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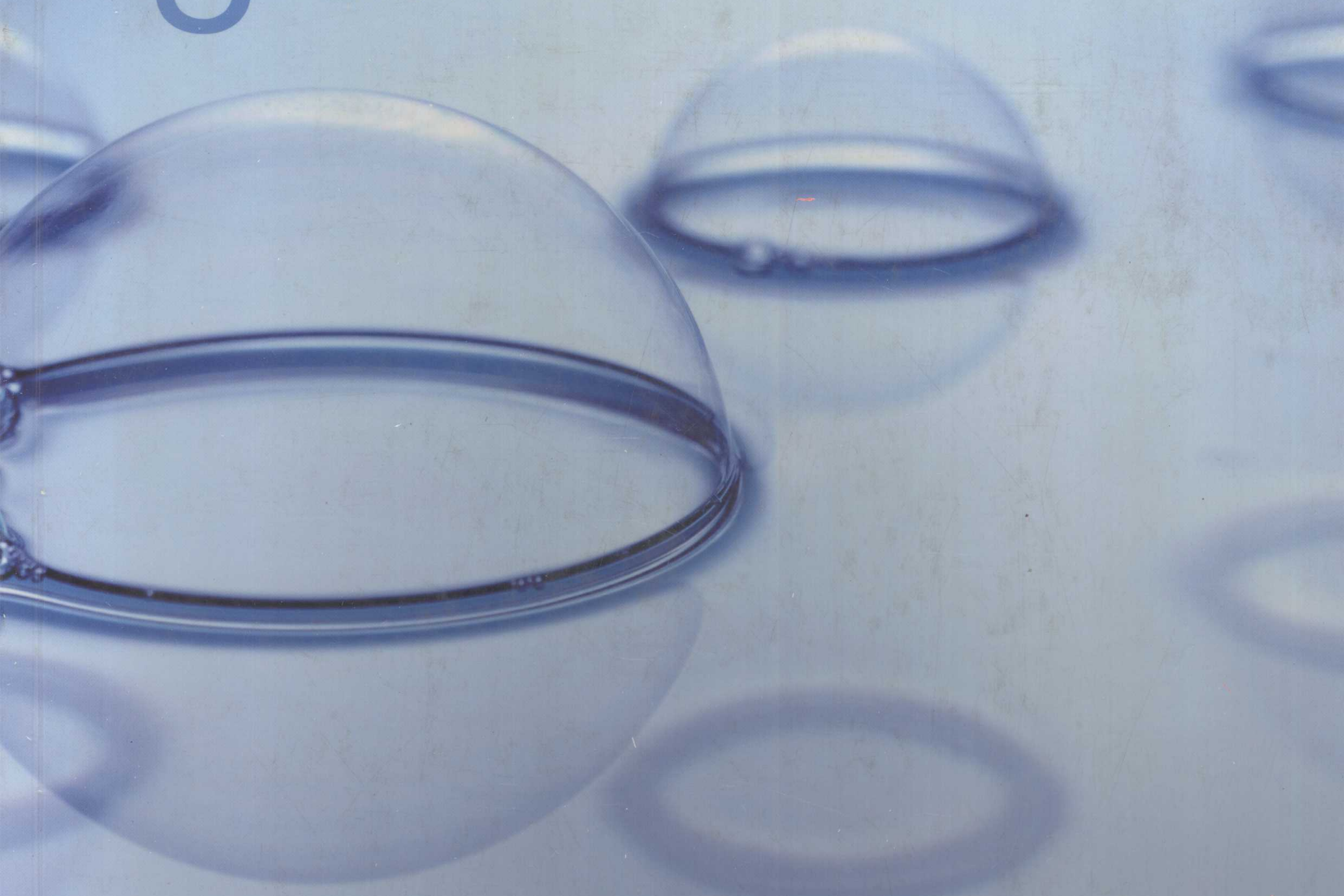

ATKINS' PHYSICAL CHEMISTRY

PETER ATKINS · JULIO DE PAULA

online resource centre

ATKINS' PHYSICAL CHEMISTRY

Eighth Edition

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ATKINS'
PHYSICAL CHEMISTRY

Preface

We have taken the opportunity to refresh both the content and presentation of this text while—as for all its editions—keeping it flexible to use, accessible to students, broad in scope, and authoritative. The bulk of textbooks is a perennial concern: we have sought to tighten the presentation in this edition. However, it should always be borne in mind that much of the bulk arises from the numerous pedagogical features that we include (such as *Worked examples* and the *Data section*), not necessarily from density of information.

The most striking change in presentation is the use of colour. We have made every effort to use colour systematically and pedagogically, not gratuitously, seeing it as a medium for making the text more attractive but using it to convey concepts and data more clearly. The text is still divided into three parts, but material has been moved between chapters and the chapters have been reorganized. We have responded to the shift in emphasis away from classical thermodynamics by combining several chapters in Part 1 (Equilibrium), bearing in mind that some of the material will already have been covered in earlier courses. We no longer make a distinction between 'concepts' and 'machinery', and as a result have provided a more compact presentation of thermodynamics with fewer artificial divisions between the approaches. Similarly, equilibrium electrochemistry now finds a home within the chapter on chemical equilibrium, where space has been made by reducing the discussion of acids and bases.

In Part 2 (Structure) the principal changes are within the chapters, where we have sought to bring into the discussion contemporary techniques of spectroscopy and approaches to computational chemistry. In recognition of the major role that physical chemistry plays in materials science, we have a short sequence of chapters on materials, which deal respectively with hard and soft matter. Moreover, we have introduced concepts of nanoscience throughout much of Part 2.

