THERMODYNAMICS Concepts and Applications

**STEPHEN R. TURNS** 

### THERMODYNAMICS Concepts and Applications

The focus of *Thermodynamics: Concepts and Applications* is on traditional engineering thermodynamics topics. The structure of this book, however, provides a broader context for thermodynamics within the thermal-fluid sciences. The subject matter is also arranged hierarchically, rather than as a collection of assorted topics. Chapter 2 epitomizes this approach with essentially all material related to thermodynamic properties contained within a single chapter. This arrangement allows students to connect topics in a logical manner, without necessarily proceeding through the chapter in a linear manner. It is expected that this chapter will be revisited many times. Similarly, Chapter 3 deals with all aspects of mass conservation, including element conservation required for reacting systems. Chapter 5 follows a similar path for energy conservation. Second-law topics are introduced hierarchically in Chapter 6, an important structure for a beginner. Here the advanced topics of chemical and phase equilibria are treated as a consequence of the second law of thermodynamics. The design of this book allows an instructor to select topics and combine them with material from other chapters seamlessly. Pedagogical devices include learning objectives; chapter overviews, summaries, and checklists; historical perspectives; numerous examples, questions and problems; and lavish illustrations. Students are encouraged to use the National Institute of Science and Technology (NIST) fluid properties database.

Stephen R. Turns has been a Professor of Mechanical Engineering at The Pennsylvania State University since completing his Ph.D. at the University of Wisconsin in 1979. Before that, Steve spent five years in the Engine Research Department of General Motors Research Laboratories in Warren, Michigan. His active research interests include the study of pollutant formation and control in combustion systems, combustion engines, combustion instrumentation, slurry fuel combustion, energy conversion, and energy policy. He has published numerous refereed journal articles on many of these topics. Steve is a member of the ASME and many other professional organizations and an ABET Program Evaluator since 1994. He is also a dedicated teacher, for which he has won numerous awards including the Penn State Teaching and Learning Consortium, Hall of Fame Faculty Award; Penn State's Milton S. Eisenhower Award for Distinguished Teaching; the Premier Teaching Award, Penn State Engineering Society; and the Outstanding Teaching Award, Penn State Engineering Society. Steve's talent as a teacher is also reflected in his best-selling advanced undergraduate textbook *Introduction to Combustion: Concepts and Applications*, 2nd ed. Steve's commitment to students and teaching is shown in the innovative approach and design of *Thermodynamics* and its companion volume, *Thermal-Fluid Sciences: An Integrated Approach*, also published by Cambridge University Press.

# THERMODYNAMICS

#### CONCEPTS AND APPLICATIONS

## Stephen R. Turns

The Pennsylvania State University



CAMBRIDGE UNIVERSITY PRESS Cambridge, New York, Melbourne, Madrid, Cape Town, Singapore, São Paulo

> Cambridge University Press 40 West 20th Street, New York, NY 10011–4211, USA

www.cambridge.org Information on this title:www.cambridge.org/9780521850421

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First published 2006

Printed in Hong Kong by Golden Cup Printing Co. Ltd.

A catalog record for this book is available from the British Library.

Library of Congress Cataloging-in-Publication Data

Turns, Stephen R. Thermodynamics : concepts and applications / Stephen R. Turns.

> p. cm. Includes bibliographical references and index. ISBN-13: 978-0-521-85042-1 (hardback) ISBN-10: 0-521-85042-8 (hardback) 1. Thermodynamics. 2. Fluid mechanics. I. Title.

> > TJ265.T86 2006 621.402'.1-dc22

#### 2005033974

ISBN-13 978-0-521-85042-1 hardback ISBN-10 0-521-85042-8 hardback

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In lecturing on any subject, it seems to be the natural course to begin with a clear explanation of the nature, purpose, and scope of the subject. But in answer to the question "What is thermo-dynamics?" I feel tempted to reply "It is a very difficult subject, nearly, if not quite, unfit for a lecture."

> Osborne Reynolds On the General Theory of Thermo-dynamics November 1883

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#### **Preface**

WHY ANOTHER THERMODYNAMICS BOOK? With a number of excellent thermodynamics textbooks available what purpose is served by publishing another? The answer to these important questions lies in the origins of this book. Although the subject matter focuses almost entirely on traditional thermodynamics topics, the structure of the book puts it in the broader context of the thermal-fluid sciences. The following specific features provide this integrated feel:

- Chapter 3 is devoted entirely to the conservation of mass principle and deals with some concepts traditionally treated in fluid mechanics textbooks.
- Rate laws for conduction, convection, and radiation heat transfer are introduced in Chapter 4—Energy and Energy Transfer. These rate laws are used subsequently in examples in this and later chapters.
- The concept of head loss, a usual topic in fluid mechanics, also is introduced in Chapter 5 and utilized in examples.

