

Thermodynamics, Statistical Thermodynamics, and Kinetics 4e

Thomas Engel
Philip Reid



PHYSICAL CHEMISTRY

Thermodynamics, Statistical Thermodynamics, and Kinetics

FOURTH EDITION

Thomas Engel

University of Washington

Philip Reid

University of Washington



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Product Manager: Elizabeth Bell
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To Walter and Juliane,
my first teachers,
and to Gloria,
Alex, Gabrielle,
and Amelie.

THOMAS ENGEL

To my family.

PHILIP REID

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About the Authors

THOMAS ENGEL 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, during 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 has published more than 80 articles and book chapters in the area of surface chemistry. 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. Other than this textbook, his current primary science interests are in energy policy and energy conservation. He serves on the citizen's advisory board of his local electrical utility, and his energy-efficient house could be heated in winter using only a hand-held hair dryer. He currently drives a hybrid vehicle and plans to transition to an electric vehicle soon to further reduce his carbon footprint.



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 140 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 fourth edition of *Thermodynamics, Statistical Thermodynamics, and Kinetics* includes many changes to the presentation and content at both a global and chapter level. These updates have been made to enhance the student learning experience and update the discussion of research areas. At the global level, changes that readers will see throughout the textbook include:

- **Review of relevant mathematics skills.** One of the primary reasons that students experience physical chemistry as a challenging course is that they find it difficult to transfer skills previously acquired in a mathematics course to their physical chemistry course. To address this issue, contents of the third edition Math Supplement have been expanded and split into 11 two- to five-page Math Essentials, which are inserted at appropriate places throughout this book, as well as in the companion volume *Quantum Chemistry & Spectroscopy*, just before the math skills are required. Our intent in doing so is to provide “just-in-time” math help and to enable students to refresh math skills specifically needed in the following chapter.
- **Concept and Connection.** A new Concept and Connection feature has been added to each chapter to present students with a quick visual summary of the most important ideas within the chapter. In each chapter, approximately 10–15 of the most important concepts and/or connections are highlighted in the margins.
- **End-of-Chapter Problems.** Numerical Problems are now organized by section number within chapters to make it easier for instructors to create assignments for specific parts of each chapter. Furthermore, a number of new Conceptual Questions and Numerical Problems have been added to the book. Numerical Problems from the previous edition have been revised.
- **Introductory chapter materials.** Introductory paragraphs of all chapters have been replaced by a set of three questions plus responses to those questions. This new feature makes the importance of the chapter clear to students at the outset.
- **Figures.** All figures have been revised to improve clarity. Also, for many figures, additional annotation has been included to help tie concepts to the visual program.
- **Key Equations.** An end-of-chapter table that summarizes Key Equations has been added to allow students to focus on the most important of the many equations in each chapter. Equations in this table are set in red type where they appear in the body of the chapter.
- **Further Reading.** A section on Further Reading has been added to each chapter to provide references for students and instructors who would like a deeper understanding of various aspects of the chapter material.
- **Guided Practice and Interactivity**
 - **MasteringTM Chemistry** with a new enhanced eBook, has been significantly expanded to include a wealth of

new end-of-chapter problems from the fourth edition, new self-guided, adaptive Dynamic Study Modules with wrong answer feedback and remediation, and the new Pearson eBook which is mobile friendly. Students who solve homework problems using MasteringTM Chemistry obtain immediate feedback, which greatly enhances learning associated with solving homework problems. This platform can also be used for pre-class reading quizzes linked directly to the eText that are useful in ensuring students remain current in their studies and in flipping the classroom.

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- Students complete a set of questions with a unique answer format that also asks them to indicate their confidence level. Questions repeat until the student can answer them all correctly and confidently. These are available as graded assignments prior to class and are accessible on smartphones, tablets, and computers.
- **Topics** include key math skills, as well as a refresher of general chemistry concepts, such as understanding matter, chemical reactions, and the periodic table and atomic structure. Topics can be added or removed to match your coverage.

In terms of chapter and section content, many changes were made. The most significant of these changes are as follows:

- A new chapter entitled Macromolecules (Chapter 20) has been added. The motivation for this chapter is that assemblies of smaller molecules form large molecules, such as proteins or polymers. The resulting macromolecules can exhibit new structures and functions that are not reflected by the individual molecular components. Understanding the factors that influence macromolecular structure is critical in understanding the chemical behavior of these important molecules.
- A more detailed discussion of system-based and surroundings-based work has been added in Chapter 2 to help clarify the confusion that has appeared in the chemical education literature about using the system or surroundings pressure in calculating work. Section 6.6

has been extensively revised to take advances in quantum computing into account.

- The discussion on entropy and the second law of thermodynamics in Chapter 5 has been substantially revised. As a result, calculations of entropy changes now appear earlier in the chapter, and the material on the reversible Carnot cycle has been shifted to a later section.
- The approach to chemical equilibrium in Chapter 6 has been substantially revised to present a formulation in terms of the extent of reaction. This change has been made to focus more clearly on changes in chemical potential as the driving force in reaching equilibrium.

For those not familiar with the third edition of *Thermodynamics, Statistical Thermodynamics, and Kinetics*, our approach to teaching physical chemistry begins with our target audience—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 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 in a limited number of areas rather than to provide a condensed encyclopedia of physical chemistry. We believe this approach teaches students how to learn and enables them to apply their newly acquired skills to master related fields.
- **Illustrate the relevance of physical chemistry to the world around us.** Physical chemistry becomes more relevant to a student if it is connected to the world around us. Therefore, example problems and specific topics are tied together to help the student develop this connection. For example, fuel cells, refrigerators, heat pumps, and real engines are discussed in connection with the second law of thermodynamics. Every attempt is made to connect fundamental ideas to applications that could be of interest to the student.
- **Link the macroscopic and atomic-level worlds.** One of the strengths of thermodynamics is that it is not dependent on a microscopic description of matter. However, students benefit from a discussion of issues such as how pressure originates from the random motion of molecules.
- **Present exciting new science in the field of physical chemistry.** Physical chemistry lies at the forefront of many emerging areas of modern chemical research. 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.
- **Provide a versatile online homework program with tutorials.** Students who submit homework problems using MasteringTM Chemistry obtain immediate feedback,

a feature that greatly enhances learning. Also, tutorials with wrong answer feedback offer students a self-paced learning environment.

- **Use web-based simulations to 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 in several chapters 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. Simulations, animations, and homework problem worksheets can be accessed at www.pearsonhighered.com/advchemistry.

Effective use of *Thermodynamics, Statistical Thermodynamics, and Kinetics* does not require proceeding sequentially through the chapters or including all sections. Some topics are discussed in supplemental sections, which can be omitted if they are not viewed as essential to the course. Also, many sections are sufficiently self-contained that they can be readily omitted if they do not serve the needs of the instructor and students. This textbook is constructed to be flexible to your needs. We welcome the comments of both students and instructors on how the material was used and how the presentation can be improved.

