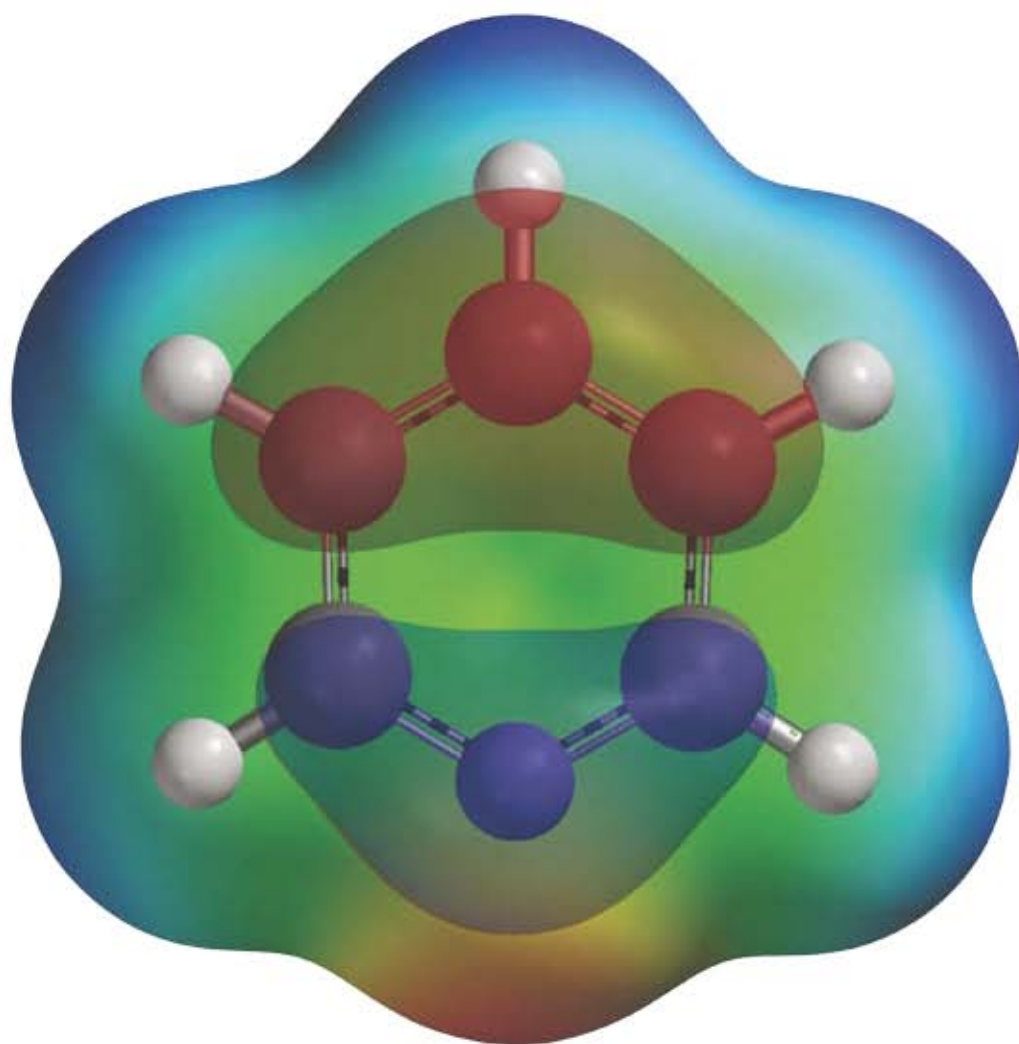# Quanta, Matter, and Change

A molecular approach to physical chemistry

Peter Atkins, Julio de Paula, and Ronald Friedman

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Quanta, Matter, and Change

A molecular approach to physical chemistry

Quanta, Matter, and Change: A molecular approach to physical chemistry

Quanta, Matter, and Change

A molecular approach to physical chemistry

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About the book

Our *Physical Chemistry* has always started with thermodynamics, progressed on to quantum mechanics, and then brought these two great rivers together by considering statistical thermodynamics. We always took care to enrich the thermodynamics with molecular understanding, and wrote the text so that it could be used flexibly to suit the pedagogical inclinations of its users. There are many, though, who consider it more appropriate to build an understanding of the subject from a firm foundation of quantum theory and then to show how the concepts of thermodynamics emerge as the microscopic evolves into the macroscopic. This text is directed at them.

