PHYSICAL CHEMISTRY

THIRD EDITION

THOMAS ENGEL | PHILIP REID

Physical Chemistry

THIRD EDITION

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University of Washington

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University of Washington

Chapter 26, "Computational Chemistry,"
was contributed by

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Values of Selected Physical Constants

Constant	Symbol	Value
Atomic mass constant	amu	$1.660\,538921 \times 10^{-27}$ kg
Avogadro's constant	N_A	$6.022\,14129 \times 10^{23}$ mol^{-1}
Bohr magneton	$\mu_B = e\hbar/2m_e$	$9.274\,00968 \times 10^{-24}$ J T^{-1}
Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2$	$5.291\,772\,1092 \times 10^{-11}$ m
Boltzmann constant	k_B	$1.380\,6488 \times 10^{-23}$ J K^{-1}
		$0.695\,03476$ cm^{-1}
Electron rest mass	m_e	$9.109\,38291 \times 10^{-31}$kg
Faraday constant	F	9.64853365×10^{4} C mol^{-1}
Gravitational constant	G	6.67384×10^{-11} m^3 kg^{-1} s^{-2}
Standard acceleration of gravity	G_n	9.80665 m s^{-2}
Molar gas constant	R	8.3144621 J K^{-1} mol^{-1}
		$0.083\,144621$ dm^3 bar K^{-1} mol^{-1}
		$0.082\,0578$ dm^3 atm K^{-1}mol^{-1}
Molar volume, ideal gas		
(1 bar, 0°C)		22.710953 L mol^{-1}
(1 atm, 0°C)		22.413968 L mol^{-1}
Nuclear magneton	$\mu_N = e\hbar/2m_p$	$5.050\,78353 \times 10^{-27}$ J T^{-1}
Permittivity of vacuum	ε_0	$8.854\,187\,817 \times 10^{-12}$ C^2 J^{-1} m^{-1}
Planck constant	h	$6.626\,069\,57 \times 10^{-34}$ J s
	$\hbar$	$1.054\,571726 \times 10^{-34}$ J s
Proton charge	e	$1.602\,176\,565 \times 10^{-19}$ C
Proton magnetogyric ratio	γ_p	$2.675\,221\,28 \times 10^{8}$ s^{-1}T^{-1}
Proton rest mass	m_p	$1.672\,621\,777 \times 10^{-27}$ kg
Rydberg constant for infinite nuclear mass	$R_\infty = m_e e^4/8\varepsilon_0^2 h^2$	$2.179\,8736 \times 10^{-18}$ J
		$109\,73731.568\,539$ m^{-1}
Rydberg constant for H	R_H	109677.581 cm^{-1}
Speed of light in vacuum	c	$2.99\,792\,458 \times 10^{8}$ m s^{-1}
Stefan-Boltzmann constant	$\sigma = 2\pi^5 k_B^4/15h^3c^2$	$5.670\,373 \times 10^{-8}$ J m^{-2} K^{-4} s^{-1}

SI Prefixes

Fraction	Prefix	Symbol	Fraction	Prefix	Symbol
10^{-1}	deci	d	10	deca	da
10^{-2}	centi	c	10^{2}	hecto	h
10^{-3}	milli	m	10^{3}	kilo	k
10^{-6}	micro	μ	10^{6}	mega	M
10^{-9}	nano	n	10^{9}	giga	G
10^{-12}	pico	p	10^{12}	tera	T
10^{-15}	femto	f	10^{15}	peta	P
10^{-18}	atto	a	10^{18}	exa	E

Greek Alphabet

Alpha	A	α	Iota	I	ι	Rho	P	ρ
Beta	B	β	Kappa	K	κ	Sigma	Σ	σ
Gamma	Γ	γ	Lambda	Λ	λ	Tau	T	τ
Delta	Δ	δ	Mu	M	μ	Upsilon	Y	υ
Epsilon	E	ε	Nu	N	ν	Phi	Φ	ϕ
Zeta	Z	ζ	Xi	Ξ	ξ	Chi	X	χ
Eta	H	η	Omicron	O	o	Psi	Ψ	ψ
Theta	Θ	θ	Pi	Π	π	Omega	Ω	ω

