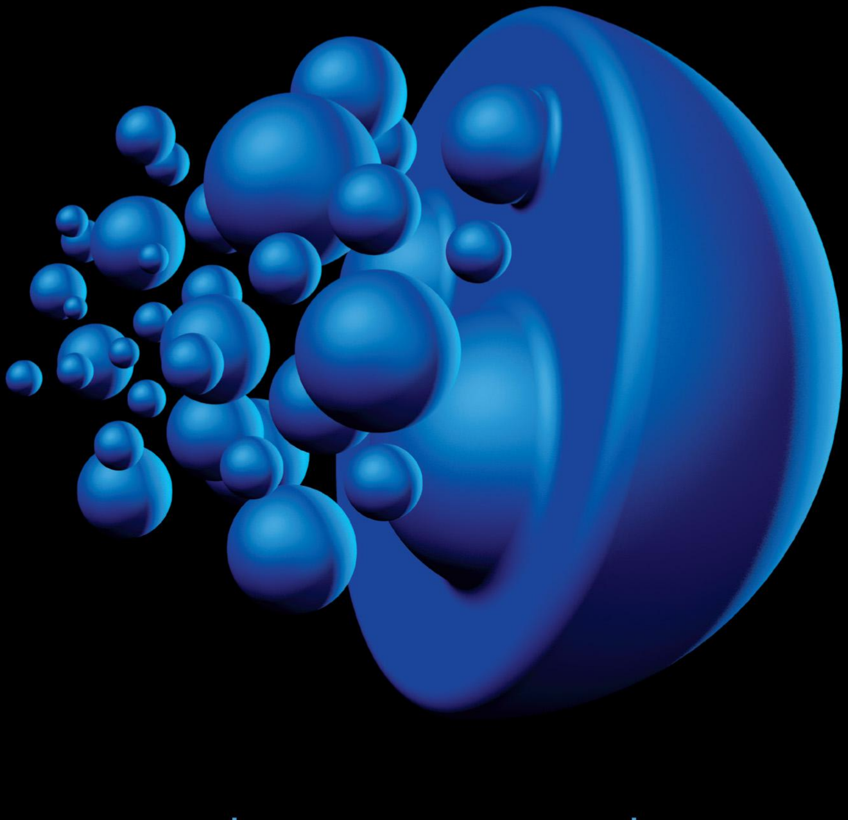
Atkins'

PHYSICAL CHEMISTRY

Thermodynamics and Kinetics

11th Edition



Peter Atkins | Julio de Paula | James Keeler

FUNDAMENTAL CONSTANTS

Constant	Symbol	Value		
			Power of 10	Units
Speed of light	c	2.997 924 58*	10^{8}	m s^{-1}
Elementary charge	e	1.602 176 565	10^{-19}	C
Planck's constant	h	6.626 069 57	10^{-34}	J s
	$\hbar = h/2\pi$	1.054 571 726	10^{-34}	J s
Boltzmann's constant	k	1.380 6488	10^{-23}	J K^{-1}
Avogadro's constant	N_A	6.022 141 29	10^{23}	mol^{-1}
Gas constant	$R = N_A k$	8.314 4621		J K^{-1} mol^{-1}
Faraday's constant	$F = N_A e$	9.648 533 65	10^{4}	C mol^{-1}
Mass				
Electron	m_e	9.109 382 91	10^{-31}	kg
Proton	m_p	1.672 621 777	10^{-27}	kg
Neutron	m_n	1.674 927 351	10^{-27}	kg
Atomic mass constant	m_u	1.660 538 921	10^{-27}	kg
Vacuum permeability	μ_0	4π*	10^{-7}	J s^{2} C^{-2} m^{-1}
Vacuum permittivity	$\varepsilon_0 = 1/\mu_0 c^2$	8.854 187 817	10^{-12}	J^{-1} C^{2} m^{-1}
	$4\pi\varepsilon_0$	1.112 650 056	10^{-10}	J^{-1} C^{2} m^{-1}
Bohr magneton	$\mu_B = e\hbar/2m_e$	9.274 009 68	10^{-24}	J T^{-1}
Nuclear magneton	$\mu_N = e\hbar/2m_p$	5.050 783 53	10^{-27}	J T^{-1}
Proton magnetic moment	μ_p	1.410 606 743	10^{-26}	J T^{-1}
g-Value of electron	g_e	2.002 319 304		
Magnetogyric ratio				
Electron	$\gamma_e = -g_e e/2m_e$	−1.001 159 652	10^{10}	C kg^{-1}
Proton	$\gamma_p = 2\mu_p/\hbar$	2.675 222 004	10^{8}	C kg^{-1}
Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar^2/e^2 m_e$	5.291 772 109	10^{-11}	m
Rydberg constant	$\tilde{R}_\infty = m_e e^4/8h^3 c\varepsilon_0^2$	1.097 373 157	10^{5}	cm^{-1}
	$hc\tilde{R}_\infty/e$	13.605 692 53		eV
Fine-structure constant	$\alpha = \mu_0 e^2 c/2h$	7.297 352 5698	10^{-3}	
	α^{-1}	1.370 359 990 74	10^{2}	
Stefan–Boltzmann constant	$\sigma = 2\pi^5 k^4/15h^3 c^2$	5.670 373	10^{-8}	W m^{-2} K^{-4}
Standard acceleration of free fall	g	9.806 65*		m s^{-2}
Gravitational constant	G	6.673 84	10^{-11}	N m^{2} kg^{-2}

* Exact value. For current values of the constants, see the National Institute of Standards and Technology (NIST) website.

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PHYSICAL CHEMISTRY
Thermodynamics and Kinetics

Eleventh edition

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The cover image symbolizes the structure of the text, as a collection of Topics that merge into a unified whole. It also symbolizes the fact that physical chemistry provides a basis for understanding chemical and physical change.

PREFACE

Our *Physical Chemistry* is continuously evolving in response to users' comments and our own imagination. The principal change in this edition is the addition of a new co-author to the team, and we are very pleased to welcome James Keeler of the University of Cambridge. He is already an experienced author and we are very happy to have him on board.

As always, we strive to make the text helpful to students and usable by instructors. We developed the popular 'Topic' arrangement in the preceding edition, but have taken the concept further in this edition and have replaced chapters by Focuses. Although that is principally no more than a change of name, it does signal that groups of Topics treat related groups of concepts which might demand more than a single chapter in a conventional arrangement. We know that many instructors welcome the flexibility that the Topic concept provides, because it makes the material easy to rearrange or trim.

We also know that students welcome the Topic arrangement as it makes processing of the material they cover less daunting and more focused. With them in mind we have developed additional help with the manipulation of equations in the form of annotations, and *The chemist's toolkits* provide further background at the point of use. As these Toolkits are often relevant to more than one Topic, they also appear in consolidated and enhanced form on the website. Some of the material previously carried in the 'Mathematical backgrounds' has been used in this enhancement. The web also provides a number of sections called *A deeper look*. As their name suggests, these sections take the material in the text further than we consider appropriate for the printed version but are there for students and instructors who wish to extend their knowledge and see the details of more advanced calculations.

Another major change is the replacement of the 'Justifications' that show how an equation is derived. Our intention has been to maintain the separation of the equation and its derivation so that review is made simple, but at the same time to acknowledge that mathematics is an integral feature of learning. Thus, the text now sets up a question and the *How is that done?* section that immediately follows develops the relevant equation, which then flows into the following text.

The worked *Examples* are a crucially important part of the learning experience. We have enhanced their presentation by replacing the 'Method' by the more encouraging *Collect your thoughts*, where with this small change we acknowledge that different approaches are possible but that students welcome guidance. The *Brief illustrations* remain: they are intended simply to show how an equation is implemented and give a sense of the order of magnitude of a property.

It is inevitable that in an evolving subject, and with evolving interests and approaches to teaching, some subjects wither and die and are replaced by new growth. We listen carefully to trends of this kind, and adjust our treatment accordingly. The topical approach enables us to be more accommodating of fading fashions because a Topic can so easily be omitted by an instructor, but we have had to remove some subjects simply to keep the bulk of the text manageable and have used the web to maintain the comprehensive character of the text without overburdening the presentation.

This book is a living, evolving text. As such, it depends very much on input from users throughout the world, and we welcome your advice and comments.

PWA
JdeP
JK

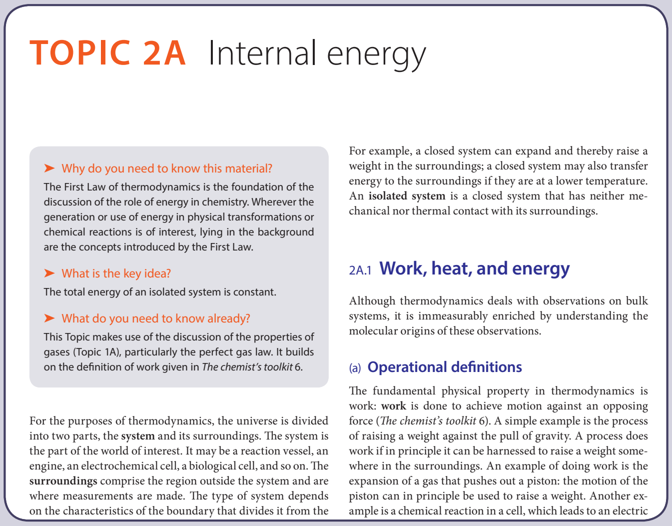
USING THE BOOK

TO THE STUDENT

For this eleventh edition we have developed the range of learning aids to suit your needs more closely than ever before. In addition to the variety of features already present, we now derive key equations in a helpful new way, through the *How is that done?* sections, to emphasize how mathematics is an interesting, essential, and integral feature of understanding physical chemistry.

Innovative structure

Short Topics are grouped into Focus sections, making the subject more accessible. Each Topic opens with a comment on why it is important, a statement of its key idea, and a brief summary of the background that you need to know.



TOPIC 2A Internal energy

➤ Why do you need to know this material?

The First Law of thermodynamics is the foundation of the discussion of the role of energy in chemistry. Wherever the generation or use of energy in physical transformations or chemical reactions is of interest, lying in the background are the concepts introduced by the First Law.

➤ What is the key idea?

The total energy of an isolated system is constant.

➤ What do you need to know already?

This Topic makes use of the discussion of the properties of gases (Topic 1A), particularly the perfect gas law. It builds on the definition of work given in *The chemist's toolkit* 6.

For the purposes of thermodynamics, the universe is divided into two parts, the **system** and its surroundings. The system is the part of the world of interest. It may be a reaction vessel, an engine, an electrochemical cell, a biological cell, and so on. The **surroundings** comprise the region outside the system and are where measurements are made. The type of system depends on the characteristics of the boundary that divides it from the

For example, a closed system can expand and thereby raise a weight in the surroundings; a closed system may also transfer energy to the surroundings if they are at a lower temperature. An **isolated system** is a closed system that has neither mechanical nor thermal contact with its surroundings.

2A.1 Work, heat, and energy

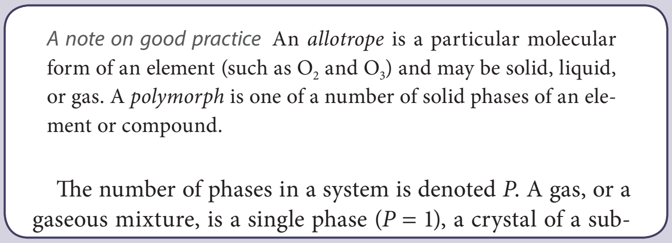
Although thermodynamics deals with observations on bulk systems, it is immeasurably enriched by understanding the molecular origins of these observations.

(a) Operational definitions

The fundamental physical property in thermodynamics is work: **work** is done to achieve motion against an opposing force (*The chemist's toolkit* 6). A simple example is the process of raising a weight against the pull of gravity. A process does work if in principle it can be harnessed to raise a weight somewhere in the surroundings. An example of doing work is the expansion of a gas that pushes out a piston: the motion of the piston can in principle be used to raise a weight. Another example is a chemical reaction in a cell, which leads to an electric

Notes on good practice

Our 'Notes on good practice' will help you avoid making common mistakes. Among other things, they encourage conformity to the international language of science by setting out the conventions and procedures adopted by the International Union of Pure and Applied Chemistry (IUPAC).

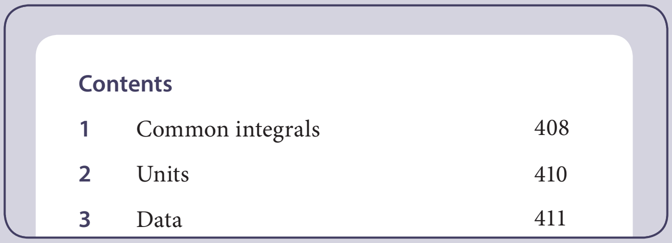


A note on good practice An *allotrope* is a particular molecular form of an element (such as O_2 and O_3) and may be solid, liquid, or gas. A *polymorph* is one of a number of solid phases of an element or compound.

The number of phases in a system is denoted *P*. A gas, or a gaseous mixture, is a single phase ($P = 1$), a crystal of a sub-

Resource section

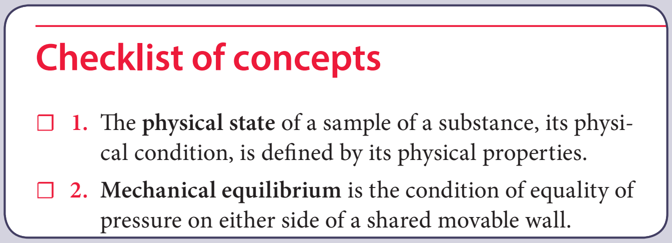
The *Resource section* at the end of the book includes a table of useful integrals, extensive tables of physical and chemical data, and character tables. Short extracts of most of these tables appear in the Topics themselves: they are there to give you an idea of the typical values of the physical quantities mentioned in the text.



Contents

Checklist of concepts

A checklist of key concepts is provided at the end of each Topic, so that you can tick off the ones you have mastered.



Checklist of concepts

☐ 1. The **physical state** of a sample of a substance, its physical condition, is defined by its physical properties.

☐ 2. **Mechanical equilibrium** is the condition of equality of pressure on either side of a shared movable wall.

PRESENTING THE MATHEMATICS

How is that done?

You need to understand how an equation is derived from reasonable assumptions and the details of the mathematical steps involved. This is accomplished in the text through the new *'How is that done?'* sections, which replace the *Justifications* of earlier editions. Each one leads from an issue that arises in the text, develops the necessary mathematics, and arrives at the equation or conclusion that resolves the issue. These sections maintain the separation of the equation and its derivation so that you can find them easily for review, but at the same time emphasize that mathematics is an essential feature of physical chemistry.

How is that done? 4A.1 Deducing the phase rule

The argument that leads to the phase rule is most easily appreciated by first thinking about the simpler case when only one component is present and then generalizing the result to an arbitrary number of components.

Step 1 *Consider the case where only one component is present*

When only one phase is present ($P = 1$), both p and T can be varied independently, so $F = 2$. Now consider the case where two phases α and β are in equilibrium ($P = 2$). If the phases are in equilibrium at a given pressure and temperature, their chemical potentials must be equal:

The chemist's toolkits

The chemist's toolkits, which are much more numerous in this edition, are reminders of the key mathematical, physical, and chemical concepts that you need to understand in order to follow the text. They appear where they are first needed. Many of these Toolkits are relevant to more than one Topic, and a compilation of them, with enhancements in the form of more information and brief illustrations, appears on the web site. **www.oup.com/uk/pchem11e/**

The chemist's toolkit 2 Properties of bulk matter

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

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

The **volume**, V, a measure of the quantity of space the sample occupies (unit: cubic metre, m^3).

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

Annotated equations and equation labels

We have annotated many equations to help you follow how they are developed. An annotation can take you across the equals sign: it is a reminder of the substitution used, an approximation made, the terms that have been assumed constant, an integral used, and so on. An annotation can also be a reminder of the significance of an individual term in an expression. We sometimes colour a collection of numbers or symbols to show how they carry from one line to the next. Many of the equations are labelled to highlight their significance.

$$C_{V,\mathrm{m}}^{\mathrm{V}} \overset{U_\mathrm{m}(T)=U_\mathrm{m}(0)+N_\mathrm{A}\langle\varepsilon^\mathrm{V}\rangle}{=} \frac{\mathrm{d}N_\mathrm{A}\langle\varepsilon^\mathrm{V}\rangle}{\mathrm{d}T} = R\theta^\mathrm{V}\frac{\mathrm{d}}{\mathrm{d}T}\frac{1}{\mathrm{e}^{\theta^\mathrm{V}/T}-1} \overset{\mathrm{d}(1/f)/\mathrm{d}x=-(1/f^2)\mathrm{d}f/\mathrm{d}x \text{ used twice}}{=} R\left(\frac{\theta^\mathrm{V}}{T}\right)^2\frac{\mathrm{e}^{\theta^\mathrm{V}/T}}{(\mathrm{e}^{\theta^\mathrm{V}/T}-1)^2}$$

By noting that $\mathrm{e}^{\theta^\mathrm{V}/T}=(\mathrm{e}^{\theta^\mathrm{V}/2T})^2$, this expression can be rearranged into

$$C_{V,\mathrm{m}}^{\mathrm{V}} = Rf(T) \quad f(T)=\left(\frac{\theta^\mathrm{V}}{T}\right)^2\left(\frac{\mathrm{e}^{-\theta^\mathrm{V}/2T}}{1-\mathrm{e}^{-\theta^\mathrm{V}/T}}\right)^2 \tag{13E.3}$$

Vibrational contribution to $C_{V,\mathrm{m}}$

Checklists of equations

A handy checklist at the end of each topic summarizes the most important equations and the conditions under which they apply. Don't think, however, that you have to memorize every equation in these checklists.

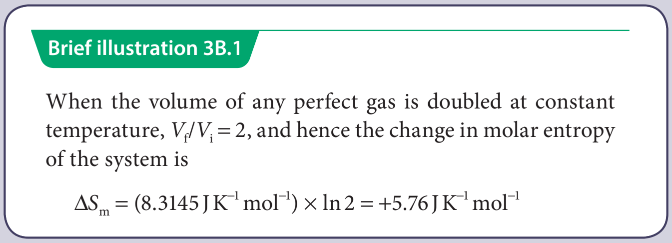
Checklist of equations

Property	Equation
Gibbs energy of mixing	$\Delta_\mathrm{mix}G = nRT(x_\mathrm{A}\ln x_\mathrm{A} + x_\mathrm{B}\ln x_\mathrm{B})$
Entropy of mixing	$\Delta_\mathrm{mix}S = -nR(x_\mathrm{A}\ln x_\mathrm{A} + x_\mathrm{B}\ln x_\mathrm{B})$

SETTING UP AND SOLVING PROBLEMS

Brief illustrations

A *Brief illustration* shows you how to use an equation or concept that has just been introduced in the text. It shows you how to use data and manipulate units correctly. It also helps you to become familiar with the magnitudes of quantities.



Brief illustration 3B.1

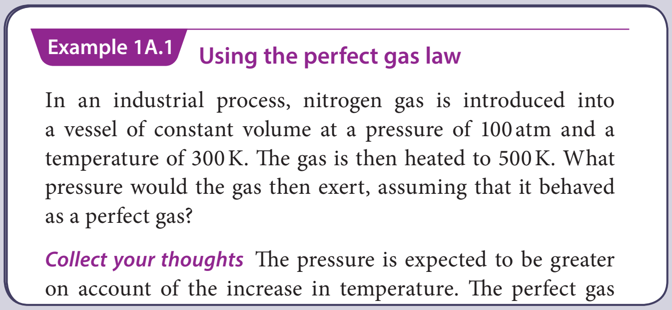
When the volume of any perfect gas is doubled at constant temperature, $V_f/V_i = 2$, and hence the change in molar entropy of the system is

$$\Delta S_m = (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times \ln 2 = +5.76\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

Examples

Worked *Examples* are more detailed illustrations of the application of the material, and typically require you to assemble and deploy the relevant concepts and equations.

