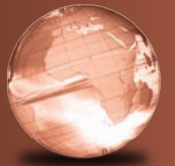


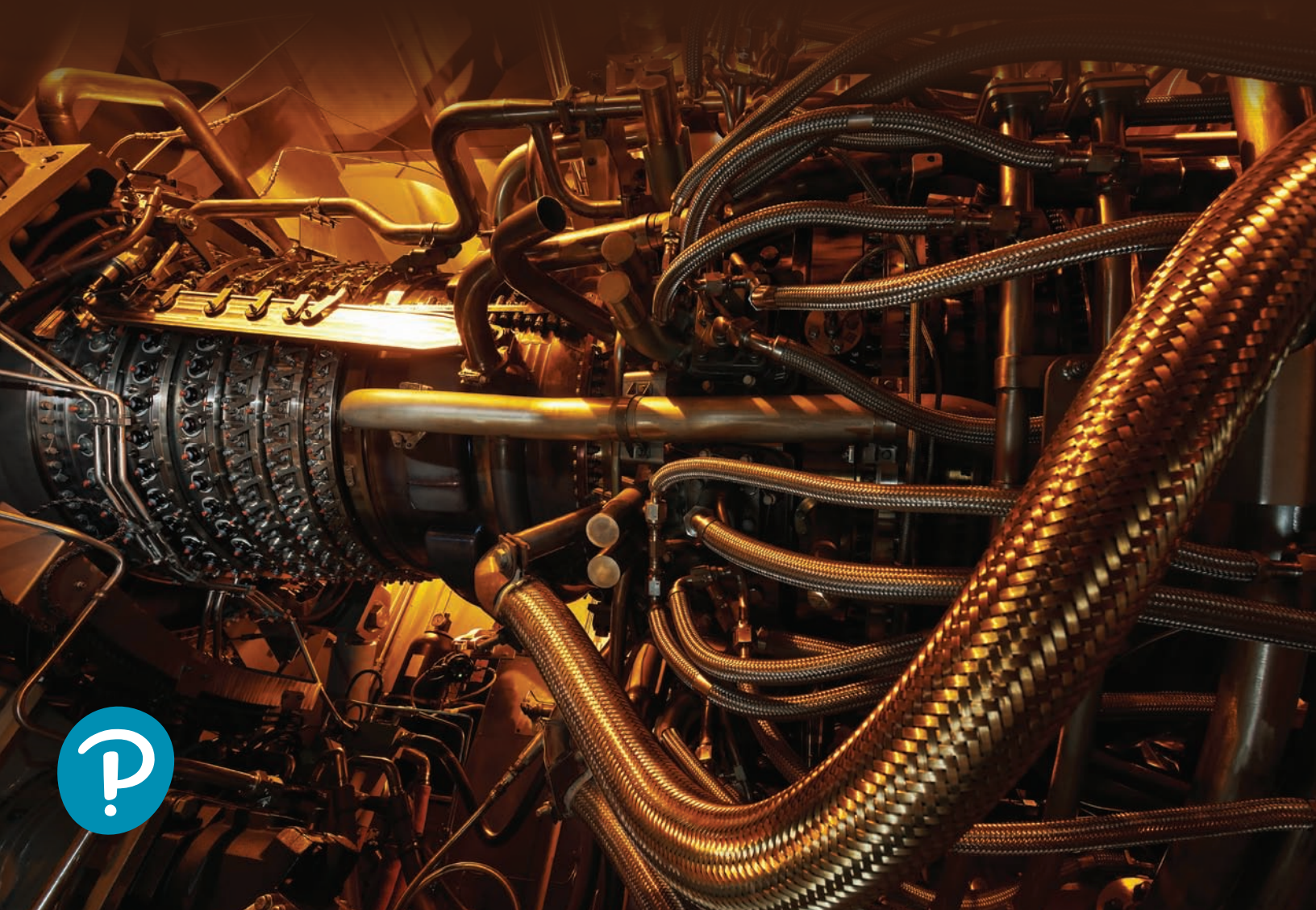
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Thermodynamics, Statistical Thermodynamics, and Kinetics

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PHYSICAL CHEMISTRY

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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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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.

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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's Math Supplement have been expanded and split into 4 two- to seven-page Math Essentials, which are inserted at appropriate places throughout this book, 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.** New Concept and Connection features have 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 Further Reading section 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**
 - **Mastering™ Chemistry** 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. Students who solve homework problems using Mastering™ Chemistry obtain immediate feedback, which greatly enhances learning associated with solving homework problems. This platform can also be used for pre-class reading quizzes that are useful in ensuring students remain current in their studies.

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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.
- 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 Mastering™ 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. Simulations, animations, and homework problem worksheets can be accessed on Mastering™ Chemistry.

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.

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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

5

Entropy and the Second and Third Laws of Thermodynamics

WHY is this material important?
Mixtures of chemically reactive species can evolve toward reactants or toward products, defining the direction of spontaneous change. How do we know which of these reactions is spontaneous? Entropy, designated by S , is the state function that predicts the direction of natural, or spontaneous, change. In this chapter, you will learn how to carry out entropy calculations.