Conversion Table for Units

Length		
meter (SI unit)	m	
centimeter	cm	$= 10^{-2}$ m
ångström	Å	$= 10^{-10}$ m
micron	μ	$= 10^{-6}$ m
Volume		
cubic meter (SI unit)	m^3	
liter	L	$= dm^3 = 10^{-3}\ m^3$
Mass		
kilogram (SI unit)	kg	
gram	g	$= 10^{-3}$ kg
metric ton	t	= 1000 kg
Energy		
joule (SI unit)	J	
erg	erg	$= 10^{-7}$ J
rydberg	Ry	$= 2.179\ 87 \times 10^{-18}$ J
electron volt	eV	$= 1.602\ 176\ 565 \times 10^{-19}$ J
inverse centimeter	cm^{-1}	$= 1.986\ 455\ 684 \times 10^{-23}$ J
calorie (thermochemical)	Cal	= 4.184 J
liter atmosphere	l atm	= 101.325 J
Pressure		
pascal (SI unit)	Pa	
atmosphere	atm	= 101325 Pa
bar	bar	$= 10^5$ Pa
torr	Torr	= 133.322 Pa
pounds per square inch	psi	$= 6.894\ 757 \times 10^3$ Pa
Power		
watt (SI unit)	W	
horsepower	hp	= 745.7 W
Angle		
radian (SI unit)	rad	
degree	°	$= \frac{2\pi}{360}\ \text{rad} = \left(\frac{1}{57.295\ 78}\right)\ \text{rad}$
Electrical dipole moment		
C m (SI unit)		
debye	D	$= 3.335\ 64 \times 10^{-30}$ C m

To Walter and Juliane,
my first teachers,
and to Gloria,
Alex,
and Gabrielle.

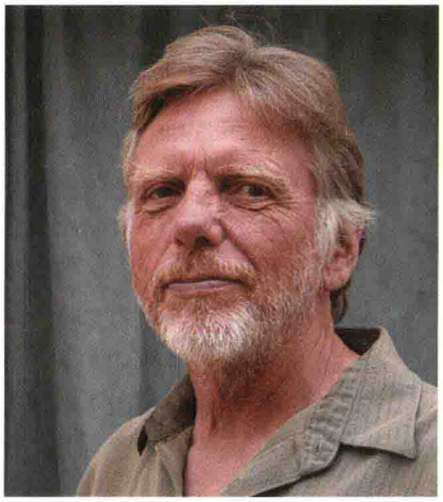
Thomas Engel

To my family.

Philip Reid

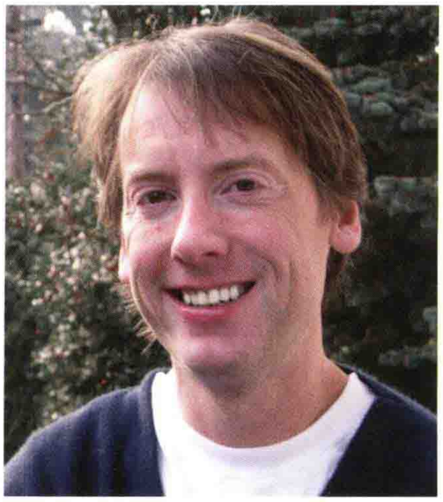
Brief Contents

About the Authors



Thomas Engel has taught chemistry at the University of Washington for more than 20 years, where he is currently professor emeritus of chemistry. Professor Engel received his bachelor's and master's degrees in chemistry from the Johns Hopkins University, and his Ph.D. in chemistry from the University of Chicago. He then spent 11 years as a researcher in Germany and Switzerland, in which time he received the Dr. rer. nat. habil. degree from the Ludwig Maximilians University in Munich. In 1980, he left the IBM research laboratory in Zurich to become a faculty member at the University of Washington.

Professor Engel's research interests are in the area of surface chemistry, and he has published more than 80 articles and book chapters in this field. He has received the Surface Chemistry or Colloids Award from the American Chemical Society and a Senior Humboldt Research Award from the Alexander von Humboldt Foundation.



Philip Reid has taught chemistry at the University of Washington since 1995. Professor Reid received his bachelor's degree from the University of Puget Sound in 1986, and his Ph.D. from the University of California, Berkeley in 1992. He performed postdoctoral research at the University of Minnesota, Twin Cities before moving to Washington.