We suggest how you should collect your thoughts (that is a new feature) and then proceed to a solution. All the worked *Examples* are accompanied by Self-tests to enable you to test your grasp of the material after working through our solution as set out in the *Example*.



Example 1A.1 **Using the perfect gas law**

In an industrial process, nitrogen gas is introduced into a vessel of constant volume at a pressure of 100 atm and a temperature of 300 K. The gas is then heated to 500 K. What pressure would the gas then exert, assuming that it behaved as a perfect gas?

Collect your thoughts The pressure is expected to be greater on account of the increase in temperature. The perfect gas

Discussion questions

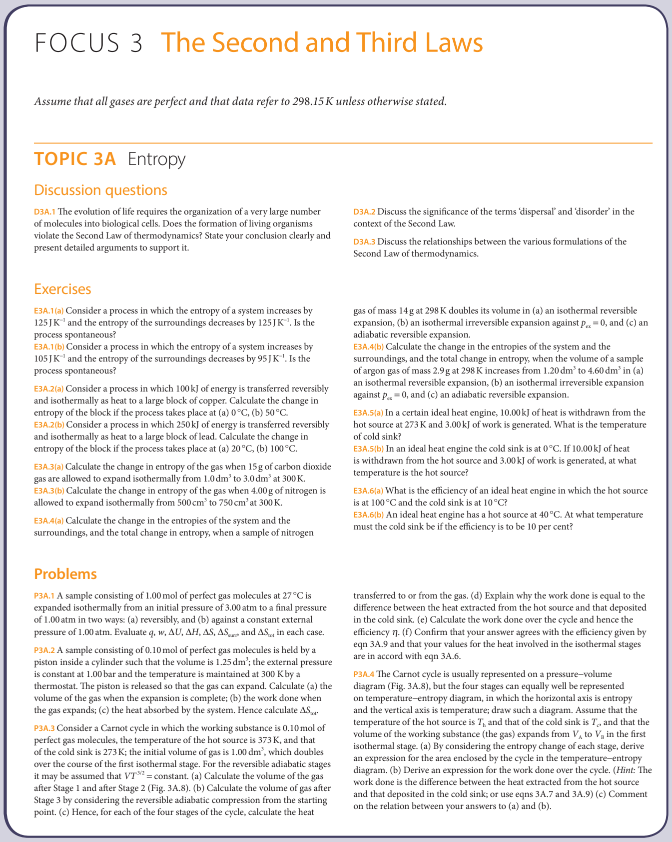
Discussion questions appear at the end of every Focus, and are organised by Topic. These questions are designed to encourage you to reflect on the material you have just read, to review the key concepts, and sometimes to think about its implications and limitations.

Exercises and problems

Exercises and Problems are also provided at the end of every Focus and organised by Topic. Exercises are designed as relatively straightforward numerical tests; the Problems are more challenging and typically involve constructing a more detailed answer. The Exercises come in related pairs, with final numerical answers available online for the 'a' questions. Final numerical answers to the odd-numbered Problems are also available online.

Integrated activities

At the end of every Focus you will find questions that span several Topics. They are designed to help you use your knowledge creatively in a variety of ways.



FOCUS 3 **The Second and Third Laws**

Assume that all gases are perfect and that data refer to 298.15 K unless otherwise stated.

TOPIC 3A Entropy

Discussion questions

D3A.1 The evolution of life requires the organization of a very large number of molecules into biological cells. Does the formation of living organisms violate the Second Law of thermodynamics? State your conclusion clearly and present detailed arguments to support it.

D3A.2 Discuss the significance of the terms 'dispersal' and 'disorder' in the context of the Second Law.

D3A.3 Discuss the relationships between the various formulations of the Second Law of thermodynamics.

Exercises

E3A.1(a) Consider a process in which the entropy of a system increases by 125 J K^{-1} and the entropy of the surroundings decreases by 125 J K^{-1}. Is the process spontaneous?
E3A.1(b) Consider a process in which the entropy of a system increases by 105 J K^{-1} and the entropy of the surroundings decreases by 95 J K^{-1}. Is the process spontaneous?

E3A.2(a) Consider a process in which 100 kJ of energy is transferred reversibly and isothermally as heat to a large block of copper. Calculate the change in entropy of the block if the process takes place at (a) 0 °C, (b) 50 °C.
E3A.2(b) Consider a process in which 250 kJ of energy is transferred reversibly and isothermally as heat to a large block of lead. Calculate the change in entropy of the block if the process takes place at (a) 20 °C, (b) 100 °C.

E3A.3(a) Calculate the change in entropy of the gas when 15 g of carbon dioxide gas are allowed to expand isothermally from 1.0 dm^3 to 3.0 dm^3 at 300 K.
E3A.3(b) Calculate the change in entropy of the gas when 4.00 g of nitrogen is allowed to expand isothermally from 500 cm^3 to 750 cm^3 at 300 K.

E3A.4(a) Calculate the change in the entropies of the system and the surroundings, and the total change in entropy, when a sample of nitrogen gas of mass 14 g at 298 K doubles its volume in (a) an isothermal reversible expansion, (b) an isothermal irreversible expansion against $p_{ex} = 0$, and (c) an adiabatic reversible expansion.
E3A.4(b) Calculate the change in the entropies of the system and the surroundings, and the total change in entropy, when the volume of a sample of argon gas of mass 2.9 g at 298 K increases from 1.20 dm^3 to 4.60 dm^3 in (a) an isothermal reversible expansion, (b) an isothermal irreversible expansion against $p_{ex} = 0$, and (c) an adiabatic reversible expansion.

E3A.5(a) In a certain ideal heat engine, 10.00 kJ of heat is withdrawn from the hot source at 273 K and 3.00 kJ of work is generated. What is the temperature of cold sink?
E3A.5(b) In an ideal heat engine the cold sink is at 0 °C. If 10.00 kJ of heat is withdrawn from the hot source and 3.00 kJ of work is generated, at what temperature is the hot source?

E3A.6(a) What is the efficiency of an ideal heat engine in which the hot source is at 100 °C and the cold sink is at 10 °C?
E3A.6(b) An ideal heat engine has a hot source at 40 °C. At what temperature must the cold sink be if the efficiency is to be 10 per cent?

Problems

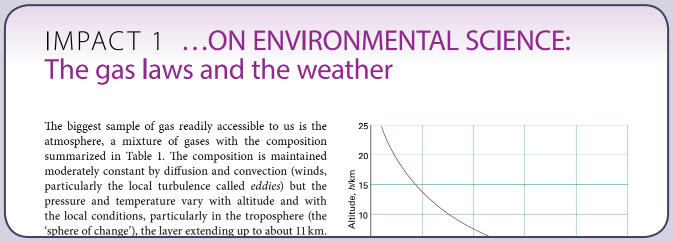
P3A.1 A sample consisting of 1.00 mol of perfect gas molecules at 27 °C is expanded isothermally from an initial pressure of 3.00 atm to a final pressure of 1.00 atm in two ways: (a) reversibly, and (b) against a constant external pressure of 1.00 atm. Evaluate q, w, ΔU, ΔH, ΔS, ΔS_{surr}, and ΔS_{tot} in each case.

P3A.2 A sample consisting of 0.10 mol of perfect gas molecules is held by a piston inside a cylinder such that the volume is 1.25 dm^3; the external pressure is constant at 1.00 bar and the temperature is maintained at 300 K by a thermostat. The piston is released so that the gas can expand. Calculate (a) the volume of the gas when the expansion is complete; (b) the work done when the gas expands; (c) the heat absorbed by the system. Hence calculate ΔS_{tot}.

P3A.3 Consider a Carnot cycle in which the working substance is 0.10 mol of perfect gas molecules, the temperature of the hot source is 373 K, and that of the cold sink is 273 K; the initial volume of gas is 1.00 dm^3, which doubles over the course of the first isothermal stage. For the reversible adiabatic stages it may be assumed that $VT^{3/2}$ = constant. (a) Calculate the volume of the gas after Stage 1 and after Stage 2 (Fig. 3A.8). (b) Calculate the volume of gas after Stage 3 by considering the reversible adiabatic compression from the starting point. (c) Hence, for each of the four stages of the cycle, calculate the heat transferred to or from the gas. (d) Explain why the work done is equal to the difference between the heat extracted from the hot source and that deposited in the cold sink. (e) Calculate the work done over the cycle and hence the efficiency η. (f) Confirm that your answer agrees with the efficiency given by eqn 3A.9 and that your values for the heat involved in the isothermal stages are in accord with eqn 3A.6.

P3A.4 The Carnot cycle is usually represented on a pressure–volume diagram (Fig. 3A.8), but the four stages can equally well be represented on temperature–entropy diagram, in which the horizontal axis is entropy and the vertical axis is temperature; draw such a diagram. Assume that the temperature of the hot source is T_h and that of the cold sink is T_c, and that the volume of the working substance (the gas) expands from V_A to V_B in the first isothermal stage. (a) By considering the entropy change of each stage, derive an expression for the area enclosed by the cycle in the temperature–entropy diagram. (b) Derive an expression for the work done over the cycle. (*Hint:* The work done is the difference between the heat extracted from the hot source and that deposited in the cold sink; or use eqns 3A.7 and 3A.9) (c) Comment on the relation between your answers to (a) and (b).

THERE IS A LOT OF ADDITIONAL MATERIAL ON THE WEB



IMPACT 1 …ON ENVIRONMENTAL SCIENCE: The gas laws and the weather

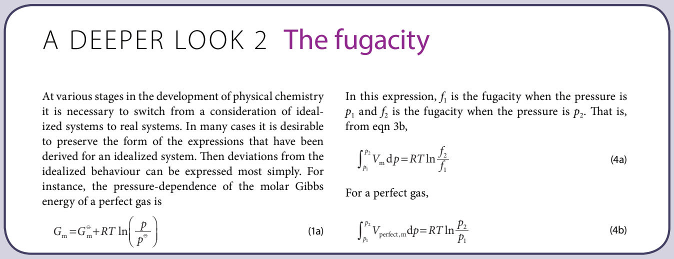
The biggest sample of gas readily accessible to us is the atmosphere, a mixture of gases with the composition summarized in Table 1. The composition is maintained moderately constant by diffusion and convection (winds, particularly the local turbulence called *eddies*) but the pressure and temperature vary with altitude and with the local conditions, particularly in the troposphere (the 'sphere of change'), the layer extending up to about 11 km.

'Impact' sections

'Impact' sections show how physical chemistry is applied in a variety of modern contexts. They showcase physical chemistry as an evolving subject. **www.oup.com/uk/pchem11e/**

A deeper look

These online sections take some of the material in the text further and are there if you want to extend your knowledge and see the details of some of the more advanced derivations **www.oup.com/uk/pchem11e/**



A DEEPER LOOK 2 The fugacity

At various stages in the development of physical chemistry it is necessary to switch from a consideration of idealized systems to real systems. In many cases it is desirable to preserve the form of the expressions that have been derived for an idealized system. Then deviations from the idealized behaviour can be expressed most simply. For instance, the pressure-dependence of the molar Gibbs energy of a perfect gas is

$$G_\mathrm{m} = G_\mathrm{m}^{\ominus} + RT\ln\left(\frac{p}{p^{\ominus}}\right) \tag{1a}$$

In this expression, f_1 is the fugacity when the pressure is p_1 and f_2 is the fugacity when the pressure is p_2. That is, from eqn 3b,

$$\int_{p_1}^{p_2} V_\mathrm{m}\,\mathrm{d}p = RT\ln\frac{f_2}{f_1} \tag{4a}$$

For a perfect gas,

$$\int_{p_1}^{p_2} V_{\mathrm{perfect,m}}\mathrm{d}p = RT\ln\frac{p_2}{p_1} \tag{4b}$$

Group theory tables

Comprehensive group theory tables are available to download.

Molecular modelling problems

Files containing molecular modelling problems can be downloaded, designed for use with the Spartan Student™ software. However they can also be completed using any modelling software that allows Hartree–Fock, density functional, and MP2 calculations. The site can be accessed at **www.oup.com/uk/pchem11e/**.

TO THE INSTRUCTOR

We have designed the text to give you maximum flexibility in the selection and sequence of Topics, while the grouping of Topics into Focuses helps to maintain the unity of the subject. Additional resources are:

Figures and tables from the book

Lecturers can find the artwork and tables from the book in ready-to-download format. These may be used for lectures without charge (but not for commercial purposes without specific permission).

Key equations

Supplied in Word format so you can download and edit them.

Lecturer resources are available only to registered adopters of the textbook. To register, simply visit **www.oup.com/uk/pchem11e/** and follow the appropriate links.

SOLUTIONS MANUALS

Two solutions manuals have been written by Peter Bolgar, Haydn Lloyd, Aimee North, Vladimiras Oleinikovas, Stephanie Smith, and James Keeler.

The *Student's Solutions Manual* (ISBN 9780198830078) provides full solutions to the 'a' Exercises and to the odd-numbered Problems.

The *Instructor's Solutions Manual* provides full solutions to the 'b' Exercises and to the even-numbered Problems (available to download online for registered adopters of the book only).

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Photograph by Natasha Ellis-Knight.

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Photograph by Nathan Pitt, ©University of Cambridge.

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Resource section

FULL CONTENTS

CONVENTIONS

To avoid intermediate rounding errors, but to keep track of values in order to be aware of values and to spot numerical errors, we display intermediate results as *n.nnn*… and round the calculation only at the final step.

Blue terms are used when we want to identify a term in an equation. An entire quotient, numerator/denominator, is coloured blue if the annotation refers to the entire term, not just to the numerator or denominator separately.

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4	The energy of the bonding molecular orbital of H_2^+
5	Rotational selection rules
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7	The van der Waals equation of state
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28	19	. . .on technology: Fuel cells

PROLOGUE Energy, temperature, and chemistry

Energy is a concept used throughout chemistry to discuss molecular structures, reactions, and many other processes. What follows is an informal first look at the important features of energy. Its precise definition and role will emerge throughout the course of this text.

The transformation of energy from one form to another is described by the laws of **thermodynamics**. They are applicable to bulk matter, which consists of very large numbers of atoms and molecules. The 'First Law' of thermodynamics is a statement about the quantity of energy involved in a transformation; the 'Second Law' is a statement about the dispersal of that energy (in a sense that will be explained).

To discuss the energy of individual atoms and molecules that make up samples of bulk matter it is necessary to use **quantum mechanics**. According to this theory, the energy associated with the motion of a particle is 'quantized', meaning that the energy is restricted to certain values, rather than being able to take on any value. Three different kinds of motion can occur: *translation* (motion through space), *rotation* (change of orientation), and *vibration* (the periodic stretching and bending of bonds). Figure 1 depicts the relative sizes and spacing of the energy states associated with these different kinds of motion of typical molecules and compares them with the typical energies of electrons in atoms and molecules. The allowed energies associated with translation are so close together in normal-sized containers that they form a continuum. In contrast, the separation between the allowed electronic energy states of atoms and molecules is very large.

The link between the energies of individual molecules and the energy of bulk matter is provided by one of the most important concepts in chemistry, the **Boltzmann distribution**. Bulk matter consists of large numbers of molecules, each of which is in one of its available energy states. The total number of molecules with a particular energy due to translation, rotation, vibration, and its electronic state is called the 'population' of that state. Most molecules are found in the lowest energy state, and higher energy states are occupied by progressively fewer molecules. The Boltzmann distribution gives the population, N_i, of any energy state in terms of the energy of the state, ε_i, and the absolute temperature, T:

$$N_i \propto \mathrm{e}^{-\varepsilon_i/kT}$$

In this expression, k is *Boltzmann's constant* (its value is listed inside the front cover), a universal constant (in the sense of having the same value for all forms of matter). Figure 2 shows the Boltzmann distribution for two temperatures: as the temperature increases higher energy states are populated at the expense of states lower in energy. According to the Boltzmann distribution, the temperature is the single parameter that governs the spread of populations over the available energy states, whatever their nature.

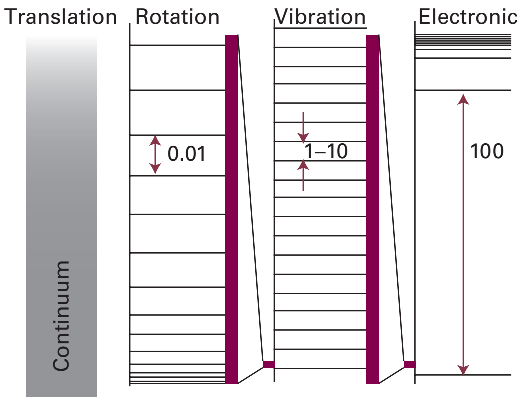
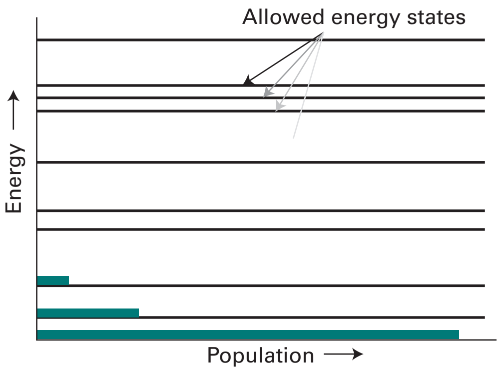
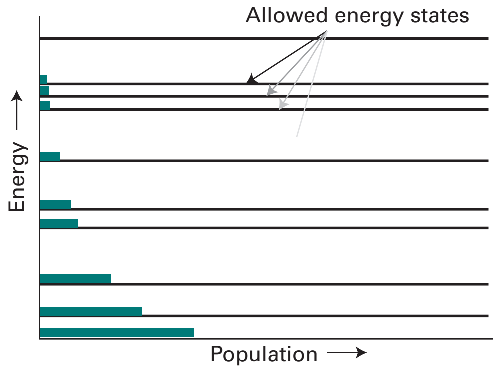


Figure 1 The relative energies of the allowed states of various kinds of atomic and molecular motion.



(a) Low temperature



(b) High temperature

Figure 2 The relative populations of states at (a) low, (b) high temperature according to the Boltzmann distribution.

The Boltzmann distribution, as well as providing insight into the significance of temperature, is central to understanding much of chemistry. That most molecules occupy states of low energy when the temperature is low accounts for the existence of compounds and the persistence of liquids and solids. That highly excited energy levels become accessible at high temperatures accounts for the possibility of reaction as one substance acquires the ability to change into another. Both features are explored in detail throughout the text.

You should keep in mind the Boltzmann distribution (which is treated in greater depth later in the text) whenever considering the interpretation of the properties of bulk matter and the role of temperature. An understanding of the flow of energy and how it is distributed according to the Boltzmann distribution is the key to understanding thermodynamics, structure, and change throughout chemistry.

FOCUS 1

The properties of gases

A gas is a form of matter that fills whatever container it occupies. This Focus establishes the properties of gases that are used throughout the text.

1A The perfect gas

This Topic is an account of an idealized version of a gas, a 'perfect gas', and shows how its equation of state may be assembled from the experimental observations summarized by Boyle's law, Charles's law, and Avogadro's principle.

1A.1 **Variables of state;** 1A.2 **Equations of state**

1B The kinetic model

A central feature of physical chemistry is its role in building models of molecular behaviour that seek to explain observed phenomena. A prime example of this procedure is the development of a molecular model of a perfect gas in terms of a collection of molecules (or atoms) in ceaseless, essentially random motion. As well as accounting for the gas laws, this model can be used to predict the average speed at which molecules move in a gas, and its dependence on temperature. In combination with the Boltzmann distribution (see the text's *Prologue*), the model can also be used to predict the spread of molecular speeds and its dependence on molecular mass and temperature.

1B.1 **The model;** 1B.2 **Collisions**

1C Real gases

The perfect gas is a starting point for the discussion of properties of all gases, and its properties are invoked throughout thermodynamics. However, actual gases, 'real gases', have properties that differ from those of perfect gases, and it is necessary to be able to interpret these deviations and build the effects of molecular attractions and repulsions into the model. The discussion of real gases is another example of how initially primitive models in physical chemistry are elaborated to take into account more detailed observations.