We have taken the cloth of *Physical Chemistry*, unravelled it, and woven a new cloth that begins from quantum theory, establishes the link with the macroscopic world by introducing statistical thermodynamics, and then shows how thermodynamics is used to describe bulk properties of matter. But this is no mere reordering of topics. As we planned the book and then progressed through its writing, we realized that we had to confront issues that required fundamentally new approaches even to very familiar material. In fact, we experienced a kind of intellectual liberation that comes from looking at a familiar subject from a new perspective. Therefore, although readers will see material that has appeared throughout the editions of *Physical Chemistry*, there is an abundance of new material, new approaches to familiar topics, and—we hope—a refreshing new insight into the familiar.

The text is divided into five parts and preceded by a *Fundamentals* section that reviews the material that we presume is already familiar to readers at this level but about which their memories might need a gentle prod. In *Part 1, Quantum theory*, we set out the foundations of quantum mechanics in terms of its postulates and then show how these principles are used to describe motion in one and more dimensions. We have acknowledged the present surge of interest in nanoscience, and have built our presentation around these exciting systems. In *Part 2, Atoms molecules, and assemblies*, we turn to the more traditional nano-systems of chemistry and work progressively through the building blocks of chemistry, ending with solids. We have paid particular attention to computational chemistry, which is, of course, of great practical significance throughout chemistry. We have confronted head on the sheer difficulty of presenting computational chemistry at this level by illustrating all the major techniques by focusing on an almost trivially simple system. Our aim in this important chapter was to give a sense of reality to this potentially recondite subject: we develop understanding and provide a launching platform for those who wish to specialize further. *Part 3, Molecular spectroscopy*, brings together all the major spectroscopic techniques, building on the principles of quantum mechanics introduced in Part 1.

Part 4, Molecular thermodynamics, was for us the most challenging—and therefore the most exciting—part to write, for here we had to make the awesome passage from the quantum theory of microscopic systems to the thermodynamic properties of bulk matter. The bridge is provided by that most extraordinary concept, the Boltzmann distribution. Once that concept has been established, it can be used to develop an understanding of the central thermodynamic properties of internal energy and entropy. We have trodden carefully through this material, trying to maintain the sense that thermodynamics is a self-contained subject dealing with phenomenological relations between properties but, at the same time, showing the illumination that comes from a molecular perspective. We hope this sensitivity to the subject is apparent and that the new insights that we ourselves have acquired in the course of developing this material will be found to be interesting and informative. There are parts of traditional thermodynamics (phase equilibria, among them), we have to admit, that are not open to this kind of elucidation or at least would be made unduly complicated, and

we have not hesitated where our judgement persuaded us to set the molecular aside and present the material from a more straightforward classical viewpoint.

In *Part 5, Chemical dynamics*, we turn to another main stream of physical chemistry, the rates of reactions. Some of this material—the setting up of rate laws, for instance—can be expressed in a purely traditional manner, but there are aspects of the dynamics of chemical reactions that draw heavily on what has gone before.

The 'Using the book' section that follows gives details of the pedagogical apparatus in the book, but there is one feature that is so important that it must be mentioned in this Preface. The principal impediment to the 'quantum first' approach adopted by this text is the level of mathematics required, or at least the *perceived* level if not the actual level, for we have taken great pains to step carefully through derivations. The actual level of mathematics needed to understand the material is not great, but the thought that it exists can be daunting. To help overcome this barrier to understanding we have included a series of *Mathematical background* features between various chapters. These sections (there are eight) give background support to the mathematics that has been used in the preceding chapter and which will be drawn on in later chapters. We are aware that many chemists prefer the concrete to the abstract, and have illustrated the material with numerous examples.

