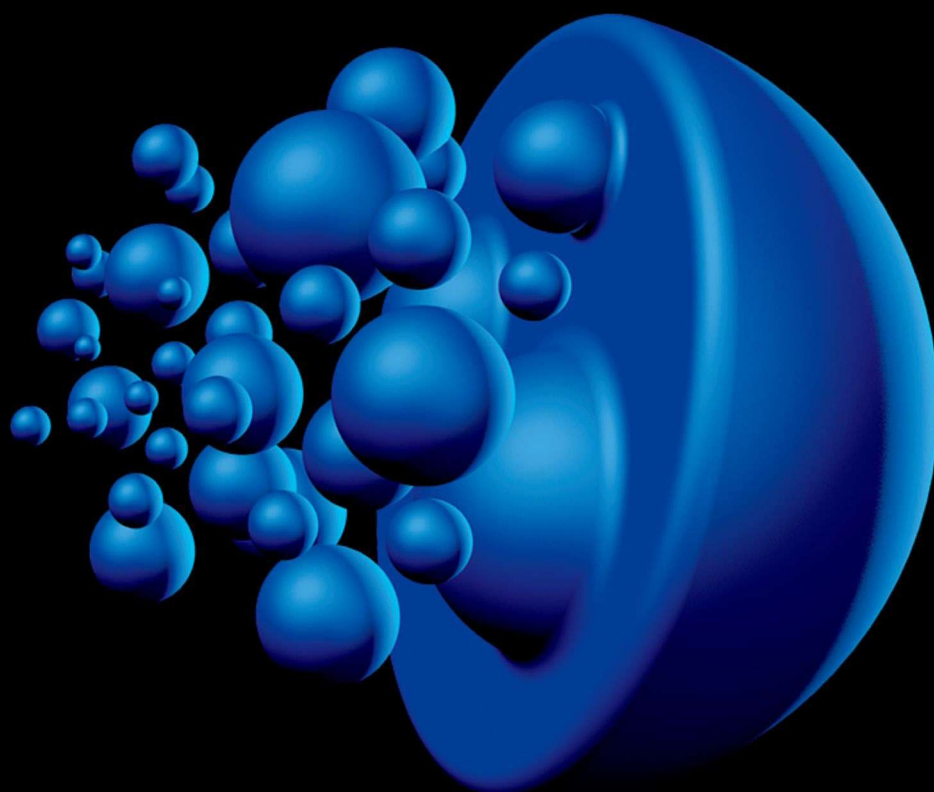


OXFORD

Atkins'  
PHYSICAL  
CHEMISTRY

11th Edition



Peter Atkins | Julio de Paula | James Keeler

# Atkins'

# PHYSICAL CHEMISTRY

Eleventh edition

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





# FUNDAMENTAL CONSTANTS

Constant	Symbol	Value		
			Power of 10	Units
Speed of light	$c$	2.997 924 58*	$10^8$	$\text{m s}^{-1}$
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	$10^{-23}$	$\text{JK}^{-1}$
Avogadro's constant	$N_A$	6.022 141 29	$10^{23}$	$\text{mol}^{-1}$
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	$10^4$	$\text{C mol}^{-1}$
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	$\mu_0$	$4\pi^*$	$10^{-7}$	$\text{Js}^2 \text{C}^{-2} \text{m}^{-1}$
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	$10^{-24}$	$\text{JT}^{-1}$
Nuclear magneton	$\mu_N = e\hbar/2m_p$	5.050 783 53	$10^{-27}$	$\text{JT}^{-1}$
Proton magnetic moment	$\mu_p$	1.410 606 743	$10^{-26}$	$\text{JT}^{-1}$
$g$ -Value of electron	$g_e$	2.002 319 304		
Magnetogyric ratio				
Electron	$\gamma_e = -g_e e/2m_e$	-1.001 159 652	$10^{10}$	$\text{C kg}^{-1}$
Proton	$\gamma_p = 2\mu_p/\hbar$	2.675 222 004	$10^8$	$\text{C kg}^{-1}$
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	$10^5$	$\text{cm}^{-1}$
	$hc\tilde{R}_\infty/e$	13.605 692 53		eV
Fine-structure constant	$\alpha = \mu_0 e^2 c/2h$	7.297 352 5698	$10^{-3}$	
	$\alpha^{-1}$	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*		$\text{m s}^{-2}$
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.



# 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 O<sub>2</sub> and O<sub>3</sub>) 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/](http://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  $\alpha$  and  $\beta$  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,  $\text{m}^3$ ).

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.