Thomas Engel and Philip Reid
University of Washington

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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, Eric Gislason, Graeme Henkelman, Lewis Johnson, Tom Pratum, Bill Reinhardt, Peter Rosky, George Schatz, Michael Schick, Gabrielle Varani, and especially Bruce Robinson, have been invaluable in advising us. 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 guided us through the first edition, to our current editor Jeanne Zalesky, to our developmental editor Spencer Cotkin, and to Jennifer Hart and Beth Sweeten at Pearson, who have led the production process.

4TH EDITION MANUSCRIPT REVIEWERS

David Coker,
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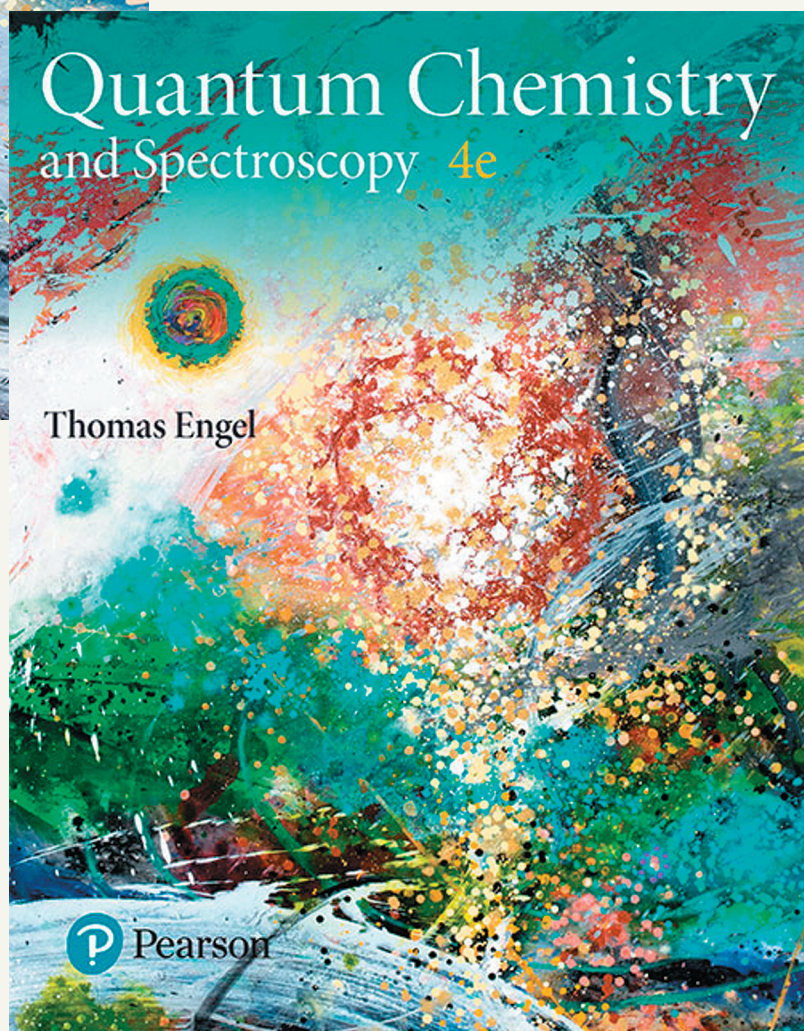
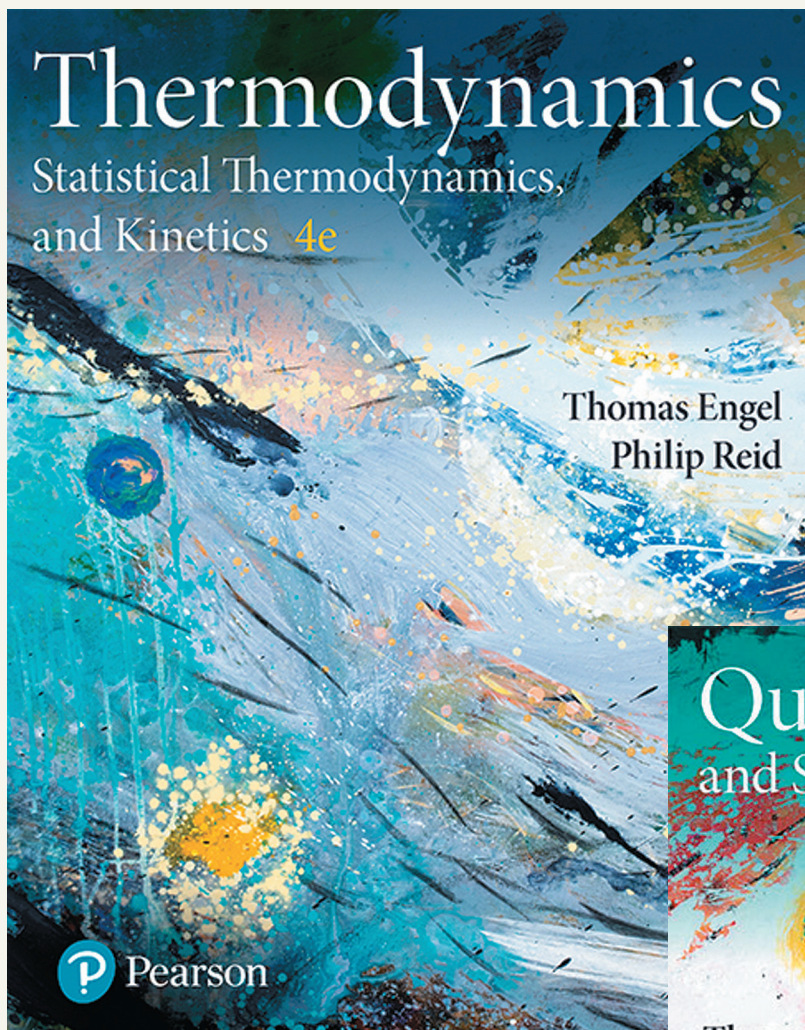
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A Visual, Conceptual, and Contemporary Approach to Physical Chemistry



A Visual, Conceptual, and Contemporary Approach to Physical Chemistry

NEW! Math Essentials provide a review of relevant math skills, offer “just in time” math help, and enable students to refresh math skills specifically needed in the chapter that follows.

UPDATED! Introductory paragraphs of all chapters have been replaced by a set of three questions plus responses to those questions making the relevance of the chapter clear at the outset.

CHAPTER 6

Commuting and Noncommuting Operators and the Surprising Consequences of Entanglement

- 6.1 Commutation Relations
- 6.2 The Stern-Gerlach Experiment
- 6.3 The Heisenberg Uncertainty Principle
- 6.4 (Supplemental Section) The Heisenberg Uncertainty Principle Expressed in Terms of Standard Deviations
- 6.5 (Supplemental Section) A Thought Experiment Using a Particle in a Three-Dimensional Box
- 6.6 (Supplemental Section) Entangled States, Teleportation, and Quantum Computers

WHY is this material important?
 The measurement process is different for a quantum-mechanical system than for a classical system. For a classical system, all observables can be measured simultaneously, and the precision and accuracy of the measurement is limited only by the instruments used to make the measurement. For a quantum-mechanical system, some observables can be measured simultaneously and exactly, whereas an uncertainty relation limits the degree to which other observables can be known simultaneously and exactly.