We hope that you will enjoy using the book as much as we have enjoyed—and learned from—writing it and will appreciate that we have aimed to produce a book that illuminates physical chemistry from a new direction.

PWA
JdeP
RSF

Using the book

We have paid attention to the needs of the student, and have provided a lot of pedagogical features to make the learning process more enjoyable and effective. This section reviews these features. Paramount among them, though, is something that pervades the entire text: we have tried throughout to *interpret* the mathematical expressions, for mathematics is a language, and it is crucially important to be able to recognize what it is seeking to convey. We have paid particular attention to the level at which we introduce information, the possibility of progressively deepening one's understanding, and providing background information to support the development in the text. We have also been very alert to the demands associated with problem solving, and have provided a variety of helpful procedures.

Organizing the information

Checklist of key ideas

We have summarized the principal concepts introduced in each chapter as a checklist at the end of the chapter. We suggest checking off the box that precedes each entry when you feel confident about the topic.

Checklist of key ideas

☐ 1. A van der Waals interaction between closed-shell molecules is inversely proportional to the sixth power of their separation.

☐ 2. The permittivity is the quantity ε in the Coulomb potential energy, $V = Q_1Q_2/4\pi\varepsilon r$.

☐ 3. A polar molecule is a molecule with a permanent electric dipole moment; the magnitude of a dipole moment is the product of the partial charge and the separation.

☐ 4. The potential energy of the dipole–dipole interaction between two fixed (non-rotating) molecules is proportional to $\mu_1\mu_2/r^3$ and that between molecules that are free to rotate

☐ 8. A hydrogen bond is an interacti where A and B are N, O, or F.

☐ 9. The Lennard-Jones (12,6) poten is a model of the total intermole

☐ 10. In real gases, molecular interact state; the true equation of state i coefficients B, C, . . . : $pV_m = RT$

☐ 11. The van der Waals equation of s the true equation of state in whi represented by a parameter a an by a parameter b: $p = nRT/(V -$

Impact sections

Where appropriate, we have separated the principles from their applications: the principles are constant; 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, especially biology and materials science.

IMPACT ON BIOCHEMISTRY
I13.1 The helix–coil transition in polypeptides

The hydrogen bonds between amino acids of a polypeptide give rise to stable helical or sheet structures, which may collapse into a random coil when certain conditions are changed. The unwinding of a helix into a random coil is a *cooperative transition*, in which the polymer becomes increasingly more susceptible to structural changes once the process has begun. We examine here a model based on the principles of statistical thermodynamics that accounts for the cooperativity of the helix–coil transition in polypeptides.

To calculate the fraction of polypeptide molecules present as helix or coil we need to set up the partition function for the vari-

ward: we simply replace the upper li

$$\frac{q}{q_0} = \sum_{i=0}^{n} C(n,i)s^i$$

A cooperative transformation is modate, and depends on building a facilitate each other's conformational *model*, conversion from h to c is alle cent to the one undergoing the conv Thus, the zipper model allows a tran . . . → . . . $hhhcc$ . . . , but not a tran . . . → . . . $hchch$ . . . . The only except the very first conversion from h to

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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 (as specified by IUPAC, the International Union of Pure and Applied Chemistry) and to help avoid common mistakes.

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bsorbed by a molecule, the angular l system is conserved. If the me sense as the spin of the reases by 1.
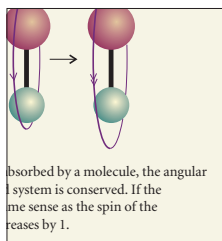
Self-test 10.4 Repeat the problem for $C^{35}ClH_3$ (see Self-test 10.2 for details).

[Lines of separation 0.944 cm^{-1} (28.3 GHz)]

A note on good practice For the discussion of spectroscopic transitions, the upper state is written first. So X → Y is an emission and X ← Y is an absorption, where X and Y specify the states in some way (such as by giving the value of the rotational quantum number J, as we have done above).