WHAT are the most important concepts and results?
Heat flows from hotter bodies to colder bodies, and gases mix rather than separate. Entropy always increases for a spontaneous change in an isolated system. For a spontaneous change in a system interacting with its environment, the sum of the entropy of the system and that of the surroundings always increases. Thermodynamics can be used to devise ways to reduce our energy use and to transition away from fossil fuels.

WHAT would be helpful for you to review for this chapter?
Because differential and integral calculus and partial derivatives are used extensively in this chapter, it would be helpful to review the material on calculus in Math Essential 2 and 3.

- 5.1 What Determines the Direction of Spontaneous Change in a Process?
- 5.2 The Second Law of Thermodynamics, Spontaneity, and the Sign of ΔS
- 5.3 Calculating Changes in Entropy as T , P , or V Change
- 5.4 Understanding Changes in Entropy at the Molecular Level
- 5.5 The Clausius Inequality
- 5.6 The Change of Entropy in the Surroundings and $\Delta S_{\text{un}} = \Delta S + \Delta S_{\text{sur}}$
- 5.7 Absolute Entropies and the Third Law of Thermodynamics
- 5.8 Standard States in Entropy Calculations
- 5.9 Entropy Changes in Chemical Reactions
- 5.10 Heat Engines and the Carnot Cycle
- 5.11 (Supplemental Section) How Does S Depend on V and T ?
- 5.12 (Supplemental Section) Dependence of S on T and P
- 5.13 (Supplemental Section) Energy Efficiency, Heat Pumps, Refrigerators, and Real Engines

5.1 WHAT DETERMINES THE DIRECTION OF SPONTANEOUS CHANGE IN A PROCESS?

The first law of thermodynamics constrains the range of possible processes to those that conserve energy and rules out machines that work indefinitely without an energy source (perpetual motion machines) that have been the dream of inventors over centuries. Any system that is not at equilibrium will evolve with time. We refer to the direction of evolution as the **spontaneous direction**. Spontaneous does not mean that the process occurs immediately, but rather that it will occur with high probability if any barrier to the change is overcome. For example, the transformation of a piece of wood to CO_2 and H_2O in the presence of oxygen is spontaneous, but it only occurs at elevated temperatures because an activation energy barrier must be overcome for the reaction to proceed. In this chapter, we discuss the second law of thermodynamics, which allows us to predict if a process is spontaneous. Before stating the second law, we discuss two processes that satisfy the first law because they conserve energy and attempt to identify criteria that can predict the spontaneous direction of evolution.

Concept

A process is defined to be spontaneous even if it occurs only for some conditions because of an energy barrier.

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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,

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

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:

$$\frac{d(ax^n)}{dx} = anx^{n-1}, \quad \text{where } a \text{ is a constant and } n \text{ is any real number} \quad (\text{ME2.4})$$

$$\frac{d(ae^x)}{dx} = ae^x, \quad \text{where } a \text{ is a constant} \quad (\text{ME2.5})$$

$$\frac{d \ln x}{dx} = \frac{1}{x} \quad (\text{ME2.6})$$

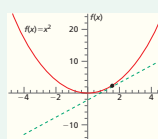


Figure ME2.1 The function $y = x^2$ plotted as a function of x . The dashed line is the tangent to the curve at $x = 1.5$.

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.

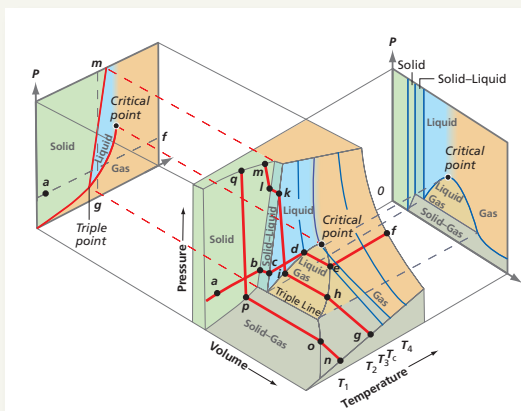


Figure 8.15 A P - V - T phase diagram for a substance that expands upon melting. The indicated processes are discussed in the text.

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Energy - Heat - Temperature

5:50 PM

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 DONT 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 Châtelier's Principle

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.

Hints

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]

double [nitrogen monoxide]

halve [nitrogen monoxide]

halve [nitrogen]

double [nitrogen]

halve [nitrogen]