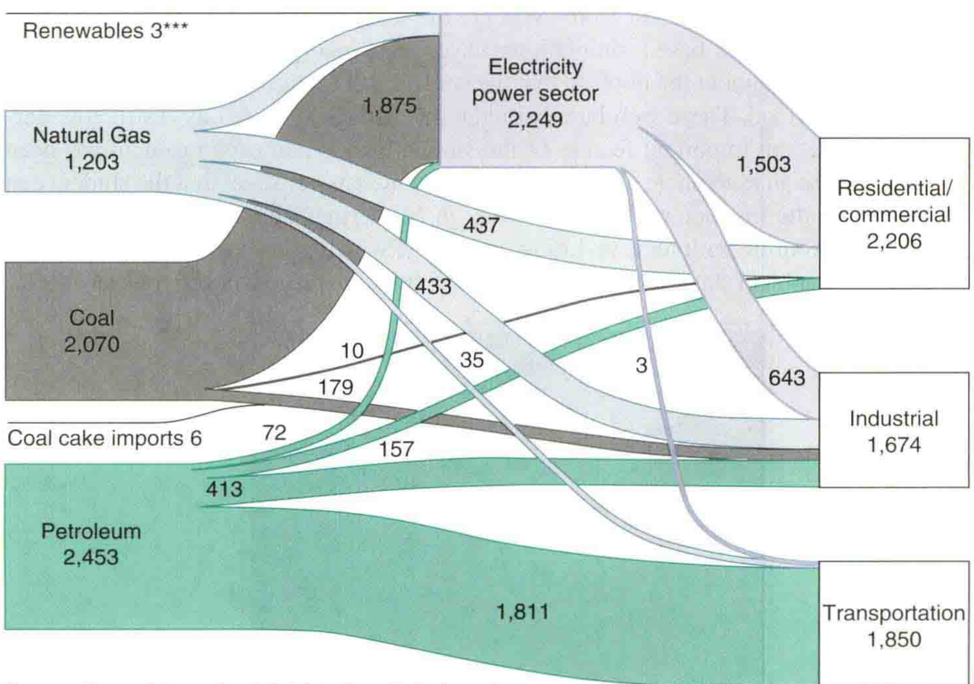
Professor Reid's research interests are in the areas of atmospheric chemistry, ultrafast condensed-phase reaction dynamics, and organic electronics. He has published more than 100 articles in these fields. Professor Reid is the recipient of a CAREER Award from the National Science Foundation, is a Cottrell Scholar of the Research Corporation, and is a Sloan Fellow. He received the University of Washington Distinguished Teaching Award in 2005.

Preface

The third edition of this book builds on user and reviewer comments on the previous editions. Our goal remains to provide students with an accessible overview of the whole field of physical chemistry while focusing on basic principles that unite the subdisciplines of the field. We continue to present new research developments in the field to emphasize the vibrancy of physical chemistry. Many chapters have been extensively revised as described below. We include additional end-of-chapter concept problems and most of the numerical problems have been revised. The target audience remains undergraduate students majoring in chemistry, biochemistry, and chemical engineering, as well as many students majoring in the atmospheric sciences and the biological sciences. The following objectives, illustrated with brief examples, outline our approach to teaching physical chemistry.

- **Focus on teaching core concepts.** The central principles of physical chemistry are explored by focusing on core ideas, and then extending these ideas to a variety of problems. The goal is to build a solid foundation of student understanding rather than cover a wide variety of topics in modest detail.
- **Illustrate the relevance of physical chemistry to the world around us.** Many students struggle to connect physical chemistry concepts to the world around them. To address this issue, example problems and specific topics are tied together to help the student develop this connection. Fuel cells, refrigerators, heat pumps, and real engines are discussed in connection with the second law of thermodynamics. The particle in the box model is used to explain why metals conduct electricity and why valence electrons rather than core electrons are important in chemical bond formation. Examples are used to show the applications of chemical spectroscopies. Every attempt is made to connect fundamental ideas to applications that are familiar to the