WHAT are the most important concepts and results?
 Measurements carried out on a system in a superposition state change the state of the system. Two observables can be measured simultaneously and exactly only if their corresponding operators commute. Two particles can be entangled, after which their properties are no longer independent of one another. Entanglement is the basis of both teleportation and quantum computing.

WHAT would be helpful for you to review for this chapter?
 It would be helpful to review the material on operators in Chapter 2.

6.1 COMMUTATION RELATIONS

In classical mechanics, a system can in principle be described completely. For instance, the position, momentum, kinetic energy, and potential energy of a mass falling in a gravitational field can be determined simultaneously at any point on its trajectory. The uncertainty in the measurements is only limited by the capabilities of the measurement technique. The values of all of these observables (and many more) can be known simultaneously. This is not generally true for a quantum-mechanical system. In the quantum world, in some cases two observables can be known simultaneously with high accuracy. However, in other cases, two observables have a fundamental uncertainty that cannot be eliminated through any measurement techniques. Nevertheless, as will be shown later,

Concept
 For a quantum mechanical system, it is not generally the case that the values of all observables can be known simultaneously.

105

MATH ESSENTIAL 2: Differentiation and Integration

Differential and integral calculus is used extensively in physical chemistry. In this unit we review the most relevant aspects of calculus needed to understand the chapter discussions and to solve the end-of-chapter problems.

ME2.1 THE DEFINITION AND PROPERTIES OF A FUNCTION

A function f is a rule that generates a value y from the value of a variable x . Mathematically, we write this as $y = f(x)$. The set of values x over which f is defined is the domain of the function. Single-valued functions have a single value of y for a given value of x . Most functions that we will deal with in physical chemistry are single-valued. However, inverse trigonometric functions and $\sqrt{\quad}$ are examples of common functions that are multivalued. A function is continuous if it satisfies these three conditions:

$$\begin{aligned} f(x) \text{ is defined at } a \\ \lim_{x \rightarrow a} f(x) \text{ exists} \\ \lim_{x \rightarrow a} f(x) = f(a) \end{aligned} \quad (\text{ME2.1})$$

ME2.2 THE FIRST DERIVATIVE OF A FUNCTION

The first derivative of a function has as its physical interpretation the slope of the function evaluated at the point of interest. In order for the first derivative to exist at a point a , the function must be continuous at $x = a$, and the slope of the function at $x = a$ must be the same when approaching a from $x < a$ and $x > a$. For example, the slope of the function $y = x^2$ at the point $x = 1.5$ is indicated by the line tangent to the curve shown in Figure ME2.1.

Mathematically, the first derivative of a function $f(x)$ is denoted $df(x)/dx$. It is defined by

$$\frac{df(x)}{dx} = \lim_{h \rightarrow 0} \frac{f(x+h) - f(x)}{h} \quad (\text{ME2.2})$$

The symbol $f'(x)$ is often used in place of $df(x)/dx$. For the function of interest,

$$\frac{df(x)}{dx} = \lim_{h \rightarrow 0} \frac{(x+h)^2 - x^2}{h} = \lim_{h \rightarrow 0} \frac{2hx + h^2}{h} = \lim_{h \rightarrow 0} 2x + h = 2x \quad (\text{ME2.3})$$

In order for $df(x)/dx$ to be defined over an interval in x , $f(x)$ must be continuous over the interval. Next, we present rules for differentiating simple functions. Some of these functions and their derivatives are as follows:

$$\begin{aligned} \frac{d(ax^n)}{dx} &= anx^{n-1}, \text{ where } a \text{ is a constant and } n \text{ is any real number} & (\text{ME2.4}) \\ \frac{d(ae^x)}{dx} &= ae^x, \text{ where } a \text{ is a constant} & (\text{ME2.5}) \\ \frac{d \ln x}{dx} &= \frac{1}{x} & (\text{ME2.6}) \end{aligned}$$

- ME2.1 The Definition and Properties of a Function
- ME2.2 The First Derivative of a Function
- ME2.3 The Chain Rule
- ME2.4 The Sum and Product Rules
- ME2.5 The Reciprocal Rule and the Quotient Rule
- ME2.6 Higher-Order Derivatives: Maxima, Minima, and Inflection Points
- ME2.7 Definite and Indefinite Integrals

21

NEW! Concept and Connection features in each chapter present students with quick visual summaries of the core concepts within the chapter, highlighting key take aways and providing students with an easy way to review the material.

UPDATED! All figures have been revised to improve clarity and for many figures, additional annotation has been included to help tie concepts to the visual program.

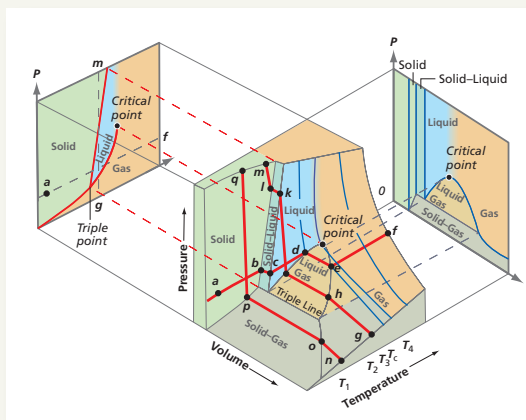


Figure 8.15
 A P - V - T phase diagram for a substance that expands upon melting. The indicated processes are discussed in the text.

Continuous Learning Before, During, and After Class

Energy - Heat - Temperature

QUESTION

A 91-g sample of gold is at an initial temperature of 22 °C. If 874 joules of heat are applied to the sample, what is the final temperature of the gold?

ANSWER

I AM UNSURE
74 °C

52 °C

36 °C

I AM UNSURE
97 °C

I DON'T KNOW YET

submit

Specific Heat Capacities of Some Common Substances	
Substance	Specific Heat Capacity, c_p (J/g · °C)*
Elements	
Lead	0.128
Gold	0.128
Silver	0.235
Copper	0.385
Iron	0.449
Aluminum	0.903
Compounds	
Ethanol	2.42
Water	4.18
Materials	
Glass (Pyrex)	0.75
Granite	0.79
Sand	0.84

*At 298 K.

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Concentration and Le Chatelier's Principle

Le Chatelier's principle concerns the reaction of systems at equilibrium to perturbations that disturb the equilibrium. Le Chatelier's principle states that systems will always respond to relieve the stress placed upon them. That is, they will respond in such a way so as to return to equilibrium.

Chemical reactions can be displaced from their equilibrium positions by changing the concentrations of reactants or products. These changes affect the value of the reaction quotient, Q . The reaction then shifts to increase or decrease Q until it is again equal to the equilibrium constant, K .

Part A

For the reaction

$$\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$$

classify each of the following actions by whether it causes a leftward shift, a rightward shift, or no shift in the direction of the reaction. Drag the appropriate items to their respective bins.