Submit My Answers Give Up

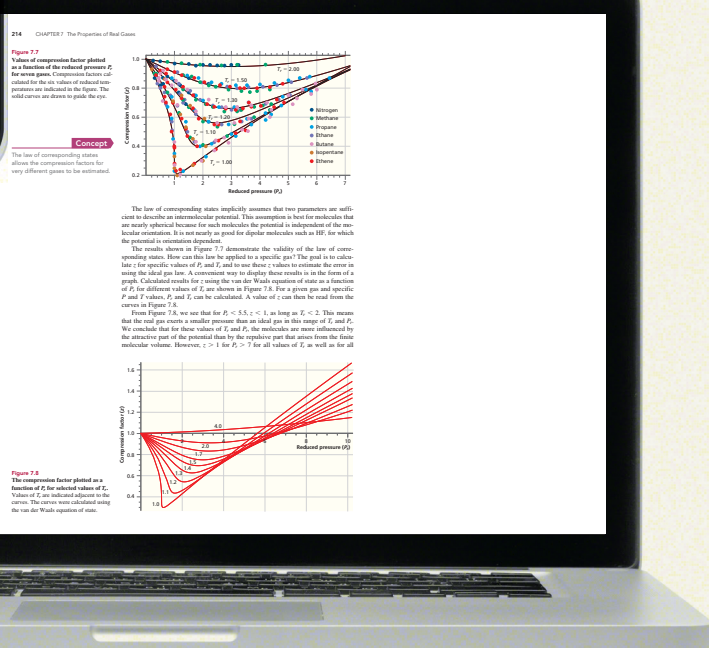
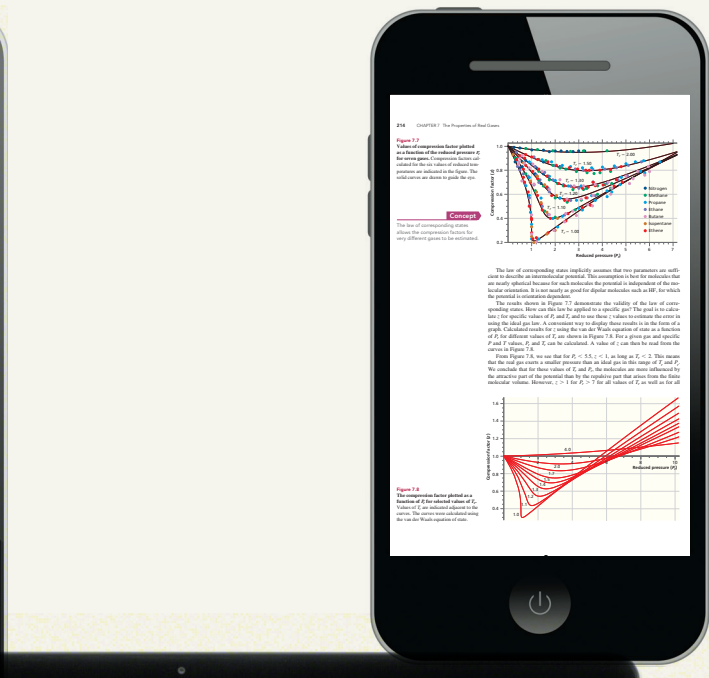
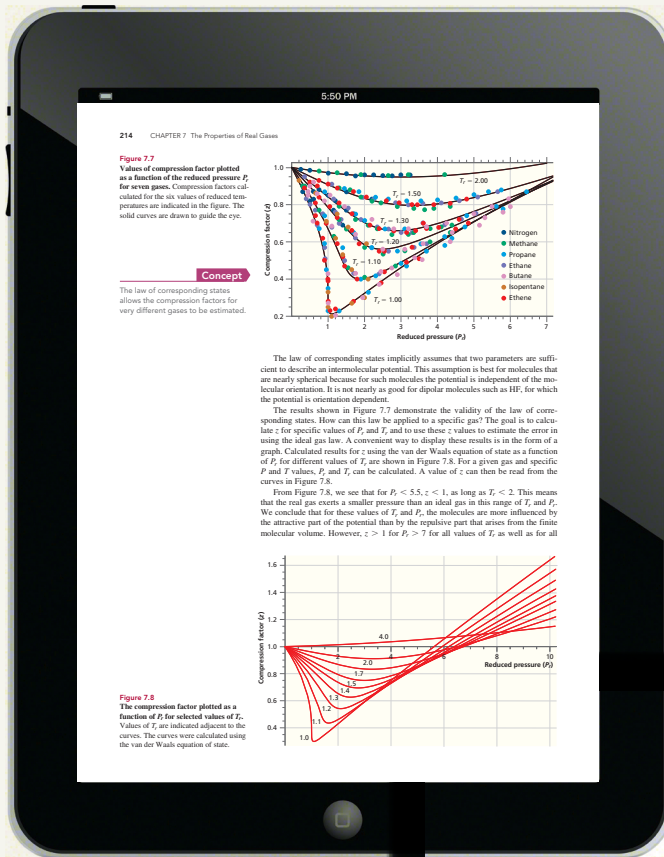
Incorrect; Try Again

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 defined by taking the value of Planck's constant h to be exactly $6.62607015 \times 10^{-34} \text{ kg} \cdot \text{m}^2/\text{s}$.
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 $2 \times 10^{-7} \text{ kg m s}^{-2}$ per meter of length. In this definition, 2 is an exact number.
Unit of thermodynamic temperature	kelvin (K)	The kelvin, unit of thermodynamic temperature, is defined by taking the value of the Boltzmann constant k to be exactly $1.380649 \times 10^{-23} \text{ J/K}$.
Unit of amount of substance	mole (mol)	The mole is the SI unit of substance. One mole contains exactly $6.02214076 \times 10^{23}$ elementary entities. 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

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

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):

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

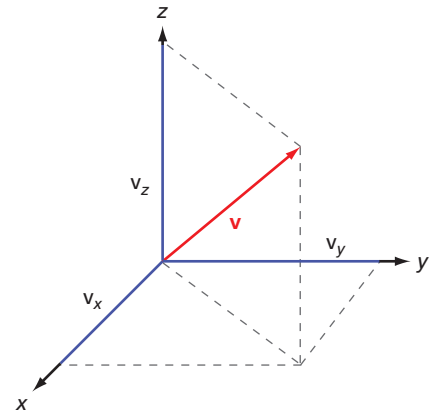


Figure 1.1
Cartesian components of velocity. The particle velocity \mathbf{v} can be resolved into three velocity components: v_x , v_y , and v_z .