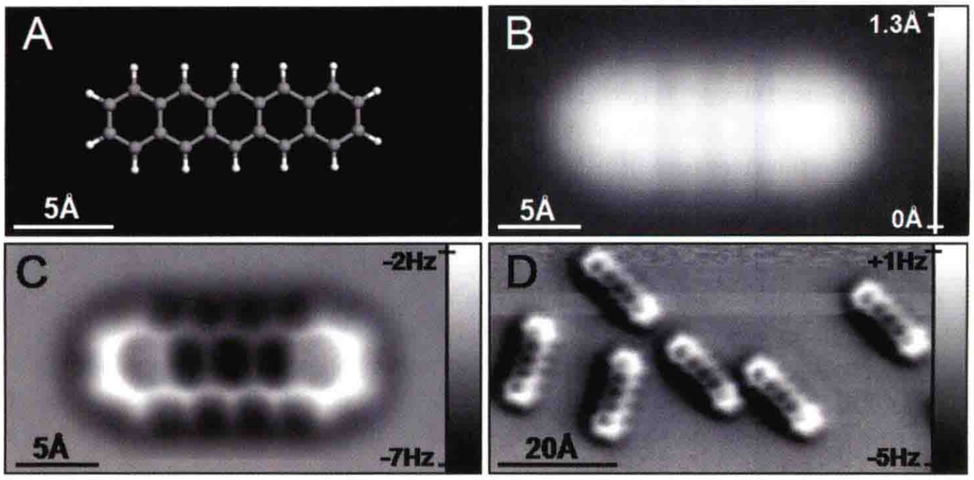
U.S. 2002 Carbon Dioxide Emissions from Energy Consumption – 5,682* Million Metric Tons of CO_2**



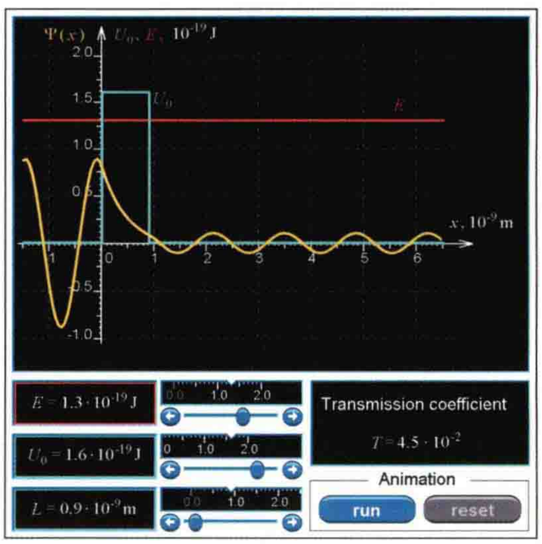
Source: Energy Information Administration. *Emissions of Greenhouse Gases in the United States 2002*. Tables 4–10.
*Includes adjustments of 42.9 million metric tons of carbon dioxide from U.S. territories, less 90.2 $MtCO_2$ from international and military bunker fuels.
**Previous versions of this chart showed emissions in metric tons of carbon, not of CO_2.
***Municipal solid waste and geothermal energy.
Note: Numbers may not equal sum of components because of independent rounding.

student. Art is used to convey complex information in an accessible manner as in the images here of U.S. carbon dioxide emissions.

- **Present exciting new science in the field of physical chemistry.** Physical chemistry lies at the forefront of many emerging areas of modern chemical research. Recent applications of quantum behavior include band-gap engineering, quantum dots, quantum wells, teleportation, and quantum computing. Single-molecule spectroscopy has led to a deeper understanding of chemical kinetics, and heterogeneous catalysis has benefited greatly from mechanistic studies carried out using the techniques of modern surface science. Atomic scale electrochemistry has become possible through scanning tunneling microscopy. The role of physical chemistry in these and other emerging areas is highlighted throughout the text. The following figure shows direct imaging of the arrangement of the atoms in pentacene as well as imaging of a delocalized molecular orbital using scanning tunneling and atomic force miscroscopies.



- **Web-based simulations illustrate the concepts being explored and avoid math overload.** Mathematics is central to physical chemistry; however, the mathematics can distract the student from "seeing" the underlying concepts. To circumvent this problem, web-based simulations have been incorporated as end-of-chapter problems throughout the book so that the student can focus on the science and avoid a math overload. These web-based simulations can also be used by instructors during lecture. An important feature of the simulations is that each problem has been designed as an assignable exercise with a printable answer sheet that the student can submit to the instructor. The Study Area in MasteringChemistry® also includes a graphing routine with a curve-fitting capability, which allows students to print and submit graphical data. The 50 web-based simulations listed in the end-of-chapter



problems are available in the Study Area of MasteringChemistry® for Physical Chemistry. MasteringChemistry® also includes a broad selection of end-of-chapter problems with answer-specific feedback.

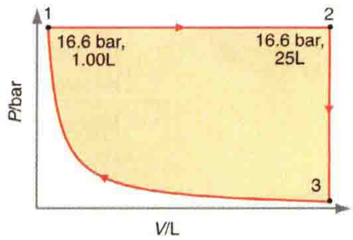
- **Show that learning problem-solving skills is an essential part of physical chemistry.** Many example problems are worked through in each chapter. They introduce the student to a useful method to solve physical chemistry problems.