Part 3 has lost its chapter on dynamic electrochemistry, but not the material. We regard this material as highly important in a contemporary context, but as a final chapter it rarely received the attention it deserves. To make it more readily accessible within the context of courses and to acknowledge that the material it covers is at home intellectually with other material in the book, the description of electron transfer reactions is now a part of the sequence on chemical kinetics and the description of processes at electrodes is now a part of the general discussion of solid surfaces.

We have discarded the Boxes of earlier editions. They have been replaced by more fully integrated and extensive *Impact* sections, which show how physical chemistry is applied to biology, materials, and the environment. By liberating these topics from their boxes, we believe they are more likely to be used and read; there are end-of-chapter problems on most of the material in these sections.

In the preface to the seventh edition we wrote that there was vigorous discussion in the physical chemistry community about the choice of a 'quantum first' or a 'thermodynamics first' approach. That discussion continues. In response we have paid particular attention to making the organization flexible. The strategic aim of this revision is to make it possible to work through the text in a variety of orders, and at the end of this Preface we once again include two suggested road maps.

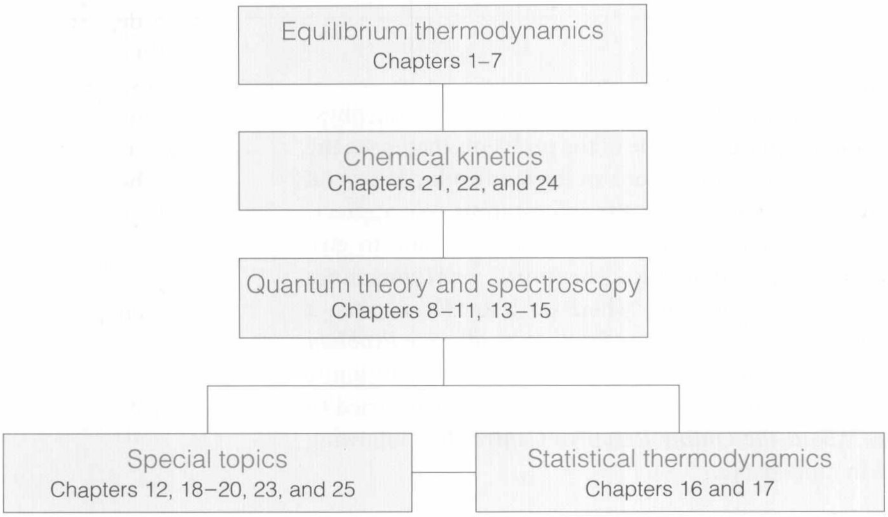
The concern expressed in the seventh edition about the level of mathematical ability has not evaporated, of course, and we have developed further our strategies for showing the absolute centrality of mathematics to physical chemistry and to make it accessible. Thus, we give more help with the development of equations, motivate them, justify them, and comment on the steps. We have kept in mind the struggling student, and have tried to provide help at every turn.

We are, of course, alert to the developments in electronic resources and have made a special effort in this edition to encourage the use of the resources in our online resource centre (at www.oxfordtextbooks.co.uk/orc/pchem8e/) where you can also access the eBook. In particular, we think it important to encourage students to use the *Living graphs* and their considerable extension as *Explorations in Physical Chemistry*. To do so, wherever we call out a *Living graph* (by an icon attached to a graph in the text), we include an *Exploration* in the figure legend, suggesting how to explore the consequences of changing parameters.

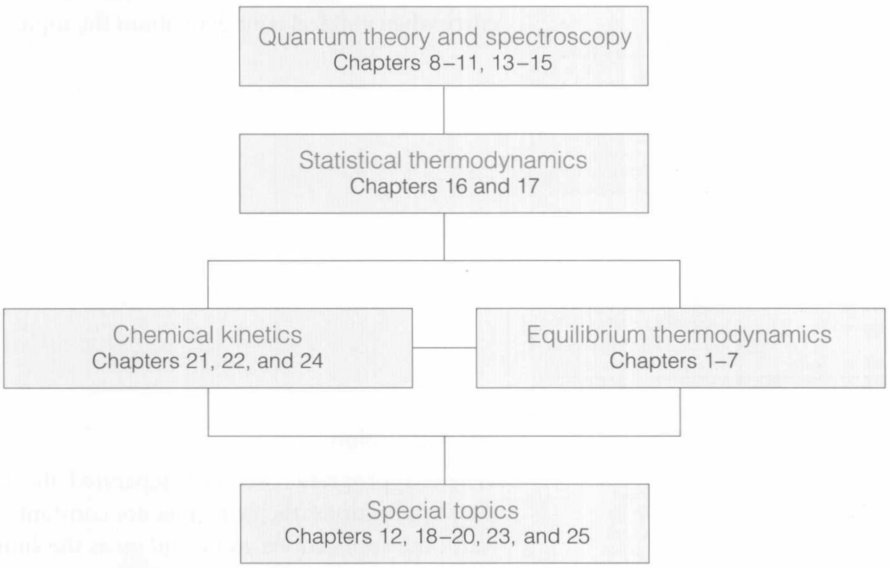
Overall, we have taken this opportunity to refresh the text thoroughly, to integrate applications, to encourage the use of electronic resources, and to make the text even more flexible and up to date.

Oxford P.W.A.
Portland J.de P.

