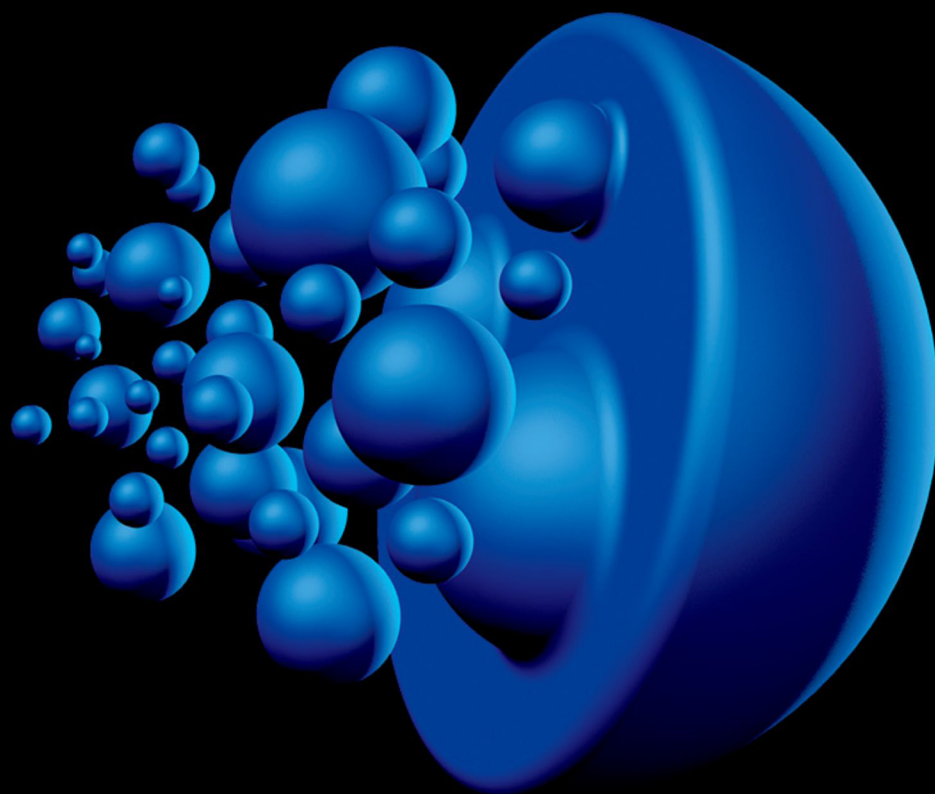


OXFORD

Atkins'
PHYSICAL
CHEMISTRY

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}	JK^{-1}
Avogadro's constant	N_A	6.022 141 29	10^{23}	mol^{-1}
Gas constant	$R = N_A k$	8.314 4621		$\text{JK}^{-1} \text{mol}^{-1}$
Faraday's constant	$F = N_A e$	9.648 533 65	10^4	Cmol^{-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}	$\text{Js}^2 \text{C}^{-2} \text{m}^{-1}$
Vacuum permittivity	$\epsilon_0 = 1/\mu_0 c^2$	8.854 187 817	10^{-12}	$\text{J}^{-1} \text{C}^2 \text{m}^{-1}$
	$4\pi\epsilon_0$	1.112 650 056	10^{-10}	$\text{J}^{-1} \text{C}^2 \text{m}^{-1}$
Bohr magneton	$\mu_B = e\hbar/2m_e$	9.274 009 68	10^{-24}	JT^{-1}
Nuclear magneton	$\mu_N = e\hbar/2m_p$	5.050 783 53	10^{-27}	JT^{-1}
Proton magnetic moment	μ_p	1.410 606 743	10^{-26}	JT^{-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}	Ckg^{-1}
Proton	$\gamma_p = 2\mu_p/\hbar$	2.675 222 004	10^8	Ckg^{-1}
Bohr radius	$a_0 = 4\pi\epsilon_0 \hbar^2/e^2 m_e$	5.291 772 109	10^{-11}	m
Rydberg constant	$\tilde{R}_\infty = m_e e^4/8h^3 c \epsilon_0^2$	1.097 373 157	10^5	cm^{-1}
	$hc\tilde{R}_\infty/e$	13.605 692 53		eV
Fine-structure constant	$\alpha = \mu_0 e^2 c/2h$	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}	$\text{W m}^{-2} \text{K}^{-4}$
Standard acceleration of free fall	g	9.806 65*		m s^{-2}
Gravitational constant	G	6.673 84	10^{-11}	$\text{N m}^2 \text{kg}^{-2}$

