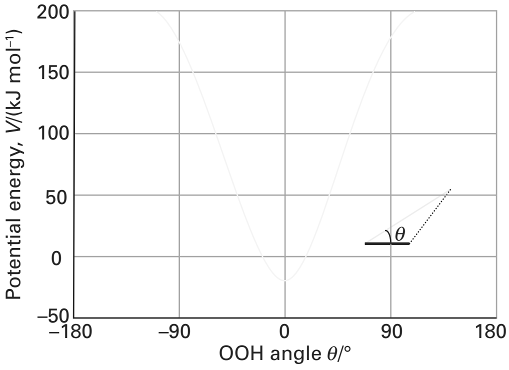


Fig. 15.6

The total interaction

15.6 Hydrogen bonding

Fig. 15.7

Box 15.1 Molecular recognition

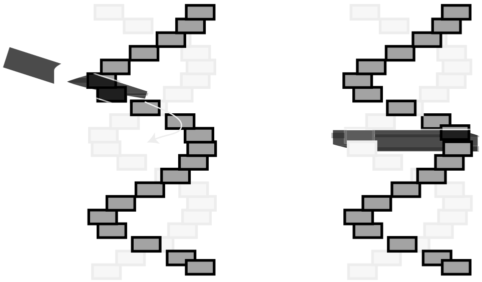


Table 15.3

Potential energy of molecular interactions

Interaction type	Distance dependence of potential energy	Typical energy (kJ mol^{-1})	Comment
Ion–ion	$1/r$	250	Only between ions
Ion–dipole	$1/r^2$	15	
Dipole–dipole	$1/r^3$	2	Between stationary polar molecules
	$1/r^6$	0.3	Between rotating polar molecules
London (dispersion)	$1/r^6$	2	Between all types of molecules and ions
Hydrogen bonding		20	The interaction is for X—H···Y and occurs on contact for X, Y = N, O, or F

Fig. 15.8

15.7 The hydrophobic effect

15.8 Modelling the total interaction

$$V = -\frac{C}{r^6}$$

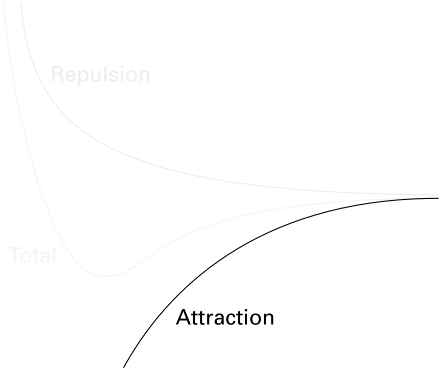


Fig. 15.9

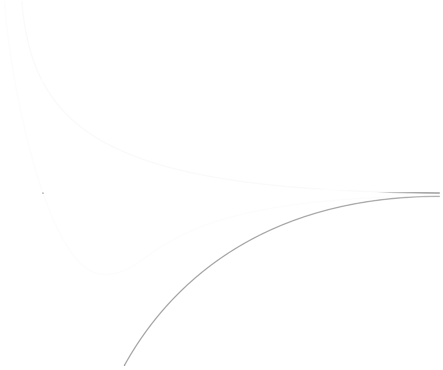


Fig. 15.10

$$V = \begin{cases} \infty & \text{for } r \le \sigma \\ 0 & \text{for } r > \sigma \end{cases}$$

$$V = +\frac{C^*}{r^n}$$

$$V = 4\varepsilon\left\{\overbrace{\left(\frac{\sigma}{r}\right)^{12}}^{\text{Repulsion}} - \overbrace{\left(\frac{\sigma}{r}\right)^{6}}^{\text{Attraction}}\right\}$$

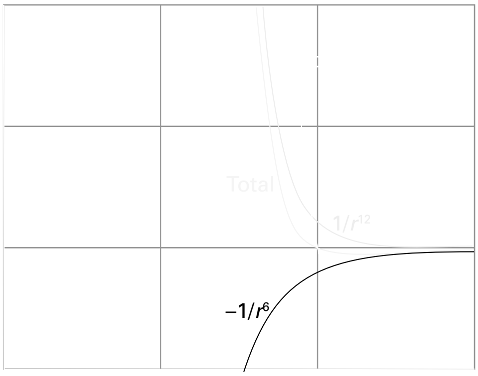


Fig. 15.11

$$F = -24\varepsilon\left\{\frac{2\sigma^{12}}{r^{13}} - \frac{\sigma^6}{r^7}\right\}$$