A second feature also sets this book apart from other engineering thermodynamics textbooks: a hierarchical structure. The following arrangements illustrate the hierarchical arrangement of subject matter:

- In Chapter 2, essentially all material related to thermodynamic properties is grouped together. In this way, we are able to show clearly the hierarchy of thermodynamic state relationships starting with the basic equation of state involving *P*, v, and *T*; adding first-law-based calorific equations of state involving *u*, *h*, *P*, *T*, and v; and ending with the second-law based state relationships involving *s*, *T*, *P*, and v, for example. Chapter 2 also treats properties of ideal gas mixtures and introduces standardized properties for reacting mixtures. Such arrangement requires that Chapter 2 be revisited at appropriate places in the study of later chapters. In this sense, Chapter 2 is a resource that is to be returned to many times.
- Element conservation, a topic central to reacting systems, is considered in Chapter 3 as just one of many ways of expressing conservation of mass.
- Constant-pressure and constant-volume combustion are considered as topics within Chapter 5—Energy Conservation.

• Chemical and phase equilibria are treated as a consequence of the 2nd law of thermodynamics and developed within Chapter 6; therefore, all topics related to the 2nd law are found hierarchically in a single chapter.

What purpose is served by such an arrangement? First, it provides an important structure for a beginning learner. Experts who have mastered and work within a discipline organize material this way in their minds, while novices tend to treat concepts in an undifferentiated way as a collection of seemingly unrelated topics.<sup>1</sup> Even through all topics will not be covered sequentially in a course, when students revisit chapters they will see the connections between new and previously covered material. It is hoped that providing a useful hierarchy from the start may speed learning and aid in retention. A second reason for a hierarchical arrangement is flexibility. In general, the book has been designed to permit an instructor to select topics from within a chapter and combine them with material from other chapters in a relatively seamless manner. This flexibility allows the book to be used in many ways depending upon the educational goals of a particular course, or a sequence of courses. To assist in selecting topics, the text distinguishes three levels; level 1 (basic) material is unmarked, level 2 (intermediate) material appears with a blue background and a blue edge stripe, and level 3 (advanced) material is denoted with a light red background and a red edge stripe. Instructors can therefore choose from the numerous topics presented to create courses that meet their specific educational objectives. The syllabus following the table of contents illustrates how the book might be used in a traditional, one-semester, engineering thermodynamics class.

In addition to structure, many other pedagogical devices are employed in this book. These include the following:

- An abundance of color photographs and images illustrate important concepts and emphasize practical applications;
- Each chapter begins with a list of learning objectives, a chapter overview, and a brief historical perspective, where appropriate, and concludes with a brief summary;
- Each chapter contains many examples that follow a standard problemsolving format;
- Self tests follow most examples;
- Key equations are denoted by colored backgrounds;
- Each chapter concludes with a checklist of key concepts and definitions linked to specific end-of-chapter questions and problems;
- The National Institute of Science and Technology (NIST) database for thermodynamic and transport properties (included in the NIST12 v.5.2 software provided with the book) is used extensively.

All of these features are intended to enhance student motivation and learning and to make teaching easier for the instructor. For example, the many color photographs make connections to real-world devices, a strong motivator for undergraduate students. Also, the learning objectives and checklists are particularly useful. For the instructor, they aid in the selection of homework problems and the creation of quizzes and exams, or other instructional tools. For students, they can be used as self tests of comprehension and can monitor progress. The checklists also cite topic-specific questions and problems. In

<sup>&</sup>lt;sup>1</sup> Larkin, J., McDermott, J., Simon, D. P., Simon, H. A., "Expert and Novice Performance in Solving Physics Problems," *Science*, 208: 1335–1342 (1980).

his use of the book, the author utilizes the learning objectives to guide reviews of the material prior to examinations. Having well-defined learning objectives is also useful in meeting engineering accreditation requirements. Many questions and problems are included at the end of each chapter. The purpose of the questions is to reinforce conceptual understanding of the material and to provide an outlet for students to articulate such understanding. Throughout the book, students are encouraged to use the National Institute of Science and Technology (NIST) databases to obtain thermodynamic properties. The online NIST property database is easily accessible and is a powerful resource. It is a tool that will always be up to date. The NIST12 v.5.2 software included with this book has features not available online. This user-friendly software provides extensive property data for eighteen fluids and has an easy-to-use plotting capability. This invaluable resource makes dealing with properties easy and can be used to enhance student understanding.