Justifications

On first reading it might be sufficient simply 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 to achieve full

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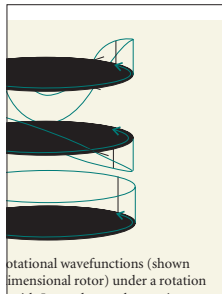
For hydrogen, $I = \frac{1}{2}$, and the ratio is 3:1. For N_2, with $I = 1$, the ratio is 1:2.
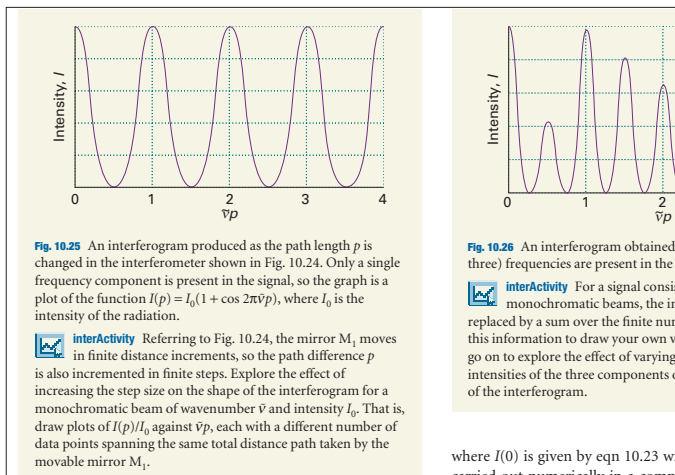
Justification 10.1 *The effect of nuclear statistics on rotational spectra*

Hydrogen nuclei are fermions (particles with half-integer spin quantum number; in their case $I = \frac{1}{2}$), so the Pauli principle requires the overall wavefunction to change sign under particle interchange. However, the rotation of an H_2 molecule through 180° has a more complicated effect than merely relabelling the nuclei, because it interchanges their spin states too if the nuclear spins are paired ($\uparrow\downarrow$) but not if they are parallel ($\uparrow\uparrow$).

For the overall wavefunction of the molecule to change

otational wavefunctions (shown imensional rotor) under a rotation

understanding 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.

interActivities

You will find that many of the graphs in the text have an *interActivity* attached: this is a suggestion about how you can use the on-line-resources of the book's website to explore the consequences of changing various parameters or of carrying out a more elaborate investigation related to the material in the illustration.

Fig. 10.25 An interferogram produced as the path length p is changed in the interferometer shown in Fig. 10.24. Only a single frequency component is present in the signal, so the graph is a plot of the function $I(p) = I_0(1 + \cos 2\pi\bar{\nu}p)$, where I_0 is the intensity of the radiation.

interActivity Referring to Fig. 10.24, the mirror M_1 moves in finite distance increments, so the path difference p is also incremented in finite steps. Explore the effect of increasing the step size on the shape of the interferogram for a monochromatic beam of wavenumber $\bar{\nu}$ and intensity I_0. That is, draw plots of $I(p)/I_0$ against $\bar{\nu}p$, each with a different number of data points spanning the same total distance path taken by the movable mirror M_1.

Fig. 10.26 An interferogram obtained when three) frequencies are present in the

interActivity For a signal consis monochromatic beams, the in replaced by a sum over the finite num this information to draw your own v go on to explore the effect of varying intensities of the three components o of the interferogram.

where $I(0)$ is given by eqn 10.23 wi carried out numerically in a comp

Further information

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.

