

PHYSICAL CHEMISTRY

Thermodynamics, Statistical Mechanics, & Kinetics



ANDREW COOKSY

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DEDICATION

To Mary, Wesley, and Owen

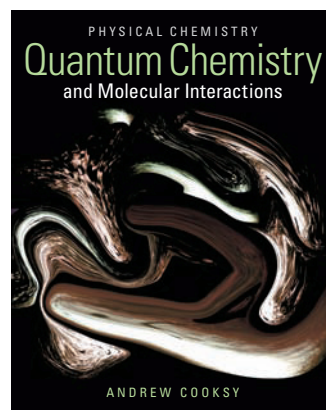
Cragged, and steep, Truth stands, and he that will
Reach her, about must, and about must go,
And what the hill's suddenness resists, winne so.
—*John Donne (1572-1631), Satire III*

Thermodynamics, Statistical Mechanics, & Kinetics

- A Introduction: Tools from Math and Physics
- 1 Classical Physical Chemistry Sets the Stage
- 2 Introduction to Statistical Mechanics: Building Up to the Bulk
- 3 Partitioning the Energy
- 4 Statistical Mechanics and Molecular Interactions
- 5 Mass Transport: Collisions and Diffusion
- 6 Energy Transport: Radiation and Matter
- 7 Introduction to Thermodynamics: Heat Capacity
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PHYSICAL CHEMISTRY

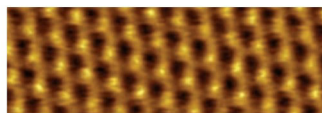
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This book is intended to provide students with a detailed guide to the reasoning that forms the basis for physical chemistry—the framework that unites all chemistry. The study of physical chemistry gives us the opportunity to look at our science as an integrated whole, with each concept connected to the next. My goal has been to trace those connections, step-by-step whenever possible, to show how each new concept makes sense given its place in the framework.

Because its ideas build upon each other in this way, physical chemistry can serve as the foundation for an intuitive understanding of chemistry in all its forms, whether synthesizing new compounds, analyzing samples in a forensic laboratory, or studying the properties of novel materials. To that end, this book emphasizes the shared, fundamental principles of chemistry, showing how we can justify the form and behavior of complex chemical systems by applying the laws of mathematics and physics to the structures of individual particles and then extrapolating to larger systems. We learn physical chemistry so that we can recognize these fundamental principles when we run into them in our other courses and in our careers. The relevance of this discipline extends beyond chemistry to engineering, physics, biology, and medicine: any field in which the molecular structure of matter is important.

A key step toward cultivating an intuition about chemistry is a thorough and convincing presentation of these fundamentals. When we see not only what the ideas are, but also how they link together, those ideas become more discernible when we examine a new chemical system or process. The following features of this text seek to achieve that objective.

- My aim is to provide a rigorous treatment of the subject in a relaxed style. A combination of qualitative summaries and annotated, step-by-step derivations illuminates the logic connecting the theory to the parameters that we can measure by experiment. Although we use a lot of math to justify the theory we are developing, the math will always make sense if we look at it carefully. We take advantage of this to strengthen our confidence in the results and our understanding of how the math relates to the physics. Nothing is more empowering in physical chemistry than finding that you can successfully predict a phenomenon using both mathematics *and* a qualitative physical argument. The manifestation of atomic and molecular structure in bulk properties of materials is a theme that informs the unhurried narrative throughout the text.
- To illustrate how our understanding in this field continues to advance, we take the time to examine several tools commonly used in the laboratory, (“Tools of the Trade”) while profiles of contemporary scientists

(“Biosketches”) showcase the ever-expanding frontiers of physical chemistry. Our intuition about chemistry operates at a deep level, held together by the theoretical framework, but these examples show how others are applying their understanding to solve real problems in the laboratory and beyond. They inspire us to think creatively about how the most fundamental chemical laws can answer our own questions about molecular structure and behavior.

- Our increasing appreciation and exploration of the interface between the molecular and the bulk scales has inspired a forward-looking coverage of topics that includes special attention to statistical mechanics throughout the volume.

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A Rigorous Standard with a Relaxed Style

“ A course in physical chemistry can describe the physical universe with uncommon depth, breadth, and clarity. The aim of this book is to help the reader make the most of the experience. ”

—Andrew Cooksy

PHYSICAL CHEMISTRY is the framework that unites all chemistry—providing powerful insight into the discipline as an integrated series of connected concepts.

As an instructor and author, Andrew Cooksy helps students uncover these connections while showing how they can be expressed in mathematical form and demonstrating the power that derives from such expressions.

The text's lively and relaxed narrative illuminates the relationship between the mathematical and the conceptual for students. By formulating the fundamental principles of physical chemistry in a mathematically precise but easily comprehensible way, students are able to acquire deeper insight—and greater mastery—than they ever thought possible.

This innovative approach is supported by several exclusive features:

- **Split quantum and thermodynamics volumes** can be taught in either order for maximum course flexibility.
- **A discrete chapter** (Chapter A) included in each volume summarizes the physics and mathematics used in physical chemistry.
- **Chapter opening sections** orient the students within the larger context of physical chemistry, provide an overview of the chapter, preview the physical and mathematical relationships that will be utilized, and set defined chapter objectives.
- **Unique pedagogical features** include annotations for key steps in derivations and an innovative use of color to identify recurring elements in equations.

Uncovering connections between foundational concepts

Reflective of the author's popular lecture strategy, chapter opening and closing features ground each topic within the larger framework of physical chemistry and help students stay oriented as they follow the development of chapter concepts.

Learning Objectives outline the skills students should expect to acquire from their study of the chapter.

Visual Roadmaps help students see the relationship between the chapters in each part of the text and the topics in each chapter.