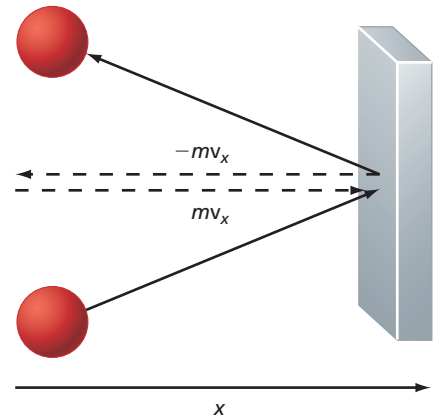


Figure 1.2
Collision between a gas particle and a wall. Before the collision, the particle has a momentum of mv_x in the x direction, whereas after the collision the momentum is $-mv_x$. Therefore, the change in particle momentum resulting from the collision is $-2mv_x$. By conservation of momentum,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

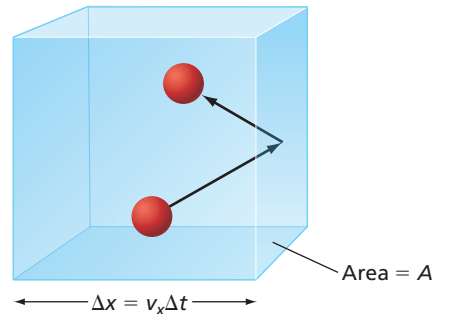


Figure 1.3
Volume element used to determine the number of collisions with a wall per unit time.

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.

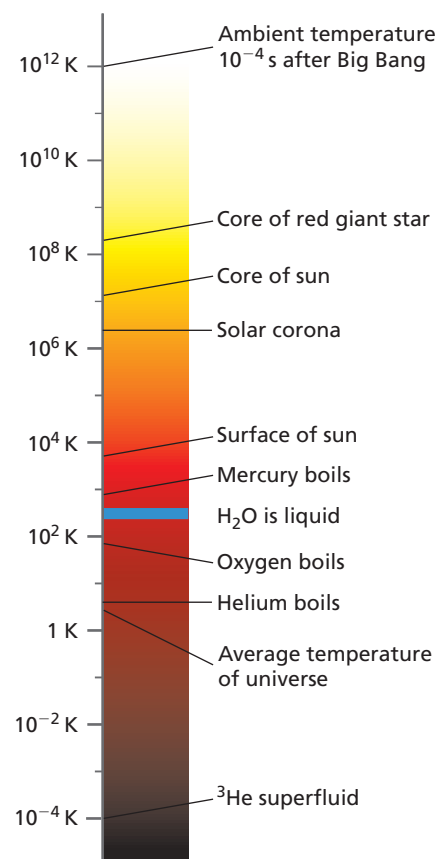


Figure 1.4 Absolute temperature displayed on a logarithmic scale. The temperature of a number of physical phenomena is also shown.

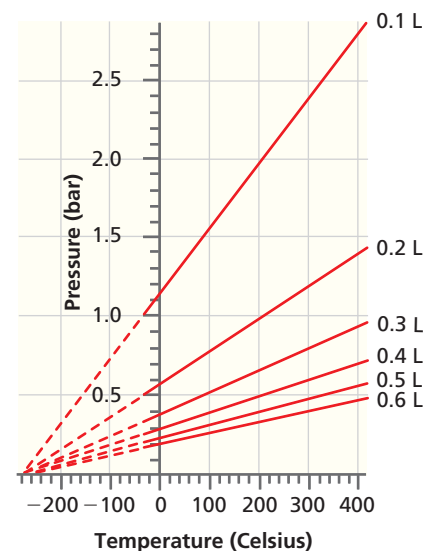


Figure 1.5 Relationship between temperature and pressure for a dilute gas. The pressure exerted by 5.00×10^{-3} mol of a dilute gas is shown as a function of the temperature measured on the Celsius scale for different fixed volumes. The dashed segments of lines indicate that the data are extrapolated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

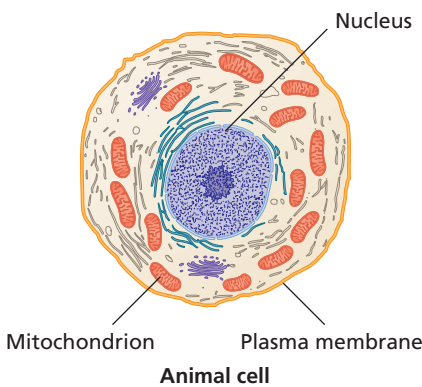
At the time of these experiments, temperatures below -30°C were not attainable in the laboratory. However, the P versus T_C (temperature on the Celsius scale) data can be extrapolated to the limiting T_C value at which $P \rightarrow 0$. It is found that these straight lines obtained for different values of V intersect at a common point on the T_C axis that lies near -273°C .