EXAMPLE PROBLEM 2.5

A system containing 2.50 mol of an ideal gas for which $C_{V,m} = 20.79\ \text{J mol}^{-1}\ \text{K}^{-1}$ is taken through the cycle in the following diagram in the direction indicated by the arrows. The curved path corresponds to $PV = nRT$, where $T = T_1 = T_3$.

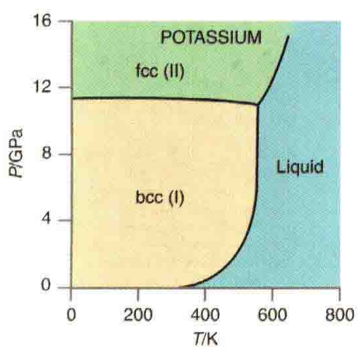
a. Calculate q, w, ΔU, and ΔH for each segment and for the cycle assuming that the heat capacity is independent of temperature.

b. Calculate q, w, ΔU, and ΔH for each segment and for the cycle in which the direction of each process is reversed.



- **The End-of-Chapter Problems cover a range of difficulties suitable for students at all levels.**

P8.6 A $P-T$ phase diagram for potassium is shown next.



Source: Phase Diagrams of the Elements by David A. Young. © 1991 Regents of the University of California. Published by the University of California Press.

a. Which phase has the higher density, the fcc or the bcc phase? Explain your answer.

b. Indicate the range of P and T in the phase diagram for which fcc and liquid potassium are in equilibrium. Does fcc potassium float on or sink in liquid potassium? Explain your answer.

c. Redraw this diagram for a different pressure range and indicate where you expect to find the vapor phase. Explain how you chose the slope of your liquid–vapor coexistence line.

- **Conceptual questions at the end of each chapter ensure that students learn to express their ideas in the language of science.**

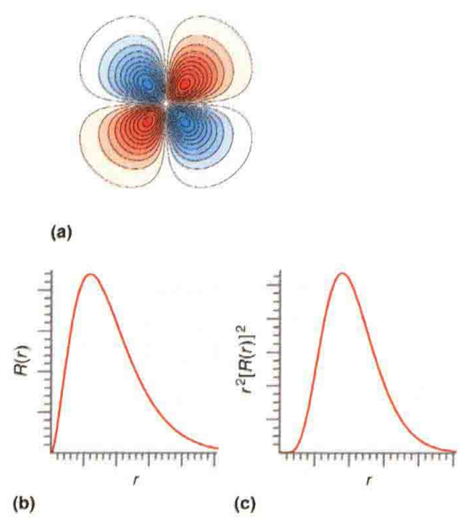
Conceptual Problems

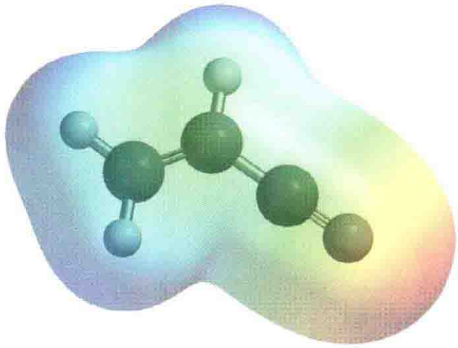
Q21.1 Why does the effective nuclear charge for the 1s orbital increase by 0.99 in going from oxygen to fluorine but only increases by 0.65 for the 2p orbital?

Q21.2 There are more electrons in the $n = 4$ shell than for the $n = 3$ shell in krypton. However, the peak in the radial distribution in Figure 21.6 is smaller for the $n = 4$ shell than for the $n = 3$ shell. Explain this fact.

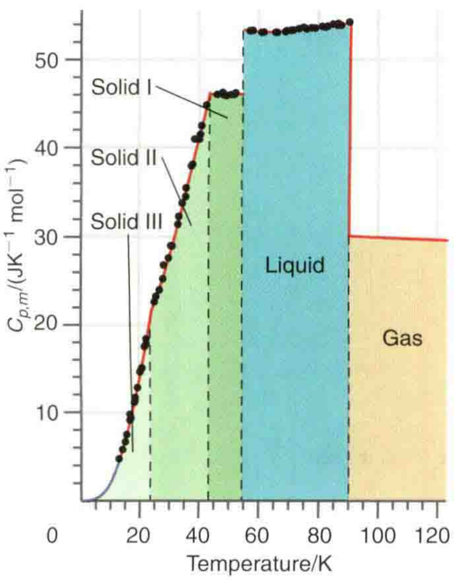
Q21.3 How is the effective nuclear charge related to the size of the basis set in a Hartree–Fock calculation?