1C.1 **Deviations from perfect behaviour;** 1C.2 **The van der Waals equation**

Web resources What is an application of this material?

The perfect gas law and the kinetic theory can be applied to the study of phenomena confined to a reaction vessel or encompassing an entire planet or star. In *Impact* 1 the gas laws are used in the discussion of meteorological phenomena—the weather. *Impact* 2 examines how the kinetic model of gases has a surprising application: to the discussion of dense stellar media, such as the interior of the Sun.

TOPIC 1A The perfect gas

➤ Why do you need to know this material?

Equations related to perfect gases provide the basis for the development of many relations in thermodynamics. The perfect gas law is also a good first approximation for accounting for the properties of real gases.

➤ What is the key idea?

The perfect gas law, which is based on a series of empirical observations, is a limiting law that is obeyed increasingly well as the pressure of a gas tends to zero.

➤ What do you need to know already?

You need to know how to handle quantities and units in calculations, as reviewed in *The chemist's toolkit* 1. You also need to be aware of the concepts of pressure, volume, amount of substance, and temperature, all reviewed in *The chemist's toolkit* 2.

The properties of gases were among the first to be established quantitatively (largely during the seventeenth and eighteenth centuries) when the technological requirements of travel in balloons stimulated their investigation. These properties set the stage for the development of the kinetic model of gases, as discussed in Topic 1B.

1A.1 Variables of state

The **physical state** of a sample of a substance, its physical condition, is defined by its physical properties. Two samples of the same substance that have the same physical properties are in the same state. The variables needed to specify the state of a system are the amount of substance it contains, n, the volume it occupies, V, the pressure, p, and the temperature, T.

(a) Pressure

The origin of the force exerted by a gas is the incessant battering of the molecules on the walls of its container. The collisions are so numerous that they exert an effectively steady force, which is experienced as a steady pressure. The SI unit of pressure, the *pascal* (Pa, 1 Pa = 1 N m^{-2}), is introduced in *The chemist's toolkit* 1. Several other units are still widely used (Table 1A.1). A pressure of 1 bar is the **standard pressure** for reporting data; it is denoted $p^\ominus$.

Table 1A.1 Pressure units*

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

* Values in bold are exact.

If two gases are in separate containers that share a common movable wall (Fig. 1A.1), the gas that has the higher pressure will tend to compress (reduce the volume of) the gas that has lower pressure. The pressure of the high-pressure gas will fall as it expands and that of the low-pressure gas will rise as it is compressed. There will come a stage when the two pressures are equal and the wall has no further tendency to move. This condition of equality of pressure on either side of a movable wall is a state of **mechanical equilibrium** between the two gases. The pressure of a gas is therefore an indication of whether a container that contains the gas will be in mechanical equilibrium with another gas with which it shares a movable wall.

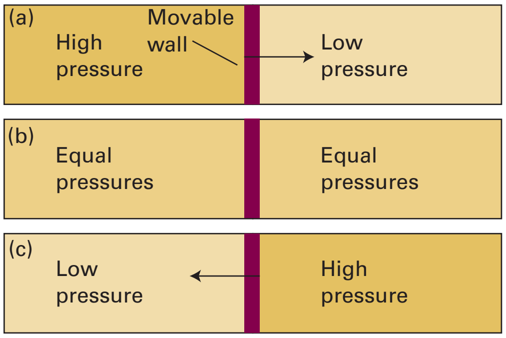


Figure 1A.1 When a region of high pressure is separated from a region of low pressure by a movable wall, the wall will be pushed into one region or the other, as in (a) and (c). However, if the two pressures are identical, the wall will not move (b). The latter condition is one of mechanical equilibrium between the two regions.

The chemist's toolkit 1 Quantities and units

The result of a measurement is a **physical quantity** that is reported as a numerical multiple of a unit:

$$\text{physical quantity} = \text{numerical value} \times \text{unit}$$

It follows that units may be treated like algebraic quantities and may be multiplied, divided, and cancelled. Thus, the expression (physical quantity)/unit is the numerical value (a dimensionless quantity) of the measurement in the specified units. For instance, the mass m of an object could be reported as $m = 2.5\,\text{kg}$ or $m/\text{kg} = 2.5$. In this instance the unit of mass is 1 kg, but it is common to refer to the unit simply as kg (and likewise for other units). See Table A.1 in the *Resource section* for a list of units.

Although it is good practice to use only SI units, there will be occasions where accepted practice is so deeply rooted that physical quantities are expressed using other, non-SI units. By international convention, all physical quantities are represented by oblique (sloping) letters (for instance, m for mass); units are given in roman (upright) letters (for instance m for metre).

Units may be modified by a prefix that denotes a factor of a power of 10. Among the most common SI prefixes are those listed in Table A.2 in the *Resource section*. Examples of the use of these prefixes are:

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

Powers of units apply to the prefix as well as the unit they modify. For example, $1\,\text{cm}^3 = 1\,(\text{cm})^3$, and $(10^{-2}\,\text{m})^3 = 10^{-6}\,\text{m}^3$. Note that $1\,\text{cm}^3$ does not mean $1\,\text{c}(\text{m}^3)$. When carrying out numerical calculations, it is usually safest to write out the numerical value of an observable in scientific notation (as $n.nnn \times 10^n$).

There are seven SI base units, which are listed in Table A.3 in the *Resource section*. All other physical quantities may be expressed as combinations of these base units. *Molar concentration* (more formally, but very rarely, *amount of substance concentration*) for example, which is an amount of substance divided by the volume it occupies, can be expressed using the derived units of $\text{mol}\,\text{dm}^{-3}$ as a combination of the base units for amount of substance and length. A number of these derived combinations of units have special names and symbols. For example, force is reported in the derived unit newton, $1\,\text{N} = 1\,\text{kg}\,\text{m}\,\text{s}^{-2}$ (see Table A.4 in the *Resource section*).

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

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

(b) Temperature

The concept of temperature is introduced in *The chemist's toolkit* 2. In the early days of thermometry (and still in laboratory practice today), temperatures were related to the length of a column of liquid, and the difference in lengths shown when the thermometer was first in contact with melting ice and then with boiling water was divided into 100 steps called 'degrees', the lower point being labelled 0. This procedure led to the **Celsius scale** of temperature. In this text, temperatures on the Celsius scale are denoted θ (theta) and expressed in *degrees Celsius* (°C). However, because different liquids expand to different extents, and do not always expand uniformly over a given range, thermometers constructed from different materials showed different numerical values of the temperature between their fixed points. The pressure of a gas, however, can be used to construct a **perfect-gas temperature scale** that is independent of the identity of the gas. The perfect-gas scale turns out to be identical to the **thermodynamic temperature scale** (Topic 3A), so the latter term is used from now on to avoid a proliferation of names.

On the thermodynamic temperature scale, temperatures are denoted T and are normally reported in *kelvins* (K; not °K). Thermodynamic and Celsius temperatures are related by the exact expression

$$T/\text{K} = \theta/{}^\circ\text{C} + 273.15 \qquad \text{Celsius scale [definition]} \qquad (1\text{A}.1)$$

This relation is the current definition of the Celsius scale in terms of the more fundamental Kelvin scale. It implies that a difference in temperature of 1 °C is equivalent to a difference of 1 K.

Brief illustration 1A.1

To express 25.00 °C as a temperature in kelvins, eqn 1A.1 is used to write

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

The chemist's toolkit 2 Properties of bulk matter

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

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

The **volume**, V, a measure of the quantity of space the sample occupies (unit: cubic metre, m^3).

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

The amount of substance, n (colloquially, 'the number of moles'), is a measure of the number of specified entities present in the sample. 'Amount of substance' is the official name of the quantity; it is commonly simplified to 'chemical amount' or simply 'amount'. A mole is currently defined as the number of carbon atoms in exactly 12 g of carbon-12. (In 2011 the decision was taken to replace this definition, but the change has not yet, in 2018, been implemented.) The number of entities per mole is called **Avogadro's constant**, N_A; the currently accepted value is $6.022 \times 10^{23}\,\mathrm{mol^{-1}}$ (note that N_A is a constant with units, not a pure number).

The **molar mass of a substance**, M (units: formally $\mathrm{kg\,mol^{-1}}$ but commonly $\mathrm{g\,mol^{-1}}$) is the mass per mole of its atoms, its molecules, or its formula units. The amount of substance of specified entities in a sample can readily be calculated from its mass, by noting that

$$n = \frac{m}{M}$$

Amount of substance

A note on good practice Be careful to distinguish atomic or molecular mass (the mass of a single atom or molecule; unit: kg) from molar mass (the mass per mole of atoms or molecules; units: $\mathrm{kg\,mol^{-1}}$). *Relative* molecular masses of atoms and molecules, $M_r = m/m_u$, where m is the mass of the atom or molecule and m_u is the atomic mass constant (see inside front cover), are still widely called 'atomic weights' and 'molecular weights' even though they are dimensionless quantities and not weights ('weight' is the gravitational force exerted on an object).

A sample of matter may be subjected to a **pressure**, p (unit: pascal, Pa; $1\,\mathrm{Pa} = 1\,\mathrm{kg\,m^{-1}\,s^{-2}}$), which is defined as the force, F, it is subjected to, divided by the area, A, to which that force is applied. Although the pascal is the SI unit of pressure, it is also common to express pressure in bar ($1\,\mathrm{bar} = 10^5\,\mathrm{Pa}$) or atmospheres ($1\,\mathrm{atm} = 101\,325\,\mathrm{Pa}$ exactly), both of which correspond to typical atmospheric pressure. Because many physical properties depend on the pressure acting on a sample, it is appropriate to select a certain value of the pressure to report their values. The **standard pressure** for reporting physical quantities is currently defined as $p^{\ominus} = 1\,\mathrm{bar}$ exactly.

To specify the state of a sample fully it is also necessary to give its **temperature**, T. The temperature is formally a property that determines in which direction energy will flow as heat when two samples are placed in contact through thermally conducting walls: energy flows from the sample with the higher temperature to the sample with the lower temperature. The symbol T is used to denote the **thermodynamic temperature** which is an absolute scale with $T = 0$ as the lowest point. Temperatures above $T = 0$ are then most commonly expressed by using the **Kelvin scale**, in which the gradations of temperature are expressed in kelvins (K). The Kelvin scale is currently defined by setting the triple point of water (the temperature at which ice, liquid water, and water vapour are in mutual equilibrium) at exactly 273.16 K (as for certain other units, a decision has been taken to revise this definition, but it has not yet, in 2018, been implemented). The freezing point of water (the melting point of ice) at 1 atm is then found experimentally to lie 0.01 K below the triple point, so the freezing point of water is 273.15 K.

Suppose a sample is divided into smaller samples. If a property of the original sample has a value that is equal to the sum of its values in all the smaller samples (as mass would), then it is said to be **extensive**. Mass and volume are extensive properties. If a property retains the same value as in the original sample for all the smaller samples (as temperature would), then it is said to be **intensive**. Temperature and pressure are intensive properties. Mass density, $\rho = m/V$, is also intensive because it would have the same value for all the smaller samples and the original sample. All molar properties, $X_m = X/n$, are intensive, whereas X and n are both extensive.

Note how the units (in this case, °C) are cancelled like numbers. This is the procedure called 'quantity calculus' in which a physical quantity (such as the temperature) is the product of a numerical value (25.00) and a unit (1 °C); see *The chemist's toolkit* 1. Multiplication of both sides by K then gives $T = 298.15\,\mathrm{K}$.

A note on good practice The zero temperature on the thermodynamic temperature scale is written $T = 0$, not $T = 0\,\mathrm{K}$. This scale is absolute, and the lowest temperature is 0 regardless of the size of the divisions on the scale (just as zero pressure is denoted $p = 0$, regardless of the size of the units, such as bar or pascal). However, it is appropriate to write 0 °C because the Celsius scale is not absolute.

1A.2 Equations of state

Although in principle the state of a pure substance is specified by giving the values of n, V, p, and T, it has been established experimentally that it is sufficient to specify only three of these variables since doing so fixes the value of the fourth variable.

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

The general form of an equation of state is

$$p = f(T,V,n) \qquad \text{General form of an equation of state} \qquad (1A.2)$$

This equation states that if the values of n, T, and V are known for a particular substance, then the pressure has a fixed value. Each substance is described by its own equation of state, but the explicit form of the equation is known in only a few special cases. One very important example is the equation of state of a 'perfect gas', which has the form $p = nRT/V$, where R is a constant independent of the identity of the gas.

The equation of state of a perfect gas was established by combining a series of empirical laws.

(a) The empirical basis

The following individual gas laws should be familiar:

Boyle's law: $pV = \text{constant, at constant } n, T$ (1A.3a)

Charles's law: $V = \text{constant} \times T\text{, at constant } n, p$ (1A.3b)

$p = \text{constant} \times T\text{, at constant } n, V$ (1A.3c)

Avogadro's principle:
$V = \text{constant} \times n \text{ at constant } p, T$ (1A.3d)

Boyle's and Charles's laws are examples of a **limiting law**, a law that is strictly true only in a certain limit, in this case $p \to 0$. For example, if it is found empirically that the volume of a substance fits an expression $V = aT + bp + cp^2$, then in the limit of $p \to 0$, $V = aT$. Many relations that are strictly true only at $p = 0$ are nevertheless reasonably reliable at normal pressures ($p \approx 1$ bar) and are used throughout chemistry.

Figure 1A.2 depicts the variation of the pressure of a sample of gas as the volume is changed. Each of the curves in the graph corresponds to a single temperature and hence is called an **isotherm**. According to Boyle's law, the isotherms of gases are hyperbolas (a curve obtained by plotting y against x with xy = constant, or y = constant/x). An alternative depiction, a plot of pressure against 1/volume, is shown in Fig. 1A.3. The linear variation of volume with temperature summarized by Charles's law is illustrated in Fig. 1A.4. The lines in this illustration are examples of **isobars**, or lines showing the variation of properties at constant pressure. Figure 1A.5 illustrates the linear variation of pressure with temperature. The lines in this diagram are **isochores**, or lines showing the variation of properties at constant volume.

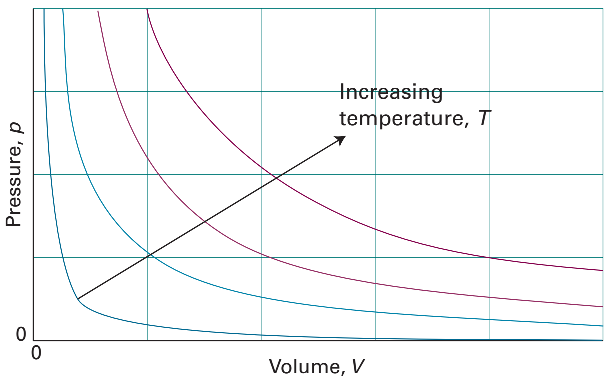


Figure 1A.2 The pressure–volume dependence of a fixed amount of perfect gas at different temperatures. Each curve is a hyperbola (pV = constant) and is called an isotherm.

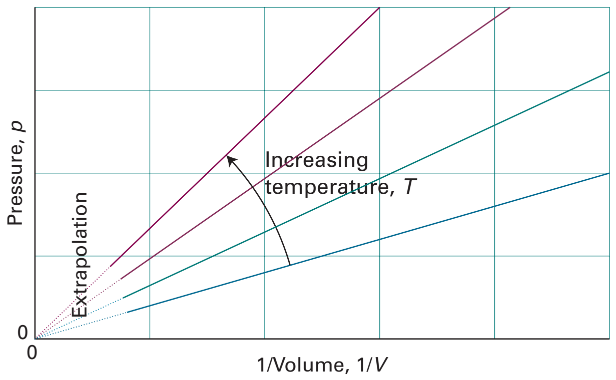


Figure 1A.3 Straight lines are obtained when the pressure of a perfect gas is plotted against $1/V$ at constant temperature. These lines extrapolate to zero pressure at $1/V = 0$.

A note on good practice To test the validity of a relation between two quantities, it is best to plot them in such a way that they should give a straight line, because deviations from a straight line are much easier to detect than deviations from a curve. The development of expressions that, when plotted, give a straight line is a very important and common procedure in physical chemistry.

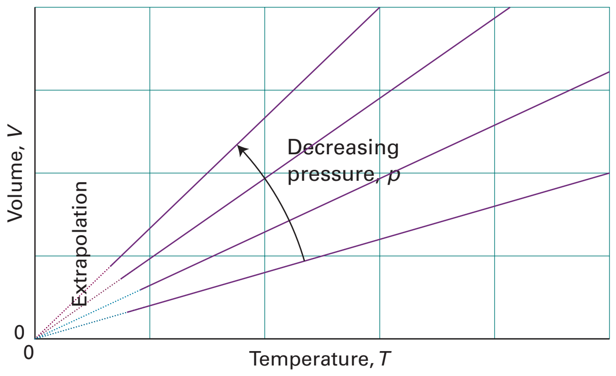


Figure 1A.4 The variation of the volume of a fixed amount of a perfect gas with the temperature at constant pressure. Note that in each case the isobars extrapolate to zero volume at $T = 0$, corresponding to $\theta = -273.15\,°\text{C}$.

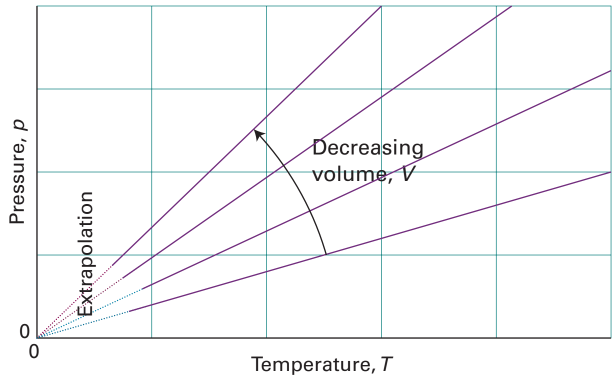


Figure 1A.5 The pressure of a perfect gas also varies linearly with the temperature at constant volume, and extrapolates to zero at $T = 0$ (–273.15 °C).

The empirical observations summarized by eqn 1A.3 can be combined into a single expression:

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

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

$$pV = nRT \quad \text{Perfect gas law} \quad (1A.4)$$

is the **perfect gas law** (or *perfect gas equation of state*). It is the approximate equation of state of any gas, and becomes increasingly exact as the pressure of the gas approaches zero. A gas that obeys eqn 1A.4 exactly under all conditions is called a **perfect gas** (or *ideal gas*). A **real gas**, an actual gas, behaves more like a perfect gas the lower the pressure, and is described exactly by eqn 1A.4 in the limit of $p \to 0$. The gas constant R can be determined by evaluating $R = pV/nT$ for a gas in the limit of zero pressure (to guarantee that it is behaving perfectly).

> *A note on good practice* Despite 'ideal gas' being the more common term, 'perfect gas' is preferable. As explained in Topic 5B, in an 'ideal mixture' of A and B, the AA, BB, and AB interactions are all the same but not necessarily zero. In a perfect gas, not only are the interactions all the same, they are also zero.

The surface in Fig. 1A.6 is a plot of the pressure of a fixed amount of perfect gas against its volume and thermodynamic temperature as given by eqn 1A.4. The surface depicts the only possible states of a perfect gas: the gas cannot exist in states that do not correspond to points on the surface. The graphs in Figs. 1A.2 and 1A.4 correspond to the sections through the surface (Fig. 1A.7).

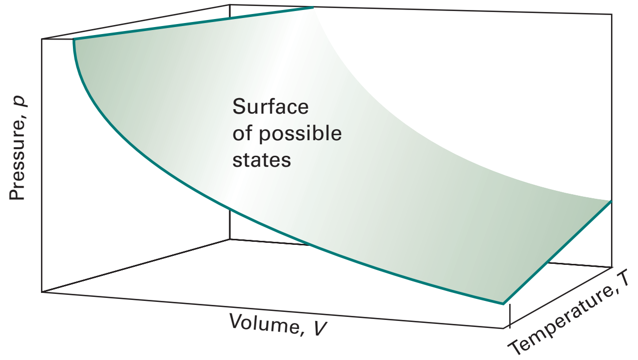


Figure 1A.6 A region of the p,V,T surface of a fixed amount of perfect gas. The points forming the surface represent the only states of the gas that can exist.