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

Atkins'

PHYSICAL CHEMISTRY

Eleventh edition

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Impression: 1

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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.

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).

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.

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.

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 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

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

A note on good practice An *allotrope* is a particular molecular form of an element (such as O₂ and O₃) 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-

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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.

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/

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.

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.

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 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).

$$C_{V,m}^V = \frac{dN_A \langle \epsilon^V \rangle}{dT} = R\theta^V \frac{d}{dT} \frac{1}{e^{\theta^V/T} - 1} = R \left(\frac{\theta^V}{T} \right)^2 \frac{e^{\theta^V/T}}{(e^{\theta^V/T} - 1)^2}$$

$U_m(T) = U_m(0) + N_A \langle \epsilon^V \rangle$
 $d(1/f)/dx = -(1/f^2)df/dx$
used twice

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

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

Vibrational contribution to $C_{V,m}$ (13E.3)

Checklist of equations

Property	Equation
Gibbs energy of mixing	$\Delta_{\text{mix}}G = nRT(x_A \ln x_A + x_B \ln x_B)$
Entropy of mixing	$\Delta_{\text{mix}}S = -nR(x_A \ln x_A + x_B \ln x_B)$

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.

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*.

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.

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

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

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

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 organisation 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 4.0 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 $p_{\text{ex}} = 0$, 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 $p_{\text{ex}} = 0$, 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_{sur} 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_{sur} .

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 the 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 $VT^{3/2} = \text{constant}$. (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

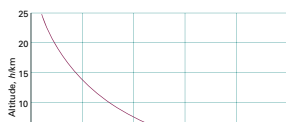
transferred to or from the gas. (d) Explain why the work done is equal to the difference between the heat extracted from the hot source and that deposited in the cold sink. (e) Calculate the work done over the cycle and hence the efficiency η . (f) Confirm that your answer agrees with the efficiency 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_1 to V_2 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/

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

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 9780198807773) provides full solutions to the 'a' Exercises and to the odd-numbered Problems.

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

$$G_m = G_m^\ominus + RT \ln \left(\frac{p}{p^\ominus} \right) \quad (1a)$$

In this expression, f_i is the fugacity when the pressure is p_i and f_j is the fugacity when the pressure is p_j . That is, from eqn 3b,

$$\int_{p_j}^{p_i} V_m dp = RT \ln \frac{f_i}{f_j} \quad (4a)$$

For a perfect gas,

$$\int_{p_j}^{p_i} V_{m, \text{perfect}} dp = RT \ln \frac{p_i}{p_j} \quad (4b)$$

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/.

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.

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).

ABOUT THE AUTHORS



Photograph by Natasha Ellis-Knight.

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



Julio de Paula is Professor of Chemistry at Lewis & Clark College. A native of Brazil, he received a B.A. degree in chemistry from Rutgers, The State University of New Jersey, and a Ph.D. in biophysical chemistry from Yale University. His research activities encompass the areas of molecular spectroscopy, photochemistry, and nanoscience. He has taught courses in general chemistry, physical chemistry, biophysical chemistry, inorganic chemistry, instrumental analysis, environmental chemistry, and writing. Among his professional honours are a Christian and Mary Lindback Award for Distinguished Teaching, a Henry Dreyfus Teacher-Scholar Award, and a Cottrell Scholar Award from the Research Corporation for Science Advancement.



Photograph by Nathan Pitt,
©University of Cambridge.