Feedback from instructors who use this book is most welcome.

THIS BOOK HAS BEEN A LONG TIME COMING and many people have contributed along the way. First I would like to thank Jonathan Plant for encouraging me to create this book. He got the ball rolling. I also would like to thank the many reviewers for their contributions. Without their candid comments and careful reading this project would not have been possible.

I am indebted to Peter Gordon at Cambridge University Press for his vision of a richly illustrated and colorful book and the managers at the Press for supporting our shared vision. To this end, I am happy to acknowledge Rick Medvitz and Jared Ahern of the Applied Research Laboratory at Penn State for their creation of the exciting computational fluid dynamics illustrations. Thanks also are owed to Joel Peltier and Eric Paterson at ARL for their support of the CFD effort. Regina Brooks and Anne Wells at Serendipity Literary Agency worked hard to find photographs, and the cooperation of AGE fotostock is gratefully acknowledged. Jessica Cepalak and Michelle Lin at Cambridge were indispensable in many ways throughout the project. The stunning book design was the effort of José Fonfrias. Thank you, José.

Special thanks go to Chris Mordaunt for his creation of the self tests and his meticulous reading of the manuscript and insightful comments. Thanks also go to the members of the solutions manual team: Jacob Stenzler and Dave Kraige, leaders of the effort, and Justin Sabourin, Yoni Malchi, and Shankar Narayanan. For nearly a decade, Mary Newby deciphered my pencil scrawls to create a word-processed manuscript. I thank Mary for her invaluable efforts.

I would like to acknowledge the production team at Cambridge—Alan Gold (Senior Production Controller) and Pauline Ireland (Director, Production and New Media Development)—who broke a great number of old rules to make a very new book. I especially want to thank Anoop Chaturvedi and his production team at TechBooks for their careful attention to detail. I also thank fellow textbook authors Dwight Look, Jr., and Harry Sauer, Jr.; Glen Myers; Alan Chapman; and David Pnueli and Chaim Gutfinger, for their permission to use selected problems from their works. Thanks also are owed to Eric Lemmon at NIST for assembling the software provided with this book and to Joan Sauerwein for making the agreement.

For the hospitality shown during a sabbatical year spent writing, I thank Allan Kirkpatrick and Charles Mitchell at Colorado State University and Taewoo Lee and Don Evans at Arizona State University. I would also like to thank good friends Kathy and Dan Wendland for opening their home to us for an extended stay in Fort Collins. Thanks also are extended to Nancy and Dave Pearson, more good friends, for their help and companionship in Tempe.

The sales and marketing team at Cambridge are a joy to work with. Thanks go to Liza Murphy, Kerry Cahill, Liz Scarpelli, Robin Silverman, Ted Guerney, Catherine Friedl, and Valerie Yaw, along with their counterparts in the UK, Rohan Seery, Ben Ashcroft, Gurdeep Pannu, and Cherrill Richardson. I would also like to thank Jae Hong for his contributions to this project.

Moral support has come from many fronts, especially from the crowd at Saints Cafe and from Bob Santoro. Three people, however, deserve my heartfelt thanks. The first is Peter Gordon at Cambridge. Peter came to the rescue in trying times and breathed new life into this project. Second is Dick Benson, friend and confidant. Without Dick's enthusiastic support, this book would not have been possible. Third, but hardly last, is Joan, my wife. I cannot thank her enough for her help, patience, and support. Thank you, Joan. THERMODYNAMICS Concepts and Applications

#### CHAPTER ONE

# BEGINNINGS



## After studying Chapter 1, you should:

- Have a basic idea of what thermodynamics is and the kinds of engineering problems to which it applies.
- Be able to distinguish between a system and a control volume.
- Be able to write and explain the generic forms of the basic conservation principles.
- Have an understanding of and be able to state the formal

definitions of thermodynamic properties, states, processes, and cycles.