PART I
EXTRAPOLATING FROM MOLECULAR TO MACROSCOPIC SYSTEMS

PART II
NON-REACTIVE MACROSCOPIC SYSTEMS

PART III
REACTIVE SYSTEMS

12 The Thermodynamics of Chemical Reactions
13 Chemical Kinetics: Elementary Reactions
14 Chemical Kinetics: Multi-Step Reactions

12 The Thermodynamics of Chemical Reactions

LEARNING OBJECTIVES
After reading this chapter, you will be able to do the following:

- 1 Identify the reactant, product, and transition state geometries on a reaction surface, and use the surface to estimate the energy of reaction and activation energy.
- 2 Calculate the enthalpy of an isothermal reaction at arbitrary temperature and pressure from the enthalpies of formation and heat capacities.
- 3 Calculate the adiabatic flame temperature of a compound.
- 4 Calculate the equilibrium constant of a reaction from the Gibbs free energies of formation, and estimate the effects of temperature.

GOAL Why Are We Here?
Our goal in this chapter is to apply the principles of thermodynamics described in Part II to chemical reactions. What motivates us is the promise of understanding how we can predict the flow of energy in and out of reactive systems, both so we know what to expect and so we can look for opportunities to control the process. While our primary thesis in this textbook has been that molecular structure determines the macroscopic properties of our system, so too can we turn that concept around and use macroscopic parameters such as pressure and temperature to influence the direction and extent of chemical reactions—processes that are defined by activity at the microscopic scale.

CONTEXT Where Are We Now?
Finally we get to real chemistry, having developed all the tools of math and physics we need to describe chemical systems in the absence of reaction. Those tools will continue to serve us well in this final stretch. Thermodynamics, for example, continues to be useful, and we shall start with its application to chemical reactions.
Our brand of thermodynamics will tell us only about the equilibrium states of the system, but that's a good place to start. By understanding the endpoints of the reaction, we can begin to see whether or not the reaction will be spontaneous, and if so what the driving force is.

SUPPORTING TEXT How Did We Get Here?
This chapter focuses a good deal on enthalpy and entropy of reaction, so our most important preparation will be a familiarity with those two parameters and how we manipulate them in solving problems about

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Context: Where Do We Go From Here? sections at the end of each chapter afford students a perspective on what they have just learned, and how it provides the foundation for the material explored in the next chapter.

Goal: Why Are We Here? chapter openers prepare students for the work ahead using one to two simple sentences.

Context: Where Are We Now? helps students understand how the chapter they are starting is related to what has come before and its place in the unfolding development of physical chemistry.

Supporting Text: How Did We Get Here? reviews previously introduced concepts, mathematical tools, and topical relationships that the new chapter will draw on.

Active research, tools, and techniques

Through learning about the instruments and methods of modern physical chemistry and meeting researchers at work today, students gain an appreciation for the practical applications of this science to many fields.

TOOLS OF THE TRADE Bomb Calorimetry

The distinction between heat and temperature was not well established until the end of the 19th century, and consequently there was no consistent theory to describe the release or absorption of heat by chemical processes such as phase changes or chemical reactions. Around 1780, Antoine Lavoisier and Pierre Laplace together developed an instrument for measuring heats of various processes, which they gauged by the amount of ice melted, but the work was ahead of its time. Nearly a century later, Marcellin Berthelot developed the first modern device for measuring the heat flow in a chemical reaction: the bomb calorimeter.

What is a bomb calorimeter? A calorimeter is any device that measures the heat flow during a process. Calorimeters are the chief diagnostic tool in thermodynamics, and we will draw on many results from calorimetry in the chapters ahead. A bomb calorimeter is any calorimeter that operates with the sample at a fixed volume.

Why do we use a bomb calorimeter? Standard bench-top conditions in the laboratory allow us to maintain a constant temperature of the system (using a water bath or

heating mantle) and a constant pressure (by exposure to the atmosphere or—for air-sensitive compounds—by working in a glove-box filled with an inert gas at fixed pressure).

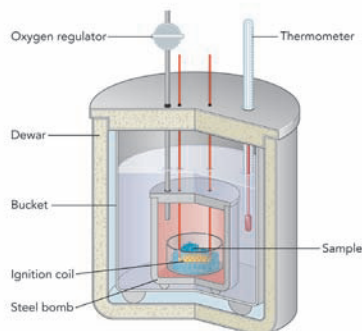
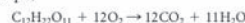
Why is fixed pressure important? Keeping the pressure fixed reduces the number of changing variables, which is convenient for record keeping alone, but it also simplifies the thermodynamics whenever we can set one parameter to a constant. By fixing the pressure, we ensure that the enthalpy change during a process is equal to the heat:

$$\Delta H = \int dH = \int (TdS + VdP)$$

$$(\Delta H)_P = \int (TdS + VdP)_P = \int (TdS) = q \text{ if } dP = 0,$$

where the subscript P indicates that the pressure is kept constant. The enthalpy was *invented* to make this relationship true.

But we have a more general definition—and a more intuitive understanding—of the *energy E*. If we want to measure ΔE instead of ΔH , however, the experiment can be much more challenging. The combustion of sucrose, for example,



► Schematic of a combustion bomb calorimeter.

Tools of the Trade sections highlight the design and operation of commonly used experimental apparatuses and how they relate to the principles discussed in the chapter.

Biosketches highlight a diverse array of contemporary scientists and engineers and their current research relating to physical chemistry.

BIOSKETCH William A. Lester, Jr.



