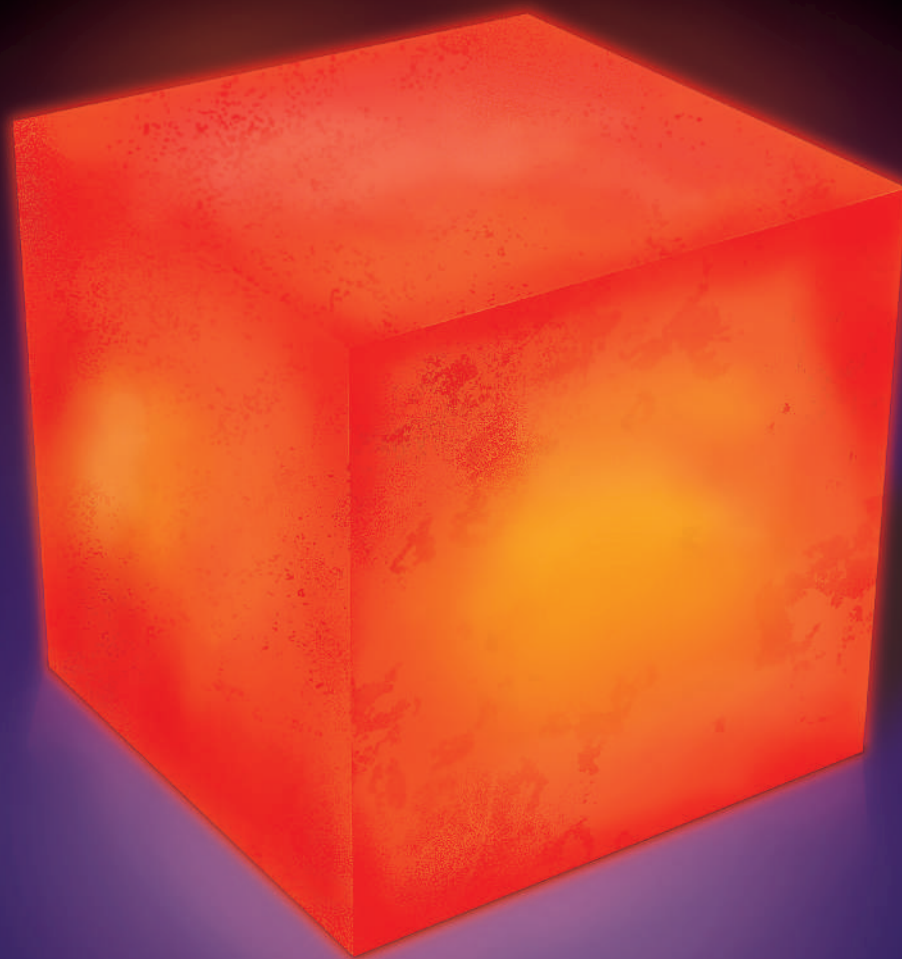


PHYSICAL CHEMISTRY

Thermodynamics, Structure, and Change

Tenth Edition



Peter Atkins | Julio de Paula

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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	$R=N_{\text{A}}k$	8.314 4621		J K ⁻¹ mol ⁻¹
Faraday's constant	$F=N_{\text{A}}e$	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	$4\pi^*$	10^{-7}	J s ² C ⁻² m ⁻¹
Vacuum permittivity	$\epsilon_0=1/\mu_0c^2$	8.854 187 817	10^{-12}	J ⁻¹ C ² m ⁻¹
	$4\pi\epsilon_0$	1.112 650 056	10^{-10}	J ⁻¹ C ² m ⁻¹
Bohr magneton	$\mu_{\text{B}}=e\hbar/2m_{\text{e}}$	9.274 009 68	10^{-24}	J T ⁻¹
Nuclear magneton	$\mu_{\text{N}}=e\hbar/2m_{\text{p}}$	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	$\gamma_{\text{e}}=-g_{\text{e}}e/2m_{\text{e}}$	-1.001 159 652	10^{10}	C kg ⁻¹
Proton	$\gamma_{\text{p}}=2\mu_{\text{p}}/\hbar$	2.675 222 004	10^8	C kg ⁻¹
Bohr radius	$a_0=4\pi\epsilon_0\hbar^2/e^2m_{\text{e}}$	5.291 772 109	10^{-11}	m
Rydberg constant	$\tilde{R}_{\infty}=m_{\text{e}}e^4/8h^3c\epsilon_0^2$	1.097 373 157	10^5	cm ⁻¹
	$hc\tilde{R}_{\infty}/e$	13.605 692 53		eV
Fine-structure constant	$\alpha=\mu_0e^2c/2h$	7.297 352 5698	10^{-3}	
	α^{-1}	1.370 359 990 74	10^2	
Second radiation constant	$c_2=hc/k$	1.438 777 0	10^{-2}	m K
Stefan-Boltzmann constant	$\sigma=2\pi^5k^4/15h^3c^2$	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.