Traditional approach



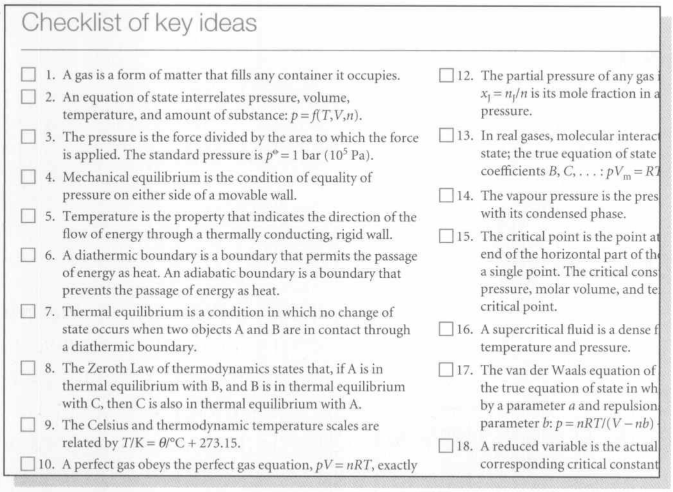
Molecular approach



About the book

There are numerous features in this edition that are designed to make learning physical chemistry more effective and more enjoyable. One of the problems that make the subject daunting is the sheer amount of information: we have introduced several devices for organizing the material: see ***Organizing the information***. We appreciate that mathematics is often troublesome, and therefore have taken care to give help with this enormously important aspect of physical chemistry: see ***Mathematics and Physics support***. Problem solving—especially, 'where do I start?'—is often a challenge, and we have done our best to help overcome this first hurdle: see ***Problem solving***. Finally, the web is an extraordinary resource, but it is necessary to know where to start, or where to go for a particular piece of information; we have tried to indicate the right direction: see ***About the Online Resource Centre***. The following paragraphs explain the features in more detail.

Organizing the information

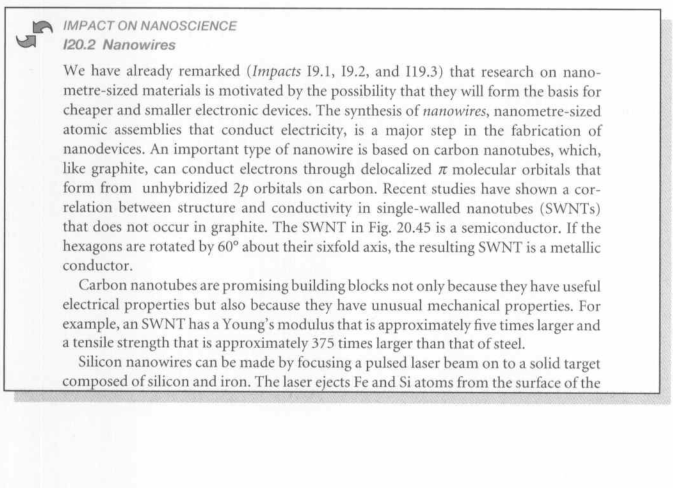


Checklist of key ideas

☐ 1. A gas is a form of matter that fills any container it occupies.
☐ 2. An equation of state interrelates pressure, volume, temperature, and amount of substance: $p = f(T,V,n)$.
☐ 3. The pressure is the force divided by the area to which the force is applied. The standard pressure is $p^\ominus = 1$ bar (10^5 Pa).
☐ 4. Mechanical equilibrium is the condition of equality of pressure on either side of a movable wall.
☐ 5. Temperature is the property that indicates the direction of the flow of energy through a thermally conducting, rigid wall.
☐ 6. A diathermic boundary is a boundary that permits the passage of energy as heat. An adiabatic boundary is a boundary that prevents the passage of energy as heat.
☐ 7. Thermal equilibrium is a condition in which no change of state occurs when two objects A and B are in contact through a diathermic boundary.
☐ 8. The Zeroth Law of thermodynamics states that, if A is in thermal equilibrium with B, and B is in thermal equilibrium with C, then C is also in thermal equilibrium with A.
☐ 9. The Celsius and thermodynamic temperature scales are related by $T/K = \theta/°C + 273.15$.
☐ 10. A perfect gas obeys the perfect gas equation, $pV = nRT$, exactly
☐ 12. The partial pressure of any gas $x_J = n_J/n$ is its mole fraction in a pressure.
☐ 13. In real gases, molecular interac state; the true equation of state coefficients $B, C, \ldots : pV_m = R$
☐ 14. The vapour pressure is the pres with its condensed phase.
☐ 15. The critical point is the point a end of the horizontal part of th a single point. The critical cons pressure, molar volume, and te critical point.
☐ 16. A supercritical fluid is a dense f temperature and pressure.
☐ 17. The van der Waals equation of the true equation of state in wh by a parameter a and repulsion parameter b: $p = nRT/(V - nb)$
☐ 18. A reduced variable is the actual corresponding critical constant

Checklist of key ideas

Here we collect together the major concepts introduced in the chapter. We suggest checking off the box that precedes each entry when you feel confident about the topic.



IMPACT ON NANOSCIENCE
I20.2 Nanowires

We have already remarked (*Impacts* I9.1, I9.2, and I19.3) that research on nanometre-sized materials is motivated by the possibility that they will form the basis for cheaper and smaller electronic devices. The synthesis of *nanowires*, nanometre-sized atomic assemblies that conduct electricity, is a major step in the fabrication of nanodevices. An important type of nanowire is based on carbon nanotubes, which, like graphite, can conduct electrons through delocalized π molecular orbitals that form from unhybridized 2p orbitals on carbon. Recent studies have shown a correlation between structure and conductivity in single-walled nanotubes (SWNTs) that does not occur in graphite. The SWNT in Fig. 20.45 is a semiconductor. If the hexagons are rotated by 60° about their sixfold axis, the resulting SWNT is a metallic conductor.