The data in Figure 1.5 show that at constant V the thermometric property P varies with temperature as

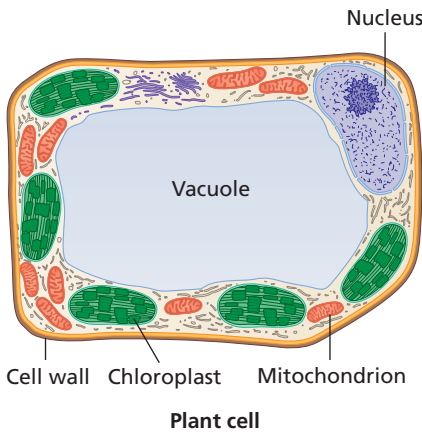
$$P = a + bT_C \quad (1.15)$$

where a and b are experimentally obtained proportionality constants. Figure 1.5 shows that all lines intersect at a single point, even for different gases. This suggests a unique reference point for temperature, rather than the two reference points used in constructing the centigrade scale. The value zero is given to the temperature at which $P \rightarrow 0$, so that $a = 0$. However, this choice is not sufficient to define the temperature scale because the size of the degree is undefined. By convention, the size of the degree on the absolute temperature scale is set equal to the size of the degree on the Celsius scale. With these two choices, the absolute and Celsius temperature scales are related by Equation (1.16). The scale measured by the ideal gas thermometer is the absolute temperature scale used in thermodynamics. The unit of temperature on this scale is called the **kelvin**, abbreviated K (without a degree sign):

$$T/\text{K} = T_C/^{\circ}\text{C} + 273.15 \quad (1.16)$$



(a)



(b)

Figure 1.6**Animal and plant cells are open systems.**

Sketch of (a) an animal cell and (b) a plant cell shown with selected organelles. The contents of the animal cell include the cytosol fluid and the numerous organelles (e.g., nucleus, mitochondria) that are separated from the surroundings by a lipid-rich plasma membrane. The plasma membrane acts as a boundary layer that can transmit energy and is selectively permeable to ions and various metabolites. A plant cell is surrounded by a cell wall that similarly encases the cytosol and organelles, including chloroplasts (in which photosynthesis occurs).

1.3 BASIC DEFINITIONS NEEDED TO DESCRIBE THERMODYNAMIC SYSTEMS

In the first two sections of this chapter, we discussed the macroscopic variables pressure, volume, and temperature. With this background information, we are now ready to introduce some important concepts used in thermodynamics. A thermodynamic **system** consists of all the materials involved in the process under study. This material could be the contents of an open beaker containing reagents, the electrolyte solution within an electrochemical cell, or the contents of a cylinder and movable piston assembly in an engine. In thermodynamics, the rest of the universe is referred to as the **surroundings**. If a system can exchange matter with the surroundings, it is called an **open system**; if not, it is a **closed system**. Living cells are open systems (see Figure 1.6). Both open and closed systems can exchange energy with the surroundings. Systems that can exchange neither matter nor energy with the surroundings are called **isolated systems**.

The interface between the system and its surroundings is called the **boundary**. Boundaries determine if energy and mass can be transferred between the system and the surroundings and lead to the distinction between open, closed, and isolated systems. Consider Earth's oceans as a system, with the rest of the universe being the surroundings. The system–surroundings boundary consists of the solid–liquid interface between the continents and the ocean floor and the water–air interface at the ocean surface. For an open beaker in which the system is the contents, the boundary surface is just inside the inner wall of the beaker, and it passes across the open top of the beaker. In this case, energy can be exchanged freely between the system and surroundings through the side and bottom walls, and both matter and energy can be exchanged between the system and surroundings through the open top boundary. The portion of the boundary formed by the beaker in the previous example is called a *wall*. Walls can be rigid or movable and permeable or nonpermeable. An example of a movable wall is the surface of a balloon. An example of a selectively permeable wall is the fabric used in raingear, which is permeable to water vapor but not to liquid water.

The exchange of energy and matter across the boundary between system and surroundings is central to the important concept of **equilibrium**. The system and surroundings can be in equilibrium with respect to one or more of several different **system variables** such as pressure (P), temperature (T), and concentration. **Thermodynamic equilibrium** refers to a condition in which equilibrium exists with respect to P , T , and

concentration. What conditions are necessary for a system to come to equilibrium with its surroundings? Equilibrium is established with respect to a given variable only if that variable does not change with time, and if it has the same value in all parts of the system and surroundings. For example, the interior of a soap bubble¹ (the system) and the surroundings (the room) are in equilibrium with respect to P because the movable wall (the bubble) can reach a position where P on both sides of the wall is the same, and because P has the same value throughout the system and surroundings. Equilibrium with respect to concentration exists only if transport of all species across the boundary in both directions is possible. If the boundary is a movable wall that is not permeable to all species, equilibrium can exist with respect to P but not to concentration. Because $N_2(g)$ and $O_2(g)$ cannot diffuse through the (idealized) bubble, the system and surroundings are in equilibrium with respect to P but not to concentration. Equilibrium with respect to temperature is a special case that is discussed next.