……

15.9 Molecules in motion

☐ **1**

☐ **2**

☐ **3**

☐ **4**

☐ **5**

☐ **6**

☐ **7**

☐ **8**

☐ **9**

Property	Equation	Comment

Discussion questions

15.1

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15.6

Exercises

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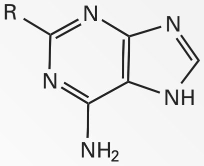
15.22

Projects

15.23‡

15.24‡

15.25



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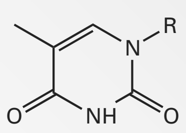
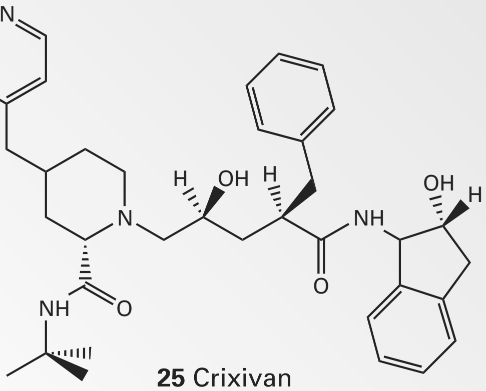


24

[illegible] helix structure of DNA. Consider methyladenine (2[illegible] = CH_3) and methylthymine (**24**, with R = CH_3) as mode[illegible] bases that can form hydrogen bonds in DNA. (a) Using [illegible] modelling software, calculate the partial charges of [illegible] in methyladenine and methylthymine. (b) Based on [illegible]tion of partial charges, identify the atoms in methyla[illegible]d methylthymine that are likely to participate in hy[illegible]onds. (c) Draw all possible adenine–thymine pairs t[illegible]linked by hydrogen bonds, keeping in mind that linea[illegible]ments of the A—H···B fragments are preferred. For [illegible]ou may want to use your molecular modelling softw[illegible]n the molecules properly. (d) Consult a biochemistry [illegible] and determine which of the pairs that you drew in part [illegible] naturally in DNA molecules.

15.26 For mature HIV particles to form in cells of the host organism, several large proteins coded for by the viral genetic material must be cleaved by a protease enzyme. The drug Crixivan (**25**) is a competitive inhibitor of HIV protease and has several molecular features that optimize binding to the active site of the enzyme. Consult the literature and prepare a brief report summarizing molecular interactions between Crixivan and HIV protease that are thought to be responsible for the drug's efficacy.



25 Crixivan

Synthetic and biological macromolecules

Box 16.1 The prediction of protein structure

Mesophases and disperse systems

Box 16.2 Biological membranes

CHECKLIST OF KEY IDEAS
TABLE OF KEY EQUATIONS
QUESTIONS AND EXERCISES

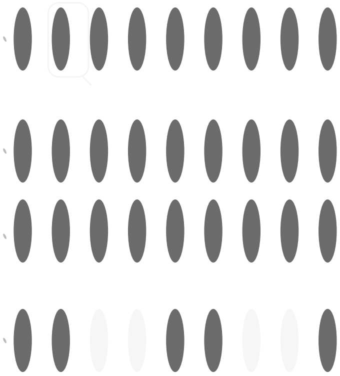


Fig. 16.1

Synthetic and biological macromolecules

16.1 Determination of size and shape

$$\bar{M}_{\mathrm{n}} = \frac{N_1 M_1 + N_2 M_2 + \cdots}{N}$$

$$\bar{M}_{\mathrm{n}} = \frac{n_1 M_1 + n_2 M_2 + \cdots}{n}$$

$$\bar{M}_{\mathrm{w}} = \frac{m_1 M_1 + m_2 M_2 + \cdots}{m}$$

$$\bar{M}_{\rm n}/({\rm kg\ mol^{-1}}) = \frac{1}{2.92}(1.3\times7.5+0.70\times12.5+0.51\times17.5$$

$$+0.25\times22.5+0.11\times27.5+0.052\times32.5) = 13$$

$$\bar{M}_{\rm w}/({\rm kg\ mol^{-1}}) = \frac{1}{37.6}(9.6\times7.5+8.7\times12.5+$$

$$8.9\times17.5+5.6\times22.5+3.1\times27.5+1.7\times32.5) = 16$$

Self-test 16.

The *Z-average molar mass* is defined as

$$\bar{M}_Z = \frac{N_1M_1^3 + N_2M_2^3 + \cdots}{N_1M_1^2 + N_2M_2^2 + \cdots}$$

Evaluate the *Z*-average molar mass of the sample described in Example 16.1.

[Answer: 19 kg mol^{-1}]

$$\left[\begin{array}{cc} \| & \\ & \| \end{array}\right]$$

Self-test 16.2

What would be the molar mass of the $N = 20$ polymer if silver trifluoroacetate were used instead of NaCl in the preparation of the matrix?