PHYSICAL CHEMISTRY

Thermodynamics, Structure, and Change

Tenth edition

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PREFACE

This new edition is the product of a thorough revision of content and its presentation. Our goal is to make the book even more accessible to students and useful to instructors by enhancing its flexibility. We hope that both categories of user will perceive and enjoy the renewed vitality of the text and the presentation of this demanding but engaging subject.

The text is still divided into three parts, but each chapter is now presented as a series of short and more readily mastered *Topics*. This new structure allows the instructor to tailor the text within the time constraints of the course as omissions will be easier to make, emphases satisfied more readily, and the trajectory through the subject modified more easily. For instance, it is now easier to approach the material either from a ‘quantum first’ or a ‘thermodynamics first’ perspective because it is no longer necessary to take a linear path through chapters. Instead, students and instructors can match the choice of Topics to their learning objectives. We have been very careful not to presuppose or impose a particular sequence, except where it is demanded by common sense.

We open with a *Foundations* chapter, which reviews basic concepts of chemistry and physics used through the text. Part 1 now carries the title *Thermodynamics*. New to this edition is coverage of ternary phase diagrams, which are important in applications of physical chemistry to engineering and materials science. Part 2 (*Structure*) continues to cover quantum theory, atomic and molecular structure, spectroscopy, molecular assemblies, and statistical thermodynamics. Part 3 (*Change*) has lost a chapter dedicated to catalysis, but not the material. Enzyme-catalysed reactions are now in Chapter 20, and heterogeneous catalysis is now part of a new Chapter 22 focused on surface structure and processes.

As always, we have paid special attention to helping students navigate and master this material. Each chapter opens with a brief summary of its Topics. Then each Topic begins with three questions: ‘Why do you need to know this material?’, ‘What is the key idea?’, and ‘What do you need to know already?’. The answers to the third question point to other Topics that we consider appropriate to have studied or at least to refer to as background to the current Topic. The *Checklists* at the end of each

Topic are useful distillations of the most important concepts and equations that appear in the exposition.

We continue to develop strategies to make mathematics, which is so central to the development of physical chemistry, accessible to students. In addition to associating *Mathematical background* sections with appropriate chapters, we give more help with the development of equations: we motivate them, justify them, and comment on the steps taken to derive them. We also added a new feature: *The chemist’s toolkit*, which offers quick and immediate help on a concept from mathematics or physics.

This edition has more worked *Examples*, which require students to organize their thoughts about how to proceed with complex calculations, and more *Brief illustrations*, which show how to use an equation or deploy a concept in a straightforward way. Both have *Self-tests* to enable students to assess their grasp of the material. We have structured the end-of-chapter *Discussion questions*, *Exercises*, and *Problems* to match the grouping of the Topics, but have added Topic- and Chapter-crossing *Integrated activities* to show that several Topics are often necessary to solve a single problem. The *Resource section* has been restructured and augmented by the addition of a list of integrals that are used (and referred to) throughout the text.

We are, of course, alert to the development of electronic resources and have made a special effort in this edition to encourage the use of web-based tools, which are identified in the *Using the book* section that follows this preface. Important among these tools are *Impact* sections, which provide examples of how the material in the chapters is applied in such diverse areas as biochemistry, medicine, environmental science, and materials science.

Overall, we have taken this opportunity to refresh the text thoroughly, making it even more flexible, helpful, and up to date. As ever, we hope that you will contact us with your suggestions for its continued improvement.

PWA, Oxford
JdeP, Portland

USING THE BOOK

For the tenth edition of *Physical Chemistry: Thermodynamics, Structure, and Change* we have tailored the text even more closely to the needs of students. First, the material within each chapter has been reorganized into discrete topics to improve accessibility, clarity, and flexibility. Second, in addition to

the variety of learning features already present, we have significantly enhanced the mathematics support by adding new Chemist's toolkit boxes, and checklists of key concepts at the end of each topic.

Organizing the information

► Innovative new structure

Each chapter has been reorganized into short topics, making the text more readable for students and more flexible for instructors. Each topic opens with a comment on why it is important, a statement of the key idea, and a brief summary of the background needed to understand the topic.

► Why do you need to know this material?

Because chemistry is about matter and the changes that it can undergo, both physically and chemically, the properties of matter underlie the entire discussion in this book.

► What is the key idea?

The bulk properties of matter are related to the identities

► Notes on good practice

Our *Notes on good practice* will help you avoid making common mistakes. 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).

applicable only to perfect gases (and other idealized systems) are labelled, as here, with a number in blue.