William A. Lester, Jr. is Professor of the Graduate School at the University of California at Berkeley, where he carries out research on the extension of Monte Carlo methods

(see Section 9.5) to quantum mechanical models of chemical reactions. Quantum Monte Carlo (QMC) calculations allow the thermodynamics of the system to be solved at the molecular scale by, for example, randomly sampling possible forms of the electron distribution. This approach allows QMC to address complex problems, because the necessary computer resources—although quite high—grow slowly (relative to other methods) with the system's number of degrees of freedom. Professor Lester and his research group have shown that QMC yields structures and energies of molecules with high accuracy, and they have extended this work to calculating thermochemical properties of reactions. Among recent projects, they have applied QMC to the prediction of bond dissociation energies and heats of formation of hydrocarbons. Theoretical studies such as these are particularly valuable for combustion science, where the several reactions occur simultaneously and often too rapidly to be well characterized by experiment.

Conceptual Insight and Mathematical Precision in a Real World Context

A discrete summary of the prerequisite mathematics and physics adds flexibility and convenience by incorporating the necessary math tools in a single chapter.

TABLE A.5 Solutions to selected integrals. In these equations, a and b are constants, n is a whole number, and C is the constant of integration.

$\int x^n dx = \frac{1}{n+1} x^{n+1} + C$	$\int a dx = a(x + C)$
$\int \frac{1}{x} dx = \ln x + C$	$\int e^x dx = e^x + C$
$\int \ln x dx = x \ln x - x + C$	$\int \frac{dx}{x(a+bx)} = \frac{1}{a} \ln \left(\frac{a+bx}{x} \right) + C$
$\int \sin x dx = -\cos x + C$	$\int \cos x dx = \sin x + C$
$\int \sin^2(ax) dx = \frac{x}{2} - \frac{\sin(2ax)}{4a} + C$	$\int \cos^2(ax) dx = \frac{x}{2} + \frac{\sin(2ax)}{4a} + C$
$\int [f(x) + g(x)] dx = \int f(x) dx + \int g(x) dx$	$\int_a^b dx = x \Big _a^b = b - a$
$\int_0^a x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$	$\int_0^a e^{-ax} dx = \frac{1}{a} \left(\frac{\pi}{a} \right)^{1/2}$
$\int_0^a x e^{-ax} dx = \frac{1}{2a}$	$\int_0^a x^2 e^{-ax} dx = \frac{1}{4} \left(\frac{\pi}{a} \right)^{3/2}$
$\int_0^a x^{2n+1} e^{-ax} dx = \frac{n!}{2a^{n+1}}$	$\int_0^a x^{2n} e^{-ax} dx = \frac{[1 \cdot 3 \cdot 5 \dots (2n-1)] \sqrt{\pi}}{2^{n+1} a^{n+1/2}}$
$\int_0^a x^n e^{-ax} dx = \frac{n!}{a^{n+1}} - e^{-a} \sum_{k=0}^n \frac{n! a^{k-1}}{(n-k)!}$	

the value of C is lost. When we undo the derivative by taking the integral, we add an unknown constant of integration to the integrated expression. Omit this constant when solving definite integrals, because the limits of integration will determine its value.

- The function being integrated is the **integrand**, and it is multiplied by the incremental change along the coordinates, called the volume element.

Most of the algebraic solutions to integrals that we need appear in Table A.5.

EXAMPLE A.4 Analytical integration

PROBLEM Evaluate the numerical value for each of the following expressions.

- $\int_1^4 \frac{dx}{x}$
- $\int_0^{\infty} e^{-2x} dx$
- $\int_0^{\pi/3} (3 \cos^2 \theta - 1) \sin \theta d\theta$

SOLUTION These can be solved by substitution of the expressions in Table A.5.

- $\int_1^4 \frac{dx}{x} = \ln x \Big|_1^4 = \ln 4 - \ln 1 = 1.386 - 0 = 1.386$
- $\int_0^{\infty} e^{-2x} dx = -\frac{1}{2} e^{-2x} \Big|_0^{\infty} = -\frac{1}{2} (e^{-\infty} - e^0) = -\frac{1}{2} (0 - 1) = \frac{1}{2}$
- $\int_0^{\pi/3} (3 \cos^2 \theta - 1) \sin \theta d\theta = [-\cos^3 \theta + \cos \theta] \Big|_0^{\pi/3}$
 $= \left[-\left(\frac{1}{2}\right)^3 + \left(\frac{1}{2}\right) \right] - [-(1)^3 + (1)] = \frac{3}{8}$

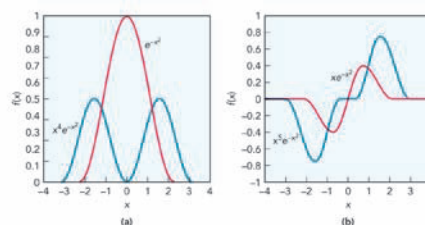
By the way, it is possible to apply rules of symmetry to extend some of the analytical solutions in Table A.5. For example, when the integrand is $x^{2n} e^{-ax^2}$, then the function is exactly the same from 0 to $-\infty$ as from 0 to $+\infty$ (Fig. A.3a). Therefore, the integral $\int_{-\infty}^{\infty} x^{2n} e^{-ax^2} dx$ is equal to 2 times $\int_0^{\infty} x^{2n} e^{-ax^2} dx$. However, if the power of x is odd, $2n+1$, then the function is negative when $x < 0$ and positive when $x > 0$ (Fig. A.3b). The integral from $-\infty$ to 0 cancels the integral from 0 to $+\infty$, so $\int_{-\infty}^{\infty} x^{2n+1} e^{-ax^2} dx = 0$.