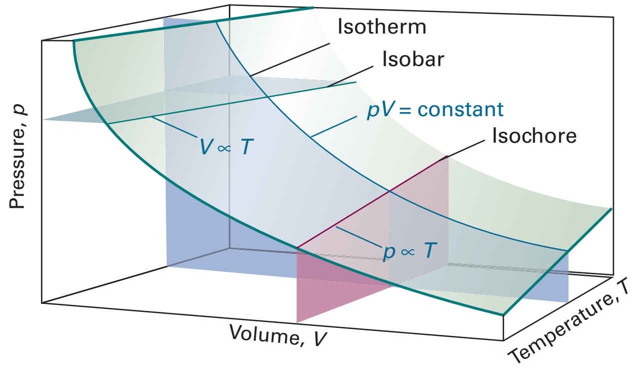


Figure 1A.7 Sections through the surface shown in Fig. 1A.6 at constant temperature give the isotherms shown in Fig. 1A.2. Sections at constant pressure give the isobars shown in Fig. 1A.4. Sections at constant volume give the isochores shown in Fig. 1A.5.

Example 1A.1 Using the perfect gas law

In an industrial process, nitrogen gas is introduced into a vessel of constant volume at a pressure of 100 atm and a temperature of 300 K. The gas is then heated to 500 K. What pressure would the gas then exert, assuming that it behaved as a perfect gas?

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

$$\frac{p_1V_1}{n_1T_1} = \frac{p_2V_2}{n_2T_2} \quad \text{Combined gas law} \quad (1A.5)$$

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

	n	p	V	T
Initial	Same	100 atm	Same	300 K
Final	Same	?	Same	500 K

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

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

which can be rearranged into

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

Substitution of the data then gives

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

Self-test 1A.1 What temperature would result in the same sample exerting a pressure of 300 atm?

Answer: 900 K

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

The molecular explanation of Boyle's law is that if a sample of gas is compressed to half its volume, then twice as many molecules strike the walls in a given period of time than before it was compressed. As a result, the average force exerted on the walls is doubled. Hence, when the volume is halved the pressure of the gas is doubled, and pV is a constant. Boyle's law applies to all gases regardless of their chemical identity (provided the pressure is low) because at low pressures the average separation of molecules is so great that they exert no influence on one another and hence travel independently. The molecular explanation of Charles's law lies in the fact that raising the temperature of a gas increases the average speed of its molecules. The molecules collide with the walls more frequently and with greater impact. Therefore they exert a greater pressure on the walls of the container. For a quantitative account of these relations, see Topic 1B.

(b) Mixtures of gases

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

$$p_J = x_J p \qquad (1A.6)$$

Partial pressure [definition]

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

$$x_J = \frac{n_J}{n} \qquad n = n_A + n_B + \cdots \qquad (1A.7)$$

Mole fraction [definition]

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

$$p_A + p_B + \cdots = (x_A + x_B + \cdots)p = p \qquad (1A.8)$$

This relation is true for both real and perfect gases.

When all the gases are perfect, the partial pressure as defined in eqn 1A.6 is also the pressure that each gas would exert if it occupied the same container alone at the same temperature. The latter is the original meaning of 'partial pressure'. That identification was the basis of the original formulation of **Dalton's law**:

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

Dalton's law

This law is valid only for mixtures of perfect gases, so it is not used to define partial pressure. Partial pressure is defined by eqn 1A.6, which is valid for all gases.

Example 1A.2 Calculating partial pressures

The mass percentage composition of dry air at sea level is approximately N_2: 75.5; O_2: 23.2; Ar: 1.3. What is the partial pressure of each component when the total pressure is 1.20 atm?

Collect your thoughts Partial pressures are defined by eqn 1A.6. To use the equation, first calculate the mole fractions of the components, by using eqn 1A.7 and the fact that the amount of atoms or molecules J of molar mass M_J in a sample of mass m_J is $n_J = m_J/M_J$. The mole fractions are independent of the total mass of the sample, so choose the latter to be exactly 100 g (which makes the conversion from mass percentages very easy). Thus, the mass of N_2 present is 75.5 per cent of 100 g, which is 75.5 g.

The solution The amounts of each type of atom or molecule present in 100 g of air are, in which the masses of N_2, O_2, and Ar are 75.5 g, 23.2 g, and 1.3 g, respectively, are

$$n(N_2) = \frac{75.5\,\mathrm{g}}{28.02\,\mathrm{g\,mol^{-1}}} = \frac{75.5}{28.02}\,\mathrm{mol} = 2.69\,\mathrm{mol}$$

$$n(O_2) = \frac{23.2\,\mathrm{g}}{32.00\,\mathrm{g\,mol^{-1}}} = \frac{23.2}{32.00}\,\mathrm{mol} = 0.725\,\mathrm{mol}$$

$$n(\mathrm{Ar}) = \frac{1.3\,\mathrm{g}}{39.95\,\mathrm{g\,mol^{-1}}} = \frac{1.3}{39.95}\,\mathrm{mol} = 0.033\,\mathrm{mol}$$

The total is 3.45 mol. The mole fractions are obtained by dividing each of the above amounts by 3.45 mol and the partial pressures are then obtained by multiplying the mole fraction by the total pressure (1.20 atm):

	N_2	O_2	Ar
Mole fraction:	0.780	0.210	0.0096
Partial pressure/atm:	0.936	0.252	0.012

Self-test 1A.2 When carbon dioxide is taken into account, the mass percentages are 75.52 (N_2), 23.15 (O_2), 1.28 (Ar), and 0.046 (CO_2). What are the partial pressures when the total pressure is 0.900 atm?

Answer: 0.703, 0.189, 0.0084, and 0.00027 atm

Checklist of concepts

☐ **1.** The **physical state** of a sample of a substance, its physical condition, is defined by its physical properties.

☐ **2.** **Mechanical equilibrium** is the condition of equality of pressure on either side of a shared movable wall.

☐ **3.** An **equation of state** is an equation that interrelates the variables that define the state of a substance.

☐ **4.** Boyle's and Charles's laws are examples of a **limiting law**, a law that is strictly true only in a certain limit, in this case $p \to 0$.

☐ **5.** An **isotherm** is a line in a graph that corresponds to a single temperature.

☐ **6.** An **isobar** is a line in a graph that corresponds to a single pressure.

☐ **7.** An **isochore** is a line in a graph that corresponds to a single volume.

☐ **8.** A **perfect gas** is a gas that obeys the perfect gas law under all conditions.

☐ **9.** **Dalton's law** states that the pressure exerted by a mixture of (perfect) gases is the sum of the pressures that each one would exert if it occupied the container alone.

Checklist of equations

Property	Equation	Comment	Equation number
Relation between temperature scales	$T/\mathrm{K} = \theta/^\circ\mathrm{C} + 273.15$	273.15 is exact	1A.1
Perfect gas law	$pV = nRT$	Valid for real gases in the limit $p \to 0$	1A.4
Partial pressure	$p_J = x_J p$	Valid for all gases	1A.6
Mole fraction	$x_J = n_J/n$ $n = n_A + n_B + \cdots$	Definition	1A.7

TOPIC 1B The kinetic model

➤ Why do you need to know this material?

This material illustrates an important skill in science: the ability to extract quantitative information from a qualitative model. Moreover, the model is used in the discussion of the transport properties of gases (Topic 16A), reaction rates in gases (Topic 18A), and catalysis (Topic 19C).

➤ What is the key idea?

A gas consists of molecules of negligible size in ceaseless random motion and obeying the laws of classical mechanics in their collisions.

➤ What do you need to know already?

You need to be aware of Newton's second law of motion, that the acceleration of a body is proportional to the force acting on it, and the conservation of linear momentum (*The chemist's toolkit* 3).

In the **kinetic theory** of gases (which is sometimes called the *kinetic-molecular theory*, KMT) it is assumed that the only contribution to the energy of the gas is from the kinetic energies of the molecules. The kinetic model is one of the most remarkable—and arguably most beautiful—models in physical chemistry, for from a set of very slender assumptions, powerful quantitative conclusions can be reached.

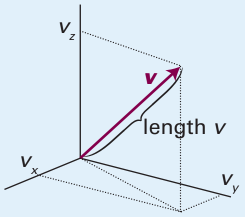
1B.1 The model

The kinetic model is based on three assumptions:

1. The gas consists of molecules of mass m in ceaseless random motion obeying the laws of classical mechanics.
2. The size of the molecules is negligible, in the sense that their diameters are much smaller than the average distance travelled between collisions; they are 'point-like'.
3. The molecules interact only through brief elastic collisions.

The chemist's toolkit 3 Momentum and force

The **speed**, v, of a body is defined as the rate of change of position. The **velocity**, $\boldsymbol{v}$, defines the direction of travel as well as the rate of motion, and particles travelling at the same speed but in different directions have different velocities. As shown in Sketch 1, the velocity can be depicted as an arrow in the direction of travel, its length being the speed v and its components v_x, v_y, and v_z along three perpendicular axes. These components have a sign: $v_x = +5\,\mathrm{m\,s^{-1}}$, for instance, indicates that a body is moving in the positive x-direction, whereas $v_x = -5\,\mathrm{m\,s^{-1}}$ indicates that it is moving in the opposite direction. The length of the arrow (the speed) is related to the components by Pythagoras' theorem: $v^2 = v_x^2 + v_y^2 + v_z^2$.



Sketch 1

The concepts of classical mechanics are commonly expressed in terms of the **linear momentum**, $\boldsymbol{p}$, which is defined as

$$\boldsymbol{p} = m\boldsymbol{v}$$

Linear momentum [definition]

Momentum also mirrors velocity in having a sense of direction; bodies of the same mass and moving at the same speed but in different directions have different linear momenta.

Acceleration, $\boldsymbol{a}$, is the rate of change of velocity. A body accelerates if its speed changes. A body also accelerates if its speed remains unchanged but its direction of motion changes. According to Newton's **second law of motion**, the acceleration of a body of mass m is proportional to the force, $\boldsymbol{F}$, acting on it:

$$\boldsymbol{F} = m\boldsymbol{a}$$

Force

Because $m\boldsymbol{v}$ is the linear momentum and $\boldsymbol{a}$ is the rate of change of velocity, $m\boldsymbol{a}$ is the rate of change of momentum. Therefore, an alternative statement of Newton's second law is that the force is equal to the rate of change of momentum. Newton's law indicates that the acceleration occurs in the same direction as the force acts. If, for an isolated system, no external force acts, then there is no acceleration. This statement is the **law of conservation of momentum**: that the momentum of a body is constant in the absence of a force acting on the body.

An **elastic collision** is a collision in which the total translational kinetic energy of the molecules is conserved.

(a) Pressure and molecular speeds

From the very economical assumptions of the kinetic model, it is possible to derive an expression that relates the pressure and volume of a gas.

How is that done? 1B.1 Using the kinetic model to derive an expression for the pressure of a gas

Consider the arrangement in Fig. 1B.1, and then follow these steps.

Step 1 *Set up the calculation of the change in momentum*

When a particle of mass m that is travelling with a component of velocity v_x parallel to the x-axis collides with the wall on the right and is reflected, its linear momentum changes from mv_x before the collision to $-mv_x$ after the collision (when it is travelling in the opposite direction). The x-component of momentum therefore changes by $2mv_x$ on each collision (the y- and z-components are unchanged). Many molecules collide with the wall in an interval Δt, and the total change of momentum is the product of the change in momentum of each molecule multiplied by the number of molecules that reach the wall during the interval.

Step 2 *Calculate the change in momentum*

Because a molecule with velocity component v_x travels a distance $v_x\Delta t$ along the x-axis in an interval Δt, all the molecules within a distance $v_x\Delta t$ of the wall strike it if they are travelling towards it (Fig. 1B.2). It follows that if the wall has area A, then all the particles in a volume $A \times v_x\Delta t$ reach the wall (if they are travelling towards it). The number density of particles is nN_A/V, where n is the total amount of molecules in the container of volume V and N_A is Avogadro's constant. It follows that the number of molecules in the volume $Av_x\Delta t$ is $(nN_A/V) \times Av_x\Delta t$.

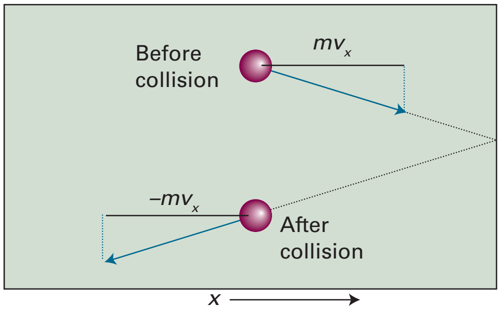


Figure 1B.1 The pressure of a gas arises from the impact of its molecules on the walls. In an elastic collision of a molecule with a wall perpendicular to the x-axis, the x-component of velocity is reversed but the y- and z-components are unchanged.

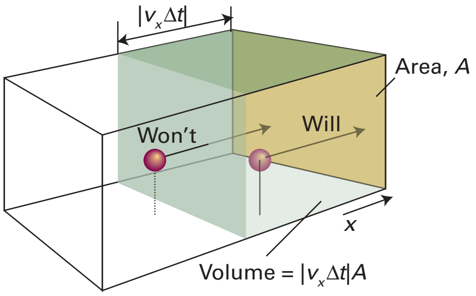


Figure 1B.2 A molecule will reach the wall on the right within an interval of time Δt if it is within a distance $v_x\Delta t$ of the wall and travelling to the right.

At any instant, half the particles are moving to the right and half are moving to the left. Therefore, the average number of collisions with the wall during the interval Δt is $\frac{1}{2}nN_AAv_x\Delta t/V$. The total momentum change in that interval is the product of this number and the change $2mv_x$:

$$\text{Momentum change} = \frac{nN_AAv_x\Delta t}{2V} \times 2mv_x$$

$$= \frac{n\overbrace{mN_A}^{M}Av_x^2\Delta t}{V} = \frac{nMAv_x^2\Delta t}{V}$$

Step 3 *Calculate the force*

The rate of change of momentum, the change of momentum divided by the interval Δt during which it occurs, is

$$\text{Rate of change of momentum} = \frac{nMAv_x^2}{V}$$

According to Newton's second law of motion this rate of change of momentum is equal to the force.

Step 4 *Calculate the pressure*

The pressure is this force ($nMAv_x^2/V$) divided by the area (A) on which the impacts occur. The areas cancel, leaving

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

Not all the molecules travel with the same velocity, so the detected pressure, p, is the average (denoted $\langle\ldots\rangle$) of the quantity just calculated:

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

The average values of v_x^2, v_y^2, and v_z^2 are all the same, and because $v^2 = v_x^2 + v_y^2 + v_z^2$, it follows that $\langle v_x^2\rangle = \frac{1}{3}\langle v^2\rangle$.

At this stage it is useful to define the **root-mean-square speed**, v_{rms}, as the square root of the mean of the squares of the speeds, v, of the molecules. Therefore

$$v_{rms} = \langle v^2\rangle^{1/2} \tag{1B.1}$$

Root-mean-square speed [definition]

The mean square speed in the expression for the pressure can therefore be written $\langle v_x^2\rangle = \frac{1}{3}\langle v^2\rangle = \frac{1}{3}v_{\mathrm{rms}}^2$ to give

$$pV = \tfrac{1}{3}nMv_{\mathrm{rms}}^2 \qquad (1B.2)$$

Relation between pressure and volume [KMT]

This equation is one of the key results of the kinetic model. If the root-mean-square speed of the molecules depends only on the temperature, then at constant temperature

$$pV = \text{constant}$$

which is the content of Boyle's law. The task now is to show that the right-hand side of eqn 1B.2 is equal to nRT.

(b) The Maxwell–Boltzmann distribution of speeds

In a gas the speeds of individual molecules span a wide range, and the collisions in the gas ensure that their speeds are ceaselessly changing. Before a collision, a molecule may be travelling rapidly, but after a collision it may be accelerated to a higher speed, only to be slowed again by the next collision. To evaluate the root-mean-square speed it is necessary to know the fraction of molecules that have a given speed at any instant. The fraction of molecules that have speeds in the range v to $v + \mathrm{d}v$ is proportional to the width of the range, and is written $f(v)\mathrm{d}v$, where $f(v)$ is called the **distribution of speeds**. An expression for this distribution can be found by recognizing that the energy of the molecules is entirely kinetic, and then using the Boltzmann distribution to describe how this energy is distributed over the molecules.

How is that done? 1B.2 Deriving the distribution of speeds

The starting point for this derivation is the Boltzmann distribution (see the text's *Prologue*).

Step 1 *Write an expression for the distribution of the kinetic energy*

The Boltzmann distribution implies that the fraction of molecules with velocity components v_x, v_y, and v_z is proportional to an exponential function of their kinetic energy: $f(v) = K\mathrm{e}^{-\varepsilon/kT}$, where K is a constant of proportionality. The kinetic energy is

$$\varepsilon = \tfrac{1}{2}mv_x^2 + \tfrac{1}{2}mv_y^2 + \tfrac{1}{2}mv_z^2$$

Therefore, use the relation $a^{x+y+z} = a^x a^y a^z$ to write

$$f(v) = K\mathrm{e}^{-(mv_x^2+mv_y^2+mv_z^2)/2kT} = K\mathrm{e}^{-mv_x^2/2kT}\mathrm{e}^{-mv_y^2/2kT}\mathrm{e}^{-mv_z^2/2kT}$$

The distribution factorizes into three terms as $f(v) = f(v_x)f(v_y)f(v_z)$ and $K = K_xK_yK_z$, with

$$f(v_x) = K_x\mathrm{e}^{-mv_x^2/2kT}$$

and likewise for the other two coordinates.

Step 2 *Determine the constants* K_x, K_y, *and* K_z

To determine the constant K_x, note that a molecule must have a velocity component somewhere in the range $-\infty < v_x < \infty$, so integration over the full range of possible values of v_x must give a total probability of 1:

$$\int_{-\infty}^{\infty} f(v_x)\mathrm{d}v_x = 1$$

(See *The chemist's toolkit* 4 for the principles of integration.) Substitution of the expression for $f(v_x)$ then gives

$$1 = K_x\overbrace{\int_{-\infty}^{\infty}\mathrm{e}^{-mv_x^2/2kT}\mathrm{d}v_x}^{\text{Integral G.1}} = K_x\left(\frac{2\pi kT}{m}\right)^{1/2}$$

Therefore, $K_x = (m/2\pi kT)^{1/2}$ and

$$f(v_x) = \left(\frac{m}{2\pi kT}\right)^{1/2}\mathrm{e}^{-mv_x^2/2kT} \qquad (1B.3)$$

The expressions for $f(v_y)$ and $f(v_z)$ are analogous.

Step 3 *Write a preliminary expression for* $f(v_x)f(v_y)f(v_z)\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z$

The probability that a molecule has a velocity in the range v_x to $v_x + \mathrm{d}v_x$, v_y to $v_y + \mathrm{d}v_y$, v_z to $v_z + \mathrm{d}v_z$, is

$$\begin{aligned} f(v_x)f(v_y)f(v_z)\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z &= \left(\frac{m}{2\pi kT}\right)^{3/2}\overbrace{\mathrm{e}^{-mv_x^2/2kT}\mathrm{e}^{-mv_y^2/2kT}\mathrm{e}^{-mv_z^2/2kT}}^{\mathrm{e}^{-m(v_x^2+v_y^2+v_z^2)/2kT}} \\ &\quad\times \mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z \\ &= \left(\frac{m}{2\pi kT}\right)^{3/2}\mathrm{e}^{-mv^2/2kT}\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z \end{aligned}$$

where $v^2 = v_x^2 + v_y^2 + v_z^2$.