Carbon nanotubes are promising building blocks not only because they have useful electrical properties but also because they have unusual mechanical properties. For example, an SWNT has a Young's modulus that is approximately five times larger and a tensile strength that is approximately 375 times larger than that of steel.

Silicon nanowires can be made by focusing a pulsed laser beam on to a solid target composed of silicon and iron. The laser ejects Fe and Si atoms from the surface of the

Impact sections

Where appropriate, we have separated the principles from their applications: the principles are constant and straightforward; the applications come and go as the subject progresses. The *Impact* sections show how the principles developed in the chapter are currently being applied in a variety of modern contexts.

A note on good practice We write $T = 0$, not $T = 0$ 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.

Notes on good practice

Science is a precise activity and its language should be used accurately. We have used this feature to help encourage the use of the language and procedures of science in conformity to international practice and to help avoid common mistakes.

5.8 **The activities of regular solutions**

The material on regular solutions presented in Section 5.4 gives further insight into the origin of deviations from Raoult's law and its relation to activity coefficients. The starting point is the expression for the Gibbs energy of mixing for a regular solution (eqn 5.31). We show in the following *Justification* that eqn 5.31 implies that the activity coefficients are given by expressions of the form

$$\ln \gamma_A = \beta x_B^2 \qquad \ln \gamma_B = \beta x_A^2 \tag{5.57}$$

These relations are called the **Margules equations.**

Justification 5.4 *The Margules equations*

The Gibbs energy of mixing to form a nonideal solution is

$$\Delta_{mix}G = nRT\{x_A \ln a_A + x_B \ln a_B\}$$

This relation follows from the derivation of eqn 5.31 with activities in place of mole fractions. If each activity is replaced by γx, this expression becomes

$$\Delta_{mix}G = nRT\{x_A \ln x_A + x_B \ln x_B + x_A \ln \gamma_A + x_B \ln \gamma_B\}$$

Now we introduce the two expressions in eqn 5.57, and use $x_A + x_B = 1$, which gives

$$\begin{aligned}\Delta_{mix}G &= nRT\{x_A \ln x_A + x_B \ln x_B + \beta x_A x_B^2 + \beta x_B x_A^2\}\\ &= nRT\{x_A \ln x_A + x_B \ln x_B + \beta x_A x_B(x_A + x_B)\}\\ &= nRT\{x_A \ln x_A + x_B \ln x_B + \beta x_A x_B\}\end{aligned}$$

as required by eqn 5.31. Note, moreover, that the activity coefficients behave correctly for dilute solutions: $\gamma_A \to 1$ as $x_B \to 0$ and $\gamma_B \to 1$ as $x_A \to 0$.

Justifications

On first reading it might be sufficient to appreciate the 'bottom line' rather than work through detailed development of a mathematical expression. However, mathematical development is an intrinsic part of physical chemistry, and it is important to see how a particular expression is obtained. The *Justifications* let you adjust the level of detail that you require to your current needs, and make it easier to review material.

Molecular interpretation 5.2 *The lowering of vapour pressure of a solvent in a mixture*

The molecular origin of the lowering of the chemical potential is not the energy of interaction of the solute and solvent particles, because the lowering occurs even in an ideal solution (for which the enthalpy of mixing is zero). If it is not an enthalpy effect, it must be an entropy effect.

The pure liquid solvent has an entropy that reflects the number of microstates available to its molecules. Its vapour pressure reflects the tendency of the solution towards greater entropy, which can be achieved if the liquid vaporizes to form a gas. When a solute is present, there is an additional contribution to the entropy of the liquid, even in an ideal solution. Because the entropy of the liquid is already higher than that of the pure liquid, there is a weaker tendency to form the gas (Fig. 5.22). The effect of the solute appears as a lowered vapour pressure, and hence a higher boiling point.

Similarly, the enhanced molecular randomness of the solution opposes the tendency to freeze. Consequently, a lower temperature must be reached before equilibrium between solid and solution is achieved. Hence, the freezing point is lowered.

Molecular interpretation sections

Historically, much of the material in the first part of the text was developed before the emergence of detailed models of atoms, molecules, and molecular assemblies. The *Molecular interpretation* sections enhance and enrich coverage of that material by explaining how it can be understood in terms of the behaviour of atoms and molecules.

Further information

Further information

Further information 5.1 *The Debye–Hückel theory of ionic solutions*

Imagine a solution in which all the ions have their actual positions, but in which their Coulombic interactions have been turned off. The difference in molar Gibbs energy between the ideal and real solutions is equal to w_e, the electrical work of charging the system in this arrangement. For a salt M_pX_q, we write

$$w_e = \overbrace{(p\mu_+ + q\mu_-)}^{G_m} - \overbrace{(p\mu_+^{ideal} + q\mu_-^{ideal})}^{G_m^{ideal}}$$
$$= p(\mu_+ - \mu_+^{ideal}) + q(\mu_- - \mu_-^{ideal})$$

From eqn 5.64 we write

$$\mu_+ - \mu_+^{ideal} = \mu_- - \mu_-^{ideal} = RT \ln \gamma_\pm$$

So it follows that

$$\ln \gamma_\pm = \frac{w_e}{sRT} \qquad s = p + q \qquad (5.73)$$

This equation tells us that we must first find the final distribution of the ions and then the work of charging them in that distribution.

The Coulomb potential at a distance r from an isolated ion of charge z_ie in a medium of permittivity ε is

$$\phi_i = \frac{Z_i}{r} \qquad Z_i = \frac{z_ie}{4\pi\varepsilon} \qquad (5.74)$$

The ionic atmosphere causes the potential to decay with distance more sharply than this expression implies. Such shielding is a familiar problem in electrostatics, and its effect is taken into account by replacing the Coulomb potential by the **shielded Coulomb potential**, an expression of the form

$$\phi_i = \frac{Z_i}{r} e^{-r/r_D} \qquad (5.75)$$

where r_D is called the **Debye length**. W
potential is virtually the same as the un
small, the shielded potential is much sn
potential, even for short distances (Fig.