[*Answer:* 4.2 kg mol^{-1}]

Example 16.2

Strategy

Solution

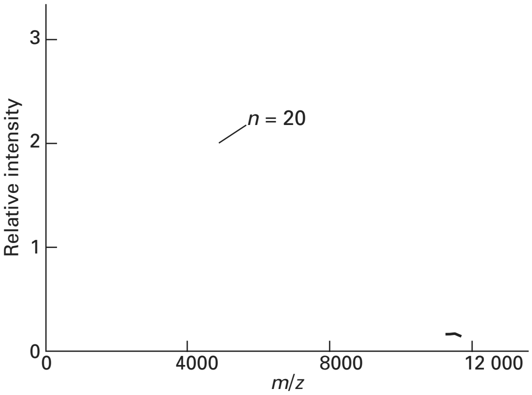


Fig. 16.2

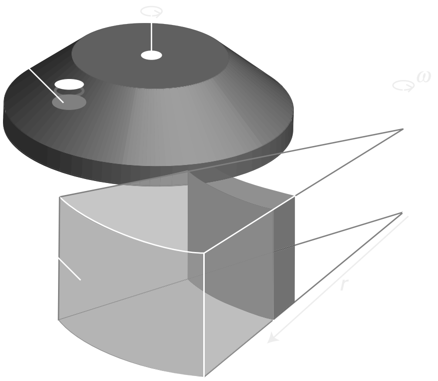


Fig. 16.3

16.2 Models of structure: random coils

$$\bar{M}_{\mathrm{w}} = \frac{2RT}{(r_2^2 - r_1^2)b\omega^2}\ln\frac{c_2}{c_1}$$

Fig. 16.4

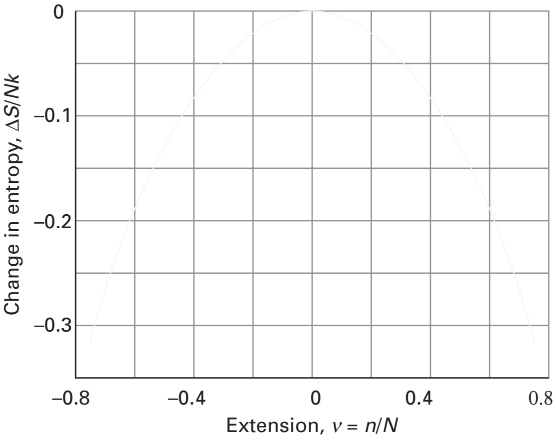


Fig. 16.5

$$R_G = \left(\frac{N}{6}\right)^{1/2} l$$

A brief illustration

$$R_G = \left(\frac{4000}{6}\right)^{1/2} \times 154\ \text{pm} = 3.98\ \text{nm}$$

$$\Delta S = -\tfrac{1}{2} kN \ln\{(1+\nu)^{1+\nu}(1-\nu)^{1-\nu}\} \qquad \nu = \frac{n}{N}$$

16.3 Models of structure: polypeptides and polynucleotides

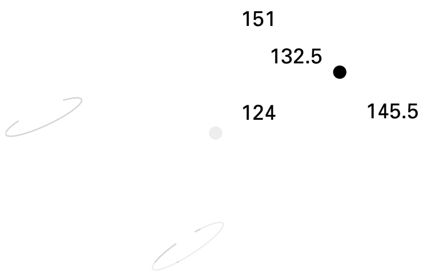


Fig. 16.6

Fig. 16.8

Fig. 16.7

Fig. 16.9

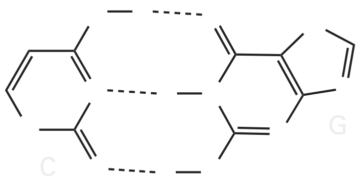
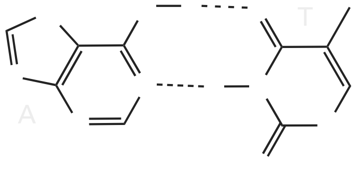


Fig. 16.10

C G A

Fig. 16.11



Box 16.1 The prediction of protein structure

$$V_{\text{Coulomb}} = \frac{Q_i Q_j}{4\pi\varepsilon r}$$

$$V_{\text{LJ}} = \frac{C}{r^{12}} - \frac{D}{r^{6}}$$

$$V_{\text{H bonding}} = \frac{E}{r^{12}} - \frac{F}{r^{10}}$$

For large molecules, a plot of potential energy against the molecular geometry often shows several local minima and a global minimum.