Step 3 *Calculate the probability that a molecule has a speed in the range* v *to* $v + \mathrm{d}v$

To evaluate the probability that a molecule has a speed in the range v to $v + \mathrm{d}v$ regardless of direction, think of the three velocity components as defining three coordinates in 'velocity space', with the same properties as ordinary space except that the axes are labelled (v_x, v_y, v_z) instead of (x, y, z). Just as the volume element in ordinary space is $\mathrm{d}x\mathrm{d}y\mathrm{d}z$, so the volume element in velocity space is $\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z$. The sum of all the volume elements in ordinary space that lie at a distance r from the centre is the volume of a spherical shell of radius r and thickness $\mathrm{d}r$. That volume is the product of the surface area of the shell,

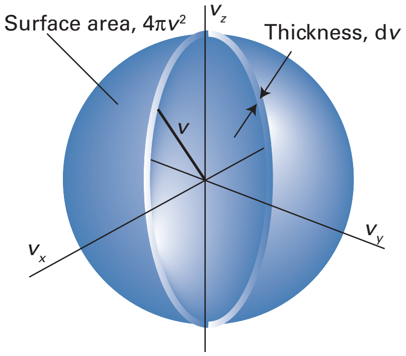


Figure 1B.3 To evaluate the probability that a molecule has a speed in the range v to $v + \mathrm{d}v$, evaluate the total probability that the molecule will have a speed that is anywhere in a thin shell of radius $v = (v_x^2 + v_y^2 + v_z^2)^{1/2}$ and thickness dv.

$4\pi r^2$, and its thickness dr, and is therefore $4\pi r^2\mathrm{d}r$. Similarly, the analogous volume in velocity space is the volume of a shell of radius v and thickness dv, namely $4\pi v^2\mathrm{d}v$ (Fig. 1B.3). Now, because $f(v_x)f(v_y)f(v_z)$, the term in blue in the last equation, depends only on v^2, and has the same value everywhere in a shell of radius v, the total probability of the molecules possessing a speed in the range v to $v + \mathrm{d}v$ is the product of the term in blue and the volume of the shell of radius v and thickness dv. If this probability is written $f(v)\mathrm{d}v$, it follows that

$$f(v)\mathrm{d}v = 4\pi v^2\mathrm{d}v\left(\frac{m}{2\pi kT}\right)^{3/2}\mathrm{e}^{-mv^2/2kT}$$

and $f(v)$ itself, after minor rearrangement, is

$$f(v) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2\mathrm{e}^{-mv^2/2kT}$$

Because $R = N_\mathrm{A}k$ (Table 1B.1), $m/k = mN_\mathrm{A}/R = M/R$, it follows that

$$f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2\mathrm{e}^{-Mv^2/2RT} \qquad \text{(1B.4)}$$

Maxwell–Boltzmann distribution [KMT]

The function $f(v)$ is called the **Maxwell–Boltzmann distribution of speeds**. Note that, in common with other distribution functions, $f(v)$ acquires physical significance only after it is multiplied by the range of speeds of interest.

Table 1B.1 The (molar) gas constant*

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

* The gas constant is now defined as $R = N_\mathrm{A}k$, where N_A is Avogadro's constant and k is Boltzmann's constant.

The chemist's toolkit 4 Integration

Integration is concerned with the areas under curves. The **integral** of a function $f(x)$, which is denoted $\int f(x)\mathrm{d}x$ (the symbol $\int$ is an elongated S denoting a sum), between the two values $x = a$ and $x = b$ is defined by imagining the x-axis as divided into strips of width δx and evaluating the following sum:

$$\int_a^b f(x)\mathrm{d}x = \lim_{\delta x \to 0}\sum_i f(x_i)\delta x$$

Integration [definition]

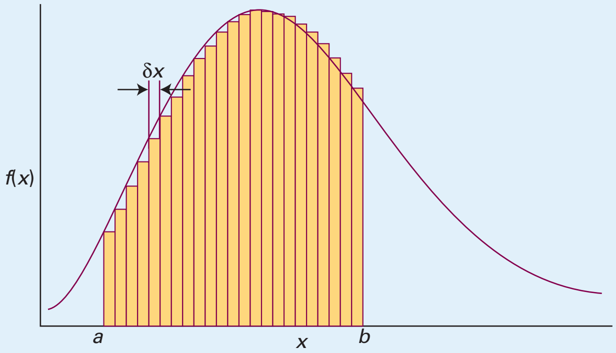
As can be appreciated from Sketch 1, the integral is the area under the curve between the limits a and b. The function to be integrated is called the **integrand**. It is an astonishing mathematical fact that the integral of a function is the inverse of the differential of that function. In other words, if differentiation of f is followed by integration of the resulting function, the result is the original function f (to within a constant).

The integral in the preceding equation with the limits specified is called a **definite integral**. If it is written without the limits specified, it is called an **indefinite integral**. If the result of carrying out an indefinite integration is $g(x) + C$, where C is a constant, the following procedure is used to evaluate the corresponding definite integral:

$$I = \int_a^b f(x)\mathrm{d}x = \{g(x) + C\}\Big|_a^b = \{g(b) + C\} - \{g(a) + C\}$$
$$= g(b) - g(a)$$

Definite integral

Note that the constant of integration disappears. The definite and indefinite integrals encountered in this text are listed in the *Resource section*. They may also be calculated by using mathematical software.



Sketch 1

The important features of the Maxwell–Boltzmann distribution are as follows (and are shown pictorially in Fig. 1B.4):

Physical interpretation

- Equation 1B.4 includes a decaying exponential function (more specifically, a Gaussian function). Its presence implies that the fraction of molecules with very high speeds is very small because e^{-x^2} becomes very small when x is large.
- The factor $M/2RT$ multiplying v^2 in the exponent is large when the molar mass, M, is large, so the exponential factor goes most rapidly towards zero when M is large. That is, heavy molecules are unlikely to be found with very high speeds.
- The opposite is true when the temperature, T, is high: then the factor $M/2RT$ in the exponent is small, so the exponential factor falls towards zero relatively slowly as v increases. In other words, a greater fraction of the molecules can be expected to have high speeds at high temperatures than at low temperatures.
- A factor v^2 (the term before the e) multiplies the exponential. This factor goes to zero as v goes to zero, so the fraction of molecules with very low speeds will also be very small whatever their mass.
- The remaining factors (the term in parentheses in eqn 1B.4 and the 4π) simply ensure that, when the fractions are summed over the entire range of speeds from zero to infinity, the result is 1.

(c) Mean values

With the Maxwell–Boltzmann distribution in hand, it is possible to calculate the mean value of any power of the speed by evaluating the appropriate integral. For instance, to evaluate the fraction, F, of molecules with speeds in the range v_1 to v_2 evaluate the integral

$$F(v_1,v_2)=\int_{v_1}^{v_2} f(v)\mathrm{d}v \qquad (1B.5)$$

This integral is the area under the graph of f as a function of v and, except in special cases, has to be evaluated numerically by using mathematical software (Fig. 1B.5). The average value of v^n is calculated as

$$\langle v^n\rangle=\int_0^\infty v^n f(v)\mathrm{d}v \qquad (1B.6)$$

In particular, integration with $n=2$ results in the mean square speed, $\langle v^2\rangle$, of the molecules at a temperature T:

$$\langle v^2\rangle=\frac{3RT}{M} \qquad (1B.7)$$

Mean square speed [KMT]

It follows that the root-mean-square speed of the molecules of the gas is

$$v_{\mathrm{rms}}=\langle v^2\rangle^{1/2}=\left(\frac{3RT}{M}\right)^{1/2} \qquad (1B.8)$$

Root-mean-square speed [KMT]

which is proportional to the square root of the temperature and inversely proportional to the square root of the molar mass. That is, the higher the temperature, the higher the root-mean-square speed of the molecules, and, at a given temperature, heavy molecules travel more slowly than light molecules.

The important conclusion, however, is that when eqn 1B.8 is substituted into eqn 1B.2, the result is $pV = nRT$, which is the equation of state of a perfect gas. This conclusion confirms that the kinetic model can be regarded as a model of a perfect gas.

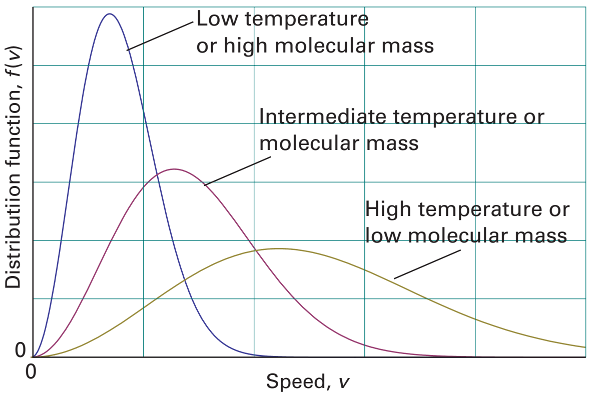


Figure 1B.4 The distribution of molecular speeds with temperature and molar mass. Note that the most probable speed (corresponding to the peak of the distribution) increases with temperature and with decreasing molar mass, and simultaneously the distribution becomes broader.

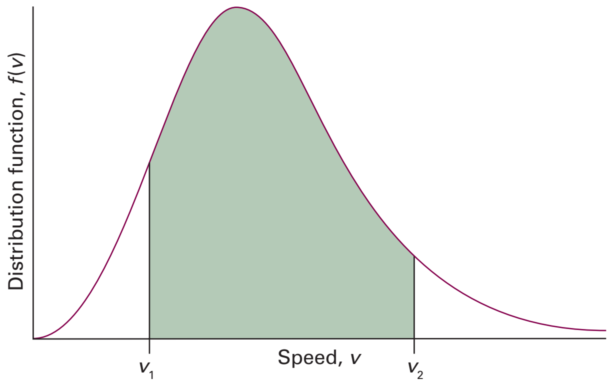


Figure 1B.5 To calculate the probability that a molecule will have a speed in the range v_1 to v_2, integrate the distribution between those two limits; the integral is equal to the area under the curve between the limits, as shown shaded here.

Example 1B.1 Calculating the mean speed of molecules in a gas

Calculate $v_{\rm rms}$ and the mean speed, $v_{\rm mean}$, of N_2 molecules at 25 °C.

Collect your thoughts The root-mean-square speed is calculated from eqn 1B.8, with $M = 28.02\,{\rm g\,mol^{-1}}$ (that is, $0.028\,02\,{\rm kg\,mol^{-1}}$) and $T = 298\,{\rm K}$. The mean speed is obtained by evaluating the integral

$$v_{\rm mean} = \int_0^\infty v f(v)\,{\rm d}v$$

with $f(v)$ given in eqn 1B.3. Use either mathematical software or the integrals listed in the *Resource section* and note that $1\,{\rm J} = 1\,{\rm kg\,m^2\,s^{-2}}$.

The solution The root-mean-square speed is

$$v_{\rm rms} = \left\{\frac{3\times(8.3145\,{\rm J\,K^{-1}\,mol^{-1}})\times(298\,{\rm K})}{0.028\,02\,{\rm kg\,mol^{-1}}}\right\}^{1/2} = 515\,{\rm m\,s^{-1}}$$

The integral required for the calculation of $v_{\rm mean}$ is

$$v_{\rm mean} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\overbrace{\int_0^\infty v^3{\rm e}^{-Mv^2/2RT}\,{\rm d}v}^{\text{Integral G.4}}$$
$$= 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\times\tfrac{1}{2}\left(\frac{2RT}{M}\right)^2 = \left(\frac{8RT}{\pi M}\right)^{1/2}$$

Substitution of the data then gives

$$v_{\rm mean} = \left(\frac{8\times(8.3145\,{\rm J\,K^{-1}\,mol^{-1}})\times(298\,{\rm K})}{\pi\times(0.028\,02\,{\rm kg\,mol^{-1}})}\right)^{1/2} = 475\,{\rm m\,s^{-1}}$$

Self-test 1B.1 Confirm that eqn 1B.7 follows from eqn 1B.6.

As shown in *Example* 1B.1, the Maxwell–Boltzmann distribution can be used to evaluate the **mean speed**, $v_{\rm mean}$, of the molecules in a gas:

$$v_{\rm mean} = \left(\frac{8RT}{\pi M}\right)^{1/2} = \left(\frac{8}{3\pi}\right)^{1/2} v_{\rm rms} \qquad (1B.9)$$

Mean speed [KMT]

The **most probable speed**, $v_{\rm mp}$, can be identified from the location of the peak of the distribution by differentiating $f(v)$ with respect to v and looking for the value of v at which the derivative is zero (other than at $v = 0$ and $v = \infty$; see Problem 1B.11):

$$v_{\rm mp} = \left(\frac{2RT}{M}\right)^{1/2} = \left(\frac{2}{3}\right)^{1/2} v_{\rm rms} \qquad (1B.10)$$

Most probable speed [KMT]

Figure 1B.6 summarizes these results.

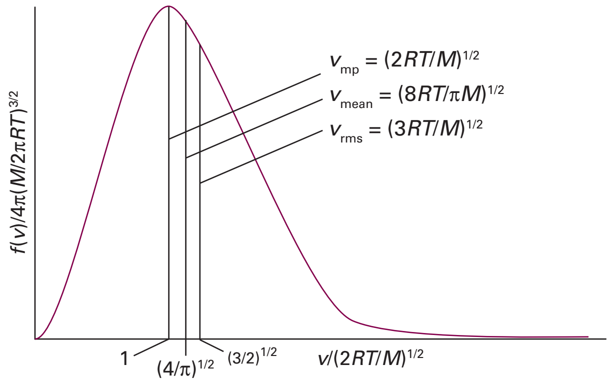


Figure 1B.6 A summary of the conclusions that can be deduced from the Maxwell distribution for molecules of molar mass M at a temperature T: $v_{\rm mp}$ is the most probable speed, $v_{\rm mean}$ is the mean speed, and $v_{\rm rms}$ is the root-mean-square speed.

The **mean relative speed**, $v_{\rm rel}$, the mean speed with which one molecule approaches another of the same kind, can also be calculated from the distribution:

$$v_{\rm rel} = 2^{1/2} v_{\rm mean} \qquad (1B.11a)$$

Mean relative speed [KMT, identical molecules]

This result is much harder to derive, but the diagram in Fig. 1B.7 should help to show that it is plausible. For the relative mean speed of two dissimilar molecules of masses $m_{\rm A}$ and $m_{\rm B}$:

$$v_{\rm rel} = \left(\frac{8kT}{\pi\mu}\right)^{1/2} \qquad \mu = \frac{m_{\rm A}m_{\rm B}}{m_{\rm A}+m_{\rm B}} \qquad (1B.11b)$$

Mean relative speed [perfect gas]

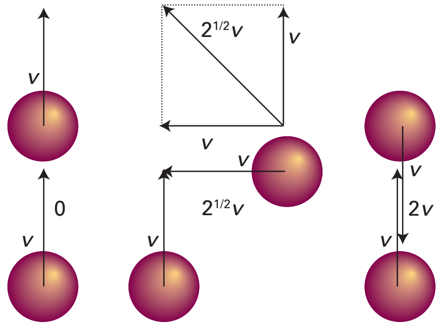


Figure 1B.7 A simplified version of the argument to show that the mean relative speed of molecules in a gas is related to the mean speed. When the molecules are moving in the same direction, the mean relative speed is zero; it is $2v$ when the molecules are approaching each other. A typical mean direction of approach is from the side, and the mean speed of approach is then $2^{1/2}v$. The last direction of approach is the most characteristic, so the mean speed of approach can be expected to be about $2^{1/2}v$. This value is confirmed by more detailed calculation.

Brief illustration 1B.1

As already seen (in *Example* 1B.1), the mean speed of N_2 molecules at 25 °C is 475 m s^{-1}. It follows from eqn 1B.11a that their relative mean speed is

$$v_{\text{rel}} = 2^{1/2} \times (475\,\text{m}\,\text{s}^{-1}) = 671\,\text{m}\,\text{s}^{-1}$$

1B.2 Collisions

The kinetic model can be used to develop the qualitative picture of a perfect gas, as a collection of ceaselessly moving, colliding molecules, into a quantitative, testable expression. In particular, it provides a way to calculate the average frequency with which molecular collisions occur and the average distance a molecule travels between collisions.

(a) The collision frequency

Although the kinetic model assumes that the molecules are point-like, a 'hit' can be counted as occurring whenever the centres of two molecules come within a distance d of each other, where d, the **collision diameter**, is of the order of the actual diameters of the molecules (for impenetrable hard spheres d is the diameter). The kinetic model can be used to deduce the **collision frequency**, z, the number of collisions made by one molecule divided by the time interval during which the collisions are counted.

How is that done? 1B.3 Using the kinetic model to derive an expression for the collision frequency

Consider the positions of all the molecules except one to be frozen. Then note what happens as this one mobile molecule travels through the gas with a mean relative speed v_{rel} for a time Δt. In doing so it sweeps out a 'collision tube' of cross-sectional area $\sigma = \pi d^2$, length $v_{\text{rel}}\Delta t$ and therefore of volume $\sigma v_{\text{rel}}\Delta t$ (Fig. 1B.8). The number of stationary molecules with centres inside the collision tube is given by the volume V of the tube multiplied by the number density $\mathcal{N} = N/V$, where N is the total number of molecules in the sample, and is $\mathcal{N}\sigma v_{\text{rel}}\Delta t$. The collision frequency z is this number divided by Δt. It follows that

$$z = \sigma v_{\text{rel}} \mathcal{N} \qquad (1\text{B}.12\text{a})$$

Collision frequency [KMT]

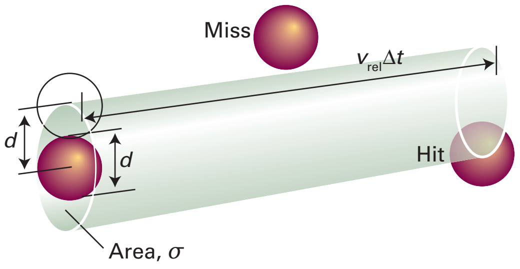


Figure 1B.8 The basis of the calculation of the collision frequency in the kinetic theory of gases.

Table 1B.2 Collision cross-sections*

	σ/nm^2
C_6H_6	0.88
CO_2	0.52
He	0.21
N_2	0.43

* More values are given in the *Resource section*.

The parameter σ is called the **collision cross-section** of the molecules. Some typical values are given in Table 1B.2.

An expression in terms of the pressure of the gas is obtained by using the perfect gas equation and $R = N_A k$ to write the number density in terms of the pressure:

$$\mathcal{N} = \frac{N}{V} = \frac{nN_A}{V} = \frac{nN_A}{nRT/p} = \frac{pN_A}{RT} = \frac{p}{kT}$$

Then

$$z = \frac{\sigma v_{\text{rel}} p}{kT} \qquad (1\text{B}.12\text{b})$$

Collision frequency [KMT]

Equation 1B.12a shows that, at constant volume, the collision frequency increases with increasing temperature, because most molecules are moving faster. Equation 1B.12b shows that, at constant temperature, the collision frequency is proportional to the pressure. The greater the pressure, the greater the number density of molecules in the sample, and the rate at which they encounter one another is greater even though their average speed remains the same.

Brief illustration 1B.2

For an N_2 molecule in a sample at 1.00 atm (101 kPa) and 25 °C, from *Brief illustration* 1B.1 v_{rel} = 671 m s^{-1}. Therefore, from eqn 1B.12b, and taking σ = 0.45 nm^2 (corresponding to 0.45×10^{-18} m^2) from Table 1B.2,

$$z = \frac{(0.45 \times 10^{-18}\,\text{m}^2) \times (671\,\text{m}\,\text{s}^{-1}) \times (1.01 \times 10^5\,\text{Pa})}{(1.381 \times 10^{-23}\,\text{J}\,\text{K}^{-1}) \times (298\,\text{K})}$$

$$= 7.4 \times 10^9\,\text{s}^{-1}$$

so a given molecule collides about 7×10^9 times each second. The timescale of events in gases is becoming clear.