Hint 1. How to approach the problem (click to open)

Hint 2. Identify the expression for the equilibrium constant (click to open)

Hint 3. Identify how changes in reactant and product concentrations affect the reaction (click to open)

Leftward shift

Rightward shift

No shift

double [oxygen]

halve [nitrogen monoxide]

double [nitrogen]

double [nitrogen monoxide]

halve [oxygen]

halve [nitrogen]

Submit My Answers Give Up

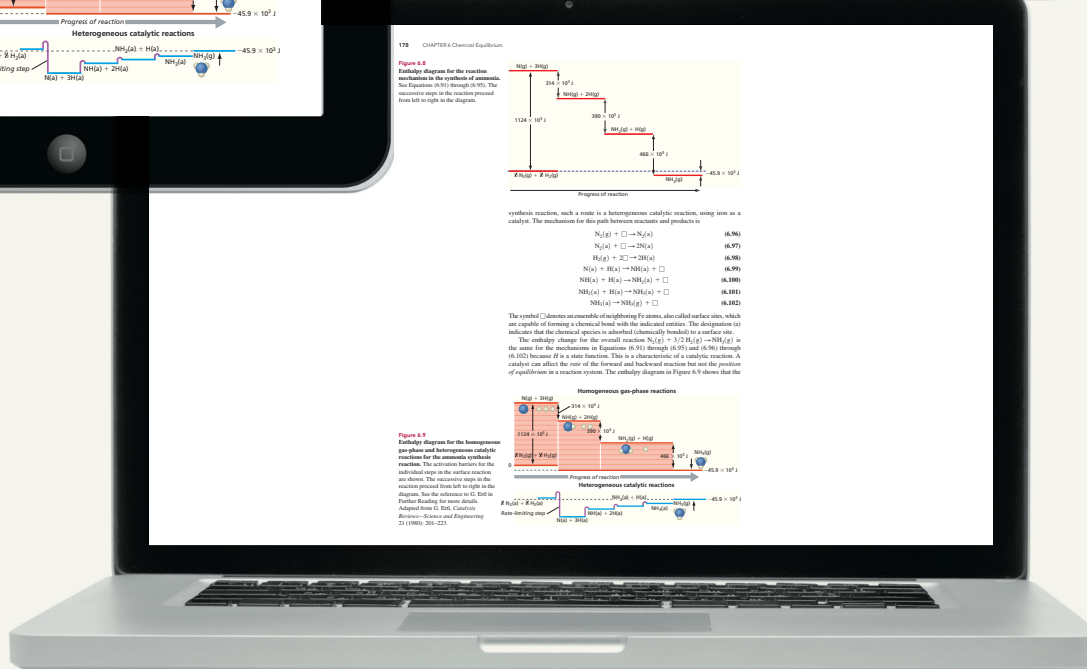
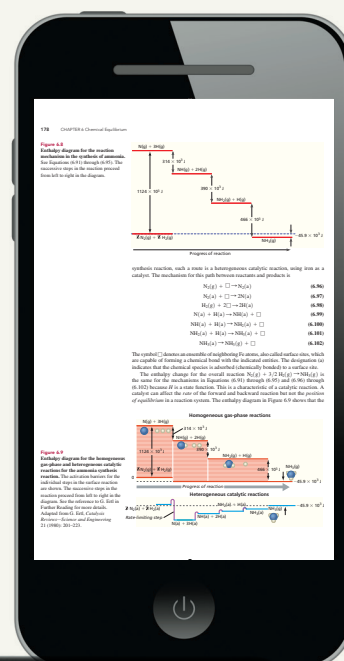
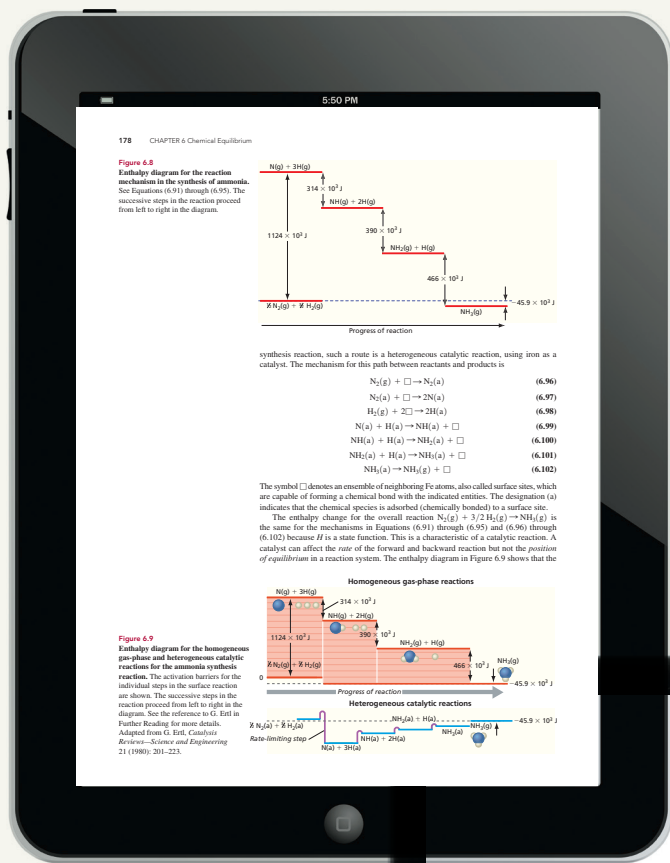
Incorrect; Try Again

You sorted 4 out of 6 items incorrectly. Increasing the concentration of a reactant will drive the reaction to consume reactants and increase products.

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MATH ESSENTIAL 1: Units, Significant Figures, and Solving End of Chapter Problems

ME1.1 UNITS

Quantities of interest in physical chemistry such as pressure, volume, or temperature are characterized by their magnitude and their units. In this textbook, we use the SI (from the French *Le Système international d'unités*) system of units. All physical quantities can be defined in terms of the seven base units listed in Table ME1.1. For more details, see <http://physics.nist.gov/cuu/Units/units.html>. The definition of temperature is based on the coexistence of the solid, gaseous, and liquid phases of water at a pressure of 1 bar.

- ME1.1 Units
- ME1.2 Uncertainty and Significant Figures
- ME1.3 Solving End-of-Chapter Problems

TABLE ME1.1 Base SI Units

Base Unit	Unit	Definition of Unit
Unit of length	meter (m)	The meter is the length of the path traveled by light in vacuum during a time interval of $1/299,792,458$ of a second.
Unit of mass	kilogram (kg)	The kilogram is the unit of mass; it is equal to the mass of the platinum iridium international prototype of the kilogram kept at the International Bureau of Weights and Measures.
Unit of time	second (s)	The second is the duration of 9,192,631,770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the cesium 133 atom.
Unit of electric current	ampere (A)	The ampere is the constant current that, if maintained in two straight parallel conductors of infinite length, is of negligible circular cross section, and if placed 1 meter apart in a vacuum would produce between these conductors a force equal to 2×10^{-7} kg m s ⁻² per meter of length. In this definition, 2 is an exact number.
Unit of thermodynamic temperature	kelvin (K)	The Kelvin is the unit of thermodynamic temperature. It is the fraction $1/273.16$ of the thermodynamic temperature of the triple point of water.
Unit of amount of substance	mole (mol)	The mole is the amount of substance of a system that contains as many elementary entities as there are atoms in 0.012 kilogram of carbon 12 where 0.012 is an exact number. When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles.
Unit of luminous intensity	candela (cd)	The candela is the luminous intensity, in a given direction, of a source that emits monochromatic radiation of frequency $540. \times 10^{12}$ hertz and that has a radiant intensity in that direction of $1/683$ watt per steradian.