A note on good practice Although the term 'ideal gas' is almost universally used in place of 'perfect gas', there are reasons for preferring the latter term. In an ideal system the interactions between molecules in a mixture are all the same. In a perfect gas not only are the interactions all the same but they are in fact zero. Few, though, make this useful distinction.

Equation A.5, the **perfect gas equation**, is a summary of three empirical conclusions, namely Boyle's law ($p \propto 1/V$ at

► Resource section

The comprehensive *Resource section* at the end of the book contains a table of integrals, data tables, a summary of conventions about units, and character tables. Short extracts of these tables often appear in the topics themselves, principally to give an idea of the typical values of the physical quantities we are introducing.

RESOURCE SECTION

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► Checklist of concepts

A *Checklist of key concepts* is provided at the end of each topic so that you can tick off those concepts which you feel you have mastered.

Checklist of concepts

- ☐ 1. The **entropy** acts as a signpost of spontaneous change.
- ☐ 2. Entropy change is defined in terms of heat transactions (the **Clausius definition**).
- ☐ 3. The **Boltzmann formula** defines absolute entropies in terms of the number of ways of achieving a configuration.

Presenting the mathematics

► Justifications

Mathematical development is an intrinsic part of physical chemistry, and to achieve full understanding you need to see how a particular expression is obtained and if any assumptions have been made. The *Justifications* are set off from the text to let you adjust the level of detail to meet your current needs and make it easier to review material.

Justification 3A.1 Heating accompanying reversible adiabatic expansion

This *Justification* is based on two features of the cycle. One feature is that the two temperatures T_h and T_c in eqn 3A.7 lie on the same adiabat in Fig. 3A.7. The second feature is that the energy transferred as heat during the two isothermal stages are

$$q_h = nRT_h \ln \frac{V_B}{V_A} \quad q_c = nRT_c \ln \frac{V_D}{V_C}$$

We now show that the two volume ratios are related in a very simple way. From the relation between temperature and volume for reversible adiabatic processes ($VT^\gamma = \text{constant}$, Topic 2D):

► Chemist's toolkits

New to the tenth edition, the *Chemist's toolkits* are succinct reminders of the mathematical concepts and techniques that you will need in order to understand a particular derivation being described in the main text.

The chemist's toolkit A.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

► Mathematical backgrounds

There are six *Mathematical background* sections dispersed throughout the text. They cover in detail the main mathematical concepts that you need to understand in order to be able to master physical chemistry. Each one is located at the end of the chapter to which it is most relevant.

Mathematical background 1 Differentiation

Two of the most important mathematical techniques in the physical sciences are differentiation and integration. They occur throughout the subject, and it is essential to be aware of the procedures involved.

MB1.1 Differentiation: definitions

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**, df/dx , of a function $f(x)$ is

► 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, the integral used, and so on. An annotation can also be a reminder of the significance of an individual term in an expression. We sometimes color 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.

$$w = -nRT \int_{V_i}^{V_f} \frac{dV}{V} \stackrel{\text{Integral A.2}}{\cong} -nRT \ln \frac{V_f}{V_i}$$

Perfect gas,
reversible,
isothermal Work of expansion (2A.9)

► Checklists of equations

You don't have to memorize every equation in the text. A checklist at the end of each topic summarizes the most important equations and the conditions under which they apply.

Checklist of equations

Property	Equation
Compression factor	$Z = V_m/V_m^\circ$
Virial equation of state	$pV_m = RT(1 + B/V_m + C/V_m^2 + \dots)$
van der Waals equation of state	$p = nRT/(V - nb) - a(n/V)^2$
Reduced variables	$X_r = X_m/X_c$

Setting up and solving problems

► Brief illustrations

A *Brief illustration* shows you how to use equations or concepts that have just been introduced in the text. They help you to learn how to use data, manipulate units correctly, and become familiar with the magnitudes of properties. They are all accompanied by a Self-test question which you can use to monitor your progress.

Brief illustration 1C.5 Corresponding states

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

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

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

$$p = 0.48 \times (72.9 \text{ atm}) = 35 \text{ atm} \quad T = 1.33 \times 304.2 \text{ K} = 405 \text{ K}$$

Self-test 1C.6 What would be the corresponding state of ammonia?

Answer: 53 atm, 539 K

► Worked examples

Worked *Examples* are more detailed illustrations of the application of the material, which require you to assemble and develop concepts and equations. We provide a suggested method for solving the problem and then implement it to reach the answer. Worked examples are also accompanied by *Self-test* questions.