(b) The mean free path

The **mean free path**, λ (lambda), is the average distance a molecule travels between collisions. If a molecule collides with a frequency z, it spends a time $1/z$ in free flight between collisions, and therefore travels a distance $(1/z)v_{\text{rel}}$. It follows that the mean free path is

$$\lambda=\frac{v_{\text{rel}}}{z} \qquad (1\text{B}.13)$$

Mean free path [KMT]

Substitution of the expression for z from eqn 1B.12b gives

$$\lambda=\frac{kT}{\sigma p} \qquad (1\text{B}.14)$$

Mean free path [perfect gas]

Doubling the pressure shortens the mean free path by a factor of 2.

Brief illustration 1B.3

From *Brief illustration* 1B.1 $v_{\text{rel}} = 671\,\text{m}\,\text{s}^{-1}$ for N_2 molecules at 25 °C, and from *Brief illustration* 1B.2 $z = 7.4\times10^{9}\,\text{s}^{-1}$ when the pressure is 1.00 atm. Under these circumstances, the mean free path of N_2 molecules is

$$\lambda=\frac{671\,\text{m}\,\text{s}^{-1}}{7.4\times10^{9}\,\text{s}^{-1}}=9.1\times10^{-8}\,\text{m}$$

or 91 nm, about 10^3 molecular diameters.

Although the temperature appears in eqn 1B.14, in a sample of constant volume, the pressure is proportional to T, so T/p remains constant when the temperature is increased. Therefore, the mean free path is independent of the temperature in a sample of gas provided the volume is constant. In a container of fixed volume the distance between collisions is determined by the number of molecules present in the given volume, not by the speed at which they travel.

In summary, a typical gas (N_2 or O_2) at 1 atm and 25 °C can be thought of as a collection of molecules travelling with a mean speed of about $500\,\text{m}\,\text{s}^{-1}$. Each molecule makes a collision within about 1 ns, and between collisions it travels about 10^3 molecular diameters.

Checklist of concepts

- ☐ **1.** The **kinetic model** of a gas considers only the contribution to the energy from the kinetic energies of the molecules.
- ☐ **2.** Important results from the model include expressions for the pressure and the **root-mean-square speed**.
- ☐ **3.** The **Maxwell–Boltzmann distribution of speeds** gives the fraction of molecules that have speeds in a specified range.
- ☐ **4.** The **collision frequency** is the average number of collisions made by a molecule in an interval divided by the length of the interval.
- ☐ **5.** The **mean free path** is the average distance a molecule travels between collisions.

Checklist of equations

Property	Equation	Comment	Equation number
Pressure of a perfect gas from the kinetic model	$pV=\frac{1}{3}nMv_{\text{rms}}^2$	Kinetic model of a perfect gas	1B.2
Maxwell–Boltzmann distribution of speeds	$f(v)=4\pi(M/2\pi RT)^{3/2}v^2\text{e}^{-Mv^2/2RT}$		1B.4
Root-mean-square speed	$v_{\text{rms}}=(3RT/M)^{1/2}$		1B.8
Mean speed	$v_{\text{mean}}=(8RT/\pi M)^{1/2}$		1B.9
Most probable speed	$v_{\text{mp}}=(2RT/M)^{1/2}$		1B.10
Mean relative speed	$v_{\text{rel}}=(8kT/\pi\mu)^{1/2}$ $\mu=m_Am_B/(m_A+m_B)$		1B.11b
The collision frequency	$z=\sigma v_{\text{rel}}p/kT,\ \sigma=\pi d^2$		1B.12b
Mean free path	$\lambda=v_{\text{rel}}/z$		1B.13

TOPIC 1C Real gases

➤ Why do you need to know this material?

The properties of actual gases, so-called 'real gases', are different from those of a perfect gas. Moreover, the deviations from perfect behaviour give insight into the nature of the interactions between molecules.

➤ What is the key idea?

Attractions and repulsions between gas molecules account for modifications to the isotherms of a gas and account for critical behaviour.

➤ What do you need to know already?

This Topic builds on and extends the discussion of perfect gases in Topic 1A. The principal mathematical technique employed is the use of differentiation to identify a point of inflexion of a curve (*The chemist's toolkit* 5).

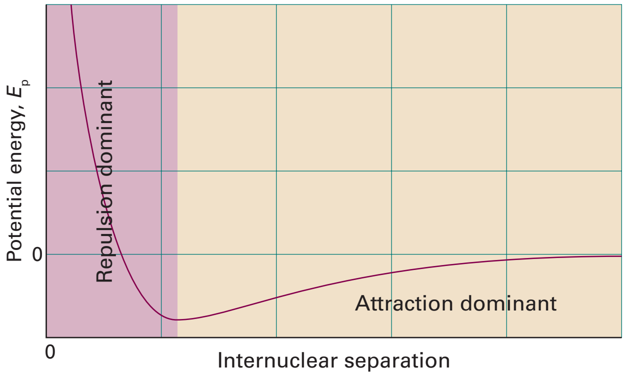


Figure 1C.1 The dependence of the potential energy of two molecules on their internuclear separation. High positive potential energy (at very small separations) indicates that the interactions between them are strongly repulsive at these distances. At intermediate separations, attractive interactions dominate. At large separations (far to the right) the potential energy is zero and there is no interaction between the molecules.

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

1C.1 Deviations from perfect behaviour

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

Repulsive forces are significant only when molecules are almost in contact: they are short-range interactions, even on a scale measured in molecular diameters (Fig. 1C.1). Because they are short-range interactions, repulsions can be expected to be important only when the average separation of the molecules is small. This is the case at high pressure, when many molecules occupy a small volume. On the other hand, attractive intermolecular forces have a relatively long range and are effective over several molecular diameters. They are important when the molecules are fairly close together but not necessarily touching (at the intermediate separations in Fig. 1C.1). Attractive forces are ineffective when the molecules are far apart (well to the right in Fig. 1C.1). Intermolecular forces are also important when the temperature is so low that the molecules travel with such low mean speeds that they can be captured by one another.

The consequences of these interactions are shown by shapes of experimental isotherms (Fig. 1C.2). At low pressures, when the sample occupies a large volume, the molecules are so far apart for most of the time that the intermolecular forces play no significant role, and the gas behaves virtually perfectly. At moderate pressures, when the average separation of the molecules is only a few molecular diameters, the attractive forces dominate the repulsive forces. In this case, the gas can be expected to be more compressible than a perfect gas because the forces help to draw the molecules together. At high pressures, when the average separation of the molecules is small, the repulsive forces dominate and the gas can be expected to be less compressible because now the forces help to drive the molecules apart.

Consider what happens when a sample of gas initially in the state marked A in Fig. 1C.2b is compressed (its volume is reduced) at constant temperature by pushing in a piston. Near A, the pressure of the gas rises in approximate agreement with Boyle's law. Serious deviations from that law begin to appear when the volume has been reduced to B.

At C (which corresponds to about 60 atm for carbon dioxide), all similarity to perfect behaviour is lost, for suddenly the

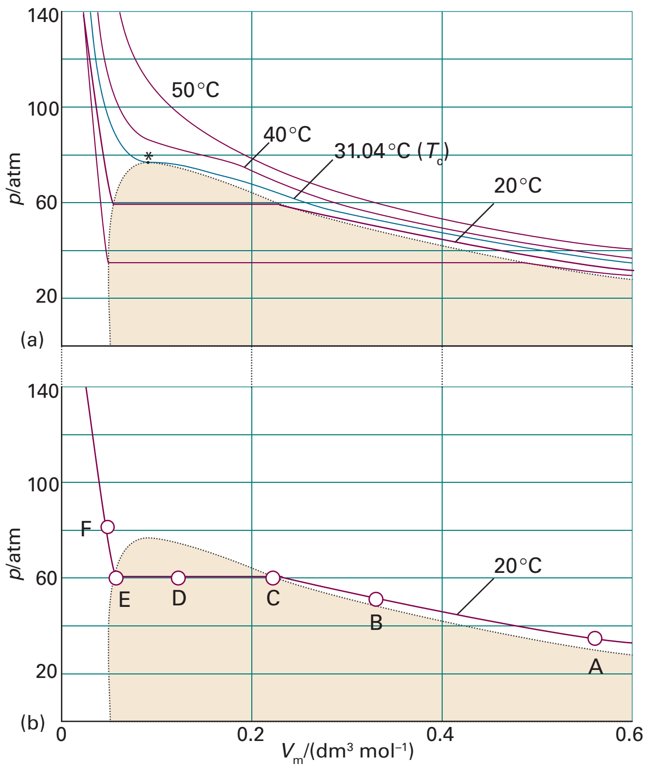


Figure 1C.2 (a) Experimental isotherms of carbon dioxide at several temperatures. The 'critical isotherm', the isotherm at the critical temperature, is at 31.04 °C (in blue). The critical point is marked with a star. (b) As explained in the text, the gas can condense only at and below the critical temperature as it is compressed along a horizontal line (such as CDE). The dotted black curve consists of points like C and E for all isotherms below the critical temperature.

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

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

(a) The compression factor

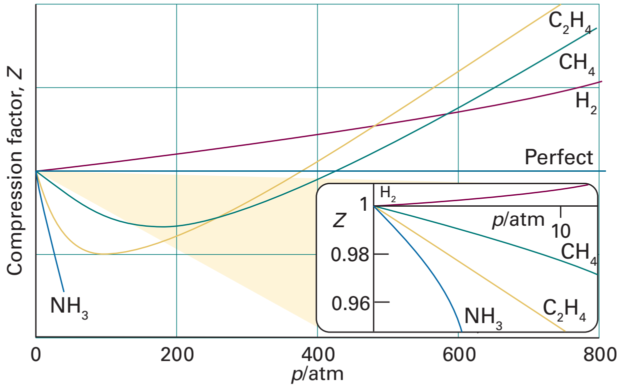


Figure 1C.3 The variation of the compression factor, Z, with pressure for several gases at 0 °C. A perfect gas has $Z = 1$ at all pressures. Notice that, although the curves approach 1 as $p \to 0$, they do so with different slopes.

As a first step in understanding these observations it is useful to introduce the **compression factor**, Z, the ratio of the measured molar volume of a gas, $V_m = V/n$, to the molar volume of a perfect gas, V_m°, at the same pressure and temperature:

$$Z = \frac{V_m}{V_m^{\circ}} \qquad (1C.1)$$

Compression factor [definition]

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

$$pV_m = RTZ \qquad (1C.2)$$

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

Some experimental values of Z are plotted in Fig. 1C.3. At very low pressures, all the gases shown have $Z \approx 1$ and behave nearly perfectly. At high pressures, all the gases have $Z > 1$, signifying that they have a larger molar volume than a perfect gas. Repulsive forces are now dominant. At intermediate pressures, most gases have $Z < 1$, indicating that the attractive forces are reducing the molar volume relative to that of a perfect gas.

Brief illustration 1C.1

The molar volume of a perfect gas at 500 K and 100 bar is $V_m^{\circ} = 0.416\,\mathrm{dm^3\,mol^{-1}}$. The molar volume of carbon dioxide under the same conditions is $V_m = 0.366\,\mathrm{dm^3\,mol^{-1}}$. It follows that at 500 K

$$Z = \frac{0.366\,\mathrm{dm^3\,mol^{-1}}}{0.416\,\mathrm{dm^3\,mol^{-1}}} = 0.880$$

The fact that $Z < 1$ indicates that attractive forces dominate repulsive forces under these conditions.

(b) Virial coefficients

At large molar volumes and high temperatures the real-gas isotherms do not differ greatly from perfect-gas isotherms.

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

	Temperature	
	273 K	600 K
Ar	−21.7	11.9
CO_2	−149.7	−12.4
N_2	−10.5	21.7
Xe	−153.7	−19.6

* More values are given in the *Resource section*.

The small differences suggest that the perfect gas law $pV_\mathrm{m} = RT$ is in fact the first term in an expression of the form

$$pV_\mathrm{m} = RT(1 + B'p + C'p^2 + \cdots) \qquad \text{(1C.3a)}$$

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

$$pV_\mathrm{m} = RT\left(1 + \frac{B}{V_\mathrm{m}} + \frac{C}{V_\mathrm{m}^2} + \cdots\right) \qquad \text{(1C.3b)}$$

Virial equation of state

These two expressions are two versions of the **virial equation of state**.[1] By comparing the expression with eqn 1C.2 it is seen that the term in parentheses in eqn 1C.3b is just the compression factor, Z.

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

Brief illustration 1C.2

To use eqn 1C.3b (up to the B term) to calculate the pressure exerted at 100 K by 0.104 mol $O_2(g)$ in a vessel of volume 0.225 dm^3, begin by calculating the molar volume:

$$V_\mathrm{m} = \frac{V}{n_{\mathrm{O_2}}} = \frac{0.225\,\mathrm{dm^3}}{0.104\,\mathrm{mol}} = 2.16\,\mathrm{dm^3\,mol^{-1}} = 2.16\times10^{-3}\,\mathrm{m^3\,mol^{-1}}$$

Then, by using the value of B found in Table 1C.1 of the *Resource section*,

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

$$= \frac{(8.3145\,\mathrm{J\,mol^{-1}\,K^{-1}})\times(100\,\mathrm{K})}{2.16\times10^{-3}\,\mathrm{m^3\,mol^{-1}}}\left(1 - \frac{1.975\times10^{-4}\,\mathrm{m^3\,mol^{-1}}}{2.16\times10^{-3}\,\mathrm{m^3\,mol^{-1}}}\right)$$

$$= 3.50\times10^5\ \mathrm{Pa,\ or\ 350\,kPa}$$

where $1\,\mathrm{Pa} = 1\,\mathrm{J\,m^{-3}}$. The perfect gas equation of state would give the calculated pressure as 385 kPa, or 10 per cent higher than the value calculated by using the virial equation of state. The difference is significant because under these conditions $B/V_\mathrm{m} \approx 0.1$ which is not negligible relative to 1.

An important point is that although the equation of state of a real gas may coincide with the perfect gas law as $p \to 0$, not all its properties necessarily coincide with those of a perfect gas in that limit. Consider, for example, the value of $\mathrm{d}Z/\mathrm{d}p$, the slope of the graph of compression factor against pressure (see *The chemist's toolkit* 5 for a review of derivatives and differentiation). For a perfect gas $\mathrm{d}Z/\mathrm{d}p = 0$ (because $Z = 1$ at all pressures), but for a real gas from eqn 1C.3a

$$\frac{\mathrm{d}Z}{\mathrm{d}p} = B' + 2pC' + \cdots \to B' \text{ as } p \to 0 \qquad \text{(1C.4a)}$$

However, B' is not necessarily zero, so the slope of Z with respect to p does not necessarily approach 0 (the perfect gas value), as can be seen in Fig. 1C.4. By a similar argument (see *The chemist's toolkit* 5 for evaluating derivatives of this kind),

$$\frac{\mathrm{d}Z}{\mathrm{d}(1/V_\mathrm{m})} \to B \text{ as } V_\mathrm{m} \to \infty \qquad \text{(1C.4b)}$$

Because the virial coefficients depend on the temperature, there may be a temperature at which $Z \to 1$ with zero slope at low pressure or high molar volume (as in Fig. 1C.4). At this temperature, which is called the **Boyle temperature**, T_B, the properties of the real gas do coincide with those of a per-

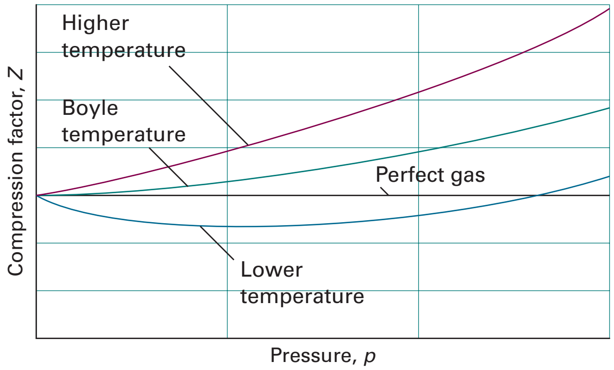


Figure 1C.4 The compression factor, Z, approaches 1 at low pressures, but does so with different slopes. For a perfect gas, the slope is zero, but real gases may have either positive or negative slopes, and the slope may vary with temperature. At the Boyle temperature, the slope is zero at $p = 0$ and the gas behaves perfectly over a wider range of conditions than at other temperatures.

---

[1] The name comes from the Latin word for force. The coefficients are sometimes denoted B_2, B_3, ….

The chemist's toolkit 5 Differentiation

Differentiation is concerned with the slopes of functions, such as the rate of change of a variable with time. The formal definition of the **derivative**, d*f*/d*x*, of a function *f*(*x*) is

$$\frac{\mathrm{d}f}{\mathrm{d}x}=\lim_{\delta x\to 0}\frac{f(x+\delta x)-f(x)}{\delta x}$$

First derivative [definition]

As shown in Sketch 1, the derivative can be interpreted as the slope of the tangent to the graph of *f*(*x*) at a given value of *x*. A positive first derivative indicates that the function slopes upwards (as *x* increases), and a negative first derivative indicates the opposite. It is sometimes convenient to denote the first derivative as *f*′(*x*). The **second derivative**, $\mathrm{d}^2f/\mathrm{d}x^2$, of a function is the derivative of the first derivative (here denoted *f*′):

$$\frac{\mathrm{d}^2f}{\mathrm{d}x^2}=\lim_{\delta x\to 0}\frac{f'(x+\delta x)-f'(x)}{\delta x}$$

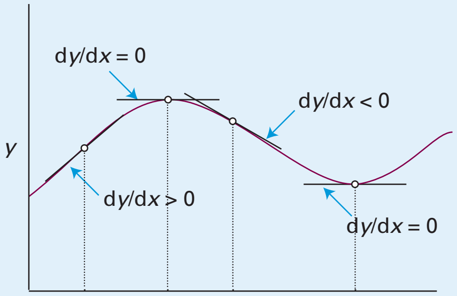
Second derivative [definition]

It is sometimes convenient to denote the second derivative *f*″. As shown in Sketch 2, the second derivative of a function can be interpreted as an indication of the sharpness of the curvature of the function. A positive second derivative indicates that the function is ∪ shaped, and a negative second derivative indicates that it is ∩ shaped. The second derivative is zero at a **point of inflection**, where the first derivative changes sign.

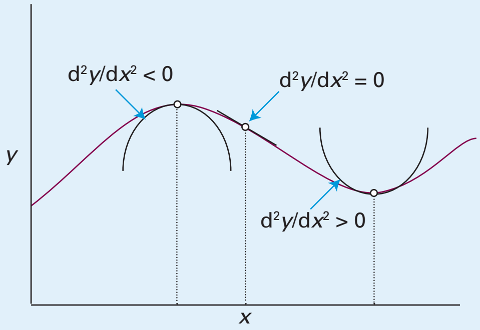
The derivatives of some common functions are as follows:

$$\frac{\mathrm{d}}{\mathrm{d}x}x^n=nx^{n-1}$$

$$\frac{\mathrm{d}}{\mathrm{d}x}\mathrm{e}^{ax}=a\mathrm{e}^{ax}$$



Sketch 1



Sketch 2

$$\frac{\mathrm{d}}{\mathrm{d}x}\sin ax=a\cos ax \qquad \frac{\mathrm{d}}{\mathrm{d}x}\cos ax=-a\sin ax$$

$$\frac{\mathrm{d}}{\mathrm{d}x}\ln ax=\frac{1}{x}$$

It follows from the definition of the derivative that a variety of combinations of functions can be differentiated by using the following rules:

$$\frac{\mathrm{d}}{\mathrm{d}x}(u+v)=\frac{\mathrm{d}u}{\mathrm{d}x}+\frac{\mathrm{d}v}{\mathrm{d}x}$$

$$\frac{\mathrm{d}}{\mathrm{d}x}uv=u\frac{\mathrm{d}v}{\mathrm{d}x}+v\frac{\mathrm{d}u}{\mathrm{d}x}$$

$$\frac{\mathrm{d}}{\mathrm{d}x}\frac{u}{v}=\frac{1}{v}\frac{\mathrm{d}u}{\mathrm{d}x}-\frac{u}{v^2}\frac{\mathrm{d}v}{\mathrm{d}x}$$

It is sometimes convenient to differentiate with respect to a function of *x*, rather than *x* itself. For instance, suppose that

$$f(x)=a+\frac{b}{x}+\frac{c}{x^2}$$

where *a*, *b*, and *c* are constants and you need to evaluate d*f*/d(1/*x*), rather than d*f*/d*x*. To begin, let *y* = 1/*x*. Then $f(y)=a+by+cy^2$ and

$$\frac{\mathrm{d}f}{\mathrm{d}y}=b+2cy$$

Because *y* = 1/*x*, it follows that

$$\frac{\mathrm{d}f}{\mathrm{d}(1/x)}=b+\frac{2c}{x}$$

fect gas as $p\to 0$. According to eqn 1C.4a, *Z* has zero slope as $p\to 0$ if $B'=0$, so at the Boyle temperature $B'=0$. It then follows from eqn 1C.3a that $pV_\mathrm{m}\approx RT_\mathrm{B}$ over a more extended range of pressures than at other temperatures because the first term after 1 (i.e. $B'p$) in the virial equation is zero and $C'p^2$ and higher terms are negligibly small. For helium $T_\mathrm{B}=22.64\,\mathrm{K}$; for air $T_\mathrm{B}=346.8\,\mathrm{K}$; more values are given in Table 1C.2.