Quantities of interest other than the seven base quantities can be expressed in terms of the units meter, kilogram, second, ampere, kelvin, mole, and candela. The most important of these derived units, some of which have special names as indicated, are listed in Table ME1.2. A more inclusive list of derived units can be found at <http://physics.nist.gov/cuu/Units/units.html>.

TABLE ME1.2 Derived Units

Unit	Definition	Relation to Base Units	Special Name	Abbreviation
Area	Size of a surface	m^2		m^2
Volume	Amount of three-dimensional space an object occupies	m^3		m^3
Velocity	Measure of the rate of motion	m s^{-1}		m s^{-1}
Acceleration	Rate of change of velocity	m s^{-2}		m s^{-2}
Linear momentum	Product of mass and linear velocity of an object	kg m s^{-1}		kg m s^{-1}
Angular momentum	Product of the moment of inertia of a body about an axis and its <i>angular</i> velocity with respect to the same axis	$\text{kg m}^2 \text{s}^{-1}$		$\text{kg m}^2 \text{s}^{-1}$
Force	Any interaction that, when unopposed, will change the motion of an object	kg m s^{-2}	newton	N
Pressure	Force acting per unit area	$\text{kg m}^{-1} \text{s}^{-2}$ N m^{-2}	pascal	Pa
Work	Product of force on an object and movement along the direction of the force	$\text{kg m}^2 \text{s}^{-2}$	joule	J
Kinetic energy	Energy an object possesses because of its motion	$\text{kg m}^2 \text{s}^{-2}$	joule	J
Potential energy	Energy an object possesses because of its position or condition	$\text{kg m}^2 \text{s}^{-2}$	joule	J
Power	Rate at which energy is produced or consumed	$\text{kg m}^2 \text{s}^{-3}$	watt	W
Mass density	Mass per unit volume	kg m^{-3}		kg m^{-3}
Radian	Angle at the center of a circle whose arc is equal in length to the radius	$\text{m/m} = 1$		$\text{m/m} = 1$
Steradian	Angle at the center of a sphere subtended by a part of the surface equal in area to the square of the radius	$\text{m}^2/\text{m}^2 = 1$		$\text{m}^2/\text{m}^2 = 1$
Frequency	Number of repeat units of a wave per unit time	s^{-1}	hertz	Hz
Electrical charge	Physical property of matter that causes it to experience an electrostatic force	A s	coulomb	C
Electrical potential	Work done in moving a unit positive charge from infinity to that point	$\text{kg m}^2 \text{s}^{-3}/\text{A}$ W/A	volt	V
Electrical resistance	Ratio of the voltage to the electric current that flows through a conductive material	$\text{kg m}^2 \text{s}^{-3}/\text{A}^2 \text{W}/\text{A}^2$	ohm	Ω

If SI units are used throughout the calculation of a quantity, the result will have SI units. For example, consider a unit analysis of the electrostatic force between two charges:

$$\begin{aligned}
 F &= \frac{q_1 q_2}{8\pi \epsilon_0 r^2} = \frac{\text{C}^2}{8\pi \times \text{kg}^{-1} \text{s}^4 \text{A}^2 \text{m}^{-3} \times \text{m}^2} = \frac{\text{A}^2 \text{s}^2}{8\pi \times \text{kg}^{-1} \text{s}^4 \text{A}^2 \text{m}^{-3} \times \text{m}^2} \\
 &= \frac{1}{8\pi} \text{kg m s}^{-2} = \frac{1}{8\pi} \text{N}
 \end{aligned}$$

Therefore, in carrying out a calculation, it is only necessary to make sure that all quantities are expressed in SI units rather than carrying out a detailed unit analysis of the entire calculation.

ME1.2 UNCERTAINTY AND SIGNIFICANT FIGURES

In carrying out a calculation, it is important to take into account the uncertainty of the individual quantities that go into the calculation. The uncertainty is indicated by the number of significant figures. For example, the mass 1.356 g has four significant figures. The mass 0.003 g has one significant figure, and the mass 0.01200 g has four significant figures. By convention, the uncertainty of a number is ± 1 in the rightmost digit. A zero at the end of a number that is not to the right of a decimal point is not significant. For example, 150 has two significant figures, but 150. has three significant figures. Some numbers are exact and have no uncertainty. For example, 1.00×10^6 has three significant figures because the 10 and 6 are exact numbers. By definition, the mass of one atom of ^{12}C is exactly 12 atomic mass units.

If a calculation involves quantities with a different number of significant figures, the following rules regarding the number of significant figures in the result apply:

- In addition and subtraction, the result has the number of digits to the right of the decimal point corresponding to the number that has the smallest number of digits to the right of the decimal point. For example $101 + 24.56 = 126$ and $0.523 + 0.10 = 0.62$.
- In multiplication or division, the result has the number of significant figures corresponding to the number with the smallest number of significant figures. For example, $3.0 \times 16.00 = 48$ and $0.05 \times 100. = 5$.

It is good practice to carry forward a sufficiently large number of significant figures in different parts of the calculation and to round off to the appropriate number of significant figures at the end.

ME1.3 SOLVING END-OF-CHAPTER PROBLEMS

Because calculations in physical chemistry often involve multiple inputs, it is useful to carry out calculations in a manner that they can be reviewed and easily corrected. For example, the input and output for the calculation of the pressure exerted by gaseous benzene with a molar volume of 2.00 L at a temperature of 595 K using the Redlich–Kwong equation of state $P = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T}} \frac{1}{V_m(V_m + b)}$ in Mathematica is shown

below. The statement in the first line clears the previous values of all listed quantities, and the semicolon after each input value suppresses its appearance in the output.

```
In[36]:= Clear[r, t, vm, a, b, prk]
         r = 8.314 × 10^-2;
         t = 595;
         vm = 2.00;
         a = 452;
         b = .08271;
         prk =  $\frac{r t}{v_m - b} - \frac{a}{\sqrt{t}} \frac{1}{v_m (v_m + b)}$ 
out[42]= 21.3526
```

Invoking the rules for significant figures, the final answer is $P = 21.4$ bar.

The same problem can be solved using Microsoft Excel as shown in the following table.

	A	B	C	D	E	F
1	R	T	V_m	a	b	$=((A2*B2)/(C2-E2))-(D2/SQRT(B2))*(1/(C2*(C2+E2)))$
2	0.08314	595	2	452	0.08271	21.35257941

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Fundamental Concepts of Thermodynamics

WHY is this material important?