Numerical integration

Not all integrals have algebraic solutions, and some have algebraic solutions only between certain limits (such as 0 and ∞). With suitable computers, any integral can be calculated without trying to cram it into some algebraic form. This is accomplished by going back to the definition in calculus,

$$\int_{x_1}^{x_2} f(x) dx = \lim_{N \rightarrow \infty} \left\{ \sum_{i=1}^N [f(x_i) + i \delta x] \right\} \delta x \quad (\text{A.20})$$

FIGURE A.3 Symmetry and definite integrals. (a) If a function $f(x)$ is equal to $f(-x)$ for all values of x , then the integral from $-\infty$ to $+\infty$ is equal to 2 times the integral from 0 to $+\infty$. (b) If $f(x)$ is equal to $-f(-x)$, then the integral from $-\infty$ to $+\infty$ is 0.



Chapter A provides a comprehensive summary of the physical laws and mathematical tools used to develop the principles of physical chemistry.

The distinctive use of color in the text's mathematical narrative allows students to identify important equation elements (such as the partition function) even as they take on different mathematical forms.

$$\begin{aligned}
 &= \sum_{\nu=0}^{\infty} \frac{e^{-\omega_e \nu / (k_B T)}}{q_{\text{vib}}(T)} \omega_e \nu \\
 &= (1 - e^{-\omega_e / (k_B T)}) \sum_{\nu=0}^{\infty} e^{-\omega_e \nu / (k_B T)} \omega_e \nu.
 \end{aligned}$$

Thoughtful **color-coding** in key equations makes it easier for students to follow the development of complex derivations as well as recognize common mathematical elements that appear in the representation of different physical situations.

Derivations Demystified

$$\begin{aligned}
 \left(\frac{\partial E}{\partial T}\right)_{V,n} &= \left(\frac{T\partial S - P\partial V}{\partial T}\right)_{V,n} && \text{by Eq. 7.12} \\
 &= \left(\frac{T\partial S}{\partial T}\right)_{V,n} && \partial V = 0 \text{ if } V \text{ constant} \\
 &= \left(\frac{dq}{dT}\right)_{V,n} && \text{by Eq. 7.43} \\
 &= C_V(T). && \text{by Eq. 7.39}
 \end{aligned}$$

Derivations are made transparent and comprehensible to students without sacrifice of mathematical rigor. **Colored annotations** provide crucial help to students by explaining important steps in key derivations.

DERIVATION SUMMARY The Maxwell-Boltzmann Distribution. Maxwell assumed that a Gaussian distribution applied to the velocity components v_x , v_y , v_z of all the velocity vectors \vec{v} of the particles in a gas, and we used this assumption to obtain a probability distribution of velocity vectors. To eliminate the dependence of direction, we integrated that distribution over all angles, which introduced a factor of v^2 in addition to the Gaussian exponential e^{-av} . We solved for the constant a in the exponential by requiring the mean square speed $\langle v^2 \rangle$ to predict the experimentally determined kinetic energy of a monatomic gas as a function of temperature. We also required the probability to be normalized, so that $\int_0^\infty \mathcal{P}_v(v) dv = 1$, in order to obtain the value of the coefficient that multiplies the entire function.

Summaries spell out the essential results of difficult derivations, making it easier to accommodate the needs of different courses, the preferences of different instructors, and the study and review habits of different students.

Supporting students' quest for deeper understanding

With numerous worked examples, robust review support, a wealth of end-of-chapter problems, and a solutions manual written by the text's author, students have everything they need to master the basics of physical chemistry.

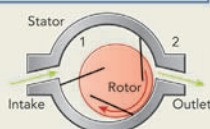
EXAMPLE 8.1 Gas Compression in a Pump

CONTEXT In many applications in chemistry and chemical engineering, we have to push gases from one place to another (for example, to get a reactant gas to the inlet of a reactor) or pull gases out of a container (for example, to create a vacuum in which we can manipulate ions in a mass spectrometer). We use gas pumps to do this. A typical configuration is a rotary vane pump, which admits gas at an inlet, traps it, compresses it to a smaller volume and higher pressure, and then releases it through an outlet at its new, higher pressure (Fig. 8.5). Pumps are rated partly by their **compression ratio**, the volume of the gas at the inlet to the gas at the outlet, $V_{\text{inlet}}/V_{\text{outlet}}$, which also gives the ratio of the outlet pressure to inlet pressure $P_{\text{outlet}}/P_{\text{inlet}}$. To achieve higher compression ratios (and therefore lower inlet pressures), a rotary vane pump may be divided into two stages, with the second stage taking the compressed gas from the first stage and compressing it still more. This can be an energy-intensive process, and we can use our results to estimate the minimum work necessary to compress a gas isothermally.

PROBLEM A vacuum chamber in a spectrometer is maintained at an operating pressure of 10.0 mtorr by a two-stage rotary vane pump with an exhaust pressure at the pump outlet of 800. torr. What is the minimum power in watts (J/s) consumed by the pump to keep the chamber at this pressure when there is a flow of 0.22 mmol/s and $T = 300.$ K?

SOLUTION The amount of gas moved in 1 second is 0.22 mol. This gas must be compressed by a factor of $800/0.010 = 80,000$ to achieve the pressure increase from inlet to outlet. The reversible work done per second gives the minimum power needed, because the reversible process wastes none of the work:

$$w_{T,\text{rev}} = -nRT \ln\left(\frac{V_2}{V_1}\right)$$
$$\frac{w_{T,\text{rev}}}{\Delta t} = -\left(\frac{n}{\Delta t}\right)RT \ln\left(\frac{P_1}{P_2}\right)$$
$$= -(0.22 \cdot 10^{-3} \text{ mol/s})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(300. \text{ K}) \ln(1/80,000) = 6.2 \text{ W}$$



▲ FIGURE 8.5 Schematic of a typical rotary-vane pump. The rotor spins inside the cavity of the stator, with vanes (shown as black lines) that slide in and out of the rotor as the gap between the rotor and stator changes. Vacuum pump oil makes a gas-tight seal between the regions separated by the vanes. As the rotor spins, gas enters through the intake into a high-volume region 1. As the rotor turns, the gas becomes trapped by the vanes and compressed until it gets pushed through the outlet.