(c) Critical constants

There is a temperature, called the **critical temperature**, T_c, which separates two regions of behaviour and plays a special role in the theory of the states of matter. An isotherm slightly below T_c behaves as already described: at a certain pressure, a liquid condenses from the gas and is distinguishable from it by

Table 1C.2 Critical constants of gases*

	p_c/atm	V_c/(cm^3 mol^{-1})	T_c/K	Z_c	T_B/K
Ar	48.0	75.3	150.7	0.292	411.5
CO_2	72.9	94.0	304.2	0.274	714.8
He	2.26	57.8	5.2	0.305	22.64
O_2	50.14	78.0	154.8	0.308	405.9

* More values are given in the *Resource section*.

the presence of a visible surface. If, however, the compression takes place at T_c itself, then a surface separating two phases does not appear and the volumes at each end of the horizontal part of the isotherm have merged to a single point, the **critical point** of the gas. The pressure and molar volume at the critical point are called the **critical pressure**, p_c, and **critical molar volume**, V_c, of the substance. Collectively, p_c, V_c, and T_c are the **critical constants** of a substance (Table 1C.2).

At and above T_c, the sample has a single phase which occupies the entire volume of the container. Such a phase is, by definition, a gas. Hence, the liquid phase of a substance does not form above the critical temperature. The single phase that fills the entire volume when $T > T_c$ may be much denser than considered typical for gases, and the name **supercritical fluid** is preferred.

Brief illustration 1C.3

The critical temperature of oxygen, 155 K, signifies that it is impossible to produce liquid oxygen by compression alone if its temperature is greater than 155 K. To liquefy oxygen the temperature must first be lowered to below 155 K, and then the gas compressed isothermally.

1C.2 The van der Waals equation

Conclusions may be drawn from the virial equations of state only by inserting specific values of the coefficients. It is often useful to have a broader, if less precise, view of all gases, such as that provided by an approximate equation of state.

(a) Formulation of the equation

The equation introduced by J.D. van der Waals in 1873 is an excellent example of an expression that can be obtained by thinking scientifically about a mathematically complicated but physically simple problem; that is, it is a good example of 'model building'.

How is that done? 1C.1 Deriving the van der Waals equation of state

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

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

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

The pressure depends on both the frequency of collisions with the walls and the force of each collision. Both the frequency of the collisions and their force are reduced by the attractive interaction, which acts with a strength proportional to the number of interacting molecules and therefore to the molar concentration, n/V, of molecules in the sample. Because both the frequency and the force of the collisions are reduced by the attractive interactions, the pressure is reduced in proportion to the square of this concentration. If the reduction of pressure is written as $a(n/V)^2$, where a is a positive constant characteristic of each gas, the combined effect of the repulsive and attractive forces is the **van der Waals equation**:

$$p = \frac{nRT}{V - nb} - a\frac{n^2}{V^2} \qquad \text{(1C.5a)}$$

van der Waals equation of state

The constants a and b are called the **van der Waals coefficients**, with a representing the strength of attractive interactions and b that of the repulsive interactions between the molecules. They are characteristic of each gas and taken to be independent of the temperature (Table 1C.3). Although a and b are not precisely defined molecular properties, they correlate with physical properties that reflect the strength of intermolecular interactions, such as critical temperature, vapour pressure, and enthalpy of vaporization.

Table 1C.3 van der Waals coefficients*

	a/(atm dm^6 mol^{-2})	b/(10^{-2} dm^3 mol^{-1})
Ar	1.337	3.20
CO_2	3.610	4.29
He	0.0341	2.38
Xe	4.137	5.16

* More values are given in the *Resource section*.

Brief illustration 1C.4

For benzene a = 18.57 atm dm^6 mol^{-2} (1.882 Pa m^6 mol^{-2}) and b = 0.1193 dm^3 mol^{-1} (1.193 × 10^{-4} m^3 mol^{-1}); its normal boiling point is 353 K. Treated as a perfect gas at T = 400 K and p = 1.0 atm, benzene vapour has a molar volume of $V_m = RT/p$ = 33 dm^3 mol^{-1}, so the criterion $V_m >> b$ for perfect gas behaviour is satisfied. It follows that $a/V_m^2 \approx$ 0.017 atm, which is 1.7 per cent of 1.0 atm. Therefore, benzene vapour is expected to deviate only slightly from perfect gas behaviour at this temperature and pressure.

Equation 1C.5a is often written in terms of the molar volume $V_m = V/n$ as

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \qquad \text{(1C.5b)}$$

Example 1C.1 Using the van der Waals equation to estimate a molar volume

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

Collect your thoughts You need to find an expression for the molar volume by solving the van der Waals equation, eqn 1C.5b. To rearrange the equation into a suitable form, multiply both sides by $(V_m - b)V_m^2$, to obtain

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

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

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

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

The solution According to Table 1C.3, a = 3.592 dm^6 atm mol^{-2} and b = 4.267 × 10^{-2} dm^3 mol^{-1}. Under the stated conditions, RT/p = 0.410 dm^3 mol^{-1}. The coefficients in the equation for V_m are therefore

$$b + RT/p = 0.453\,\text{dm}^3\,\text{mol}^{-1}$$
$$a/p = 3.61 \times 10^{-2}\,(\text{dm}^3\,\text{mol}^{-1})^2$$
$$ab/p = 1.55 \times 10^{-3}\,(\text{dm}^3\,\text{mol}^{-1})^3$$

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

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

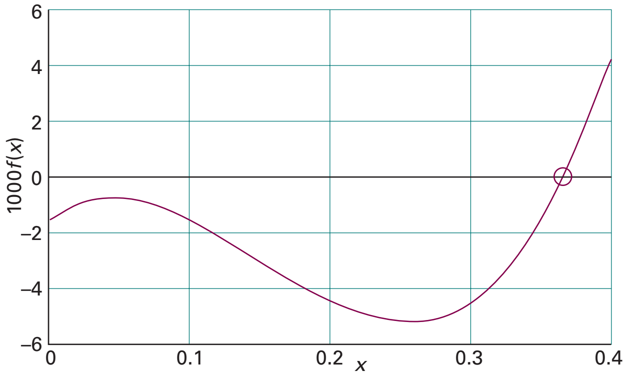


Figure 1C.5 The graphical solution of the cubic equation for V in *Example* 1C.1.

The acceptable root is x = 0.366 (Fig. 1C.5), which implies that V_m = 0.366 dm^3 mol^{-1}. The molar volume of a perfect gas under these conditions is 0.410 dm^3 mol^{-1}.

Self-test 1C.1 Calculate the molar volume of argon at 100 °C and 100 atm on the assumption that it is a van der Waals gas.

Answer: 0.298 dm^3 mol^{-1}

(b) The features of the equation

To what extent does the van der Waals equation predict the behaviour of real gases? It is too optimistic to expect a single, simple expression to be the true equation of state of all substances, and accurate work on gases must resort to the virial equation, use tabulated values of the coefficients at various temperatures, and analyse the system numerically. The advantage of the van der Waals equation, however, is that it is analytical (that is, expressed symbolically) and allows some general conclusions about real gases to be drawn. When the equation fails another equation of state must be used (some are listed in Table 1C.4), yet another must be invented, or the virial equation is used.

The reliability of the equation can be judged by comparing the isotherms it predicts with the experimental isotherms in Fig. 1C.2. Some calculated isotherms are shown in Figs. 1C.6 and 1C.7. Apart from the oscillations below the critical temperature, they do resemble experimental isotherms quite well. The oscillations, the **van der Waals loops**, are unrealistic because they suggest that under some conditions an increase of pressure results in an increase of volume. Therefore they are replaced by horizontal lines drawn so the loops define equal areas above and below the lines: this procedure is called the **Maxwell construction** (**1**). The van der Waals coefficients, such as those in Table 1C.3, are found by fitting the calculated curves to the experimental curves.

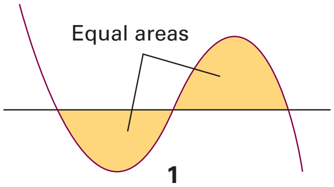


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Table 1C.4 Selected equations of state

	Equation	Reduced form*	Critical constants		
			p_c	V_c	T_c
Perfect gas	$p=\dfrac{nRT}{V}$				
van der Waals	$p=\dfrac{nRT}{V-nb}-\dfrac{n^2a}{V^2}$	$p_r=\dfrac{8T_r}{3V_r-1}-\dfrac{3}{V_r^2}$	$\dfrac{a}{27b^2}$	$3b$	$\dfrac{8a}{27bR}$
Berthelot	$p=\dfrac{nRT}{V-nb}-\dfrac{n^2a}{TV^2}$	$p_r=\dfrac{8T_r}{3V_r-1}-\dfrac{3}{T_rV_r^2}$	$\dfrac{1}{12}\left(\dfrac{2aR}{3b^3}\right)^{1/2}$	$3b$	$\dfrac{2}{3}\left(\dfrac{2a}{3bR}\right)^{1/2}$
Dieterici	$p=\dfrac{nRTe^{-na/RTV}}{V-nb}$	$p_r=\dfrac{T_re^{2(1-1/T_rV_r)}}{2V_r-1}$	$\dfrac{a}{4e^2b^2}$	$2b$	$\dfrac{a}{4bR}$
Virial	$p=\dfrac{nRT}{V}\left\{1+\dfrac{nB(T)}{V}+\dfrac{n^2C(T)}{V^2}+\cdots\right\}$				

* Reduced variables are defined as $X_r = X/X_c$ with $X = p$, V_m, and T. Equations of state are sometimes expressed in terms of the molar volume, $V_m = V/n$.

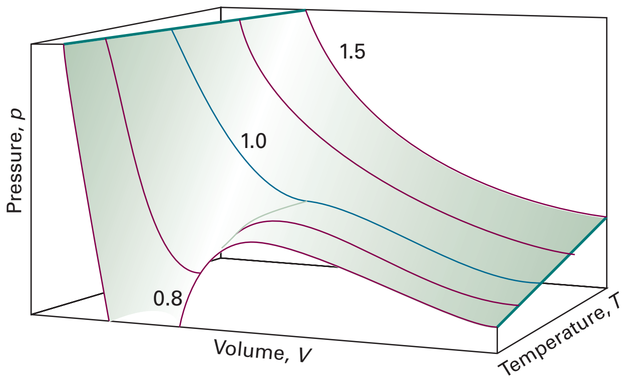


Figure 1C.6 The surface of possible states allowed by the van der Waals equation. The curves drawn on the surface are isotherms, labelled with the value of T/T_c, and correspond to the isotherms in Fig. 1C.7.

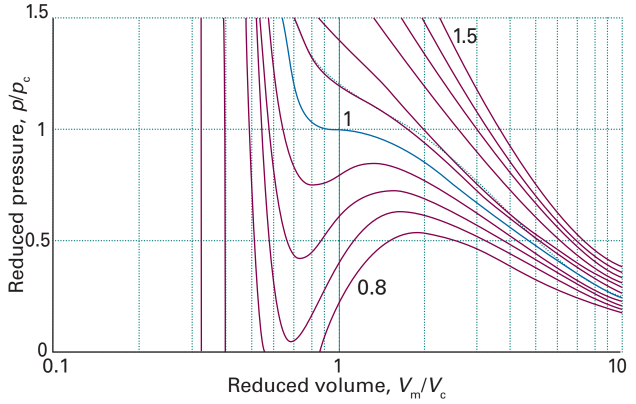


Figure 1C.7 Van der Waals isotherms at several values of T/T_c. The van der Waals loops are normally replaced by horizontal straight lines. The critical isotherm is the isotherm for $T/T_c = 1$, and is shown in blue.

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

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

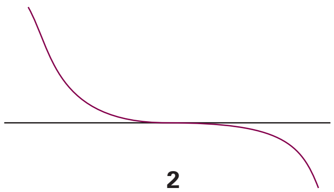
When the temperature is high, RT may be so large that the first term in eqn 1C.5b greatly exceeds the second. Furthermore, if the molar volume is large in the sense $V_m >> b$, then the denominator $V_m - b \approx V_m$. Under these conditions, the equation reduces to $p = RT/V_m$, the perfect gas equation.

2. Liquids and gases coexist when the attractive and repulsive effects are in balance.

The van der Waals loops occur when both terms in eqn 1C.5b have similar magnitudes. The first term arises from the kinetic energy of the molecules and their repulsive interactions; the second represents the effect of the attractive interactions.

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

For $T < T_c$, the calculated isotherms oscillate, and each one passes through a minimum followed by a maximum. These extrema converge as $T \to T_c$ and coincide at $T = T_c$; at the critical point the curve has a flat inflexion (2). From the properties of curves, an inflexion of this type occurs when both the first and second derivatives are zero. Hence, the critical constants can be found by calculating these derivatives and setting them equal to zero at the critical point:



2

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

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

The solutions of these two equations (and using eqn 1C.5b to calculate p_c from V_c and T_c; see Problem 1C.12) are

$$V_c=3b \qquad p_c=\frac{a}{27b^2} \qquad T_c=\frac{8a}{27bR} \tag{1C.6}$$

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

$$Z_c=\frac{p_cV_c}{RT_c}=\frac{3}{8} \tag{1C.7}$$

for all gases that are described by the van der Waals equation near the critical point. Table 1C.2 shows that although $Z_c < \frac{3}{8} = 0.375$, it is approximately constant (at 0.3) and the discrepancy is reasonably small.

(c) The principle of corresponding states

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

$$V_r=\frac{V_m}{V_c} \qquad p_r=\frac{p}{p_c} \qquad T_r=\frac{T}{T_c} \tag{1C.8}$$

Reduced variables [definition]

If the reduced pressure of a gas is given, its actual pressure is calculated by using $p = p_rp_c$, and likewise for the volume and temperature. Van der Waals, who first tried this procedure, hoped that gases confined to the same reduced volume, V_r, at the same reduced temperature, T_r, would exert the same reduced pressure, p_r. The hope was largely fulfilled (Fig. 1C.8). The illustration shows the dependence of the compression factor on the reduced pressure for a variety of gases at various reduced temperatures. The success of the procedure is strikingly clear: compare this graph with Fig. 1C.3, where similar data are plotted without using reduced variables.

The observation that real gases at the same reduced volume and reduced temperature exert the same reduced pressure is called the **principle of corresponding states**. The principle is only an approximation. It works best for gases composed of spherical molecules; it fails, sometimes badly, when the molecules are non-spherical or polar.

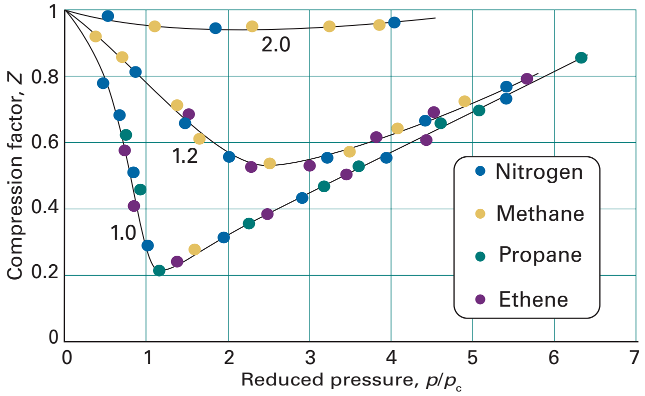


Figure 1C.8 The compression factors of four of the gases shown in Fig. 1C.3 plotted using reduced variables. The curves are labelled with the reduced temperature $T_r = T/T_c$. The use of reduced variables organizes the data on to single curves.

Brief illustration 1C.5

The critical constants of argon and carbon dioxide are given in Table 1C.2. Suppose argon is at 23 atm and 200 K, its reduced pressure and temperature are then

$$p_r=\frac{23\,\text{atm}}{48.0\,\text{atm}}=0.48 \qquad T_r=\frac{200\,\text{K}}{150.7\,\text{K}}=1.33$$

For carbon dioxide to be in a corresponding state, its pressure and temperature would need to be

$$p=0.48\times(72.9\,\text{atm})=35\,\text{atm} \qquad T=1.33\times304.2\,\text{K}=405\,\text{K}$$

The van der Waals equation sheds some light on the principle. When eqn 1C.5b is expressed in terms of the reduced variables it becomes

$$p_rp_c=\frac{RT_rT_c}{V_rV_c-b}-\frac{a}{V_r^2V_c^2}$$

Now express the critical constants in terms of a and b by using eqn 1C.6:

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

and, after multiplying both sides by $27b^2/a$, reorganize it into

$$p_r=\frac{8T_r}{3V_r-1}-\frac{3}{V_r^2} \tag{1C.9}$$

This equation has the same form as the original, but the coefficients a and b, which differ from gas to gas, have disappeared. It follows that if the isotherms are plotted in terms of the reduced variables (as done in fact in Fig. 1C.7 without drawing attention to the fact), then the same curves are obtained whatever the gas. This is precisely the content of the principle of corresponding states, so the van der Waals equation is compatible with it.

Looking for too much significance in this apparent triumph is mistaken, because other equations of state also accommodate the principle. In fact, any equation of state (such as those in Table 1C.4) with two parameters playing the roles of a and b can be manipulated into a reduced form. The observation that real gases obey the principle approximately amounts to saying that the effects of the attractive and repulsive interactions can each be approximated in terms of a single parameter. The importance of the principle is then not so much its theoretical interpretation but the way that it enables the properties of a range of gases to be coordinated on to a single diagram (e.g. Fig. 1C.8 instead of Fig. 1C.3).

Checklist of concepts

☐ **1.** The extent of deviations from perfect behaviour is summarized by introducing the **compression factor**.
☐ **2.** The **virial equation** is an empirical extension of the perfect gas equation that summarizes the behaviour of real gases over a range of conditions.
☐ **3.** The isotherms of a real gas introduce the concept of **critical behaviour**.
☐ **4.** A gas can be liquefied by pressure alone only if its temperature is at or below its **critical temperature**.
☐ **5.** The **van der Waals equation** is a model equation of state for a real gas expressed in terms of two parameters, one (a) representing molecular attractions and the other (b) representing molecular repulsions.
☐ **6.** The van der Waals equation captures the general features of the behaviour of real gases, including their critical behaviour.
☐ **7.** The properties of real gases are coordinated by expressing their equations of state in terms of **reduced variables**.

Checklist of equations

Property	Equation	Comment	Equation number
Compression factor	$Z = V_m/V_m^\circ$	Definition	1C.1
Virial equation of state	$pV_m = RT(1 + B/V_m + C/V_m^2 + \cdots)$	B, C depend on temperature	1C.3b
van der Waals equation of state	$p = nRT/(V - nb) - a(n/V)^2$	a parameterizes attractions, b parameterizes repulsions	1C.5a
Reduced variables	$X_r = X/X_c$	$X = p$, V_m, or T	1C.8

FOCUS 1 The properties of gases

TOPIC 1A The perfect gas

Discussion questions

D1A.1 Explain how the perfect gas equation of state arises by combination of Boyle's law, Charles's law, and Avogadro's principle.