Example 3A.2 Calculating the entropy change for a composite process

Calculate the entropy change when argon at 25 °C and 1.00 bar in a container of volume 0.500 dm³ is allowed to expand to 1.000 dm³ and is simultaneously heated to 100 °C.

Method As remarked in the text, use reversible isothermal expansion to the final volume, followed by reversible heating at constant volume to the final temperature. The entropy change in the first step is given by eqn 3A.16 and that of the second step, provided C_V is independent of temperature, by eqn 3A.20 (with C_V in place of C_p). In each case we need to

► Discussion questions

Discussion questions appear at the end of every chapter, where they are organized by topic. These questions are designed to encourage you to reflect on the material you have just read, and to view it conceptually.

► Exercises and Problems

Exercises and *Problems* are also provided at the end of every chapter, and organized by topic. They prompt you to test your understanding of the topics in that chapter. Exercises are designed as relatively straightforward numerical tests whereas the problems are more challenging. The Exercises come in related pairs, with final numerical answers available on the Book Companion Site for the 'a' questions. Final numerical answers to the odd-numbered problems are also available on the Book Companion Site.

► Integrated activities

At the end of most chapters, you will find questions that cross several topics and chapters, and are designed to help you use your knowledge creatively in a variety of ways. Some of the questions refer to the Living Graphs on the Book Companion Site, which you will find helpful for answering them.

► Solutions manuals

Two solutions manuals have been written by Charles Trapp, Marshall Cady, and Carmen Giunta to accompany this book.

The *Student Solutions Manual* (ISBN 1-4641-2449-3) provides full solutions to the 'a' exercises and to the odd-numbered problems.

TOPIC 3A Entropy

Discussion questions

3A.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.

3A.2 Discuss the significance of the terms 'dispersal' and 'disorder' in the context of the Second Law.

Exercises

3A.1(a) During a hypothetical process, the entropy of a system increases by 125 J K⁻¹ while the entropy of the surroundings decreases by 125 J K⁻¹. Is the process spontaneous?

3A.1(b) During a hypothetical process, the entropy of a system increases by 105 J K⁻¹ while the entropy of the surroundings decreases by 95 J K⁻¹. Is the process spontaneous?

3A.2(a) A certain ideal heat engine uses water at the triple point as the hot source and an organic liquid as the cold sink. It withdraws 10.00 kJ of heat from the hot source and generates 3.00 kJ of work. What is the temperature of the organic liquid?

3A.2(b) A certain ideal heat engine uses water at the triple point as the hot source and an organic liquid as the cold sink. It withdraws 2.71 kJ of heat from the hot source and generates 0.71 kJ of work. What is the temperature of the organic liquid?

The *Instructor's Solutions Manual* provides full solutions to the 'b' exercises and to the even-numbered problems (available to download from the Book Companion Site for registered adopters of the book only).

BOOK COMPANION SITE

The Book Companion Site to accompany *Physical Chemistry: Thermodynamics, Structure, and Change*, tenth edition provides a number of useful teaching and learning resources for students and instructors.

The site can be accessed at:

<http://www.whfreeman.com/pchem10e/>

Instructor resources are available only to registered adopters of the textbook. To register, simply visit <http://www.whfreeman.com/pchem10e/> and follow the appropriate links.

Student resources are openly available to all, without registration.



Materials on the Book Companion Site include:

'Impact' sections

'Impact' sections show how physical chemistry is applied in a variety of modern contexts. New for this edition, the Impacts are linked from the text by QR code images. Alternatively, visit the URL displayed next to the QR code image.

Group theory tables

Comprehensive group theory tables are available to download.

Figures and tables from the book

Instructors 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).

Molecular modeling problems

PDFs containing molecular modeling problems can be downloaded, designed for use with the Spartan Student™ software. However they can also be completed using any modeling software that allows Hartree-Fock, density functional, and MP2 calculations.

Living graphs

These interactive graphs can be used to explore how a property changes as various parameters are changed. Living graphs are sometimes referred to in the Integrated activities at the end of a chapter.

ACKNOWLEDGEMENTS

A book as extensive as this could not have been written without significant input from many individuals. We would like to reiterate our thanks to the hundreds of people who contributed to the first nine editions. Many people gave their advice based on the ninth edition, and others, including students, reviewed the draft chapters for the tenth edition as they emerged. We wish to express our gratitude to the following colleagues:

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Because we prepared this edition at the same time as its sister volume, *Physical Chemistry: Quanta, matter, and change*, it goes without saying that our colleague on that book, Ron Friedman, has had an unconscious but considerable impact on this text too, and we cannot thank him enough for his contribution to this book. Our warm thanks also go to Charles Trapp, Carmen Giunta, and Marshall Cady who once again have produced the *Solutions manuals* that accompany this book and whose comments led us to make a number of improvements. Kerry Karukstis contributed helpfully to the Impacts that are now on the web.