Further information 13.2 *The partition functions of polyatomic rotors*

The energies of a symmetric rotor are

$$E_{J,K,M_J} = hc\bar{B}J(J+1) + hc(\bar{A} - \bar{B})K^2$$

with $J = 0, 1, 2, \ldots$, $K = J, J-1, \ldots, -J$, and $M_J = J, J-1, \ldots, -J$. Instead of considering these ranges, we can cover the same values by allowing K to range from $-\infty$ to ∞, with J confined to $|K|, |K|+1, \ldots, \infty$ for each value of K (Fig. 13.23). Because the energy is independent of M_J, and there are $2J+1$ values of M_J for each value of J, each value of J is $(2J+1)$-fold degenerate. It follows that the partition function

$$q = \sum_{J=0}^{\infty} \sum_{K=-J}^{J} \sum_{M_J=-J}^{J} e^{-E_{J,K,M_J}/kT}$$

can be written equivalently as

$$q = \sum_{K=-\infty}^{\infty} \sum_{J=|K|}^{\infty} (2J+1) e^{-E_{J,K,M_J}/kT}$$

$$= \sum_{K=-\infty}^{\infty} \sum_{J=|K|}^{\infty} (2J+1) e^{-hc\{\bar{B}J(J+1)+(\bar{A}-\bar{B})K^2\}/kT} \qquad (13.59)$$

Now we assume that the temperature is s occupied and that the sums may be appro

$$q = \int_{-\infty}^{\infty} e^{-\{hc(\bar{A}-\bar{B})/kT\}K^2} \int_{|K|}^{\infty} (2J+1)e^{-hc}$$

As before, the integral over J can be recog derivative of a function, which is the func

$$\int_{|K|}^{\infty} (2J+1)e^{-hc\bar{B}J(J+1)/kT}\,dJ = \int_{|K|}^{\infty} \left(-\frac{kT}{hc}\right)$$

$$= \left(-\frac{kT}{hc\bar{B}}\right)e^{-}$$

$$= \left(\frac{kT}{hc\bar{B}}\right)e^{-}$$

$$\approx \left(\frac{kT}{hc\bar{B}}\right)e^{-}$$

Synoptic tables and the Resource section

Long tables of data are helpful for assembling and solving exercises and problems, but can break up the flow of the text. The *Resource section* at the end of the text consists of a *Data section* with a lot of useful numerical information and a collection of other useful tables. Short extracts in the *Synoptic tables* in the text itself give an idea of the typical values of the physical quantities we are introducing.

Part 1 Data section

Physical properties of selected materials

	$\rho/(\text{g cm}^{-3})$ at 293 K†	T_f/K	T_b/K		$\rho/(\text{g cm}^{-3})$ at 293 K†
Elements				**Inorganic compounds**	
Aluminium(s)	2.698	933.5	2740	$CaCO_3$(s, calcite)	2.71
Argon(g)	1.381	83.8	87.3	$CuSO_4 \cdot 5H_2O$(s)	2.284
Boron(s)	2.340	2573	3931	HBr(g)	2.77
Bromine(l)	3.123	265.9	331.9	HCl(g)	1.187
Carbon(s, gr)	2.260	3700s		HI(g)	2.85
Carbon(s, d)	3.513			H_2O(l)	0.997
Chlorine(g)	1.507	172.2	239.2	D_2O(l)	1.104
Copper(s)	8.960	1357	2840	NH_3(g)	0.817
Fluorine(g)	1.108	53.5	85.0	KBr(s)	2.750
Gold(s)	19.320	1338	3080	KCl(s)	1.984
Helium(g)	0.125		4.22	NaCl(s)	2.165
Hydrogen(g)	0.071	14.0	20.3	H_2SO_4(l)	1.841
Iodine(s)	4.930	386.7	457.5		
Iron(s)	7.874	1808	3023	**Organic compounds**	
Krypton(g)	2.413	116.6	120.8	Acetaldehyde, CH_3CHO(l)	0.788
Lead(s)	11.350	600.6	2013	Acetic acid, CH_3COOH(l)	1.049

Mathematics support

A brief comment

A topic often needs to draw on a mathematical procedure or a concept of physics; *A brief comment* is a quick reminder of the procedure or concept.
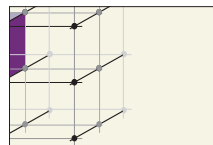
sided (but not necessarily the entire crystal structure can be slations (not reflections, rotations,

A brief comment A *symmetry operation* is an action (such as a rotation, reflection, or inversion) that leaves an object looking the same after it has been carried out. There is a corresponding *symmetry element* for each symmetry operation, which is the point, line, or plane with respect to which the symmetry operation is performed. For instance, an *n-fold rotation* (the symmetry operation) about an *n-fold axis of symmetry* (the corresponding symmetry element) is a rotation through $360°/n$. See Chapter 7 for a more detailed discussion of symmetry.