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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 $n.nnn\dots$ 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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13	The BET isotherm

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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

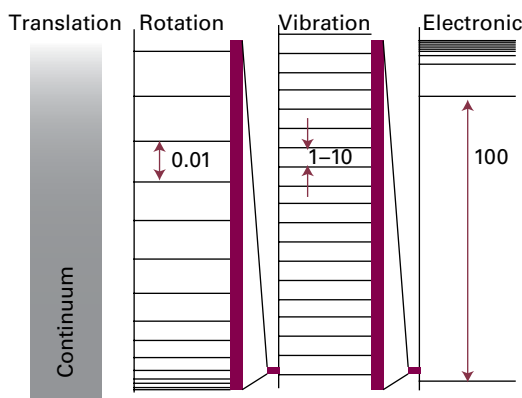


Figure 1 The relative energies of the allowed states of various kinds of atomic and molecular motion.

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 :

$$N_i \propto e^{-\epsilon_i/kT}$$

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.

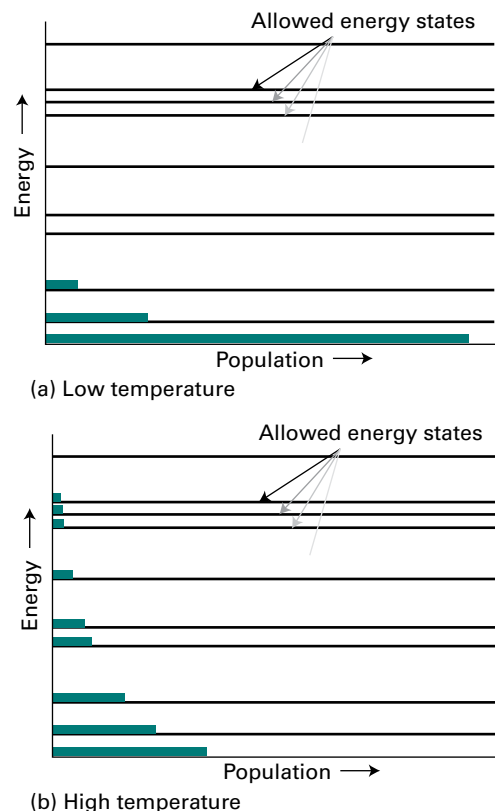


Figure 2 The relative populations of states at (a) low, (b) high temperature according to the Boltzmann distribution.

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

Table 1A.1 Pressure units*

Name	Symbol	Value
pascal	Pa	$1 \text{ Pa} = 1 \text{ N m}^{-2}$, $1 \text{ kg m}^{-1} \text{ s}^{-2}$
bar	bar	$1 \text{ bar} = 10^5 \text{ Pa}$
atmosphere	atm	$1 \text{ atm} = 101.325 \text{ kPa}$
torr	Torr	$1 \text{ Torr} = (101\,325/760) \text{ Pa} = 133.32\dots \text{ Pa}$
millimetres of mercury	mmHg	$1 \text{ mmHg} = 133.322\dots \text{ Pa}$
pounds per square inch	psi	$1 \text{ psi} = 6.894757\dots \text{ kPa}$

* Values in bold are exact.

of pressure, the *pascal* (Pa, $1 \text{ Pa} = 1 \text{ N m}^{-2}$), 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 .

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.

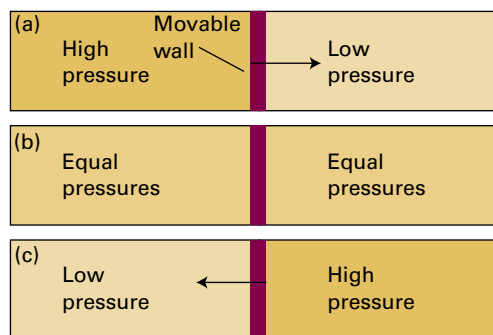


Figure 1A.1 When a region of high pressure is separated from a region of low pressure by a movable wall, the wall will be pushed into one region or the other, as in (a) and (c). However, if the two pressures are identical, the wall will not move (b). The latter condition is one of mechanical equilibrium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

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

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 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 mol 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, $1 \text{ N} = 1 \text{ kg m s}^{-2}$ (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* ($^{\circ}\text{C}$). 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** (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 $^{\circ}\text{K}$). Thermodynamic and Celsius temperatures are related by the exact expression

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

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 $6.022 \times 10^{23} \text{ mol}^{-1}$ (note that N_A is a constant with units, not a pure number).