Worked Examples provide students with context of the problem, clearly describe the parameters of the problem, and walk students step-by-step toward the solution.

KEY CONCEPTS AND EQUATIONS

KEY TERMS

OBJECTIVES REVIEW

PROBLEMS

A **comprehensive online solutions manual**, written by author Andrew Cooksy, is filled with unique solution sets emphasizing qualitative results to help students move beyond the math to a deeper conceptual understanding.

End-of-chapter materials bring students full circle, helping them assess their grasp of current chapter concepts and synthesize information from prior chapters.

MasteringChemistry[®] for Students

www.masteringchemistry.com

MasteringChemistry provides dynamic, engaging experiences that personalize and activate learning for each student. Research shows that Mastering's immediate feedback and tutorial assistance helps students understand and master concepts and skills—allowing them to retain more knowledge and perform better in this course and beyond.

The screenshot shows a tutorial titled "Formation Reactions". It defines the standard heat of formation, ΔH_f° , as the enthalpy change for the formation of one mole of substance from its constituent elements in their standard states. It provides a table of ΔH_f° values for NO(g), O(g), and NO₂(g). The tutorial includes a "Part A" question asking for the ΔH_f° of a reaction and a "Try Again" button.

Substance	ΔH_f° (kJ/mol)
NO(g)	90.2
O(g)	0
NO ₂ (g)	33.2

StudentTutorials

Physical chemistry tutorials reinforce conceptual understanding. Over 460 tutorials are available in MasteringChemistry for Physical Chemistry, including new ones on The Cyclic Rule and Thermodynamic Relation of Proofs.

The screenshot shows a tutorial titled "Problem 13.4". It asks the student to evaluate the function $f(x)$ for a given x . The tutorial includes a "Part A" question and a "Try Again" button.

End-of-Chapter Content Available in MasteringChemistry:

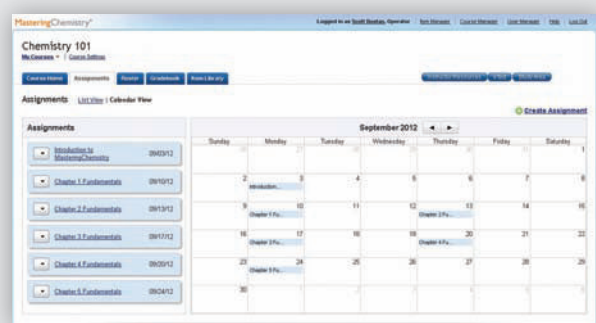
Selected end-of-chapter problems are assignable within MasteringChemistry, including:

- Numerical answer hints and feedback are only with tutorials in this course
- Equation and Symbolic answer types so that the results of a self-derivation can be entered to check for correctness, feedback, and assistance
- A Solution View that allows students to see intermediate steps involved in calculations of the final numerical result

The screenshot shows a tutorial titled "Problem 7.3". It asks the student to derive an expression for β in terms of N , k_B , T , P , and V . The tutorial includes a "Part A" question and a "Try Again" button.

Easy to get started. Easy to use.

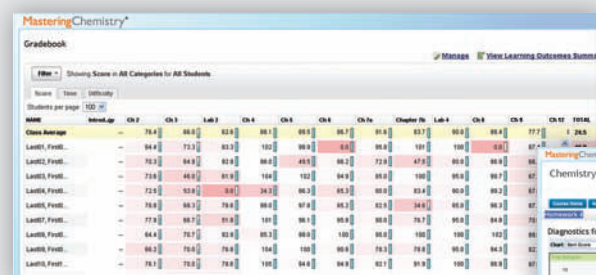
MasteringChemistry provides a rich and flexible set of course materials to get you started quickly, including homework, tutorial, and assessment tools that you can use *as is* or customize to fit your needs.



NEW! Calendar Features

The Course Home default page now features a **Calendar View** displaying upcoming assignments and due dates.

- Instructors can schedule assignments by dragging and dropping the assignment onto a date in the calendar. If the due date of an assignment needs to change, instructors can drag the assignment to the new due date and change the "available from and to dates" accordingly.
- The calendar view gives students a syllabus-style overview of due dates, making it easy to see all assignments due in a given month.



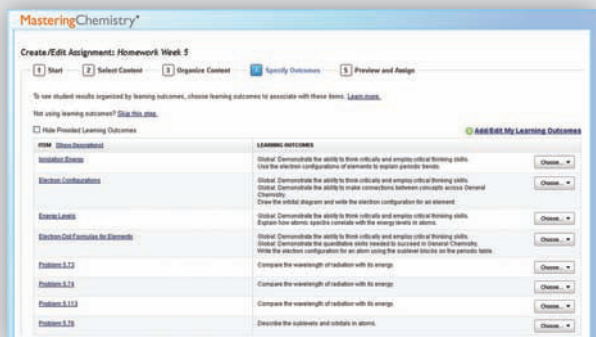
Gradebook

Every assignment is automatically graded. Shades of red highlight struggling students and challenging assignments at a glance.



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.



NEW! Learning Outcomes

Let Mastering do the work in tracking student performance against your learning outcomes:

- Add your own or use the publisher-provided learning outcomes.
- View class performance against the specified learning outcomes.
- Export results to a spreadsheet that you can further customize and share with your chair, dean, administrator, or accreditation board.



Introduction: Tools from Math and Physics

GOAL *Why Are We Here?*

The goal of this textbook is a concise and elegant exposition of the theoretical framework that forms the basis for all modern chemistry. To accomplish this, we are going to draw regularly on your knowledge of algebra, geometry, calculus, mechanics, electromagnetism, and chemistry. Physical chemistry is both rewarding and challenging in this way.