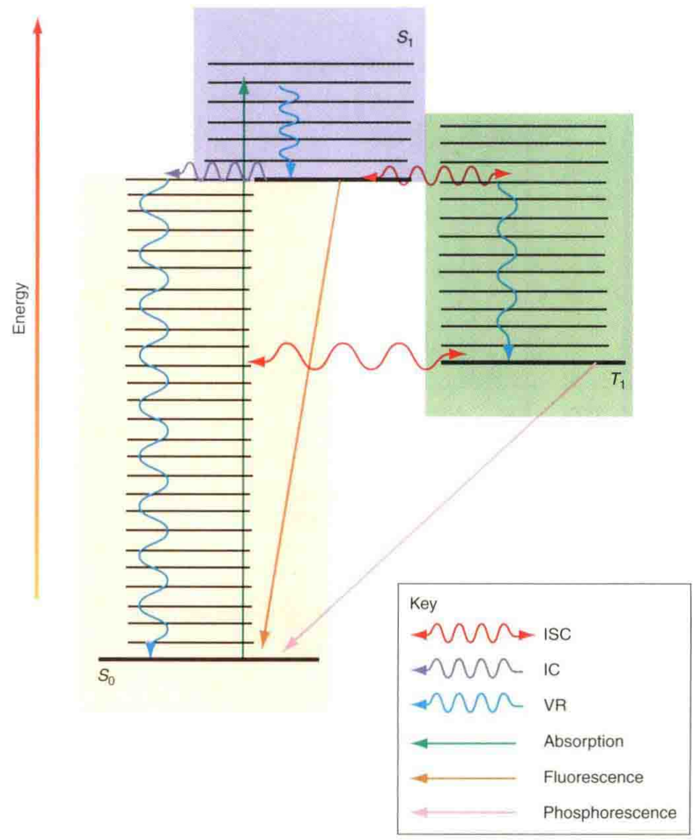
Q21.4 The angular functions, $\Theta(\theta)\Phi(\phi)$, for the one-electron Hartree–Fock orbitals are the same as for the hydrogen atom, and the radial functions and radial probability functions are similar to those for the hydrogen atom. The contour coloring is explained in the caption to figure 20.7. The following figure shows (a) a contour plot in the xy plane with the y axis being the vertical axis, (b) the radial function, and (c) the radial probability distribution for a one-electron orbital. Identify the orbital (2s, 4d_{xz}, and so on).





- **Integrate computational chemistry into the standard curriculum.** The teaching of quantum mechanics has not taken advantage of the widespread availability of Ab Initio Software. Many chapters include computational problems for which detailed instructions for the student are available in the Study Area in MasteringChemistry®. It is our experience that students welcome this material, (see L. Johnson and T. Engel, *Journal of Chemical Education* 2011, 88 [569-573]) which transforms the teaching of chemical bonding and molecular structure from being qualitative to quantitative. For example, an electrostatic potential map of acetonitrile built in Spartan Student is shown here.
- **Key equations.** Physical chemistry is a chemistry subdiscipline that is mathematics intensive in nature. Key equations that summarize fundamental relationships between variables are colored in red for emphasis.
- **Green boxes.** Fundamental principles such as the laws of thermodynamics and the quantum mechanical postulates are displayed in green boxes.
- **Updated graph design.** Color is used in graphs to clearly display different relationships in a single figure as shown in the heat capacity for oxygen as a function of temperature and important transitions in the electron spectroscopy of molecules.





This text contains more material than can be covered in an academic year, and this is entirely intentional. Effective use of the text does not require a class to proceed sequentially through the chapters, or to include all sections. Some topics are discussed in supplemental sections that can be omitted if they are not viewed as essential to the course. Also, many sections are self contained so that they can be readily omitted if they do not serve the needs of the instructor. This text is constructed to be flexible to your needs, not the other way around. We welcome the comments of both students and instructors how the material was used and how the presentation can be improved.