Two systems that have the same temperature are in **thermal equilibrium**. We use the concepts of temperature and thermal equilibrium to characterize the walls between a system and its surroundings. Consider the two systems with rigid walls shown in Figure 1.7a. Each system has the same molar density and is equipped with a pressure gauge. If we bring the two systems into direct contact, two limiting behaviors are observed. If neither pressure gauge changes, as in Figure 1.7b, the wall has not allowed the transfer of energy, and we refer to the wall as being **adiabatic**. Because $P_1 \neq P_2$, the systems are not in thermal equilibrium and, therefore, have different temperatures. An example of a system surrounded by adiabatic walls is coffee in a Styrofoam cup with a Styrofoam lid.² Experience shows that it is not possible to bring two systems enclosed by adiabatic walls into thermal equilibrium by bringing them into contact because adiabatic walls insulate against the transfer of “heat.” If we push a Styrofoam cup containing hot coffee against one containing ice water, they will not reach the same temperature. Rely on experience at this point regarding the meaning of heat; a thermodynamic definition will be given in Chapter 2.

The second limiting case is shown in Figure 1.7c. In bringing the systems into intimate contact, both pressures change and reach the same value after some time. We conclude that the systems have the same temperature, $T_1 = T_2$, and say that they are in thermal equilibrium. We refer to the walls as being **diathermal**. Two systems in contact separated by diathermal walls reach thermal equilibrium because diathermal walls conduct heat. Hot coffee stored in a copper cup is an example of a system surrounded by diathermal walls. Because the walls are diathermal, the coffee will quickly reach room temperature.

The **zeroth law of thermodynamics** generalizes the experiments illustrated in Figure 1.7 and asserts the existence of an objective temperature that can be used to define the condition of thermal equilibrium. The formal statement of this law is as follows:

Two systems that are separately in thermal equilibrium with a third system are also in thermal equilibrium with one another.

The unfortunate name was assigned to the “zeroth” law because it was formulated after the first law of thermodynamics, but logically it precedes it. The zeroth law tells us that we can determine if two systems are in thermal equilibrium without bringing them into contact. Imagine the third system to be a thermometer, which is defined more precisely in the next section. The third system can be used to compare the temperatures of the other two systems; if they have the same temperature, they will be in thermal equilibrium if placed in contact.

¹For this example, the surface tension of the bubble is assumed to be so small that it can be set equal to zero. This is in keeping with the thermodynamic tradition of weightless pistons and frictionless pulleys.

²In this discussion, Styrofoam is assumed to be a perfect insulator.

Concept

Two systems are in thermodynamic equilibrium if pressure, temperature, and all concentrations are the same in both systems.

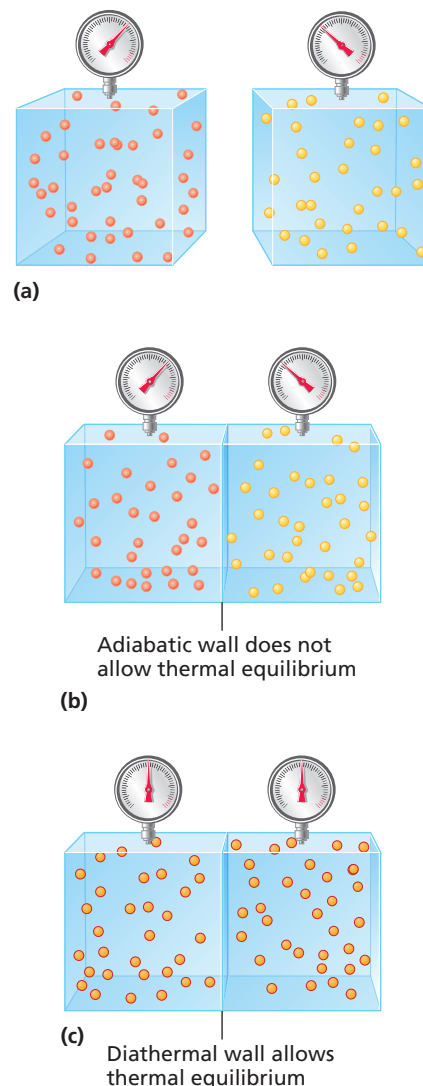


Figure 1.7
Comparison of adiabatic and diathermal walls. (a) Two separated systems with rigid walls and the same molar density have different temperatures. (b) Two systems are brought together so that their adiabatic walls are in intimate contact. The pressure in each system will not change unless heat transfer is possible. (c) As in part (b), two systems are brought together so that their diathermal walls are in intimate contact. The pressures become equal.

1.4 EQUATIONS OF STATE AND THE IDEAL GAS LAW

Concept

An equation of state links the variables that define the system.