- Understand the concept of thermodynamic equilibrium and its requirement of simultaneously satisfying thermal, mechanical, phase, and chemical equilibria.
- Be able to explain the meaning of a quasi-equilibrium process.
- Understand the distinction between primary dimensions and derived dimensions, and the distinction between dimensions and units.
- Be able to convert SI units of force, mass, energy, and power to U.S. customary units, and vice versa.

## Chapter 1 Overview

IN THIS CHAPTER, we introduce the subject of thermodynamics. We also introduce three fairly complex, practical applications of our study of thermodynamics: the fossil-fueled steam power plant, jet engines, and the spark-ignition reciprocating engine. To set the stage for more detailed developments later in the book, several of the most important concepts and definitions are presented here: These include the concepts of thermodynamic systems and control volumes; the fundamental conservation principles; thermodynamic properties, states, and cycles; and equilibrium and quasi-equilibrium processes. The chapter concludes with some ideas of how you might optimize the use of this textbook based on your particular educational objectives.

#### 1.1 WHAT IS THERMODYNAMICS?

Thermodynamics is one of three disciplines collectively known as the thermalfluid sciences, or sometimes, just the thermal sciences: thermodynamics, heat transfer, and fluid dynamics. Although the focus of our study in this book is thermodynamics, we touch on the other disciplines as necessary to provide a more thorough understanding of and context for thermodynamics.

We begin with a dictionary definition [1] of thermodynamics:

## Thermodynamics is the science that deals with the relationship of heat and mechanical energy and conversion of one into the other.

The Greek roots, *therme*, meaning heat, and *dynamis*, meaning power or strength, suggest a more elegant definition: *the power of heat*. In its common usage in engineering, thermodynamics has come to mean the broad study of energy and its various interconversions from one form to another. The following are but a few examples that motivate our study of thermodynamics.



Examples of energy conversion systems: Fuel cells convert energy stored in chemical bonds to electricity to power a low-pollution bus (left); solar concentrators collect radiant energy from the sun (middle); wind turbines, Tehachapi, California produce electricity (right).







Coal-fired power plant in North Rhine-Westphalia, Germany.



**1.2 SOME APPLICATIONS** 

We present here, and revisit throughout the book, the following three practical applications:

- Fossil-fueled steam power plants,
- Spark-ignition engines, and
- Jet engines.

These applications, and others, provide a practical context for our study of thermodynamics. Many of the examples presented in subsequent chapters revisit these specific applications, as do many of the end-of-chapter problems. Where these particular examples appear, a note reminds the reader that the example relates to one of these three applications.

#### 1.2a Fossil-Fueled Steam Power Plants

There are many reasons to choose the fossil-fueled steam power plant as an application of thermodynamics. First, and foremost, is the overwhelming importance of such power plants to our daily existence. Imagine how your life would be changed if you did not have access to electrical power, or less severely, if electricity had to be rationed so that it would be available to you only a few hours each day! It is easy to forget the blessings of essentially limitless electrical power available to residents of the United States. That the source of our electricity is dominated by the combustion of fossil fuels is evident from an examination of Table 1.1. Here we see that approximately 71% of the electricity produced in the United States in 2002 had its origin in the combustion of a fossil fuel, that is, coal, gas, or oil. A second reason for our choice of steam power plants as an integrating application is the historical significance of steam power. The science of thermodynamics was born, in part, from a desire to understand and improve the earliest steam engines. John Newcomen's first coal-fired steam engine (1712) predates the discovery of the fundamental principles of thermodynamics by more than a hundred years! The idea later to be known as the second law of thermodynamics was published by Sadi Carnot in 1824; the conservation of energy principle, or the first law of thermodynamics, was first presented by Julius Mayer in 1842.<sup>1</sup>

In this chapter we present the basic steam power plant cycle and illustrate some of the hardware used to accomplish this cycle. In subsequent chapters, we will add devices and complexity to the basic cycle. Figure 1.1 shows the basic steam power cycle, or Rankine<sup>2</sup> cycle. Water (liquid and vapor) is the working fluid in the closed loop 1–2–3–4–1. The water undergoes four processes:

- **Process 1–2** A pump boosts the pressure of the liquid water prior to entering the boiler. To operate the pump, an input of energy is required.
- Process 2-3 Energy is added to the water in the boiler, resulting, first, in an increase in the water temperature and, second, in a phase change. The hot products of combustion provide this energy. The working fluid is all liquid at state 2 and all vapor (steam) at state 3.

John Newcomen's steam engine was used to pump water from coal mines.