#### 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

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

### Examples

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

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

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

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

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

### Discussion questions

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

### Exercises and problems

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

### Integrated activities

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

## FOCUS 3 The Second and Third Laws

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

### TOPIC 3A Entropy

#### Discussion questions

**D3A.1** The evolution of life requires the 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  $125 \text{ J K}^{-1}$  and the entropy of the surroundings decreases by  $125 \text{ J K}^{-1}$ . Is the process spontaneous?

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

**E3A.2(a)** Consider a process in which  $100 \text{ kJ}$  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)  $0^\circ \text{C}$ , (b)  $50^\circ \text{C}$ .

**E3A.2(b)** Consider a process in which  $250 \text{ kJ}$  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)  $20^\circ \text{C}$ , (b)  $100^\circ \text{C}$ .

**E3A.3(a)** Calculate the change in entropy of the gas when  $15 \text{ g}$  of carbon dioxide gas are allowed to expand isothermally from  $1.0 \text{ dm}^3$  to  $3.0 \text{ dm}^3$  at  $300 \text{ K}$ .

**E3A.3(b)** Calculate the change in entropy of the gas when  $4.00 \text{ g}$  of nitrogen is allowed to expand isothermally from  $500 \text{ cm}^3$  to  $750 \text{ cm}^3$  at  $300 \text{ K}$ .

**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  $14 \text{ g}$  at  $298 \text{ K}$  doubles its volume in (a) an isothermal reversible expansion, (b) an isothermal irreversible expansion against  $p_{\text{ext}} = 0$ , 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  $2.9 \text{ g}$  at  $298 \text{ K}$  increases from  $1.20 \text{ dm}^3$  to  $4.60 \text{ dm}^3$  in (a) an isothermal reversible expansion, (b) an isothermal irreversible expansion against  $p_{\text{ext}} = 0$ , and (c) an adiabatic reversible expansion.

**E3A.5(a)** In a certain ideal heat engine,  $10.00 \text{ kJ}$  of heat is withdrawn from the hot source at  $273 \text{ K}$  and  $3.00 \text{ kJ}$  of work is generated. What is the temperature of cold sink?

**E3A.5(b)** In an ideal heat engine the cold sink is at  $0^\circ \text{C}$ . If  $10.00 \text{ kJ}$  of heat is withdrawn from the hot source and  $3.00 \text{ kJ}$  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  $100^\circ \text{C}$  and the cold sink is at  $10^\circ \text{C}$ ?

**E3A.6(b)** An ideal heat engine has a hot source at  $40^\circ \text{C}$ . At what temperature must the cold sink be if the efficiency is to be 10 per cent?

#### Problems

**P3A.1** A sample consisting of  $1.00 \text{ mol}$  of perfect gas molecules at  $27^\circ \text{C}$  is expanded isothermally from an initial pressure of  $3.00 \text{ atm}$  to a final pressure of  $1.00 \text{ atm}$  in two ways: (a) reversibly, and (b) against a constant external pressure of  $1.00 \text{ atm}$ . Evaluate  $q$ ,  $w$ ,  $\Delta U$ ,  $\Delta H$ ,  $\Delta S$ ,  $\Delta S_{\text{sys}}$ , and  $\Delta S_{\text{sur}}$  in each case.

**P3A.2** A sample consisting of  $0.10 \text{ mol}$  of perfect gas molecules is held by a piston inside a cylinder such that the volume is  $1.25 \text{ dm}^3$ ; the external pressure is constant at  $1.00 \text{ bar}$  and the temperature is maintained at  $300 \text{ K}$  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  $\Delta S_{\text{sys}}$ .

**P3A.3** Consider a Carnot cycle in which the working substance is  $0.10 \text{ mol}$  of perfect gas molecules, the temperature of the hot source is  $373 \text{ K}$ , and that of the cold sink is  $273 \text{ K}$ ; the initial volume of gas is  $1.00 \text{ dm}^3$ , which doubles over the course of the first isothermal stage. For the reversible adiabatic stages it may be assumed that  $\gamma T^{-\gamma} = \text{constant}$ . (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  $\eta$ . (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  $V_i$  to  $V_f$  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/](http://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/](http://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  $f_i^\ominus$  is the fugacity when the pressure is  $p^\ominus$ . That is, from eqn 3b,

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

For a perfect gas,

$$\int_{p_i}^{p_i^\ominus} V_m dp = RT \ln \frac{p_i^\ominus}{p_i} \quad (4b)$$

### 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/](http://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/](http://www.oup.com/uk/pchem11e/) and follow the appropriate links.

# ABOUT THE AUTHORS



Photograph by Natasha Ellis-Knight.

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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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