Mathematical background

It is often the case that you need a more full-bodied account of a mathematical concept, either because it is important to understand the procedure more fully or because you need to use a series of tools to develop an equation. The eight *Mathematical background* sections are located between chapters, primarily where they are first needed, and include many illustrations of how each concept is used.

MATHEMATICAL BACKGROUND 8: MULTIVA

MATHEMATICAL BACKGROUND 8
Multivariate calculus

A property of a system typically depends on a number of variables, such as the pressure depending on the amount, volume, and temperature according to an equation of state, $p = f(n,T,V)$. To understand how these properties vary with the conditions we need to understand how to manipulate their derivatives. This is the field of **multivariate calculus**, the calculus of several variables.

MB8.1 Partial derivatives

A **partial derivative** of a function of more than one variable, such as $f(x,y)$, is the slope of the function with respect to one of the variables, all the other variables being held constant (Fig. MB8.1). Although a partial derivative shows how a function changes when one variable changes, it may be used to determine how the function changes when more than one variable changes by an infinitesimal amount. Thus, if f is a function of x and y then, when x and y change by dx and dy, respectively, f changes by

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy \qquad \text{(MB8.1)}$$

● **A BRIEF ILLUSTRATION**

Suppose that $f(x,y) = ax^3y + b$
Fig. MB8.1), then

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

Then, when x and y undergo inf
by

$$df = 3ax^2y\,dx + (ax^3 + 2by)d$$

To verify that the order of taking
is irrelevant, we form

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

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

Self test **MB8.1** Evaluate df for
verify that the order of taking the
is irrelevant. $[df = 4x$

Problem solving

A brief illustration

A brief illustration 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.

● **A BRIEF ILLUSTRATION**

Consider a complex salt with three unpaired electrons per complex cation at 298 K, of mass density 3.24 g cm^{-3}, and molar mass 200 g mol^{-1}. First note that

$$\frac{N_A g_e^2 \mu_0 \mu_B^2}{3k} = 6.3001 \times 10^{-6} \text{ m}^3 \text{ K}^{-1} \text{ mol}^{-1}$$

Consequently,

$$\chi_m = 6.3001 \times 10^{-6} \times \frac{S(S+1)}{T/K} \text{ m}^3 \text{ mol}^{-1}$$

Substitution of the data with $S = \frac{3}{2}$ gives $\chi_m = 7.9 \times 10^{-8}$ m^3 mol^{-1}. Note that the density is not needed at this stage. To obtain the volume magnetic susceptibility, the molar susceptibility is divided by the molar volume $V_m = M/\rho$, where ρ is the mass density. In this *illustration*, $V_m = 61.7$ cm^3 mol^{-1}, so $\chi = 1.3 \times 10^{-3}$. ●

(c) Induced magnetic moments

An applied magnetic field induces the ci currents. These currents give rise to a ma opposes the applied field, so the substan few cases the induced field augments the substance is then paramagnetic.

The great majority of molecules with spins are diamagnetic. In these cases, the rents occur within the orbitals of the mol in its ground state. In the few cases in whi magnetic despite having no unpaired e electron currents flow in the opposite c can make use of unoccupied orbitals that in energy. This orbital paramagnetism from spin paramagnetism by the fact that pendent: this is why it is called **temperat magnetism** (TIP).