<sup>&</sup>lt;sup>1</sup>A timeline of important people and events in the history of the thermal sciences is presented in Appendix A.

<sup>&</sup>lt;sup>2</sup> William Rankine (1820–1872), a Scottish engineer, was the author of the Manual of the Steam Engine and Other Prime Movers (1859) and made significant contributions to the fields of civil and mechanical engineering.

Source	Billion kW · hr	%	
Fossil Fuels			
Coal	1926.4	50.2	
Petroleum	89.9	2.3	
Natural Gas	685.8	17.9	
Other Gases	12.1	0.3	
Subtotal	2714.2	70.7	
Nuclear	780.2	20.3	
Hydro Pumped Storage	-8.8	-0.2	
Renewables			
Hydro	263.6	6.9	
Wood	36.5	1.0	
Waste	22.9	0.6	
Geothermal	13.4	0.3	
Solar	0.5	—	
Wind	10.5	0.3	
Other	5.6	0.1	
Subtotal	353.0	9.2	
TOTAL	3838.6	100.0	

#### Table 1.1 Electricity Generation in the United States for 2002 [2]





#### FIGURE 1.2

Cutaway view of boiler showing gasor oil-fired burners on the right wall. Liquid water flowing through the tubes is heated by the hot combustion products. The steam produced resides in the steam drum (tank) at the top left. The boiler has a nominal 8-m width, 12-m height, and 10-m depth. Adapted from Ref. [3] with permission.



- **Process 3–4** Energy is removed from the high-temperature, high-pressure steam as it expands through a steam turbine. The output shaft of the turbine is connected to an electrical generator for the production of electricity.
- **Process 4–1** The low-pressure steam is returned to the liquid state as it flows through the condenser. The energy from the condensing steam is transferred to the cooling water.

Figures 1.2–1.6 illustrate the various generic components used in the Rankine cycle. Figure 1.2 shows a cutaway view of an industrial boiler; a much larger central power station utility boiler is shown in Fig. 1.3. Although the design of boilers [3–6] is well beyond the scope of this book, the text offers much about the fundamental principles of their operation. For example,



FIGURE 1.3 Boilers for public utility central power generation can be quite large, as are these oil-fired units. Photograph courtesy of Florida Power and Light Company.
Steam turbine for power generation. Photograph and original caption reproduced with permission of the Smithsonian Institution.



Westinghouse Turbine Rotor, 1925 © Smithsonian Institution

The "Heart" of the Huge Westinghouse Turbine – An unusual detailed picture showing the maze of minutely fashioned blades – approximately five thousand—of the Westinghouse turbine rotor, or "spindle". Though only twenty-five feet in length this piece of machinery weighs one hundred and fifteen thousand pounds. At full speed the outside diameter of the spindle, on the left, is running nearly ten miles per minute, or a little less than 600 miles per hour. The problem of excessive heat resulting from such tremendous speed has been overcome by working the bearings under forced lubrication, about two barrels of oil being circulated through the bearings every sixty seconds to lubricate and carry away the heat generated by the rotation. The motor is that of the 45000 H.P. generating unit built by the South Philadelphia Works, Westinghouse Electric & Mfg. Co. for the Los Angeles Gas and Electric Company.

Original Caption by Science Service © Westinghouse



As we begin our study, we emphasize the importance of safety in both the design and operation of power generation equipment. Fluids at high pressure contain enormous quantities of energy, as do spinning turbine rotors. Figure 1.7 shows the results of a catastrophic boiler explosion. Similarly, environmental concerns are extremely important in power generation. Examples here are the emission of potential air pollutants from



Smog in Lujiazui financial district in Shanghai, China.

#### FIGURE 1.5

Cutaway view of shell-and-tube heat exchanger. Energy is transferred from the hot fluid passing through the shell to the cold fluid flowing through the tubes.



#### FIGURE 1.6 Typical electric-motor-driven feedwater pump. Larger pumps may be driven from auxiliary steam turbines. Adapted from Ref. [4] with permission.





Pollution controls are important components of fossil-fueled power plants.

#### FIGURE 1.7

Safety is of paramount importance in the design and operation of power generation equipment. This photograph shows the catastrophic results of a boiler explosion at the Courbevoie power station (France). the combustion process and thermal interactions with the environment associated with steam condensation. You can find entire textbooks devoted to these topics [7, 8].