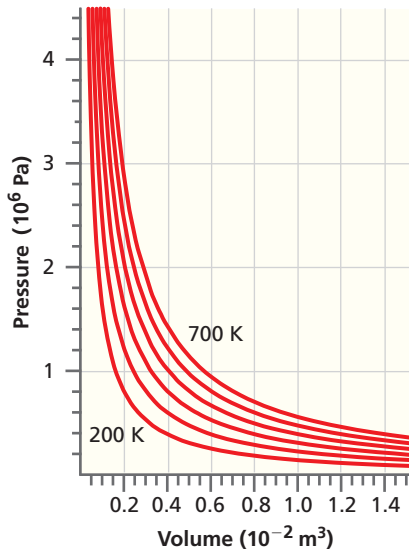


Figure 1.8 Plot showing the relationship between pressure and volume. Red curves represent fixed values of temperature for 1.00 mol of He. The interval of curves is 100 K.

Macroscopic models in which the system is described by a set of variables are based on experience. It is particularly useful to formulate an **equation of state** that relates the state variables. A dilute gas can be modeled as consisting of point masses that do not interact with one another; we call this an ideal gas. The equation of state for an ideal gas was first determined from experiments by the English chemist Robert Boyle in the 17th century. If the pressure of He is measured as a function of the volume for different values of temperature, the set of nonintersecting hyperbolas as shown in Figure 1.8 is obtained. The curves in this figure can be quantitatively fit by the functional form

$$PV = \alpha T \quad (1.17)$$

where T is the absolute temperature as defined by Equation (1.16), allowing α to be determined. The constant α is found to be directly proportional to the mass of gas used. It is useful to separate this dependence by writing $\alpha = nR$, where n is the number of moles of the gas and R is a constant that is independent of the size of the system. The result is the ideal gas equation of state

$$PV = Nk_B T = nRT \quad (1.18)$$

as derived in Equation (1.11). The equation of state given in Equation (1.18) is familiar as the ideal gas law. Because the four variables P , V , T , and n are related through the equation of state, any three of these variables are sufficient to completely describe the ideal gas.

Of these four variables, P and T are independent of the amount of gas, whereas V and n are proportional to the amount of gas. A variable that is independent of the size of the system (for example, P and T) is referred to as an **intensive variable**, and one that is proportional to the size of the system (for example, V) is referred to as an **extensive variable**. Equation (1.18) can be written in terms of intensive variables exclusively:

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

For a fixed number of moles, the ideal gas equation of state has only two independent intensive variables: any two of P , T , and ρ_m .

For an ideal gas mixture

$$PV = \sum_i n_i RT \quad (1.19)$$

because ideal gas molecules do not interact with one another. Equation (1.19) can be rewritten in the form

$$P = \sum_i \frac{n_i RT}{V} = \sum_i P_i = P_1 + P_2 + P_3 + \dots \quad (1.20)$$

In Equation (1.20), P_i is the **partial pressure** of each gas. This equation states that each ideal gas exerts a pressure that is independent of the other gases in the mixture. We also have

$$\frac{P_i}{P} = \frac{\frac{n_i RT}{V}}{\sum_i \frac{n_i RT}{V}} = \frac{\frac{n_i RT}{V}}{\frac{nRT}{V}} = \frac{n_i}{n} = x_i \quad (1.21)$$

Concept

In an ideal gas mixture, the total pressure is the sum of the partial pressures.

which relates the partial pressure of a component in the mixture P_i with its **mole fraction**, $x_i = n_i/n$, and the total pressure P .

In the SI system of units, pressure is measured in Pascal (Pa) units, where $1 \text{ Pa} = 1 \text{ N/m}^2$. Volume is measured in cubic meters, and temperature is measured in kelvin. However, other units of pressure are frequently used; these other units are related to the Pascal, as indicated in Table 1.1. In this table, numbers that are not exact have been given to five significant figures. The other commonly used unit of volume is the liter (L), where $1 \text{ m}^3 = 10^3 \text{ L}$ and $1 \text{ L} = 1 \text{ dm}^3 = 10^{-3} \text{ m}^3$.

TABLE 1.1 Units of Pressure and Conversion Factors

Unit of Pressure	Symbol	Numerical Value
Pascal	Pa	$1 \text{ N m}^{-2} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$
Atmosphere	atm	$1 \text{ atm} = 101,325 \text{ Pa}$ (exactly)
Bar	bar	$1 \text{ bar} = 10^5 \text{ Pa}$
Torr or millimeters of Hg	Torr	$1 \text{ Torr} = 101,325/760 = 133.32 \text{ Pa}$
Pounds per square inch	psi	$1 \text{ psi} = 6,894.8 \text{ Pa}$

EXAMPLE PROBLEM 1.1

Before you begin a day trip, you inflate the tires on your automobile to a recommended pressure of $3.21 \times 10^5 \text{ Pa}$ on a day when the temperature is -5.00°C . On your trip you drive to the beach, where the temperature is 28.0°C . (a) What is the final pressure in the tires, assuming constant volume? (b) Derive a formula for the final pressure, assuming more realistically that the volume of the tires increases with increasing pressure as $V_f = V_i(1 + \gamma[P_f - P_i])$ where γ is an experimentally determined constant.