Thermodynamics is a powerful science that allows predictions to be made about chemical reactions, the efficiency of engines, and the potential of new energy sources. It is a macroscopic science and does not depend on a description of matter at the molecular scale. In this chapter, we introduce basic concepts such as the system variables pressure, temperature, and volume, and equations of state that relate these variables with one another.

WHAT are the most important concepts and results?

Processes such as chemical reactions occur in an apparatus whose contents we call the system. The rest of the universe is the surroundings. The exchange of energy and matter between the system and surroundings is central to thermodynamics. We will show that the macroscopic gas property pressure arises through the random thermal motion of atoms and molecules. Equations of state such as the ideal gas law allow us to calculate how one system variable changes when another variable is increased or decreased.

WHAT would be helpful for you to review for this chapter?

It would be useful to review the material on units and problem solving discussed in Math Essential 1.

1.1 WHAT IS THERMODYNAMICS AND WHY IS IT USEFUL?

Thermodynamics is the branch of science that describes the behavior of matter and the transformation between different forms of energy on a **macroscopic scale**, which is the scale of phenomena experienced by humans, as well as larger-scale phenomena (e.g., astronomical scale). Thermodynamics describes a system of interest in terms of its bulk properties. Only a few variables are needed to describe such a system, and the variables are generally directly accessible through measurements. A thermodynamic description of matter does not make reference to its structure and behavior at the microscopic level. For example, 1 mol of gaseous water at a sufficiently low density is completely described by two of the three **macroscopic variables** of pressure, volume, and temperature. By contrast, the microscopic scale refers to dimensions on the order of the size of molecules. At the microscopic level, water is described as a dipolar triatomic molecule, H_2O , with a bond angle of 104.5° that forms a network of hydrogen bonds.

In the first part of this book (Chapters 1–11), we will discuss thermodynamics. Later in the book, we will turn to statistical thermodynamics. Statistical thermodynamics

- 1.1 What Is Thermodynamics and Why Is It Useful?
- 1.2 The Macroscopic Variables Volume, Pressure, and Temperature
- 1.3 Basic Definitions Needed to Describe Thermodynamic Systems
- 1.4 Equations of State and the Ideal Gas Law
- 1.5 A Brief Introduction to Real Gases

Concept

Because thermodynamics does not make reference to a description of matter at the microscopic level, it is equally applicable to a liter of garbage and a liter of pure water.

uses atomic and molecular properties to calculate the macroscopic properties of matter. For example, statistical thermodynamic analysis shows that liquid water is the stable form of aggregation at a pressure of 1 bar and a temperature of 90°C, whereas gaseous water is the stable form at 1 bar and 110°C. Using statistical thermodynamics, we can calculate the macroscopic properties of matter from underlying molecular properties.

Given that the microscopic nature of matter is becoming increasingly well understood using theories such as quantum mechanics, why is the macroscopic science thermodynamics relevant today? The usefulness of thermodynamics can be illustrated by describing four applications of thermodynamics that you will have mastered after working through this book:

- You have built an industrial plant to synthesize $\text{NH}_3(\text{g})$ gas from $\text{N}_2(\text{g})$ and $\text{H}_2(\text{g})$. You find that the yield is insufficient to make the process profitable, and you decide to try to improve the NH_3 output by changing either the temperature or pressure of synthesis, or both. However, you do not know whether to increase or decrease the values of these variables. As will be shown in Chapter 6, the ammonia yield will be higher at equilibrium if the temperature is decreased and the pressure is increased.
- You wish to use methanol to power a car. One engineer provides a design for an internal combustion engine that will burn methanol efficiently according to the reaction $\text{CH}_3\text{OH}(\text{l}) + 3/2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$. A second engineer designs an electrochemical fuel cell that carries out the same reaction. He claims that the vehicle will travel much farther if it is powered by the fuel cell rather than by the internal combustion engine. As will be shown in Chapter 5, this assertion is correct, and an estimate of the relative efficiencies of the two propulsion systems can be made.
- You are asked to design a new battery that will be used to power a hybrid car. Because the voltage required by the driving motors is much higher than can be generated in a single electrochemical cell, many cells must be connected in series. Because the space for the battery is limited, as few cells as possible should be used. You are given a list of possible cell reactions and told to determine the number of cells needed to generate the required voltage. As you will learn in Chapter 11, this problem can be solved using tabulated values of thermodynamic functions.
- Your attempts to synthesize a new and potentially very marketable compound have consistently led to yields that make it unprofitable to begin production. A supervisor suggests a major effort to make the compound by first synthesizing a catalyst that promotes the reaction. How can you decide if this effort is worth the required investment? As will be shown in Chapter 6, the maximum yield expected under equilibrium conditions should be calculated first. If this yield is insufficient, a catalyst is useless.

1.2 THE MACROSCOPIC VARIABLES VOLUME, PRESSURE, AND TEMPERATURE

We begin our discussion of thermodynamics by considering a bottle of a gas such as He or CH_4 . At a macroscopic level, the sample of known chemical composition is completely described by the measurable quantities volume, pressure, and temperature for which we use the symbols V , P , and T . The volume V is just that of the bottle. What physical association do we have with P and T ?

Concept

The origin of pressure in a gas is the random thermally induced motion of individual molecules.

Pressure is the force exerted by the gas per unit area of the container. It is most easily understood by considering a microscopic model of the gas known as the kinetic theory of gases. The gas is described by two assumptions: first, the atoms or molecules of an **ideal gas** do not interact with one another, and second, the atoms or molecules can be treated as point masses. The pressure exerted by a gas on the container that confines the gas arises from collisions of randomly moving gas molecules with the container walls. Because the number of molecules in a small volume of the gas is on the order of Avogadro's number N_A , the number of collisions between molecules is also

large. To describe pressure, a molecule is envisioned as traveling through space with a velocity vector \mathbf{v} that can be resolved into three Cartesian components: v_x , v_y , and v_z , as illustrated in Figure 1.1.

The square of the magnitude of the velocity v^2 in terms of the three velocity components is

$$v^2 = \mathbf{v} \cdot \mathbf{v} = v_x^2 + v_y^2 + v_z^2 \quad (1.1)$$

The particle kinetic energy is $1/2 mv^2$ such that

$$\varepsilon_{tr} = \frac{1}{2}mv^2 = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 = \varepsilon_{tr_x} + \varepsilon_{tr_y} + \varepsilon_{tr_z} \quad (1.2)$$

where ε is kinetic energy and the subscript *tr* indicates that the energy corresponds to translational motion of the particle. Furthermore, this equation states that the total translational energy is the sum of translational energy along each Cartesian dimension.