The **molar mass of a substance**, M (units: formally kg mol^{-1} but commonly 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

$$n = \frac{m}{M} \quad \text{Amount of substance}$$

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: 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).

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* 1. Multiplication of both sides by K then gives $T = 298.15 \text{ K}$.

A note on good practice The zero temperature on the thermodynamic temperature scale is written $T = 0$, not $T = 0 \text{ K}$. 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

A sample of matter may be subjected to a **pressure**, p (unit: pascal, Pa; $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$), 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 ($1 \text{ bar} = 10^5 \text{ Pa}$) or atmospheres ($1 \text{ atm} = 101\,325 \text{ Pa}$ 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 $p^\ominus = 1 \text{ bar}$ 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.

$p = 0$, 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

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

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

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

Avogadro's principle:

$V = \text{constant} \times n$ 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 $p \rightarrow 0$. 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 $p \rightarrow 0$, $V = aT$. 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

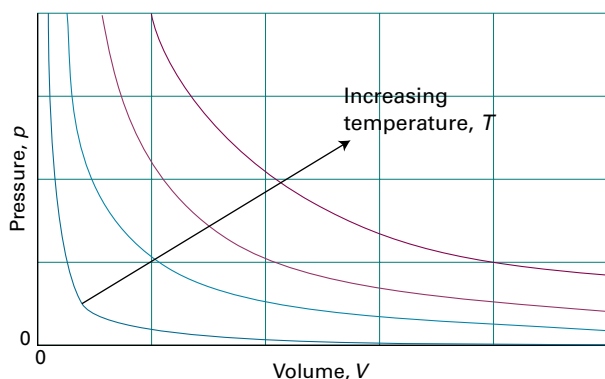


Figure 1A.2 The pressure–volume dependence of a fixed amount of perfect gas at different temperatures. Each curve is a hyperbola ($pV = \text{constant}$) and is called an isotherm.

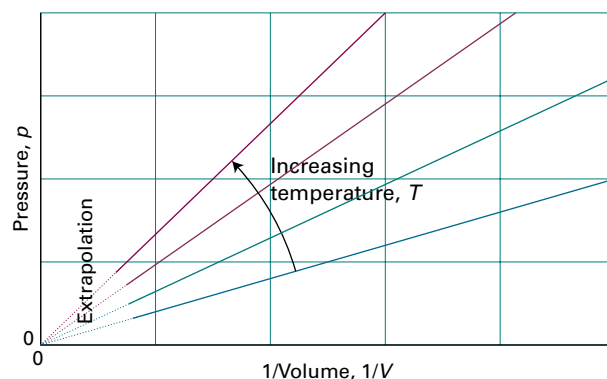


Figure 1A.3 Straight lines are obtained when the pressure of a perfect gas is plotted against $1/V$ at constant temperature. These lines extrapolate to zero pressure at $1/V = 0$.

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, 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.

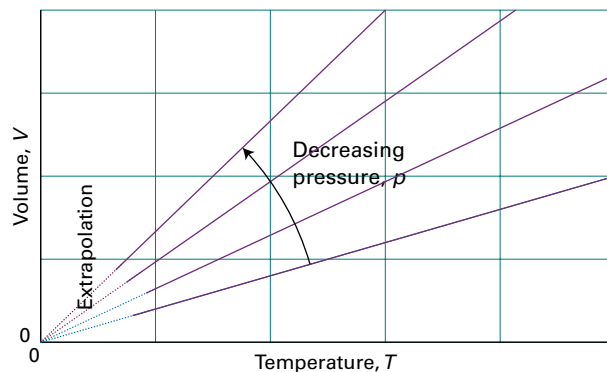


Figure 1A.4 The variation of the volume of a fixed amount of a perfect gas with the temperature at constant pressure. Note that in each case the isobars extrapolate to zero volume at $T = 0$, corresponding to $\theta = -273.15$ °C.