#### 1.2b Spark-Ignition Engines

We choose the spark-ignition engine as one of our applications to revisit because there are so many of them (approximately 200 million are installed in automobiles and light-duty trucks in the United States alone) and because many



The mechanical cycle of the fourstroke spark-ignition engine consists of the intake stroke (a), the compression stroke (b), the expansion stroke (c), and the exhaust stroke (d). This sequence of events, however, does not execute a thermodynamic cycle. Adapted from Ref. [9] with permission.









students are particularly interested in engines. Owing to these factors, and others, many schools offer entire courses dealing with internal combustion engines, and many books are devoted to this subject, among them Refs. [9-12].

Although you may be familiar with the four-stroke engine cycle, we present it here to make sure that all readers have the same understanding. Figure 1.8 illustrates the following sequence of events:

- **Intake Stroke** The inlet valve is open and a fresh fuel-air mixture is pulled into the cylinder by the downward motion of the piston. At some point near the bottom of the stroke, the intake valve closes.
- **Compression Stroke** The piston moves upward, compressing the mixture. The temperature and pressure increase. Prior to the piston reaching the top of its travel (i.e., top center), the spark plug ignites the mixture and a flame begins to propagate across the combustion chamber. Pressure rises above that owing to compression alone.
- **Expansion Stroke** The flame continues its travel across the combustion chamber, ideally burning all of the mixture before the piston descends much from top center. The high pressure in the cylinder pushes the piston downward. Energy is extracted from the burned gases in the process.
- Exhaust Stroke When the piston is near the bottom of its travel (bottom center), the exhaust valve opens. The hot combustion products flow rapidly out of the cylinder because of the relatively high pressure within the cylinder compared to that in the exhaust port. The piston ascends, pushing most of the remaining combustion products out of the cylinder. When the piston is somewhere near top center, the exhaust valve closes and the intake valve opens. The mechanical cycle now repeats.

In Chapter 5, we will analyze the processes that occur during the times in the cycle that both valves are closed and the gas contained within the cylinder can be treated as a thermodynamic system. With this analysis, we can model the compression, combustion, and expansion processes. Chapters 2 and 6 also deal with idealized compression and expansion processes. Note that Appendix 1A defines many engine-related terms and provides equations relating the cylinder volume, and its time derivative, to crank-angle position and other parameters.

Schematic drawings of a single-shaft turbojet engine (top) and a two-shaft high-bypass turbofan engine (bottom). Adapted from Ref. [13] with permission.





#### 1.2c Jet Engines

Air travel is becoming more and more popular each year as suggested by the number of passenger miles flown in the United States increasing from 433 billion in 1989 to 651 billion in 1999. Since you are likely to entrust your life from time to time to the successful performance of jet engines, you may find learning about these engines interesting. Figure 1.9 schematically illustrates the two general types of aircraft engines.

The schematic at the top shows a pure turbojet engine in which all of the thrust is generated by the jet of combustion products passing through the exhaust nozzle. This type of engine powered the supersonic J4 Phantom military jet fighter and the recently retired Concorde supersonic transport aircraft. In the turbojet, a multistage compressor boosts the pressure of the entering air. A portion of the high-pressure air enters the combustor, where fuel is added and burned, while the remaining air is used to cool the combustion chamber. The hot products of combustion then mix with the cooling air, and these gases expand through a multistage turbine. In the final process, the gases accelerate through a nozzle and exit to the atmosphere to produce a high-velocity propulsive jet.<sup>3</sup> The compressor and turbine are rotary machines with spinning wheels of blades. Rotational speeds vary over a wide range but are of the order of 10,000–20,000 rpm. Other than that needed to drive accessories, all of the power delivered by the turbine is used to drive the compressor in the pure turbojet engine.

The second major type of jet engine is the turbofan engine (Fig. 1.9 bottom). This is the engine of choice for commercial aircraft. (See Fig. 1.10.) In the turbofan, a bypass air jet generates a significant proportion of the engine thrust. The large fan shown at the front of the engine creates this jet.

<sup>&</sup>lt;sup>3</sup> The basic principle here is similar to that of a toy balloon that is propelled by a jet of escaping air.







A portion of the total air entering the engine bypasses the core of the engine containing the compressor and turbine, while the remainder passes through the core. The turbines drive the fan and the core compressors, generally using separate shafts for each. In the turbofan configuration, the exiting jets from both the bypass flow and the core flow provide the propulsive force.