Last, but by no means least, we would also like to thank our two commissioning editors, Jonathan Crowe of Oxford University Press and Jessica Fiorillo of W. H. Freeman & Co., and their teams for their encouragement, patience, advice, and assistance.

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PART ONE

Thermodynamics

Part 1 of the text develops the concepts of thermodynamics, the science of the transformations of energy. Thermodynamics provides a powerful way to discuss equilibria and the direction of natural change in chemistry. Its concepts apply to both physical change, such as fusion and vaporization, and chemical change, including electrochemistry. We see that through the concepts of energy, enthalpy, entropy, Gibbs energy, and the chemical potential it is possible to obtain a unified view of these core features of chemistry and to treat equilibria quantitatively.

The chapters in Part 1 deal with the bulk properties of matter; those of Part 2 show how these properties stem from the behaviour of individual atoms.

1 The properties of gases

Mathematical background 1: Differentiation and integration

2 The First Law

Mathematical background 2: Multivariate calculus

3 The Second and Third Laws

4 Physical transformations of pure substances

5 Simple mixtures

6 Chemical equilibrium

CHAPTER 1

The properties of gases

A **gas** is a form of matter that fills whatever container it occupies. This chapter establishes the properties of gases that will be used throughout the text.

1A The perfect gas

The chapter begins with 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.

1B The kinetic model

One 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. This model is the basis of ‘kinetic molecular theory’. As well as accounting for the gas laws, this theory can be used to predict the average speed at which molecules move in a gas, and that speed’s dependence on temperature. In combination with the Boltzmann distribution (*Foundations* B), the kinetic theory can also be used to predict the spread of molecular speeds and its dependence on molecular mass and temperature.

1C Real gases

The perfect gas is an excellent starting point for the discussion of properties of all gases, and its properties are invoked throughout the chapters on thermodynamics that follow this chapter. However, actual gases, ‘real gases’, have properties that differ from those of perfect gases, and we need to be able to interpret these deviations and build the effects of molecular attractions and repulsions into our 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.

What is the impact 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. We have identified two applications. In *Impact* I1.1 we see how the gas laws are used in the discussion of meteorological phenomena—the weather. In *Impact* I1.2 we examine how the kinetic model of gases has a surprising application: to the discussion of dense stellar media, such as the interior of the Sun.



To read more about the impact of this material, scan the QR code, or go to bcs.whfreeman.com/webpub/chemistry/pchem10e/impact/pchem-1-1.html

1A The perfect gas

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► Why do you need to know this material?

Equations related to perfect gases provide the basis for the development of many equations 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 be aware of the concepts of pressure and temperature introduced in *Foundations A*.

In molecular terms, a gas consists of a collection of molecules that are in ceaseless motion and which interact significantly with one another only when they collide. 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.

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, $1 \text{ Pa} = 1 \text{ N m}^{-2}$) is introduced in *Foundations A*. As discussed there, several other units are still widely used (Table 1A.1). A pressure of 1 bar is the **standard pressure** for reporting data; we denote it $p^\ominus$.

If two gases are in separate containers that share a common movable wall (a ‘piston’, 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.

Table 1A.1 Pressure units*

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

* Values in bold are exact.

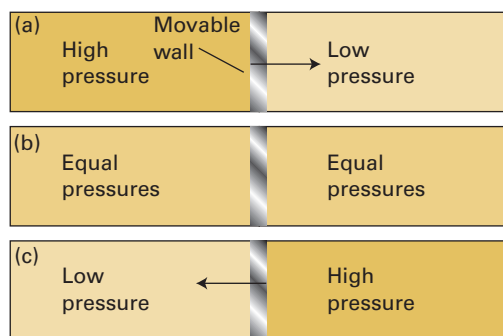


Figure 1A.1 When a region of high pressure is separated from a region of low pressure by a movable wall, the wall will be pushed into one region or the other, as in (a) and (c). However, if the two pressures are identical, the wall will not move (b). The latter condition is one of mechanical equilibrium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

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

Example 1A.1 Calculating the pressure exerted by a column of liquid

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

Method According to *Foundations A*, the pressure is the force, F , divided by the area, A , to which the force is applied: $p = F/A$. For a mass m subject to a gravitational field at the surface of the earth, $F = mg$, where g is the acceleration of free fall. To calculate F we need to know the mass m of the column of liquid, which is its mass density, ρ , multiplied by its volume, V : $m = \rho V$. The first step, therefore, is to calculate the volume of a cylindrical column of liquid.