Mathematics of several varieties is our most valuable tool, and in this text we shall be interested in it only as a tool. It is not necessary, for example, that you remember how to derive the algebraic solution to the integral $\int \ln x \, dx$, but it will help if you know that an algebraic solution exists and how to use it (because with it we will obtain a useful equation for diffusion). This chapter is a summary of the math and physics that serve as our starting point as we explore the theory of chemistry. If you are embarking on this course, you may wish to review any of the following topics that appear alarmingly unfamiliar at first glance.

A.1 Mathematics

Algebra and Units

Basic Formula Manipulations

The use of algebra in this text is similar to its use in introductory physics and chemistry courses. We will routinely encounter the basic manipulations of variables in equations, especially to solve for one unknown in terms of several known constants. A tough example would be to solve for n_B in the equation

$$T_B = T'_B \left[\frac{V_T - V_A}{V_T - V'_A} \right]^{-n_B R / C_B}$$

The key is to see that a solution must be available, because the variable we are solving for appears in only one place, and a series of operations will allow us to isolate it on one side of the equation. Once we recognize that, then we can methodically undo the operations on one side of the equation to leave n_B : divide both sides by T'_B , take the logarithm of both sides to bring n_B down to earth from the exponent, and finally divide both sides by the factor that leaves n_B alone on one side of the equation. Those steps eventually bring us to

$$n_B = -\frac{C_B}{R} \frac{\ln\left(\frac{T_B}{T'_B}\right)}{\ln\left(\frac{V_T - V_A}{V_T - V'_A}\right)}.$$

One issue that makes the algebra something of a challenge is the notation. To put it mildly, we will use a lot of algebraic symbols. In fact, with the exception of “O,” which looks too much like a zero, we use the entire Roman alphabet at least twice, and most of the Greek.¹ The symbols have been chosen in hopes of an optimal combination of (a) preventing the same symbol from appearing with different meanings in the same chapter; (b) adherence to the conventional usage in the scientific literature, and (c) clarity of meaning. Unfortunately, these three aims cannot always be satisfied simultaneously. Physical chemistry is a synthesis of work done by pioneers in mathematics, physics, and chemistry, often without any intention that the results would one day become integrated into a general theory of chemistry. We bring together many fields that evolved independently, and the way these fields fit together is one of the joys of this course. Admittedly, the complexity of the notation is not.

The text provides guides to the notation used in long derivations and sample calculations to show how the notation is used. Please be aware, however, that no textbook gimmick can substitute for the reader’s understanding of the parameters represented by these symbols. If you recognize the difference between the fundamental charge e and the base of the natural logarithm e , you are in no danger of confusing the two, even though they are both represented by the letter “e,” sometimes appearing in the same equation.

Unit Analysis and Reasonable Answers

One of the most helpful tools for checking algebra and for keeping these many symbols under control is unit analysis. If a problem asks you to solve for the value of some variable Y , and you’re not certain what units you will get in the end, then it’s likely that the meaning of Y has not been made entirely clear. In many cases, including viscosities and wavefunctions, the units are not obvious from the variable’s definition in words but are easily determined from an important equation in which the variable appears. Quick: how do you write the units for pressure in terms of mass and distance and time? If you recall the definition of the pressure as force per unit area

$$P = \frac{F}{A}$$

¹If the lower case Greek letter upsilon (υ) didn’t look so much like an italic “v” (ν), there are at least two places it would have been used. It’s bad enough that ν and the Greek nu (ν) are so similar and sometimes appear in the same equation.

and know that force has units of mass times acceleration, then pressure must have units of

$$\begin{aligned} \frac{\text{force}}{\text{distance}^2} &= \frac{\text{mass} \times \text{speed}/\text{time}}{\text{distance}^2} = \frac{\text{mass} \times \text{distance}/\text{time}^2}{\text{distance}^2} \\ &= \frac{\text{mass}}{\text{distance} \times \text{time}^2} = \text{kg m}^{-1} \text{s}^{-2}. \end{aligned} \quad (\text{A.1})$$

It will not be worthwhile to attempt a problem before understanding the variables involved.

Unit analysis is also a useful guard against algebraic mistakes. An error in setting up an algebraic solution often changes the units of the answer, and a check of the answer's units will show the mistake. This does not protect against many other mistakes, however, such as dividing instead of multiplying by 10^{10} to convert a length from meters to angstroms. In such cases, there is no replacement for knowing what range of values is appropriate for the quantity. Recognizing a reasonable value for a particular variable is primarily a matter of familiarity with some typical parameters. The values given in Table A.1 are meant only to give common orders of magnitude for various quantities. Answers differing by factors of 10 from these may be possible, but not common.

TABLE A.1 Some typical values for parameters in chemical problems. These are meant only as a rough guide to expected values under typical conditions.

Parameter	Value (in typical units)
chemical bond length	1.5 Å
chemical bond energy	400 kJ mol ⁻¹
molecular speed	200 m s ⁻¹
mass density (solid or liquid)	1 g cm ⁻³

EXAMPLE A.1 Unreasonable Answers

PROBLEM Unit analysis and recognition of a reasonable value can prevent errors such as those that resulted in the following answers. Identify the problem with these results for the requested quantity:

Quantity	Wrong answer
the density of NaCl(s)	$1.3 \cdot 10^{-24} \text{ g cm}^{-3}$
the density of NaCl(s)	$3.3 \cdot 10^7 \text{ g cm}^{-1}$
bond length of CsI	12.3 m
speed of a molecule	$4.55 \cdot 10^{11} \text{ m s}^{-1}$
momentum of electron	$5 \cdot 10^{-10} \text{ m s}^{-1}$

SOLUTION Each of those examples gives an answer of entirely the wrong magnitude (which could arise from using the wrong conversion factor, the wrong units, or both).