Thomas Engel
University of Washington

Philip Reid
University of Washington

New to This Edition

The third edition of *Physical Chemistry* includes changes at several levels. The most far-reaching change is the introduction of MasteringChemistry® for Physical Chemistry. Over 460 tutorials will augment the example problems in the book and enhance active learning and problem solving. Selected end of chapter problems are now assignable within MasteringChemistry® and numerical, equation and symbolic answer types are automatically graded.

The art program has been updated and expanded, and several levels of accuracy checking have been incorporated to increase accuracy throughout the text. Many new conceptual problems have been added to the book and most of the numerical problems have been revised. Significant content updates include moving part of the kinetic gas theory to Chapter 1 to allow a molecular level discussion of P and T. The heat capacity discussion previously in sections 2.5 and 3.2 have been consolidated in Chapter 2, and a new section on doing work and changing the system energy from a molecular level perspective has been added. The discussion of differential scanning calorimetry in Chapter 4 has been expanded and a molecular level discussion of entropy has been added to Chapter 5. The discussion of batteries and fuel cells in Chapter 11 has been revised and updated. Problems have been added to the end of Chapter 14 and a new section entitled on superposition wave functions has been added. A new section on traveling waves and potential energy barriers has been added to Chapter 16. The discussion of the classical harmonic oscillator and rigid rotor has been better integrated by placing these sections before the corresponding quantum models in Chapter 18. Chapter 23 has been revised to better introduce molecular orbital theory. A new section on computational results and a set of new problems working with molecular orbitals has been added to Chapter 24. The number and breadth of the numerical problems has been increased substantially in Chapter 25. The content on transition state theory in Chapter 32 has been updated. A discussion of oscillating reactions has been added to Chapter 36 and the material on electron transfer has been expanded.

Acknowledgments

Many individuals have helped us to bring the text into its current form. Students have provided us with feedback directly and through the questions they have asked, which has helped us to understand how they learn. Many of our colleagues including Peter Armentrout, Doug Doren, Gary Drobny, Graeme Henkelman, Lewis Johnson, Tom Pratum, Bill Reinhardt, Peter Rosky, George Schatz, Michael Schick, Gabrielle Varani, and especially Wes Borden and Bruce Robinson have been invaluable in advising us. Paul Siders generously provided problems for Chapter 24. We are also fortunate to have access to some end-of-chapter problems that were originally presented in *Physical Chemistry,* 3rd edition, by Joseph H. Noggle and in *Physical Chemistry,* 3rd edition, by Gilbert W. Castellan. The reviewers, who are listed separately, have made many suggestions for improvement, for which we are very grateful. All those involved in the production process have helped to make this book a reality through their efforts. Special thanks are due to Jim Smith, who helped initiate this project, to our editors Jeanne Zalesky and Jessica Neumann, and to the staff at Pearson, who have guided the production process.

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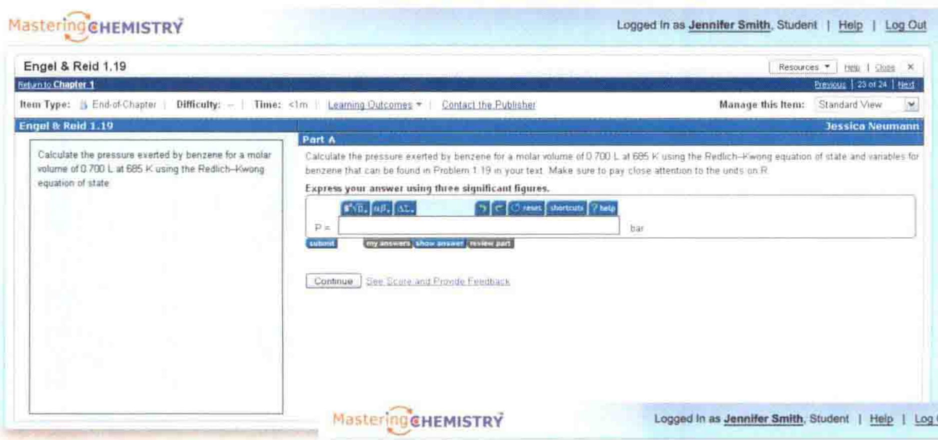