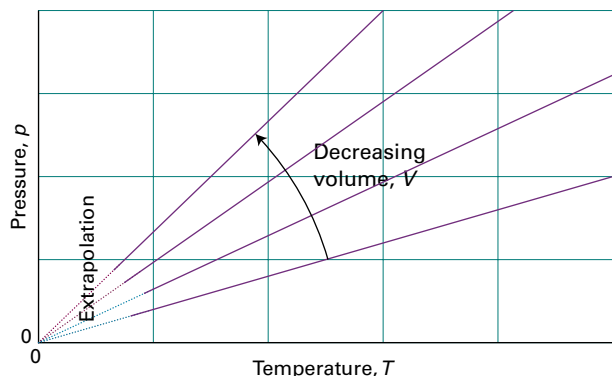


Figure 1A.5 The pressure of a perfect gas also varies linearly with the temperature at constant volume, and extrapolates to zero at $T = 0$ (-273.15°C).

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 $p \rightarrow 0$. 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).

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).

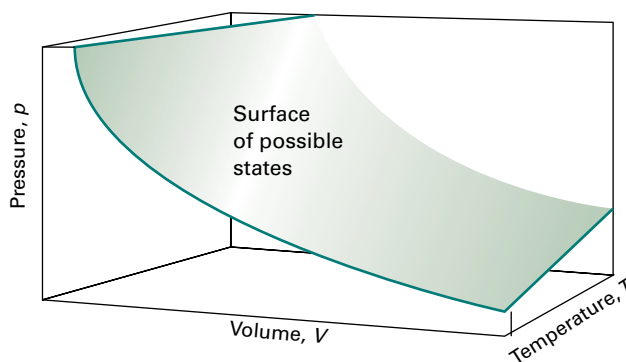


Figure 1A.6 A region of the p, V, T surface of a fixed amount of perfect gas. The points forming the surface represent the only states of the gas that can exist.

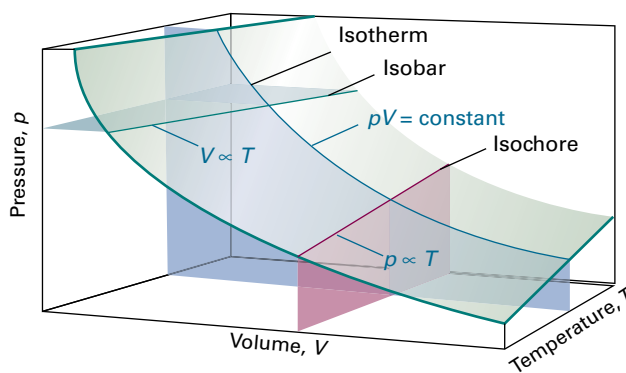


Figure 1A.7 Sections through the surface shown in Fig. 1A.6 at constant temperature give the isotherms shown in Fig. 1A.2. Sections at constant pressure give the isobars shown in Fig. 1A.4. Sections at constant volume give the isochores shown in Fig. 1A.5.

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'

$$\frac{p_1 V_1}{n_1 T_1} = \frac{p_2 V_2}{n_2 T_2} \quad \text{Combined gas law} \quad (1A.5)$$

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

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

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 $24.789\text{ dm}^3\text{ mol}^{-1}$. 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, 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

$$p_J = x_J p \quad \text{Partial pressure [definition]} \quad (1A.6)$$

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:

$$x_J = \frac{n_J}{n} \quad n = n_A + n_B + \dots \quad \text{Mole fraction [definition]} \quad (1A.7)$$

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:

$$p_A + p_B + \dots = (x_A + x_B + \dots)p = p \quad (1A.8)$$

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.