Solution

a. Because the number of moles is constant,

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}; \quad P_f = \frac{P_i V_i T_f}{V_f T_i};$$

$$P_f = \frac{P_i V_i T_f}{V_f T_i} = 3.21 \times 10^5 \text{ Pa} \times \frac{V_i}{V_i} \times \frac{(273.15 + 28.0)}{(273.15 - 5.00)} = 3.61 \times 10^5 \text{ Pa}$$

b.
$$\frac{P_i V_i}{T_i} = \frac{P_f V_i (1 + \gamma [P_f - P_i])}{T_f};$$

$$P_i T_f = P_f T_i (1 + \gamma [P_f - P_i])$$

$$P_f^2 T_i \gamma + P_f T_i (1 - P_i \gamma) - P_i T_f = 0$$

$$P_f = \frac{-T_i(1 - P_i \gamma) \pm \sqrt{T_i^2(1 - P_i \gamma)^2 + 4T_i T_f \gamma P_i}}{2T_i \gamma}$$

We leave it to the end-of-chapter problems to show that this expression for P_f has the correct limit as $\gamma \rightarrow 0$.

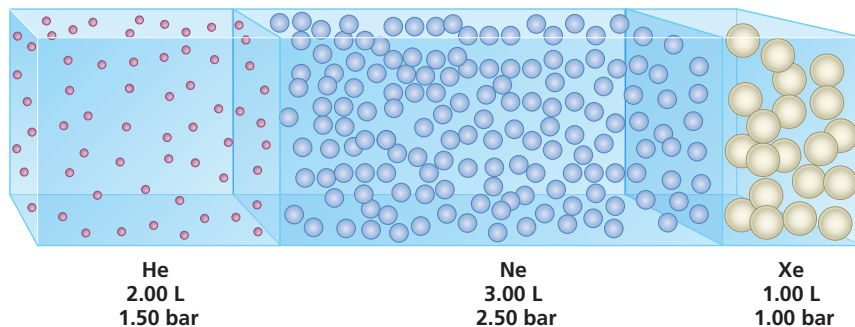
In the SI system, the constant R that appears in the ideal gas law has the value $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, where the joule (J) is the unit of energy in the SI system. To simplify calculations for other units of pressure and volume, the values of the constant R with different combinations of units are given in Table 1.2.

TABLE 1.2 The Ideal Gas Constant, R , in Various Units

$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
$R = 8.314 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1}$
$R = 8.314 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1}$
$R = 8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}$
$R = 62.36 \text{ L Torr K}^{-1} \text{ mol}^{-1}$

EXAMPLE PROBLEM 1.2

Consider the composite system, which is held at 298 K, shown in the following figure. Assuming ideal gas behavior, calculate the total pressure and the partial pressure of each component if the barriers separating the compartments are removed. Assume that the volume of the barriers is negligible.



Solution

The number of moles of He, Ne, and Xe is given by

$$n_{\text{He}} = \frac{PV}{RT} = \frac{1.50 \text{ bar} \times 2.00 \text{ L}}{8.314 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}} = 0.121 \text{ mol}$$

$$n_{\text{Ne}} = \frac{PV}{RT} = \frac{2.50 \text{ bar} \times 3.00 \text{ L}}{8.314 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}} = 0.303 \text{ mol}$$

$$n_{\text{Xe}} = \frac{PV}{RT} = \frac{1.00 \text{ bar} \times 1.00 \text{ L}}{8.314 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}} = 0.0403 \text{ mol}$$

$$n = n_{\text{He}} + n_{\text{Ne}} + n_{\text{Xe}} = 0.464$$

The mole fractions are

$$x_{\text{He}} = \frac{n_{\text{He}}}{n} = \frac{0.121}{0.464} = 0.261$$

$$x_{\text{Ne}} = \frac{n_{\text{Ne}}}{n} = \frac{0.303}{0.464} = 0.653$$

$$x_{\text{Xe}} = \frac{n_{\text{Xe}}}{n} = \frac{0.0403}{0.464} = 0.0860$$

The total pressure is given by

$$\begin{aligned} P &= \frac{(n_{\text{He}} + n_{\text{Ne}} + n_{\text{Xe}})RT}{V} \\ &= \frac{0.464 \text{ mol} \times 8.314 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{6.00 \text{ L}} \\ &= 1.92 \text{ bar} \end{aligned}$$

The partial pressures are given by

$$P_{\text{He}} = x_{\text{He}}P = 0.261 \times 1.92 \text{ bar} = 0.501 \text{ bar}$$

$$P_{\text{Ne}} = x_{\text{Ne}}P = 0.653 \times 1.92 \text{ bar} = 1.25 \text{ bar}$$

$$P_{\text{Xe}} = x_{\text{Xe}}P = 0.0860 \times 1.92 \text{ bar} = 0.165 \text{ bar}$$

1.5 A BRIEF INTRODUCTION TO REAL GASES

The ideal gas law provides a useful means of describing a system in terms of macroscopic parameters. However, we should also emphasize the downside of not taking the microscopic nature of the system into account. For example, the ideal gas law only holds for gases at low densities. In practice, deviations from the ideal gas law that occur for real gases must be taken into account in such applications as a gas thermometer.