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

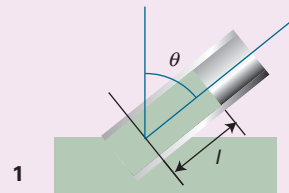
$$F = mg = \rho Ahg$$

The pressure at the base of the column is therefore

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

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

Self-test 1A.1 Derive an expression for the pressure at the base of a column of liquid of length l held at an angle θ (theta) to the vertical (1).



Answer: $p = \rho gl \cos \theta$

The pressure of a sample of gas inside a container is measured by using a pressure gauge, which is a device with 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 *Foundations A*. 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* ($^{\circ}\text{C}$). However, because different liquids expand to different extents, and do not always expand uniformly over a given range, thermometers constructed from different materials showed different numerical values of the temperature between their fixed points. The pressure of a gas, however, can be used to construct a **perfect-gas temperature scale** that is independent of the identity of the gas. The perfect-gas scale turns out to be identical to the **thermodynamic temperature scale** introduced in Topic 3A, so we shall use the latter term from now on to avoid a proliferation of names.

On the thermodynamic temperature scale, temperatures are denoted T and are normally reported in *kelvins* (K; not $^{\circ}\text{K}$). Thermodynamic and Celsius temperatures are related by the exact expression

$$T/\text{K} = \theta/^{\circ}\text{C} + 273.15 \quad \text{Definition of Celsius scale} \quad (1\text{A.2})$$

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.

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

Brief illustration 1A.1 Temperature conversion

To express 25.00°C as a temperature in kelvins, we use eqn 1A.4 to write

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

Note how the units (in this case, $^{\circ}\text{C}$) 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* A.1 of *Foundations*. Multiplication of both sides by the unit K then gives $T=298.15\text{K}$.

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

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, for then the fourth variable is fixed. That is, it is an experimental fact that each substance is described by an **equation of state**, an equation that interrelates these four variables.

The general form of an equation of state is

$$p = f(T, V, n) \quad \text{General form of an equation of state} \quad (1\text{A.3})$$

This equation tells us that if we know the values of n , T , and V for a particular substance, then the pressure has a fixed value. Each substance is described by its own equation of state, but

we know the explicit form of the equation in only a few special cases. One very important example is the equation of state of a ‘perfect gas’, which has the form $p = nRT/V$, where R is a constant 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

We assume that the following individual gas laws are familiar:

$$\text{Boyle’s law: } pV = \text{constant, at constant } n, T \quad (1\text{A.4a})$$

$$\text{Charles’s law: } V = \text{constant} \times T, \text{ at constant } n, p \quad (1\text{A.4b})$$

$$p = \text{constant} \times T, \text{ at constant } n, V \quad (1\text{A.4c})$$

Avogadro’s principle:

$$V = \text{constant} \times n \text{ at constant } p, T \quad (1\text{A.4d})$$

Boyle’s and Charles’s laws are examples of a **limiting law**, a law that is strictly true only in a certain limit, in this case $p \rightarrow 0$. 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 $p \rightarrow 0$, $V = aT$. Throughout this text, equations valid in this limiting sense are labelled with a blue equation number, as in these expressions. Although these relations are strictly true only at $p=0$, they are reasonably reliable at normal pressures ($p \approx 1\text{ bar}$) and are used widely throughout chemistry.

Avogadro’s principle is commonly expressed in the form ‘equal volumes of gases at the same temperature and pressure contain the same numbers of molecules’. It is a principle rather than a law (a summary of experience) because it depends on the validity of a model, in this case the existence of molecules. Despite there now being no doubt about the existence of molecules, it is still a model-based principle rather than a law.

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

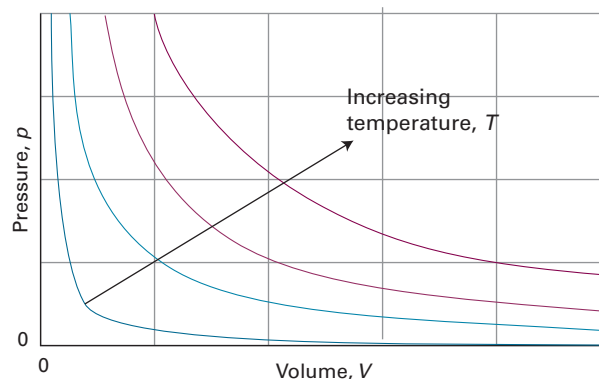


Figure 1A.2 The pressure–volume dependence of a fixed amount of perfect gas at different temperatures. Each curve is a hyperbola ($pV = \text{constant}$) and is called an isotherm.