We can summarize these remarks as

Worked examples

Each *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) and use or find the necessary data. Then there is the worked-out *Answer*, where we emphasize the importance of using units correctly.

Example 13.5 *Evaluating the rotational partition function explicitly*

Evaluate the rotational partition function of $^1H^{35}Cl$ at 25°C, given that $\tilde{B} = 10.591$ cm^{-1}.

Method We use eqn 13.19 and evaluate it term by term. Once again, we use $kT/hc = 207.224$ cm^{-1} at 298.15 K. The sum is readily evaluated by using mathematical software.

Answer To show how successive terms contribute, we draw up the following table by using $hc\tilde{B}/kT = 0.051\,11$ (Fig. 13.8):

J	0	1	2	3	4	$\cdots$ 10
$(2J+1)e^{-0.05111J(J+1)}$	1	2.71	3.68	3.79	3.24	$\cdots$ 0.08

The sum required by eqn 13.19 (the sum of the numbers in the second row of the table) is 19.9, hence $q^R = 19.9$ at this temperature. Taking J up to 50 gives $q^R = 19.902$. Notice that about ten J-levels are significantly populated but the number of populated *states* is larger on account of the $(2J+1)$-fold degeneracy of each level. We shall shortly encounter the approximation that $q^R \approx kT/hc\tilde{B}$, which in the present case gives $q^R = 19.6$, in good agreement with the exact value and with much less work.

CO_2	ν_1
	ν_2
	ν_3

* For more values, see Table 10.
and use $hc/k = 1.439$ K cm.

At room temperature $kT/hc \approx 20$ stants of many molecules are close 13.2) and often smaller (though the which $\tilde{B} = 60.9$ cm^{-1}, is one excep rotational levels are populated at n this is the case, the partition functio

Linear rotors: $q^R = \dfrac{kT}{hc\tilde{B}}$

Non-linear rotors: $q^R = \left(\dfrac{kT}{hc}\right)^3$

where $\tilde{A}$, $\tilde{B}$, and $\tilde{C}$ are the rotationa expressed as wavenumbers. Howeve sions, read on (to eqns 13.21 and 13

Self-tests

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

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.

Discussion questions

17.1 Explain how the mixing of reactants and products affects the position of chemical equilibrium.

17.2 Explain how a reaction that is not spontaneous may be driven forward by coupling to a spontaneous reaction.

17.3 Use concepts of statistical thermodynamics to describe the molecular features that determine the magnitudes of equilibrium constants and their variation with temperature.

17.4 Suggest how the thermodynamic equilibrium constant may respond differently to changes in pressure and temperature from the equilibrium constant expressed in terms of partial pressures.

17.5 Account for Le Chatelier's principle in terms of thermodynamic quantities. Can you think of a reason why the principle might fail?

17.6 State the limits to the generality of th as in eqn 17.28.

17.7 Distinguish between galvanic, electr

17.8 Explain why salt bridges are routinel measurements.

17.9 Discuss how the electrochemical ser redox reaction is spontaneous.

17.10 Describe a method for the determin of a redox couple.

17.11 Describe at least one non-calorime determining a standard reaction enthalpy

Exercises and Problems

The 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. Although this text includes many of the hundreds of *Exercises* and *Problems* that are present in the 8th edition of *Physical chemistry*, well more than half of them are entirely new or have been modified.

Exercises

17.1(a) Write the expressions for the equilibrium constants of the following reactions in terms of (i) activities and (ii) where appropriate, the ratios p/p° and the products $\gamma b/b^\circ$:

(a) $CO(g) + Cl_2(g) \rightleftharpoons COCl(g) + Cl(g)$
(b) $2 SO_2(g) + O_2(g) \rightleftharpoons 2 SO_3(g)$
(c) $Fe(s) + PbSO_4(aq) \rightleftharpoons FeSO_4(aq) + Pb(s)$
(d) $Hg_2Cl_2(s) + H_2(g) \rightleftharpoons 2 HCl(aq) + 2 Hg(l)$
(e) $2 CuCl(aq) \rightleftharpoons Cu(s) + CuCl_2(aq)$