To appreciate the physical size and performance of a typical turbojet engine, consider the GE F103 engine. These engines power the Airbus A300B, the DC-10-30, and the Boeing 747. The F103 engine has a nominal diameter of 2.7 m (9 ft) and a length of 4.8 m (16 ft), produces a maximum thrust of 125 kN (28,000 lb<sub>f</sub>), and weighs 37 kN (8,325 lb<sub>f</sub>). Typical core and fan speeds are 14,500 and 8000 rpm, respectively [14].

Jet engines afford many opportunities to apply the theoretical concepts developed throughout this book. Analyzing a turbojet engine cycle is a major topic in Chapter 8, and individual components are treated in Chapter 7.



FIGURE 1.11 The system boundary separates a fixed mass, the system, from its surroundings.

#### **1.3 PHYSICAL FRAMEWORKS FOR ANALYSIS**

In this section, we define a **thermodynamic system** and a **control volume**. These concepts are central to almost any analysis of a thermal-fluid problem.

#### 1.3a Systems

In a generic sense, a **system** is anything that we wish to analyze and distinguish from its **surroundings** or **environment**. To denote a system, all one needs to do is create a **boundary** between the system of interest and everything else, that is, the surroundings. The boundary may be a real surface or an imaginary construct indicated by a dashed line on a sketch. Figure 1.11 illustrates the separation of a system from its surroundings by a boundary.



The gas sealed within the cylinder of a spark-ignition engine constitutes a system, provided there is no gas leakage past the valves or the piston rings. The boundaries of this system deform as the piston moves. A more specific definition of a system used in the thermal sciences is the following:

# A *system* is a specifically identified fixed mass of material separated from its surroundings by a real or imaginary boundary.

To emphasize that the mass of the system is always unchanged regardless of what other changes might occur, the word **system** is frequently modified by adjectives, for example, **fixed-mass system** or **closed system**. In this book, we usually use the word *system* without modifiers to indicate a fixed mass.

The boundaries of a system need not be fixed in space but may, out of necessity, move. For example, consider the gas as the system of interest in the piston–cylinder arrangement shown Fig. 1.12. As the gas is compressed, the system boundary shrinks to always enclose the same mass.

Depending upon one's objectives, a system may be simple or complex, homogeneous or nonhomogenous. Our example of the gas enclosed in an engine cylinder (Fig. 1.12) is a relatively simple system. There is only one substance comprising the system: the fuel–air mixture. To further simplify an analysis of this particular system, we might assume that the fuel–air mixture has a uniform temperature, although in an operating engine the temperature will vary throughout the system. The matter comprising the system need not be a gas. Liquids and solids, of course, can be the whole system or a part of it. Again, the key distinguishing feature of a system is that it contains a fixed quantity of matter. No mass can cross the system boundary.

To further illustrate the thermodynamic concept of a system, consider the computer chip module schematically illustrated in Fig. 1.13. One might perform a thermal analysis of this device to ensure that the chip stays sufficiently cool. Considering the complexity of this module, a host of possible





#### FIGURE 1.13

A computer chip is housed in a module designed to keep the chip sufficiently cool. Various systems can be defined for thermal analyses of this relatively complex device. Two such choices are shown. Basic module sketch courtesy of Mechanical Engineering magazine, Vol. 108/No. 3, March, 1986, page 41; © Mechanical Engineering magazine (The American Society of Mechanical Engineers International).

The indicated control surface surrounds a control volume containing hot liquid coffee, air, and moisture. Water vapor or droplets exit through the upper portion of the control surface.



systems exist. For example, one might choose a system boundary surrounding the entire device and cutting through the connecting wires, as indicated as system 1. Alternatively, one might choose the chip itself (system 2) to be a thermodynamic system.

Choosing system boundaries is critical to any thermodynamic analysis. One of the goals of this book is to help you develop the skills required to define and analyze thermodynamic systems.

#### 1.3b Control Volumes<sup>4</sup>

In contrast to a system, mass may enter and/or exit a **control volume** through a **control surface**. We formally define these as follows:

## A *control volume* is a region in space separated from its surroundings by a real or imaginary boundary, the *control surface*, across which mass may pass.

Figure 1.14 illustrates a control volume and its attendant control surface. Here, mass in the form of water vapor or water droplets crosses the upper boundary as a result of evaporation from the hot liquid coffee. For this example, we chose a fixed control surface near the top of the cup; however, we could have chosen the regressing liquid surface to be the upper boundary. A choice of a moving control surface may or may not simplify an analysis, depending on the particular situation.