Contour plots of potential energy against the angles ψ and ϕ, also known as a Ramachandran diagram, for (a) a glycyl residue of a polypeptide chain and (b) an alanyl residue. (Hovmoller, et al., *Acta Crystallogr.* **D58**, 768 (2002).)

minima and a global minimum (see the second illustration). The software packages include schemes for modifying the locations of the atoms and searching for these minima systematically.

The third illustration shows the potential energy contours for the helical form of polypeptide chains formed from the nonchiral amino acid glycine (R = H) and the chiral amino acid L-alanine (R = CH_3). The contours were computed by summing all the contributions described above for each choice of angles, and then plotting contours of equal potential energy. The glycine map is symmetrical, with minima of equal depth at $\phi = -80°$, $\psi = +90°$ and at $\phi = +80°$, $\psi = -90°$. In contrast, the map for L-alanine is unsymmetrical, and there are three distinct low-energy conformations (marked I, II, III). The minima of regions I and II lie close to the angles typical of right- and left-handed α-helices, but the former has a lower minimum, which is consistent with the formation of right-handed helices from the naturally occurring L-amino acids.

The structure corresponding to the global minimum of a molecular mechanics simulation is a snapshot of the molecule at $T = 0$ because only the potential energy is included in the calculation; contributions to the total energy from kinetic energy are excluded. In a *molecular dynamics* simulation, the molecule is set in motion by heating it to a specified temperature. The possible trajectories of all atoms under the influence of the intermolecular potentials are then calculated by integration of Newton's equations of motion. These trajectories correspond to the conformations that the molecule can sample at the temperature of the simulation. At very low temperatures, the molecule cannot overcome some of the potential energy barriers described above, atomic motion is restricted, and only a few conformations are possible. At high temperatures, more potential energy barriers can be overcome and more conformations are possible. Therefore, molecular dynamics calculations are useful tools for the visualization of the flexibility of polymers.

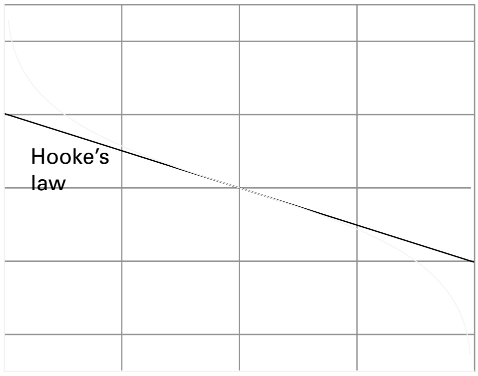


Fig. 16.13

Fig. 16.12

$$F = \frac{kT}{2l} \ln\left(\frac{1+v}{1-v}\right)$$

$$F \approx \frac{nkT}{Nl}$$

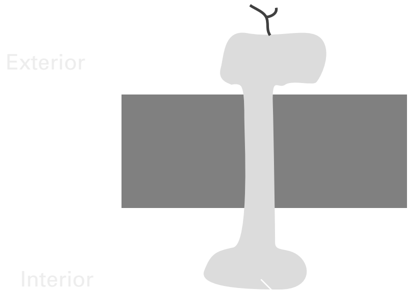
16.5 Liquid crystals

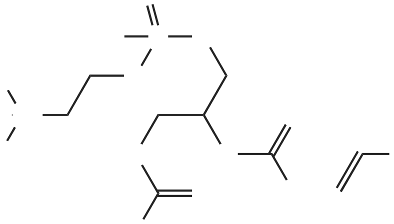
Mesophases and disperse systems

Fig. 16.14

Fig. 16.15

Box 16.2 Biological membranes





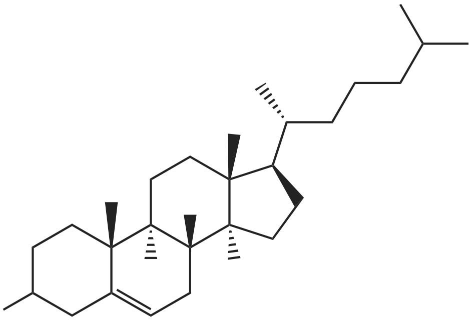


Fig. 16.16

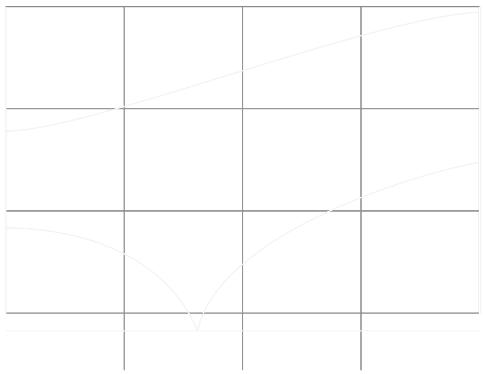


Fig. 16.17

16.6 Classification of disperse systems