17.1(b) Write the expressions for the equilibrium constants of the following reactions in terms of (i) activities and (ii) where appropriate, the ratios p/p° and the products $\gamma b/b^\circ$:

(a) $H_2(g) + Br_2(g) \rightleftharpoons 2 HBr(g)$
(b) $2 O_3(g) \rightleftharpoons 3 O_2(g)$
(c) $2 H_2(g) + O_2(g) \rightleftharpoons 2 H_2O(l)$
(d) $H_2(g) + O_2(g) \rightleftharpoons H_2O_2(aq)$
(e) $H_2(g) + I_2(g) \rightleftharpoons 2 HI(aq)$

17.2(a) Identify the stoichiometric numbers in the reaction $Hg_2Cl_2(s) + H_2(g) \rightarrow 2 HCl(aq) + 2 Hg(l)$.

17.2(b) Identify the stoichiometric numbers in the reaction $CH_4(g) + 2 O_2(g) \rightarrow CO_2(g) + 2 H_2O(l)$.

17.4(b) The equilibrium pressure of H_2 ov hydride, UH_3, at 500 K is 139 Pa. Calculat formation of $UH_3(s)$ at 500 K.

17.5(a) From information in the *Data sec* Gibbs energy and the equilibrium constan for the reaction $PbO(s) + CO(g) \rightleftharpoons Pb(s)$ reaction enthalpy is independent of temp

17.5(b) From information in the *Data sec* Gibbs energy and the equilibrium constan the reaction $CH_4(g) + 3 Cl_2(g) \rightleftharpoons CHCl_3$ reaction enthalpy is independent of temp

17.6(a) For $CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2 F^-(aq$ the standard Gibbs energy of formation o Calculate the standard Gibbs energy of fo

17.6(b) For $PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2 I^-(aq)$ the standard Gibbs energy of formation o Calculate the standard Gibbs energy of fo

17.7(a) In the gas-phase reaction $2 A + B$ when 1.00 mol A, 2.00 mol B, and 1.00 m come to equilibrium at 25°C, the resultin at a total pressure of 1.00 bar. Calculate (a

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The Book Companion Site to accompany *Quanta, Matter, and Change* provides teaching and learning resources to augment the printed book. It is free of charge, and provides additional material for download, which can be incorporated into a virtual learning environment.

The book companion site can be accessed by visiting

www.whfreeman.com/pchem.

Note that instructor resources are available only to registered adopters of the textbook. To register, simply visit www.whfreeman.com/pchem and follow the appropriate links. You will be given the opportunity to select your own username and password, which will be activated once your adoption has been verified.

Student resources are openly available to all, without registration.

The materials on the book companion site include:

Living graphs

A *Living graph* 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;* see below), we have included a suggested *interActivity* to many of the illustrations in the text.

Artwork

An instructor may wish to use the figures from this text in a lecture. Almost all the figures are available in PowerPoint® format and can be used for lectures without charge (but not for commercial purposes without specific permission).

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 artwork.

Group theory tables

Comprehensive group theory tables are available for downloading.

Weblinks

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 website might suggest where to find the specific data or indicate where additional data can be found.

Other resources

Explorations in Physical Chemistry by Valerie Walters, Julio de Paula, and Peter Atkins

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 can be purchased at www.whfreeman.com/explorations; ISBN 0-7167-0841-8.

Solutions manuals

Two solutions manuals accompany this book; both are written by Charles Trapp, Marshall Cady, and Carmen Giunta.

A *Student's Solutions Manual* (ISBN 1-4292-2375-8) provides full solutions to the 'a' exercises, and the odd-numbered problems.

An *Instructor's Solutions Manual* (1-4292-2374-x) provides full solutions to the 'b' exercises, and the even-numbered problems.

About the authors

Peter Atkins is a fellow of Lincoln College in the University of Oxford and the author of more than sixty 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, 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.

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Acknowledgements

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