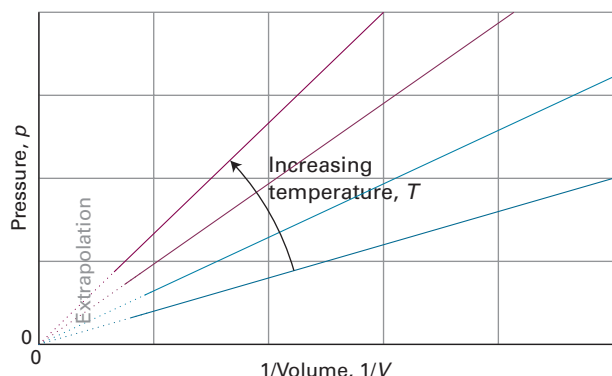


Figure 1A.3 Straight lines are obtained when the pressure is plotted against $1/V$ at constant temperature.

graph corresponds to a single temperature and hence is called an **isotherm**. According to Boyle's law, the isotherms of gases are hyperbolas (a curve obtained by plotting y against x with $xy = \text{constant}$, or $y = \text{constant}/x$). An alternative depiction, a plot of pressure against $1/\text{volume}$, 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.

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

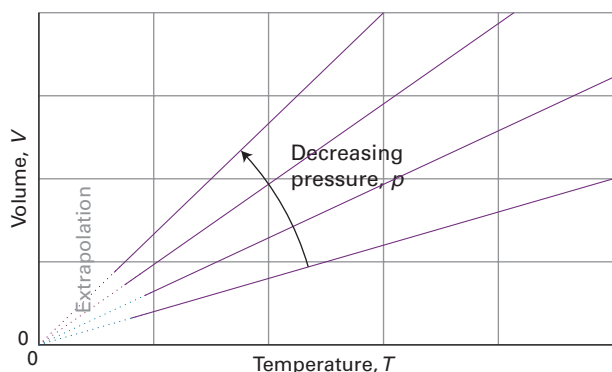


Figure 1A.4 The variation of the volume of a fixed amount of gas with the temperature at constant pressure. Note that in each case the isobars extrapolate to zero volume at $T=0$, or $\theta = -273^\circ\text{C}$.

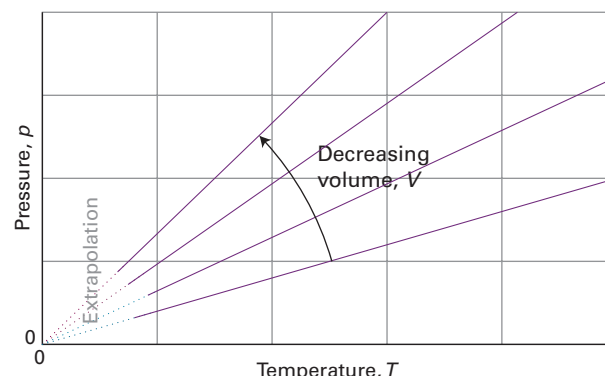


Figure 1A.5 The pressure also varies linearly with the temperature at constant volume, and extrapolates to zero at $T=0$ (-273°C).

The empirical observations summarized by eqn 1A.5 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

$$pV = nRT \quad \text{Perfect gas law} \quad (1A.5)$$

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.5 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.5 in the limit of $p \rightarrow 0$. The gas constant R can be determined by evaluating $R = pV/nT$ for a gas in the limit of zero pressure (to guarantee that it is behaving perfectly). However, a more accurate value can be obtained by measuring the speed of sound in a low-pressure gas (argon is used in practice), for the speed of sound depends on the value of R and extrapolating its value to zero pressure. Another route to its value is to recognize (as explained in *Foundations B*) that it is related to Boltzmann's constant, k , by

$$R = N_A k \quad \text{The (molar) gas constant} \quad (1A.6)$$

where N_A is Avogadro's constant. There are currently (in 2014) plans to use this relation as the sole route to R , with defined values of N_A and k . Table 1A.2 lists the values of R in a variety of units.

A note on good practice Despite 'ideal gas' being the more common term, we prefer 'perfect gas'. As explained in Topic 5A, in an 'ideal mixture' of A and B, the AA, BB, and AB

Table 1A.2 The gas constant ($R=N_A k$)

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

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.5. 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).

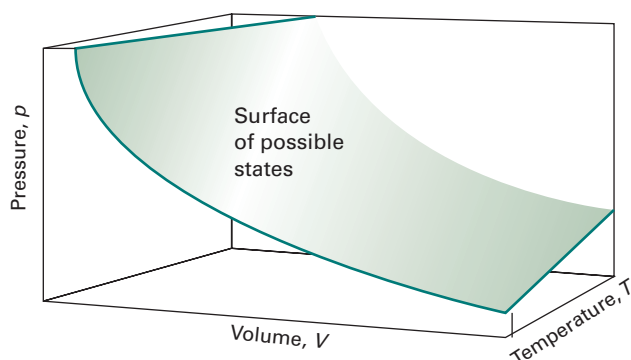


Figure 1A.6 A region of the p, V, T surface of a fixed amount of perfect gas. The points forming the surface represent the only states of the gas that can exist.