Quantity	Wrong answer	Why unreasonable
the density of NaCl(s)	$1.3 \cdot 10^{-24} \text{ g cm}^{-3}$	too small
the density of NaCl(s)	$3.3 \cdot 10^7 \text{ g cm}^{-1}$	wrong units
bond length of CsI	12.3 m	too big
speed of a molecule	$4.55 \cdot 10^{11} \text{ m s}^{-1}$	too big (greater than speed of light)
momentum of electron	$5 \cdot 10^{-10} \text{ m s}^{-1}$	wrong units

In many problems, the units themselves require some algebraic manipulation because several units are products of other units. For example, the unit of pressure, $1 \text{ kg m}^{-1} \text{ s}^{-2}$, obtained in Eq. A.1, is called the “pascal.” We shall also encounter an equation

$$E_n = -\frac{Z^2 m_e e^4}{2(4\pi\epsilon_0)^2 n^2 \hbar^2},$$

in which E_n has units of energy, Z and n are unitless, m_e has units of mass, e has units of charge, ϵ_0 has units of charge² energy⁻¹ distance⁻¹, and \hbar has units of energy \times time. The units on each side of the equation must be identical, and this we can show by substituting in the appropriate units for mass, charge, and energy:

$$\begin{aligned} 1 \text{ J} &= 1 \frac{(\text{kg})(\text{C})^4}{(\text{C}^2 \text{ J}^{-1} \text{ m}^{-1})^2 (\text{Js})^2} \\ &= 1 \frac{(\text{kg})(\text{C})^4}{\text{C}^4 \text{ s}^2/\text{m}^2} \\ &= 1 \text{ kg m}^2 \text{ s}^{-2} = 1 \text{ J}. \end{aligned} \tag{A.2}$$

This may be a good place to remind you about that bothersome factor of $4\pi\epsilon_0$ and some other aspects of the SI units convention.

SI Units

The accepted standard for units in the scientific literature is the *Système International* (SI), based on the meter, kilogram, second, coulomb, kelvin, mole, and candela.² It is acceptable SI practice to use combinations of these units and to convert up or down by factors of 1000. So, for example, the SI unit of force should have units of (mass \times acceleration), or kg m s^{-2} , a unit commonly called the newton and abbreviated N. Energy has units of force \times distance, so the SI unit is $\text{kg m}^2 \text{ s}^{-2}$, also called the joule and abbreviated J. But the joule is inconveniently small for measuring, say, the energy released in a chemical reaction, so one could use the kilojoule (10^3 J) and remain true to the SI standard. We’ll give special attention to energy units shortly.

A practical advantage of a single system for all physical units is that—if you’re careful—the units take care of themselves. Allowing for the factors of 1000, if all the quantities on one side of an equation are in SI units, the value

²If you don’t recall the candela, that’s understandable. It’s the unit of luminous intensity, and with that, makes its last appearance in this text.

on the other side will also be in SI units. If an object of mass 2.0 kg rests on a table, subject to the gravitational acceleration of 9.8 m s^{-2} , then I can calculate the force it exerts on the table by multiplying the mass and the acceleration,

$$F = ma = (2.0 \text{ kg})(9.8 \text{ m s}^{-2}) = 20 \text{ N},$$

and I can be certain that the final value is in SI units for force, namely newtons.

Standardization of units takes time, however, and you can be certain that the chemical data you encounter in your career will not adhere to one standard. One formerly common set of units, now widely discouraged, is the **Gaussian** or **CGS system**, similar to SI except that it replaces the meter, kilogram, and coulomb with the centimeter, gram, and electrostatic unit, respectively. Another convention, now on the rise, is the set of atomic units, for which all units are expressed as combinations of fundamental physical constants such as the electron mass m_e and the elementary charge e .

The SI system, while having some features convenient to engineering, suffers from one inconvenience in our applications: elementary calculations that include electric charges or magnetic fields require the use of constants called the permeability μ_0 and permittivity ϵ_0 of free space. Although these constants originally appeared with a physical meaning attached, for our purposes they are merely conversion factors. In particular, the factor $4\pi\epsilon_0$ converts SI units of coulomb squared to units of energy times distance, $\text{J} \cdot \text{m}$. For example, the energy of repulsion between two electrons at a separation of $d = 1.0 \cdot 10^{-10} \text{ m}$ is

$$\frac{e^2}{4\pi\epsilon_0 d} = \frac{(1.602 \cdot 10^{-19} \text{ C})^2}{(1.113 \cdot 10^{-10} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1})(1.0 \cdot 10^{-10} \text{ m})} = 2.306 \cdot 10^{-18} \text{ J}. \quad (\text{A.3})$$

In contrast, the atomic and CGS units fold this conversion into the definition of the charge, and the factor of $4\pi\epsilon_0$ would *not* appear in the calculation. For all equations in this text involving the forces between charged particles, we conform to the standards of the day and use SI units and the associated factor of $4\pi\epsilon_0$.

In other cases, however, we will not adhere strictly to the SI standard. Even allowing for factors of 1000, I don't know any chemists who express molecular dipole moments in coulomb meters, a unit too large for its purpose by 30 orders of magnitude (not even prefixes like "micro-" and "nano-" are enough to save it). The conventional unit remains the debye, which is derived from CGS units (adjusted by 18 orders of magnitude, it must be said) and just the right size for measuring typical bond dipoles. The angstrom (\AA) also remains in wide use in chemistry because it is a metric unit ($1 \text{ \AA} = 10^{-10} \text{ m}$) that falls within a factor of 2 of almost any chemical bond length.