D1A.2 Explain the term 'partial pressure' and explain why Dalton's law is a limiting law.

Exercises

E1A.1(a) Express (i) 108 kPa in torr and (ii) 0.975 bar in atmospheres.
E1A.1(b) Express (i) 22.5 kPa in atmospheres and (ii) 770 Torr in pascals.

E1A.2(a) Could 131 g of xenon gas in a vessel of volume 1.0 $\mathrm{dm^3}$ exert a pressure of 20 atm at 25 °C if it behaved as a perfect gas? If not, what pressure would it exert?
E1A.2(b) Could 25 g of argon gas in a vessel of volume 1.5 $\mathrm{dm^3}$ exert a pressure of 2.0 bar at 30 °C if it behaved as a perfect gas? If not, what pressure would it exert?

E1A.3(a) A perfect gas undergoes isothermal compression, which reduces its volume by 2.20 $\mathrm{dm^3}$. The final pressure and volume of the gas are 5.04 bar and 4.65 $\mathrm{dm^3}$, respectively. Calculate the original pressure of the gas in (i) bar, (ii) atm.
E1A.3(b) A perfect gas undergoes isothermal compression, which reduces its volume by 1.80 $\mathrm{dm^3}$. The final pressure and volume of the gas are 1.97 bar and 2.14 $\mathrm{dm^3}$, respectively. Calculate the original pressure of the gas in (i) bar, (ii) torr.

E1A.4(a) A car tyre (an automobile tire) was inflated to a pressure of 24 lb $\mathrm{in^{-2}}$ (1.00 atm = 14.7 lb $\mathrm{in^{-2}}$) on a winter's day when the temperature was −5 °C. What pressure will be found, assuming no leaks have occurred and that the volume is constant, on a subsequent summer's day when the temperature is 35 °C? What complications should be taken into account in practice?
E1A.4(b) A sample of hydrogen gas was found to have a pressure of 125 kPa when the temperature was 23 °C. What can its pressure be expected to be when the temperature is 11 °C?

E1A.5(a) A sample of 255 mg of neon occupies 3.00 $\mathrm{dm^3}$ at 122 K. Use the perfect gas law to calculate the pressure of the gas.
E1A.5(b) A homeowner uses $4.00 \times 10^3\ \mathrm{m^3}$ of natural gas in a year to heat a home. Assume that natural gas is all methane, CH_4, and that methane is a perfect gas for the conditions of this problem, which are 1.00 atm and 20 °C. What is the mass of gas used?

E1A.6(a) At 500 °C and 93.2 kPa, the mass density of sulfur vapour is 3.710 kg $\mathrm{m^{-3}}$. What is the molecular formula of sulfur under these conditions?
E1A.6(b) At 100 °C and 16.0 kPa, the mass density of phosphorus vapour is 0.6388 kg $\mathrm{m^{-3}}$. What is the molecular formula of phosphorus under these conditions?

E1A.7(a) Calculate the mass of water vapour present in a room of volume 400 $\mathrm{m^3}$ that contains air at 27 °C on a day when the relative humidity is 60 per cent. *Hint:* Relative humidity is the prevailing partial pressure of water vapour expressed as a percentage of the vapour pressure of water vapour at the same temperature (in this case, 35.6 mbar).
E1A.7(b) Calculate the mass of water vapour present in a room of volume 250 $\mathrm{m^3}$ that contains air at 23 °C on a day when the relative humidity is 53 per cent (in this case, 28.1 mbar).

E1A.8(a) Given that the mass density of air at 0.987 bar and 27 °C is 1.146 kg $\mathrm{m^{-3}}$, calculate the mole fraction and partial pressure of nitrogen and oxygen assuming that (i) air consists only of these two gases, (ii) air also contains 1.0 mole per cent Ar.
E1A.8(b) A gas mixture consists of 320 mg of methane, 175 mg of argon, and 225 mg of neon. The partial pressure of neon at 300 K is 8.87 kPa. Calculate (i) the volume and (ii) the total pressure of the mixture.

E1A.9(a) The mass density of a gaseous compound was found to be 1.23 kg $\mathrm{m^{-3}}$ at 330 K and 20 kPa. What is the molar mass of the compound?
E1A.9(b) In an experiment to measure the molar mass of a gas, 250 $\mathrm{cm^3}$ of the gas was confined in a glass vessel. The pressure was 152 Torr at 298 K, and after correcting for buoyancy effects, the mass of the gas was 33.5 mg. What is the molar mass of the gas?

E1A.10(a) The densities of air at −85 °C, 0 °C, and 100 °C are 1.877 g $\mathrm{dm^{-3}}$, 1.294 g $\mathrm{dm^{-3}}$, and 0.946 g $\mathrm{dm^{-3}}$, respectively. From these data, and assuming that air obeys Charles' law, determine a value for the absolute zero of temperature in degrees Celsius.
E1A.10(b) A certain sample of a gas has a volume of 20.00 $\mathrm{dm^3}$ at 0 °C and 1.000 atm. A plot of the experimental data of its volume against the Celsius temperature, θ, at constant p, gives a straight line of slope 0.0741 $\mathrm{dm^3\ {}^\circ C^{-1}}$. From these data alone (without making use of the perfect gas law), determine the absolute zero of temperature in degrees Celsius.

E1A.11(a) A vessel of volume 22.4 $\mathrm{dm^3}$ contains 2.0 mol $H_2(g)$ and 1.0 mol $N_2(g)$ at 273.15 K. Calculate (i) the mole fractions of each component, (ii) their partial pressures, and (iii) their total pressure.
E1A.11(b) A vessel of volume 22.4 $\mathrm{dm^3}$ contains 1.5 mol $H_2(g)$ and 2.5 mol $N_2(g)$ at 273.15 K. Calculate (i) the mole fractions of each component, (ii) their partial pressures, and (iii) their total pressure.

Problems

P1A.1 A manometer consists of a U-shaped tube containing a liquid. One side is connected to the apparatus and the other is open to the atmosphere. The pressure p inside the apparatus is given $p = p_{\mathrm{ex}} + \rho g h$, where p_{ex} is the external pressure, ρ is the mass density of the liquid in the tube, $g = 9.806\ \mathrm{m\ s^{-2}}$ is the acceleration of free fall, and h is the difference in heights of the liquid in the two sides of the tube. (The quantity $\rho g h$ is the *hydrostatic pressure* exerted by a column of liquid.) (i) Suppose the liquid in a manometer is mercury, the external pressure is 760 Torr, and the open side is 10.0 cm higher than the side connected to the apparatus. What is the pressure in the apparatus? The mass density of mercury at 25 °C is 13.55 g $\mathrm{cm^{-3}}$. (ii) In an attempt to determine an accurate value of the gas constant, R, a student heated a container of volume 20.000 $\mathrm{dm^3}$ filled with 0.251 32 g of helium gas to 500 °C and measured the pressure as 206.402 cm in a manometer filled with water at 25 °C. Calculate the value of R from these data. The mass density of water at 25 °C is 0.997 07 g $\mathrm{cm^{-3}}$.

P1A.2 Recent communication with the inhabitants of Neptune have revealed that they have a Celsius-type temperature scale, but based on the melting point (0 °N) and boiling point (100 °N) of their most common substance, hydrogen. Further communications have revealed that the Neptunians know about perfect gas behaviour and they find that in the limit of zero pressure, the value of pV is 28 dm^3 atm at 0 °N and 40 dm^3 atm at 100 °N. What is the value of the absolute zero of temperature on their temperature scale?

P1A.3 The following data have been obtained for oxygen gas at 273.15K. From the data, calculate the best value of the gas constant R.

p/atm	0.750 000	0.500 000	0.250 000
$V_m/(dm^3\,mol^{-1})$	29.8649	44.8090	89.6384

P1A.4 Charles's law is sometimes expressed in the form $V = V_0(1 + \alpha\theta)$, where θ is the Celsius temperature, α is a constant, and V_0 is the volume of the sample at 0 °C. The following values for have been reported for nitrogen at 0 °C:

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

For these data estimate the absolute zero of temperature on the Celsius scale.

P1A.5 Deduce the relation between the pressure and mass density, ρ, of a perfect gas of molar mass M. Confirm graphically, using the following data on methoxymethane (dimethyl ether) at 25 °C, that perfect behaviour is reached at low pressures and find the molar mass of the gas.

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

P1A.6 The molar mass of a newly synthesized fluorocarbon was measured in a gas microbalance. This device consists of a glass bulb forming one end of a beam, the whole surrounded by a closed container. The beam is pivoted, and the balance point is attained by raising the pressure of gas in the container, so increasing the buoyancy of the enclosed bulb. In one experiment, the balance point was reached when the fluorocarbon pressure was 327.10 Torr; for the same setting of the pivot, a balance was reached when CHF_3 ($M = 70.014\,g\,mol^{-1}$) was introduced at 423.22 Torr. A repeat of the experiment with a different setting of the pivot required a pressure of 293.22 Torr of the fluorocarbon and 427.22 Torr of the CHF_3. What is the molar mass of the fluorocarbon? Suggest a molecular formula.

P1A.7 A constant-volume perfect gas thermometer indicates a pressure of 6.69 kPa at the triple point temperature of water (273.16 K). (a) What change of pressure indicates a change of 1.00 K at this temperature? (b) What pressure indicates a temperature of 100.00 °C? (c) What change of pressure indicates a change of 1.00 K at the latter temperature?

P1A.8 A vessel of volume 22.4 dm^3 contains 2.0 mol H_2(g) and 1.0 mol N_2(g) at 273.15 K initially. All the H_2 then reacts with sufficient N_2 to form NH_3. Calculate the partial pressures of the gases in the final mixture and the total pressure.

P1A.9 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 (1 t = 10^3 kg) of SO_2 each day. If this gas is emitted at 800 °C and 1.0 atm, what volume of gas is emitted?

P1A.10 Ozone is a trace atmospheric gas which plays an important role in screening the Earth from harmful ultraviolet radiation, and the abundance of ozone is commonly reported in *Dobson units*. Imagine a column passing up through the atmosphere. The total amount of O_3 in the column divided by its cross-sectional area is reported in Dobson units with 1 Du = 0.4462 mmol m^{-2}. What amount of O_3 (in moles) is found in a column of atmosphere with a cross-sectional area of 1.00 dm^2 if the abundance is 250 Dobson units (a typical midlatitude value)? In the seasonal Antarctic ozone hole, the column abundance drops below 100 Dobson units; how many moles of O_3 are found in such a column of air above a 1.00 dm^2 area? Most atmospheric ozone is found between 10 and 50 km above the surface of the Earth. If that ozone is spread uniformly through this portion of the atmosphere, what is the average molar concentration corresponding to (a) 250 Dobson units, (b) 100 Dobson units?

P1A.11[‡] In a commonly used model of the atmosphere, the atmospheric pressure varies with altitude, h, according to the *barometric formula:*

$$p = p_0 e^{-h/H}$$

where p_0 is the pressure at sea level and H is a constant approximately equal to 8 km. More specifically, $H = RT/Mg$, where M is the average molar mass of air and T is the temperature at the altitude h. This formula represents the outcome of the competition between the potential energy of the molecules in the gravitational field of the Earth and the stirring effects of thermal motion. Derive this relation by showing that the change in pressure dp for an infinitesimal change in altitude dh where the mass density is ρ is $dp = -\rho g dh$. Remember that ρ depends on the pressure. Evaluate (a) the pressure difference between the top and bottom of a laboratory vessel of height 15 cm, and (b) the external atmospheric pressure at a typical cruising altitude of an aircraft (11 km) when the pressure at ground level is 1.0 atm.

P1A.12[‡] Balloons are still used to deploy sensors that monitor meteorological phenomena and the chemistry of the atmosphere. It is possible to investigate some of the technicalities of ballooning by using the perfect gas law. Suppose your balloon has a radius of 3.0 m and that it is spherical. (a) What amount of H_2 (in moles) is needed to inflate it to 1.0 atm in an ambient temperature of 25 °C at sea level? (b) What mass can the balloon lift (the payload) at sea level, where the mass density of air is 1.22 kg m^{-3}? (c) What would be the payload if He were used instead of H_2?

P1A.13[‡] Chlorofluorocarbons such as CCl_3F and CCl_2F_2 have been linked to ozone depletion in Antarctica. In 1994, these gases were found in quantities of 261 and 509 parts per trillion by volume (World Resources Institute, *World resources* 1996–97). Compute the molar concentration of these gases under conditions typical of (a) the mid-latitude troposphere (10 °C and 1.0 atm) and (b) the Antarctic stratosphere (200 K and 0.050 atm). *Hint:* The composition of a mixture of gases can be described by imagining that the gases are separated from one another in such a way that each exerts the same pressure. If one gas is present at very low levels it is common to express its concentration as, for example, 'x parts per trillion by volume'. Then the volume of the separated gas at a certain pressure is $x \times 10^{-12}$ of the original volume of the gas mixture at the same pressure. For a mixture of perfect gases, the volume of each separated gas is proportional to its partial pressure in the mixture and hence to the amount in moles of the gas molecules present in the mixture.

P1A.14 At sea level the composition of the atmosphere is approximately 80 per cent nitrogen and 20 per cent oxygen by mass. At what height above the surface of the Earth would the atmosphere become 90 per cent nitrogen and 10 per cent oxygen by mass? Assume that the temperature of the atmosphere is constant at 25 °C. What is the pressure of the atmosphere at that height? *Hint:* Use a barometric formula, see Problem P1A.11, for each partial pressure.

[‡] These problems were supplied by Charles Trapp and Carmen Giunta.

TOPIC 1B The kinetic model

Discussion questions

D1B.1 Specify and analyse critically the assumptions that underlie the kinetic model of gases.

D1B.2 Provide molecular interpretations for the dependencies of the mean free path on the temperature, pressure, and size of gas molecules.

D1B.3 Use the kinetic model of gases to explain why light gases, such as He, are rare in the Earth's atmosphere but heavier gases, such as O_2, CO_2, and N_2, once formed remain abundant.

Exercises

E1B.1(a) Determine the ratios of (i) the mean speeds, (ii) the mean translational kinetic energies of H_2 molecules and Hg atoms at 20 °C.
E1B.1(b) Determine the ratios of (i) the mean speeds, (ii) the mean translational kinetic energies of He atoms and Hg atoms at 25 °C.

E1B.2(a) Calculate the root-mean-square speeds of H_2 and O_2 molecules at 20 °C.
E1B.2(b) Calculate the root-mean-square speeds of CO_2 molecules and He atoms at 20 °C.

E1B.3(a) Use the Maxwell–Boltzmann distribution of speeds to estimate the fraction of N_2 molecules at 400 K that have speeds in the range 200–210 $\mathrm{m\,s^{-1}}$. *Hint:* The fraction of molecules with speeds in the range v to $v + \mathrm{d}v$ is equal to $f(v)\mathrm{d}v$, where $f(v)$ is given by eqn 1B.4.
E1B.3(b) Use the Maxwell–Boltzmann distribution of speeds to estimate the fraction of CO_2 molecules at 400 K that have speeds in the range 400–405 $\mathrm{m\,s^{-1}}$. See the hint in Exercise E1B.3(a).

E1B.4(a) What is the relative mean speed of N_2 and H_2 molecules in a gas at 25 °C?
E1B.4(b) What is the relative mean speed of O_2 and N_2 molecules in a gas at 25 °C?

E1B.5(a) Calculate the most probable speed, the mean speed, and the mean relative speed of CO_2 molecules at 20 °C.
E1B.5(b) Calculate the most probable speed, the mean speed, and the mean relative speed of H_2 molecules at 20 °C.

E1B.6(a) Evaluate the collision frequency of H_2 molecules in a gas at 1.00 atm and 25 °C.
E1B.6(b) Evaluate the collision frequency of O_2 molecules in a gas at 1.00 atm and 25 °C.

E1B.7(a) Assume that air consists of N_2 molecules with a collision diameter of 395 pm. Calculate (i) the mean speed of the molecules, (ii) the mean free path, (iii) the collision frequency in air at 1.0 atm and 25 °C.
E1B.7(b) The best laboratory vacuum pump can generate a vacuum of about 1 nTorr. At 25 °C and assuming that air consists of N_2 molecules with a collision diameter of 395 pm, calculate at this pressure (i) the mean speed of the molecules, (ii) the mean free path, (iii) the collision frequency in the gas.

E1B.8(a) At what pressure does the mean free path of argon at 20 °C become comparable to the diameter of a 100 $\mathrm{cm^3}$ vessel that contains it? Take $\sigma = 0.36\,\mathrm{nm^2}$.
E1B.8(b) At what pressure does the mean free path of argon at 20 °C become comparable to 10 times the diameters of the atoms themselves? Take $\sigma = 0.36\,\mathrm{nm^2}$.

E1B.9(a) At an altitude of 20 km the temperature is 217 K and the pressure is 0.050 atm. What is the mean free path of N_2 molecules? ($\sigma = 0.43\,\mathrm{nm^2}$).
E1B.9(b) At an altitude of 15 km the temperature is 217 K and the pressure is 12.1 kPa. What is the mean free path of N_2 molecules? ($\sigma = 0.43\,\mathrm{nm^2}$).

Problems

P1B.1 A rotating slotted-disc apparatus consists of five coaxial 5.0 cm diameter discs separated by 1.0 cm, the radial slots being displaced by 2.0° between neighbours. The relative intensities, I, of the detected beam of Kr atoms for two different temperatures and at a series of rotation rates were as follows:

ν/Hz	20	40	80	100	120
I (40 K)	0.846	0.513	0.069	0.015	0.002
I (100 K)	0.592	0.485	0.217	0.119	0.057

Find the distributions of molecular velocities, $f(v_x)$, at these temperatures, and check that they conform to the theoretical prediction for a one-dimensional system for this low-pressure, collision-free system.

P1B.2 Consider molecules that are confined to move in a plane (a two-dimensional gas). Calculate the distribution of speeds and determine the mean speed of the molecules at a temperature T.

P1B.3 A specially constructed velocity-selector accepts a beam of molecules from an oven at a temperature T but blocks the passage of molecules with a speed greater than the mean. What is the mean speed of the emerging beam, relative to the initial value? Treat the system as one-dimensional.

P1B.4 What, according to the Maxwell–Boltzmann distribution, is the proportion of gas molecules having (i) more than, (ii) less than the root mean square speed? (iii) What are the proportions having speeds greater and smaller than the mean speed? *Hint:* Use mathematical software to evaluate the integrals.

P1B.5 Calculate the fractions of molecules in a gas that have a speed in a range Δv at the speed nv_{mp} relative to those in the same range at v_{mp} itself. This calculation can be used to estimate the fraction of very energetic molecules (which is important for reactions). Evaluate the ratio for $n = 3$ and $n = 4$.

P1B.6 Derive an expression for $\langle v^n \rangle^{1/n}$ from the Maxwell–Boltzmann distribution of speeds. *Hint:* You will need the integrals given in the *Resource section*, or use mathematical software.

P1B.7 Calculate the escape velocity (the minimum initial velocity that will take an object to infinity) from the surface of a planet of radius R. What is the value for (i) the Earth, $R = 6.37 \times 10^6$ m, $g = 9.81\,\mathrm{m\,s^{-2}}$, (ii) Mars, $R = 3.38 \times 10^6$ m, $m_{\mathrm{Mars}}/m_{\mathrm{Earth}} = 0.108$. At what temperatures do H_2, He, and O_2 molecules have mean speeds equal to their escape speeds? What proportion of the molecules have enough speed to escape when the temperature is (i) 240 K, (ii) 1500 K? Calculations of this kind are very important in considering the composition of planetary atmospheres.

P1B.8 Plot different Maxwell–Boltzmann speed distributions by keeping the molar mass constant at 100 $\mathrm{g\,mol^{-1}}$ and varying the temperature of the sample between 200 K and 2000 K.

P1B.9 Evaluate numerically the fraction of O_2 molecules with speeds in the range 100 $\mathrm{m\,s^{-1}}$ to 200 $\mathrm{m\,s^{-1}}$ in a gas at 300 K and 1000 K.