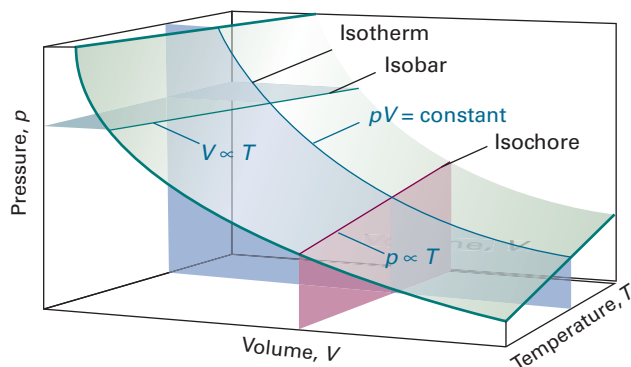


Figure 1A.7 Sections through the surface shown in Fig. 1A.6 at constant temperature give the isotherms shown in Fig. 1A.2, the isobars shown in Fig. 1A.4, and the isochores shown in Fig. 1A.5.

Example 1A.2 Using the perfect gas law

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

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

$$\frac{p_1 V_1}{n_1 T_1} = \frac{p_2 V_2}{n_2 T_2} \quad \text{Combined gas law} \quad (1A.7)$$

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	Same	300
Final	Same	?	Same	500

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

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

which can be rearranged into

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

Substitution of the data then gives

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

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

Self-test 1A.2 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 (that is, exactly 10^5 Pa), is easily calculated from $V_m = RT/p$ to be $24.789 \text{ dm}^3 \text{ mol}^{-1}$. An earlier definition, **standard temperature and pressure (STP)**, was 0°C and 1 atm; at STP, the molar volume of a perfect gas is $22.414 \text{ dm}^3 \text{ mol}^{-1}$.

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

$$p_J = x_J p \quad \text{Definition} \quad \text{Partial pressure} \quad (1A.8)$$

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

$$x_J = \frac{n_J}{n} \quad n = n_A + n_B + \dots \quad \text{Definition} \quad \text{Mole fraction} \quad (1A.9)$$

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

$$p_A + p_B + \dots = (x_A + x_B + \dots)p = p \quad (1A.10)$$

This relation is true for both real and perfect gases.

When all the gases are perfect, the partial pressure as defined in eqn 1A.9 is also the pressure that each gas would exert if it occupied the same container alone at the same temperature. The latter is the original meaning of 'partial pressure'. That identification was the basis of the original formulation of **Dalton's law**:

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

Dalton's law

Now, however, the relation between partial pressure (as defined in eqn 1A.8) and total pressure (as given by eqn 1A.10) is true for all gases and the identification of partial pressure with the pressure that the gas would exert on its own is valid only for a perfect gas.

Example 1A.3 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?

Method We expect species with a high mole fraction to have a proportionally high partial pressure. Partial pressures are defined by eqn 1A.8. To use the equation, we need the mole fractions of the components. To calculate mole fractions, which are defined by eqn 1A.9, we use the fact that the amount of molecules J of molar mass M_J in a sample of mass m_J is $n_J = m_J/M_J$. The mole fractions are independent of the total mass of the sample, so we can choose the latter to be exactly 100 g (which makes the conversion from mass percentages very easy). Thus, the mass of N_2 present is 75.5 per cent of 100 g, which is 75.5 g.

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

$$\begin{aligned} n(\text{N}_2) &= \frac{75.5 \text{ g}}{28.02 \text{ g mol}^{-1}} = \frac{75.5}{28.02} \text{ mol} = 2.69 \text{ mol} \\ n(\text{O}_2) &= \frac{23.2 \text{ g}}{32.00 \text{ g mol}^{-1}} = \frac{23.2}{32.00} \text{ mol} = 0.725 \text{ mol} \\ n(\text{Ar}) &= \frac{1.3 \text{ g}}{39.95 \text{ g mol}^{-1}} = \frac{1.3}{39.95} \text{ mol} = 0.033 \text{ mol} \end{aligned}$$

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

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

Self-test 1A.3 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, 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 $p \rightarrow 0$.
- ☐ 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	$T/K = \theta/^{\circ}\text{C} + 273.15$	273.15 is exact	1A.2
Equation of state	$p = f(n, V, T)$		1A.3
Perfect gas law	$pV = nRT$	Valid for real gases in the limit $p \rightarrow 0$	1A.5
Partial pressure	$p_i = x_i p$	Valid for all gases	1A.8