Pressure arises from the collisions of gas particles with the walls of the container; therefore, to describe pressure, we must consider what occurs when a gas particle collides with the wall. First, we assume that the collisions with the wall are **elastic collisions**, meaning that translational energy of the particle is conserved. Although the collision is elastic, this does not mean that nothing happens. As a result of the collision, linear momentum is imparted to the wall, which results in pressure. The definition of pressure is force per unit area, and, by Newton's second law, force is equal to the product of mass and acceleration. Using these two definitions, we find that the pressure arising from the collision of a single molecule with the wall is expressed as

$$P = \frac{F}{A} = \frac{ma_i}{A} = \frac{m}{A} \left(\frac{dv_i}{dt} \right) = \frac{1}{A} \left(\frac{dmv_i}{dt} \right) = \frac{1}{A} \left(\frac{dp_i}{dt} \right) \quad (1.3)$$

In Equation (1.3), F is the force of the collision, A is the area of the wall with which the particle has collided, m is the mass of the particle, v_i is the velocity component along the i direction ($i = x, y, \text{ or } z$), and p_i is the particle linear momentum in the i direction. Equation (1.3) illustrates that pressure is related to the change in linear momentum with respect to time that occurs during a collision. Due to conservation of momentum, any change in particle linear momentum must result in an equal and opposite change in momentum of the container wall. A single collision is depicted in Figure 1.2. This figure illustrates that the particle linear momentum change in the x direction is $-2mv_x$ (note that there is no change in momentum in the y or z direction). Accordingly, a corresponding momentum change of $2mv_x$ must occur for the wall.

The pressure measured at the container wall corresponds to the sum of collisions involving a large number of particles that occur per unit time. Therefore, the total momentum change that gives rise to the pressure is equal to the product of the momentum change from a single-particle collision and the total number of particles that collide with the wall:

$$\Delta p_{\text{total}} = \frac{\Delta p}{\text{molecule}} \times (\text{number of molecules}) \quad (1.4)$$

How many molecules strike the side of the container in a given period of time? To answer this question, the time over which collisions are counted must be considered. Consider a volume element defined by the area of the wall A multiplied by length Δx , as illustrated in Figure 1.3. The collisional volume element depicted in Figure 1.3 is given by

$$V = A\Delta x \quad (1.5)$$

The length of the box Δx is related to the time period over which collisions will be counted Δt and the component of particle velocity parallel to the side of the box (taken to be the x direction):

$$\Delta x = v_x \Delta t \quad (1.6)$$

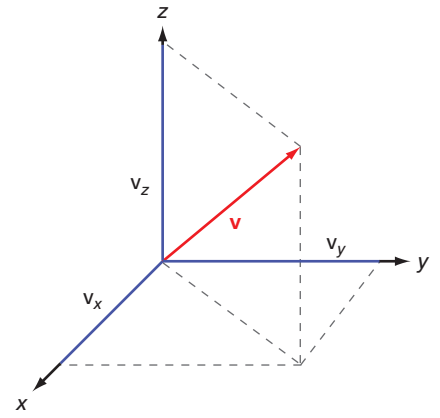


Figure 1.1
Cartesian components of velocity. The particle velocity \mathbf{v} can be resolved into three velocity components: v_x , v_y , and v_z .

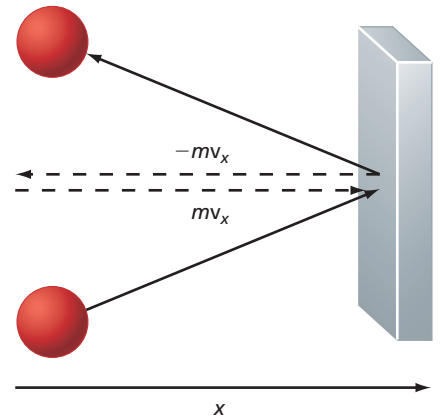


Figure 1.2
Collision between a gas particle and a wall. Before the collision, the particle has a momentum of mv_x in the x direction, whereas after the collision the momentum is $-mv_x$. Therefore, the change in particle momentum resulting from the collision is $-2mv_x$. By conservation of momentum, the change in momentum of the wall must be $2mv_x$. The incoming and outgoing trajectories are offset to show the individual momentum components.

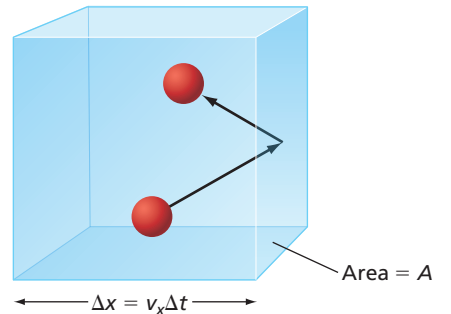


Figure 1.3
Volume element used to determine the number of collisions with a wall per unit time.

In this expression, v_x is for a single particle; however, an average of this quantity will be used when describing the collisions from a collection of particles. Finally, the number of particles that will collide with the container wall N_{coll} in the time interval Δt is equal to the number density \tilde{N} . This quantity is equal to the number of particles in the container N divided by the container volume V and multiplied by the collisional volume element depicted in Figure 1.3:

$$N_{\text{coll}} = \tilde{N} \times (Av_x \Delta t) \left(\frac{1}{2} \right) = \frac{nN_A}{V} (Av_x \Delta t) \left(\frac{1}{2} \right) \quad (1.7)$$

We have used the equality $N = nN_A$ where N_A is Avogadro's number and n is the number of moles of gas in the second part of Equation (1.7). Because particles travel in either the $+x$ or $-x$ direction with equal probability, only those molecules traveling in the $+x$ direction will strike the area of interest. Therefore, the total number of collisions is divided by two to take the direction of particle motion into account. Employing Equation (1.7), we see that the total change in linear momentum of the container wall imparted by particle collisions is given by

$$\begin{aligned} \Delta p_{\text{total}} &= (2mv_x)(N_{\text{coll}}) \\ &= (2mv_x) \left(\frac{nN_A}{V} Av_x \Delta t \right) \\ &= \frac{nN_A}{V} A \Delta t m \langle v_x^2 \rangle \end{aligned} \quad (1.8)$$

In Equation (1.8), angle brackets appear around v_x^2 to indicate that this quantity represents an average value, given that the particles will demonstrate a distribution of velocities. This distribution is considered in detail later in Chapter 13. With the total change in linear momentum provided in Equation (1.8), the force and corresponding pressure exerted by the gas on the container wall [Equation (1.3)] are as follows:

$$\begin{aligned} F &= \frac{\Delta p_{\text{total}}}{\Delta t} = \frac{nN_A}{V} Am \langle v_x^2 \rangle \\ P &= \frac{F}{A} = \frac{nN_A}{V} m \langle v_x^2 \rangle \end{aligned} \quad (1.9)$$

Equation (1.9) can be converted into a more familiar expression once $1/2 m \langle v_x^2 \rangle$ is recognized as the translational energy in the x direction. In Chapter 14, it will be shown that the average translational energy for an individual particle in one dimension is

$$\frac{m \langle v_x^2 \rangle}{2} = \frac{k_B T}{2} \quad (1.10)$$

where T is the gas temperature.