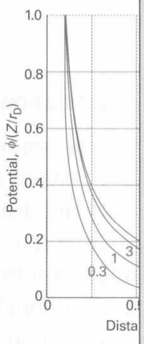


Fig. 5.36 The variation of the shielded C
distance for different values of the Deb
Debye length, the more sharply the pot
case, a is an arbitrary unit of length.

Exploration Write an expression
unshielded and shielded Coulon
Then plot this expression against r_D an
interpretation for the shape of the plot.

In some cases, we have judged that a derivation is too long, too detailed, or too different in level for it to be included in the text. In these cases, the derivations will be found less obtrusively at the end of the chapter.

Appendices

966 Appendix 2 MATHEMATICAL TECHNIQUES

A2.6 **Partial derivatives**

A **partial derivative** of a function of more than one variabl
of the function with respect to one of the variables, all th
constant (see Fig. 2.*). Although a partial derivative sho
when one variable changes, it may be used to determine
when more than one variable changes by an infinitesimal
tion of x and y, then when x and y change by dx and dy, re

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

where the symbol ∂ is used (instead of d) to denote a part
df is also called the **differential** of f. For example, if $f = ax^3$

$$\left(\frac{\partial f}{\partial x}\right)_y = 3ax^2y \qquad \left(\frac{\partial f}{\partial y}\right)_x = ax^3 + 2by$$

Physical chemistry draws on a lot of background material, especially in mathematics and physics. We have included a set of *Appendices* to provide a quick survey of some of the information relating to units, physics, and mathematics that we draw on in the text.

Synoptic tables and the Data section

1000 DATA SECTION

Table 2.8 Expansion coefficients, α, and isothermal compressibilities, κ_T

	$\alpha/(10^{-4}\,K^{-1})$	$\kappa_T/(10^{-6}\,atm^{-1})$
Liquids		
Benzene	12.4	92.1
Carbon tetrachloride	12.4	90.5
Ethanol	11.2	76.8
Mercury	1.82	38.7
Water	2.1	49.6
Solids		
Copper	0.501	0.735
Diamond	0.030	0.187
Iron	0.354	0.589
Lead	0.861	2.21

The values refer to 20°C.
Data: AIP(α), KL(κ_T).

Table 2.9 Inversion temperatures, n
points, and Joule–Thomson coefficien

	T_I/K	T_f/K
Air	603	
Argon	723	83.8
Carbon dioxide	1500	194.7s
Helium	40	
Hydrogen	202	14.0
Krypton	1090	116.6
Methane	968	90.6
Neon	231	24.5
Nitrogen	621	63.3
Oxygen	764	54.8

s: sublimes.
Data: AIP, JL, and M.W. Zemansky, *Heat and*
New York (1957).

Long tables of data are helpful for assembling and solving exercises and problems, but can break up the flow of the text. We provide a lot of data in the *Data section* at the end of the text and short extracts in the *Synoptic tables* in the text itself to give an idea of the typical values of the physical quantities we are introducing.

Mathematics and Physics support

Comment 1.2
A hyperbola is a curve obtained by plotting y against x with xy = constant.

Comment 2.5
The partial-differential operation $(\partial z/\partial x)_y$ consists of taking the first derivative of $z(x,y)$ with respect to x, treating y as a constant. For example, if $z(x,y) = x^2y$, then

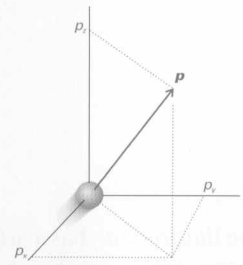
$$\left(\frac{\partial z}{\partial x}\right)_y = \left(\frac{\partial [x^2y]}{\partial x}\right)_y = y\frac{\mathrm{d}x^2}{\mathrm{d}x} = 2yx$$

Partial derivatives are reviewed in *Appendix 2.*

Comments

A topic often needs to draw on a mathematical procedure or a concept of physics; a *Comment* is a quick reminder of the procedure or concept.

978 Appendix 3 ESSENTIAL CONCEPTS OF PHYSICS



A3.1 The linear momentum of a particle is a vector property and points in the direction of motion.

Classical mechanics

Classical mechanics describes the behaviour of objects in expresses the fact that the total energy is constant in the a other expresses the response of particles to the forces acti

A3.3 The trajectory in terms of the energy

The **velocity**, v, of a particle is the rate of change of its po

$$v = \frac{\mathrm{d}r}{\mathrm{d}t}$$

The velocity is a vector, with both direction and magni velocity is the **speed**, v. The **linear momentum**, p, of a pa its velocity, v, by

$$p = mv$$

Like the velocity vector, the linear momentum vector po of the particle (Fig. A3.1). In terms of the linear momentu ticle is

Appendices

There is further information on mathematics and physics in Appendices 2 and 3, respectively. These appendices do not go into great detail, but should be enough to act as reminders of topics learned in other courses.