Of all the physical parameters, energy has the greatest diversity in commonly used scientific units. There are several ways to express energy, even after excluding all sorts of nonmetric energy units (such as the British thermal unit, kilowatt-hour, foot-pound, ton of TNT, and—most beloved of chemists—the calorie). Other conventions appear when discussing the interaction of radiation with matter, for which it is common to quantify energy in terms of the frequency (s^{-1}) or reciprocal wavelength (cm^{-1}) of the radiation. Under the proper assumptions, it may also be informative to convert an energy to a corresponding

temperature, in units of kelvin. Typical laboratory samples of a compound have numbers of molecules in the range of 10^{20} or more, and molecular energies are therefore often given in terms of the energy per mole of the compound (e.g., kJ mol^{-1}). These cases will be explained as they appear, and they are summarized in the conversion table for energies on this textbook's back endpapers.

Once these non-SI units are introduced, please make sure you are comfortable with the algebra needed to convert from one set of units to another. This one skill, mundane as it may seem, will likely be demanded of you in any career in science or engineering. Famous and costly accidents have occurred because this routine procedure was not given its due attention.³

Complex Numbers

Complex numbers are composed of a real number and an imaginary number added together. For our purposes, a complex number serves as a sort of two-dimensional number; the imaginary part contains data on a measurement distinct from the data given by the real part. For example, a sinusoidal wave that varies in time may be described by a complex number in which the real part gives the shape of the wave at the current time and the imaginary part describes what the wave will look like a short time later.

The imaginary part of any complex number is a real number multiplied by $i \equiv \sqrt{-1}$. (The symbol “ \equiv ” is used throughout this text to indicate a definition, as opposed to the “ $=$ ” symbol, used for equalities that can be proved mathematically.) This relationship between i and -1 allows the imaginary part of a complex number to influence the real-number results of an algebraic operation. For example, if a and b are both real numbers, then $a + ib$ is complex, with a the real part and ib the imaginary part. The **complex conjugate** of $a + ib$, written $(a + ib)^*$, is equal to $a - ib$, and the product of any number with its complex conjugate is a real number:

$$(a + ib)(a - ib) = a^2 - iba + iba - i^2b^2 = a^2 + b^2. \quad (\text{A.4})$$

Notice that the value of b —even though it was contained entirely in the imaginary parts of the two original complex numbers—contributes to the value of the real number quantity that results from this operation.

Many of the mathematical functions in the text are complex, but multiplication by the complex conjugate yields a real function, which can correspond directly to a measurable property. For that reason, we often judge the validity of the functions by whether we can integrate over the product f^*f . In this text, a well-behaved function f is single-valued, finite at all points, and yields a finite value when f^*f is integrated over all points in space. To be very well-behaved, the function and its derivatives should also be continuous functions, but we will use a few functions that are naughty in this regard.

³A prominent example is the loss in 1999 of the unmanned Mars Climate Orbiter, a probe that entered the Martian atmosphere too low and burned up because engineers were sending course correction data calculated using forces in pounds to an on-board system that was designed to accept the data in newtons.

EXAMPLE A.2 Complex Conjugates

PROBLEM Write the complex conjugate f^* for each of the following expressions f and show that the value of f^*f is real.

- $5 + 5i$
- $-x/i$
- $\cos x - i\sin x$

SOLUTION

1. $f^* = 5 - 5i$

$$f^*f = (5 + 5i)(5 - 5i) = 25 + 25 = 50$$

2. First we would like to put this in the form $a + ib$, so we multiply by $\frac{i}{i}$ to bring the factor of i into the numerator:

$$f = -\frac{x}{i}\left(\frac{i}{i}\right) = -\frac{ix}{-1} = ix$$

The real part of this function is zero, but for any complex conjugate, we change the sign on the imaginary term: $f^* = -ix$

$$f^*f = (ix)(-ix) = -i^2x^2 = x^2$$

3. $f^* = \cos x + i\sin x$

$$f^*f = \cos^2x - i^2\sin^2x = \cos^2x + \sin^2x = 1$$

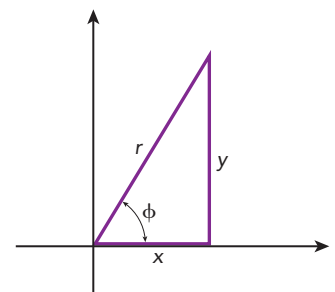
Trigonometry

Elementary results from trigonometry play an important role in our equations of motion, and therefore you should know the definitions of the sine, cosine, and tangent functions (and their inverses) as signed ratios of the lengths of the sides of a right triangle. Using the triangle drawn in Fig. A.1, with sides of length y , x , and r , we would define these functions as follows:

$$\begin{aligned} \sin \phi &\equiv \frac{y}{r} & \csc \phi &\equiv \frac{1}{\sin \phi} = \frac{r}{y} \\ \cos \phi &\equiv \frac{x}{r} & \sec \phi &\equiv \frac{1}{\cos \phi} = \frac{r}{x} \\ \tan \phi &\equiv \frac{y}{x} & \cot \phi &\equiv \frac{1}{\tan \phi} = \frac{x}{y} \end{aligned} \quad (\text{A.5})$$

The sign is important. If ϕ lies between 90° and 270° , then the x value becomes negative, so $\cos \phi$ and $\sec \phi$ would be less than zero. Similarly, $\sin \phi$ and $\csc \phi$ are negative for ϕ between 180° and 360° .

Please also make sure you are comfortable using the trigonometric identities listed in Table A.2. These are algebraic manipulations that may allow us to simplify equations or to isolate an unknown variable.



▲ **FIGURE A.1** Right triangle used to define trigonometric functions of the angle ϕ .