Substituting this result into Equation (1.9) results in the following expression for pressure:

$$P = \frac{nN_A}{V} m \langle v_x^2 \rangle = \frac{nN_A}{V} k_B T = \frac{nRT}{V} \quad (1.11)$$

Concept

The ideal gas law assumes that individual molecules are point masses that do not interact.

Concept

Temperature can only be measured indirectly through a physical property such as the volume of a gas or the voltage across a thermocouple.

We have used the equality $N_A k_B = R$ where k_B is the **Boltzmann constant** and R is the **ideal gas constant** in the last part of Equation (1.11). The Boltzmann constant relates the average kinetic energy of molecules to the temperature of the gas, whereas the ideal gas constant relates average kinetic energy per mole to temperature. Equation (1.11) is the **ideal gas law**. Although this relationship is familiar, we have derived it by employing a classical description of a single molecular collision with the container wall and then scaling this result up to macroscopic proportions. We see that the origin of the pressure exerted by a gas on its container is the momentum exchange of the randomly moving gas molecules with the container walls.

What physical association can we make with the temperature T ? At the microscopic level, **temperature** is related to the mean kinetic energy of molecules as shown by

Equation (1.10). We defer the discussion of temperature at the microscopic level until Chapter 13 and focus on a macroscopic level discussion here. Although each of us has a sense of a “temperature scale” based on the qualitative descriptors *hot* and *cold*, a more quantitative and transferable measure of temperature that is not grounded in individual experience is needed. The quantitative measurement of temperature is accomplished using a **thermometer**. For any useful thermometer, the measured temperature, T , must be a single-valued, continuous, and monotonic function of some thermometric system property such as the volume of mercury confined to a narrow capillary, the electromotive force generated at the junction of two dissimilar metals, or the electrical resistance of a platinum wire.

The simplest case that one can imagine is when T is linearly related to the value of the thermometric property x :

$$T(x) = a + bx \quad (1.12)$$

Equation (1.12) defines a **temperature scale** in terms of a specific thermometric property, once the constants a and b are determined. The constant a determines the zero of the temperature scale because $T(0) = a$ and the constant b determines the size of a unit of temperature, called a degree.

One of the first practical thermometers was the mercury-in-glass thermometer. This thermometer utilizes the thermometric property that the volume of mercury increases monotonically over the temperature range -38.8°C to 356.7°C in which Hg is a liquid. In 1745, Carolus Linnaeus gave this thermometer a standardized scale by arbitrarily assigning the values 0 and 100 to the freezing and boiling points of water, respectively. Because there are 100 degrees between the two calibration points, this scale is known as the **centigrade scale**.

The centigrade scale has been superseded by the **Celsius scale**. The Celsius scale (denoted in units of $^\circ\text{C}$) is similar to the centigrade scale. However, rather than being determined by two fixed points, the Celsius scale is determined by one fixed reference point at which ice, liquid water, and gaseous water are in equilibrium. This point is called the triple point (see Section 8.2) and is assigned the value 0.01°C . On the Celsius scale, the boiling point of water at a pressure of 1 atmosphere is 99.975°C . The size of the degree is chosen to be the same as on the centigrade scale.

Although the Celsius scale is used widely throughout the world today, the numerical values for this temperature scale are completely arbitrary because a liquid other than water could have been chosen as a reference. It would be preferable to have a temperature scale derived directly from physical principles. There is such a scale, called the **thermodynamic temperature scale** or **absolute temperature scale**. For such a scale, the temperature is independent of the substance used in the thermometer, and the constant a in Equation (1.12) is zero. The **gas thermometer** is a practical thermometer with which the absolute temperature can be measured. A gas thermometer contains a dilute gas under conditions in which the ideal gas law of Equation (1.11) describes the relationship among P , T , and the molar density $\rho_m = n/V$ with sufficient accuracy:

$$P = \rho_m RT \quad (1.13)$$

Equation (1.13) can be rewritten as

$$T = \frac{P}{\rho_m R} \quad (1.14)$$

showing that for a gas thermometer, the thermometric property is the temperature dependence of P for a dilute gas at constant V . The gas thermometer provides the international standard for thermometry at very low temperatures. At intermediate temperatures, the electrical resistance of platinum wire is the standard, and at higher temperatures the radiated energy emitted from glowing silver is the standard. The absolute temperature is shown in Figure 1.4 on a logarithmic scale together with associated physical phenomena.

Equation (1.14) implies that as $T \rightarrow 0$, $P \rightarrow 0$. Measurements carried out by Guillaume Amontons in the 17th century demonstrated that the pressure exerted by a fixed amount of gas at constant V varies linearly with temperature as shown in Figure 1.5.

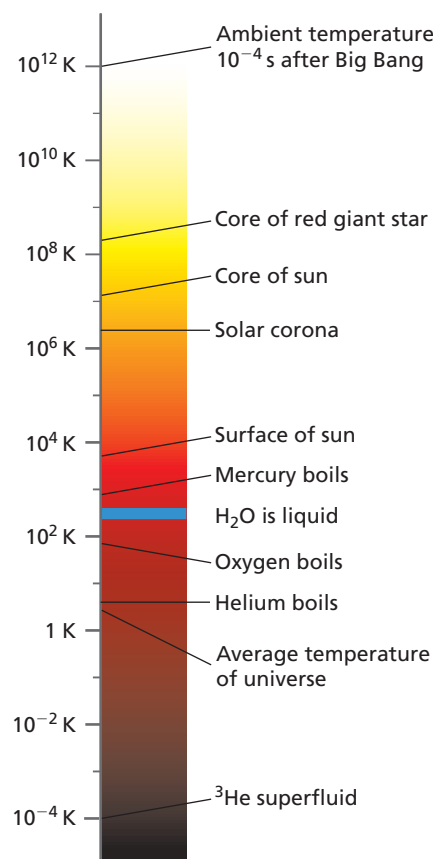


Figure 1.4 Absolute temperature displayed on a logarithmic scale. The temperature of a number of physical phenomena is also shown.

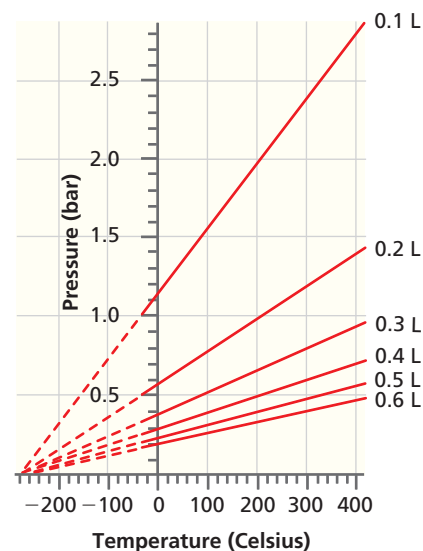


Figure 1.5 Relationship between temperature and pressure for a dilute gas. The pressure exerted by 5.00×10^{-3} mol of a dilute gas is shown as a function of the temperature measured on the Celsius scale for different fixed volumes. The dashed segments of lines indicate that the data are extrapolated to lower temperatures than could be achieved experimentally by early investigators.