Problem solving

Illustration 5.2 *Using Henry's law*

To estimate the molar solubility of oxygen in water at 25°C and a partial pressure of 21 kPa, its partial pressure in the atmosphere at sea level, we write

$$b_{O_2} = \frac{p_{O_2}}{K_{O_2}} = \frac{21\ \text{kPa}}{7.9\times 10^4\ \text{kPa kg mol}^{-1}} = 2.9\times 10^{-4}\ \text{mol kg}^{-1}$$

The molality of the saturated solution is therefore 0.29 mmol kg^{-1}. To convert this quantity to a molar concentration, we assume that the mass density of this dilute solution is essentially that of pure water at 25°C, or $\rho_{H_2O} = 0.99709$ kg dm^{-3}. It follows that the molar concentration of oxygen is

$$[O_2] = b_{O_2}\times \rho_{H_2O} = 0.29\ \text{mmol kg}^{-1}\times 0.99709\ \text{kg dm}^{-3} = 0.29\ \text{mmol dm}^{-3}$$

A note on good practice The number of significant figures in the result of a calculation should not exceed the number in the data (only two in this case).

Self-test 5.5 Calculate the molar solubility of nitrogen in water exposed to air at 25°C; partial pressures were calculated in *Example 1.3*. [0.51 mmol dm^{-3}]

Illustrations

An *Illustration* (don't confuse this with a diagram!) is a short example of how to use an equation that has just been introduced in the text. In particular, we show how to use data and how to manipulate units correctly.

Example 8.1 *Calculating the number of photons*

Calculate the number of photons emitted by a 100 W yellow lamp in 1.0 s. Take the wavelength of yellow light as 560 nm and assume 100 per cent efficiency.

Method Each photon has an energy $h\nu$, so the total number of photons needed to produce an energy E is $E/h\nu$. To use this equation, we need to know the frequency of the radiation (from $\nu = c/\lambda$) and the total energy emitted by the lamp. The latter is given by the product of the power (P, in watts) and the time interval for which the lamp is turned on ($E = P\Delta t$).

Answer The number of photons is

$$N = \frac{E}{h\nu} = \frac{P\Delta t}{h(c/\lambda)} = \frac{\lambda P \Delta t}{hc}$$

Substitution of the data gives

$$N = \frac{(5.60\times 10^{-7}\ \mathrm{m})\times(100\ \mathrm{J\ s^{-1}})\times(1.0\ \mathrm{s})}{(6.626\times 10^{-34}\ \mathrm{J\ s})\times(2.998\times 10^{8}\ \mathrm{m\ s^{-1}})} = 2.8\times 10^{20}$$

Note that it would take nearly 40 min to produce 1 mol of these photons.

A note on good practice To avoid rounding and other numerical errors, it is best to carry out algebraic mainpulations first, and to substitute numerical values into a single, final formula. Moreover, an analytical result may be used for other data without having to repeat the entire calculation.

Self-test 8.1 How many photons does a monochromatic (single frequency) infrared rangefinder of power 1 mW and wavelength 1000 nm emit in 0.1 s?

[5×10^{14}]

Worked examples

A *Worked example* is a much more structured form of *Illustration*, often involving a more elaborate procedure. Every *Worked example* has a Method section to suggest how to set up the problem (another way might seem more natural: setting up problems is a highly personal business). Then there is the worked-out Answer.

Self-test 3.12 Calculate the change in G_m for ice at −10°C, with density 917 kg m^{-3}, when the pressure is increased from 1.0 bar to 2.0 bar. [+2.0 J mol^{-1}]

Self-tests

Each *Worked example*, and many of the *Illustrations*, has a *Self-test*, with the answer provided as a check that the procedure has been mastered. There are also free-standing *Self-tests* where we thought it a good idea to provide a question to check understanding. Think of *Self-tests* as in-chapter *Exercises* designed to help monitor your progress.

Discussion questions

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

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

1.3 Explain how the compression factor varies with pressure and temperature and describe how it reveals information about intermolecular interactions in real gases.

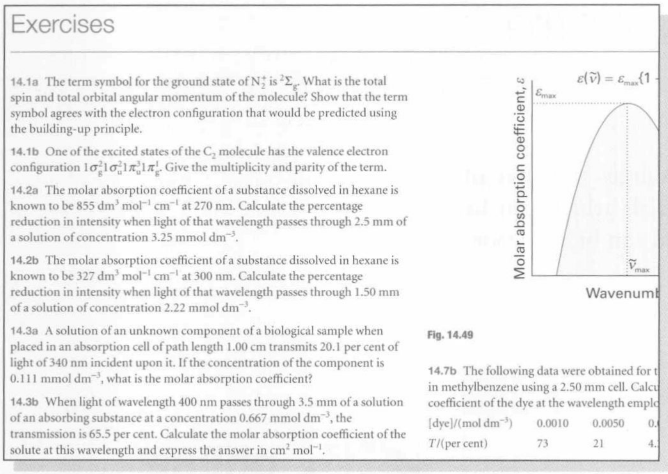
1.4 What is the significance of the critical c

1.5 Describe the formulation of the van de rationale for one other equation of state in

1.6 Explain how the van der Waals equatio behaviour.

Discussion questions

The end-of-chapter material starts with a short set of questions that are intended to encourage reflection on the material and to view it in a broader context than is obtained by solving numerical problems.


Exercises

14.1a The term symbol for the ground state of N_2^+ is $^2\Sigma_g$. What is the total spin and total orbital angular momentum of the molecule? Show that the term symbol agrees with the electron configuration that would be predicted using the building-up principle.

14.1b One of the excited states of the C_2 molecule has the valence electron configuration $1\sigma_g^2 1\sigma_u^2 1\pi_u^3 1\pi_g^1$. Give the multiplicity and parity of the term.

14.2a The molar absorption coefficient of a substance dissolved in hexane is known to be 855 $dm^3\,mol^{-1}\,cm^{-1}$ at 270 nm. Calculate the percentage reduction in intensity when light of that wavelength passes through 2.5 mm of a solution of concentration 3.25 mmol dm^{-3}.