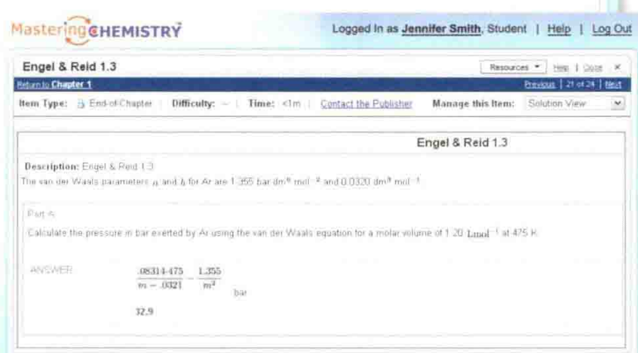

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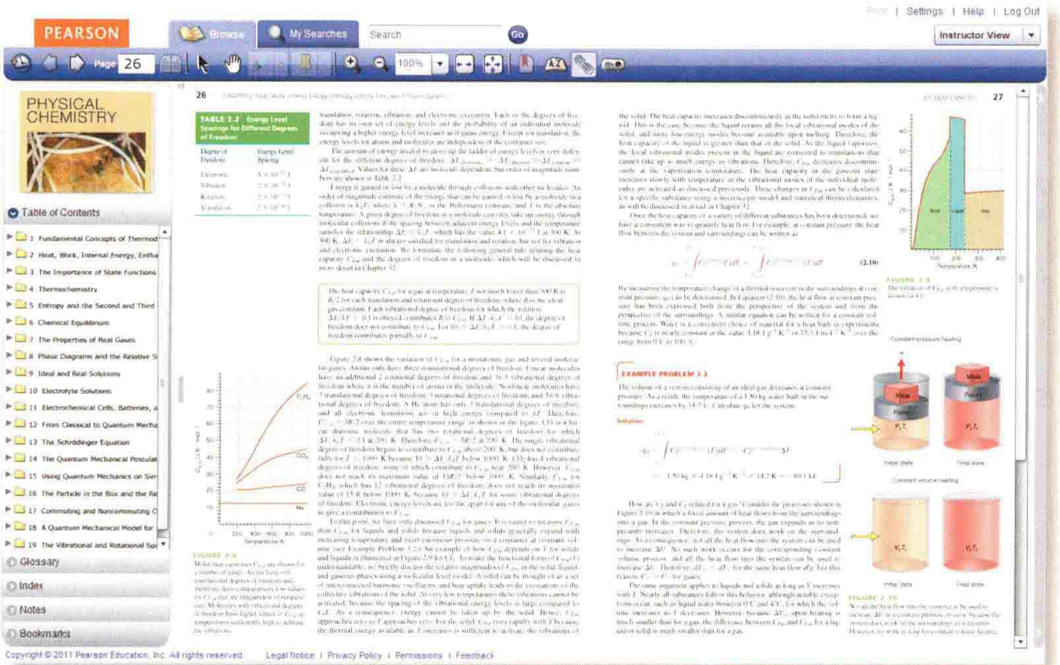

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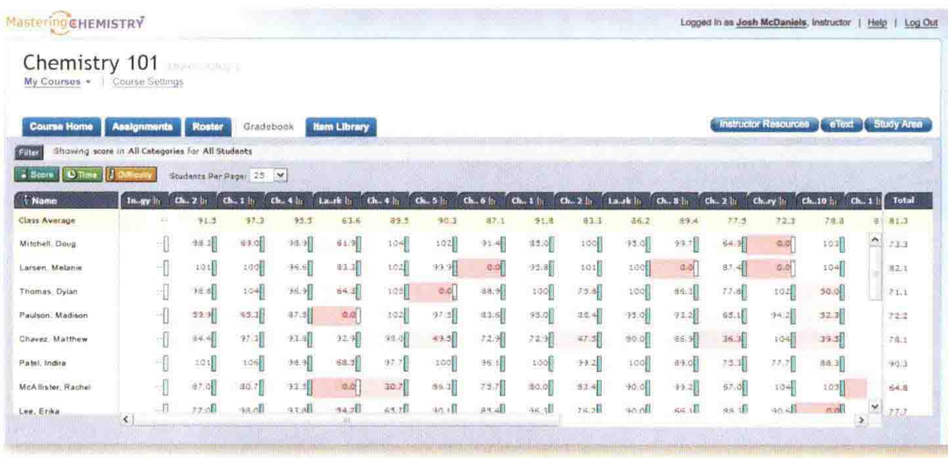

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Every assignment is automatically graded. Shades of red highlight vulnerable students and challenging assignments.

GRADEBOOK DIAGNOSTICS

This screen provides you with your favorite diagnostics. With a single click, charts summarize the most difficult problems, vulnerable students, grade distribution, and even score improvement over the course.