14.2b The molar absorption coefficient of a substance dissolved in hexane is known to be 327 $dm^3\,mol^{-1}\,cm^{-1}$ at 300 nm. Calculate the percentage reduction in intensity when light of that wavelength passes through 1.50 mm of a solution of concentration 2.22 mmol dm^{-3}.

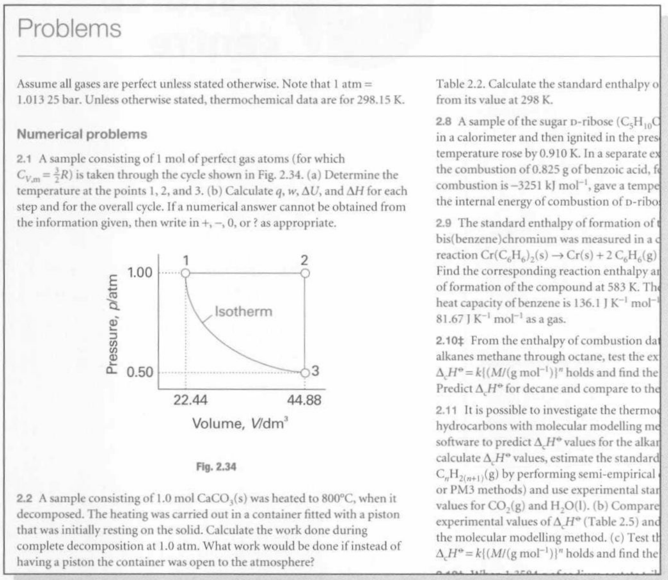
14.3a A solution of an unknown component of a biological sample when placed in an absorption cell of path length 1.00 cm transmits 20.1 per cent of light of 340 nm incident upon it. If the concentration of the component is 0.111 mmol dm^{-3}, what is the molar absorption coefficient?

14.3b When light of wavelength 400 nm passes through 3.5 mm of a solution of an absorbing substance at a concentration 0.667 mmol dm^{-3}, the transmission is 65.5 per cent. Calculate the molar absorption coefficient of the solute at this wavelength and express the answer in $cm^2\,mol^{-1}$.

Fig. 14.49

14.7b The following data were obtained for t
in methylbenzene using a 2.50 mm cell. Calcu
coefficient of the dye at the wavelength emplo

[dye]/(mol dm^{-3})	0.0010	0.0050	0.
T/(per cent)	73	21	4.


Problems

Assume all gases are perfect unless stated otherwise. Note that 1 atm = 1.013 25 bar. Unless otherwise stated, thermochemical data are for 298.15 K.

Numerical problems

2.1 A sample consisting of 1 mol of perfect gas atoms (for which $C_{V,m} = \frac{3}{2}R$) is taken through the cycle shown in Fig. 2.34. (a) Determine the temperature at the points 1, 2, and 3. (b) Calculate q, w, ΔU, and ΔH for each step and for the overall cycle. If a numerical answer cannot be obtained from the information given, then write in +, −, 0, or ? as appropriate.

Fig. 2.34

2.2 A sample consisting of 1.0 mol $CaCO_3$(s) was heated to 800°C, when it decomposed. The heating was carried out in a container fitted with a piston that was initially resting on the solid. Calculate the work done during complete decomposition at 1.0 atm. What work would be done if instead of having a piston the container was open to the atmosphere?

Table 2.2. Calculate the standard enthalpy o
from its value at 298 K.

2.8 A sample of the sugar D-ribose (C_5H_{10}C
in a calorimeter and then ignited in the pres
temperature rose by 0.910 K. In a separate ex
the combustion of 0.825 g of benzoic acid, f
combustion is −3251 kJ mol^{-1}, gave a tempe
the internal energy of combustion of D-ribo

2.9 The standard enthalpy of formation of t
bis(benzene)chromium was measured in a c
reaction $Cr(C_6H_6)_2(s) \rightarrow Cr(s) + 2\,C_6H_6(g)$
Find the corresponding reaction enthalpy a
of formation of the compound at 583 K. Th
heat capacity of benzene is 136.1 J $K^{-1}\,mol^{-1}$
81.67 J $K^{-1}\,mol^{-1}$ as a gas.

2.10‡ From the enthalpy of combustion da
alkanes methane through octane, test the ex
$\Delta_c H^\ominus = k\{(M/(g\,mol^{-1}))\}^n$ holds and find the
Predict $\Delta_c H^\ominus$ for decane and compare to the

2.11 It is possible to investigate the thermo
hydrocarbons with molecular modelling me
software to predict $\Delta_c H^\ominus$ values for the alka
calculate $\Delta_c H^\ominus$ values, estimate the standard
$C_nH_{2(n+1)}$(g) by performing semi-empirical
or PM3 methods) and use experimental sta
values for CO_2(g) and H_2O(l). (b) Compare
experimental values of $\Delta_c H^\ominus$ (Table 2.5) and
the molecular modelling method. (c) Test th
$\Delta_c H^\ominus = k\{(M/(g\,mol^{-1}))\}^n$ holds and find the

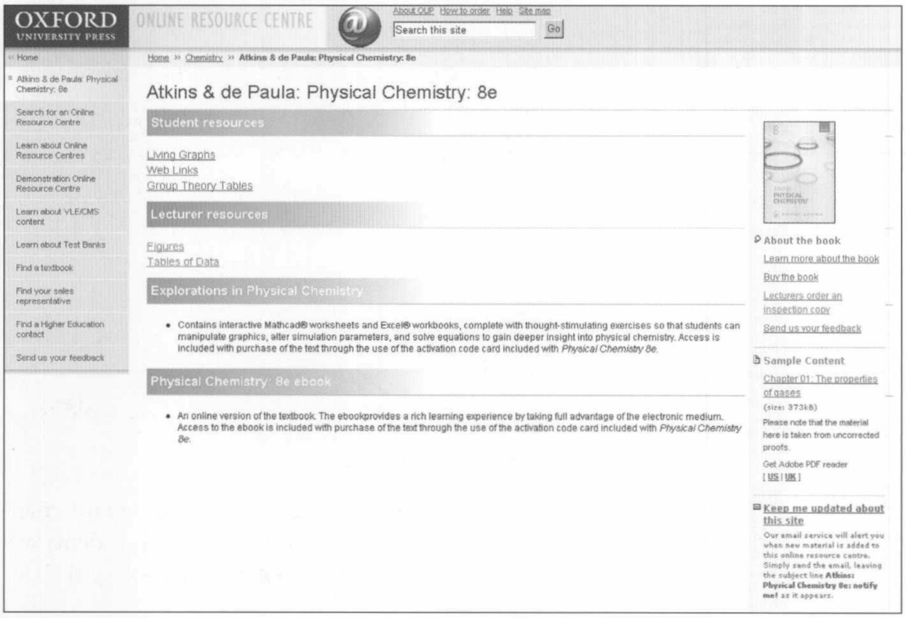
Exercises and Problems

The real core of testing understanding is the collection of end-of-chapter *Exercises* and *Problems*. The *Exercises* are straightforward numerical tests that give practice with manipulating numerical data. The *Problems* are more searching. They are divided into 'numerical', where the emphasis is on the manipulation of data, and 'theoretical', where the emphasis is on the manipulation of equations before (in some cases) using numerical data. At the end of the *Problems* are collections of problems that focus on practical applications of various kinds, including the material covered in the *Impact* sections.

About the Online Resource Centre

The Online Resource Centre provides teaching and learning resources. It is free of charge, complements the textbook, and offers additional materials which can be downloaded. The resources it provides are fully customizable and can be incorporated into a virtual learning environment. Go to:

www.oxfordtextbooks.co.uk/orc/pchem8e/



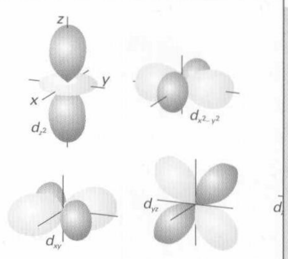
The material includes:

Living graphs

A *Living graph* is indicated in the text by the icon attached to a graph. This feature can be used to explore how a property changes as a variety of parameters are changed. To encourage the use of this resource (and the more extensive *Explorations in Physical Chemistry*) we have added a question to each figure where a *Living graph* is called out.

10.16 The boundary surfaces of d orbitals. Two nodal planes in each orbital intersect at the nucleus and separate the lobes of each orbital. The dark and light areas denote regions of opposite sign of the wavefunction.

Exploration To gain insight into the shapes of the f orbitals, use mathematical software to plot the boundary surfaces of the spherical harmonics $Y_{3,m_l}(\theta,\varphi)$.



Artwork

An instructor may wish to use the illustrations from this text in a lecture. Almost all the illustrations are available and can be used for lectures without charge (but not for commercial purposes without specific permission). This edition is in full colour: we have aimed to use colour systematically and helpfully, not just to make the page prettier.

Tables of data

All the tables of data that appear in the chapter text are available and may be used under the same conditions as the figures.

Web links

There is a huge network of information available about physical chemistry, and it can be bewildering to find your way to it. Also, a piece of information may be needed that we have not included in the text. The web site might suggest where to find the specific data or indicate where additional data can be found.

Group theory tables

Comprehensive group theory tables are available for downloading.

Explorations in Physical Chemistry

Physical chemistry describes the dynamic processes that shape the world around us; it is far removed from the perception of abstract theories and relationships held by so many students. But how can students make the jump from abstract equation to the reality of physical chemistry in action? *Explorations in Physical Chemistry* offers a unique way to bring physical chemistry to life.

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

Explorations in Physical Chemistry is available on-line at www.oxfordtextbooks.co.uk/orc/explorations/, using the activation code card included with *Atkins' Physical Chemistry* 8e. It can also be purchased as a CD-ROM (978-019-928894-6).

Physical Chemistry, Eighth Edition eBook

A complete online version of the textbook. The eBook provides a rich learning experience by taking full advantage of the electronic medium integrating all student media resources and adds features unique to the eBook. The eBook also offers lecturers unparalleled flexibility and customization options not previously possible with any printed textbook. Access to the eBook is included with purchase of the text through the use of the activation code card included with *Atkins' Physical Chemistry* 8e.

Key features of the eBook include:

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Solutions manuals

As with previous editions, Charles Trapp, Carmen Giunta, and Marshall Cady have produced the solutions manuals to accompany this book. A *Student's Solutions Manual* (978-019-928858-8) provides full solutions to the 'a' exercises and the odd-numbered problems. An *Instructor's Solutions Manual* (978-019-928857-1) provides full solutions to the 'b' exercises and the even-numbered problems.

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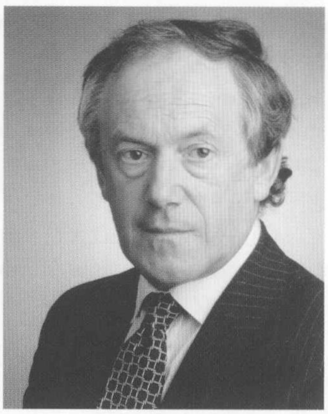

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