Control volumes may be simple or complex. Fixing the control surface in space yields the simplest control volume, whereas moving control volumes with deforming control surfaces are the most complex. Figure 1.15 illustrates the latter, where an inflated balloon is propelled by the exiting jet of air. In this example, the control volume both moves with respect to a fixed observer and shrinks with time. Figure 1.16 illustrates a simple, fixed control volume associated with an analysis of a water pump. Note that the control surface cuts through flanged connections at the inlet and outlet of the pump. The particular choice of a control volume and its control surface frequently is of overwhelming importance to an analysis. A wise choice can make an analysis simple, whereas a poor choice can make the analysis more difficult, or perhaps, impossible. Examples presented throughout this book provide guidance in selecting control volumes.



#### FIGURE 1.15

A rubber balloon and the air it contains constitute a control volume. The control volume moves through space and shrinks as the air escapes.

A sliding-vane pump and the fluid it contains constitute a simple control volume. Mass crosses the control surface at both the pump inlet and outlet. Adapted from Ref. [15] with permission.



#### **1.4 PREVIEW OF CONSERVATION PRINCIPLES**

In your study of physics, you have already encountered conservation of mass, conservation of energy, and conservation of momentum. These fundamental principles form the bedrock of the thermal-fluid sciences. A wise first step in analyzing any new problem addresses the following questions: Do any fundamental conservation principles apply here? If so, which ones? Because of the overriding importance of these principles to the thermal-fluid sciences, we offer a preview here in this first chapter.

A major focus of this book is the conservation of energy principle, which we elaborate in Chapter 5. Conservation of mass is also important to our study of engineering thermodynamics and its application. We discuss mass conservation in Chapter 3. Although conservation of momentum is central to the study of fluid dynamics, we only invoke this principle to supplement our analysis of jet engines in Chapter 8 to find the thrust.

#### 1.4a Generalized Formulation



A moving train possesses large quantities of mass, momentum, and energy.

It is quite useful to cast all three conservation principles in a common form. We do this for two reasons: first, to show the unity among the three conservation principles and, second, to provide an easy-to-remember single relationship that can be converted to more specific statements as needed. To do this, we define X to be the conserved quantity of interest, that is,

$$X \equiv \begin{cases} Mass \ or \\ Energy \ or \\ Momentum \end{cases}$$

We now express the general conservation law as follows: For a finite time interval,  $\Delta t = t_2 - t_1$ ,

$X_{\rm in}$ ·	$-X_{out}$ +	- X <sub>generated</sub>	=	$\Delta X_{\text{stored}} \equiv X(t_2) - X(t_1).$	(1.1)
Quantity of X crossing boundary and passing into system or control volume	Quantity of X crossing boundary and passing out of system or control	Quantity of X generated within system or control volume		Change of quantity of X stored within system or control volume during time interval	
	volume				









To interpret and understand these relationships, consider Fig. 1.17. The top drawing of Fig. 1.17 illustrates the situation for a system or control volume that experiences various exchanges of a conserved quantity during a finite time period. To make our discussion less abstract, let us assume for the time being, first, that X is mass and, second, that we are dealing with a control volume, not a system. During the time interval of interest, a certain quantity of mass,  $X_{in}$ , crosses the control surface into the control volume. Also during this interval, another quantity of mass,  $X_{out}$ , leaves the control volume. Straight arrows represent these two quantities. Note that these arrows are drawn external to the control volume and that they begin or end at the control surface without crossing the boundary. (Attention to such details helps distinguish interactions at the boundary from what is happening within the control volume.) Furthermore, if we allow for nuclear transformations, some mass can be generated (or destroyed). This mass is represented as the squiggly arrow within the control volume labeled  $X_{\text{generated}}$ . If more mass enters or is generated  $(X_{in} + X_{generated})$  than exits  $(X_{out})$ , the control volume will experience an increase in mass. This mass increase is also represented by a squiggly arrow within the control volume labeled  $\Delta X_{\text{stored}}$ . The subscript *stored* refers to the idea that during the time interval of interest additional mass is stored within the control volume. Of course,  $X_{\text{out}}$  could be greater than  $X_{\text{in}} + X_{\text{generated}}$ , in which case the storage term is negative. This accounting procedure involving quantities in, out, generated, and *stored* is intuitively satisfying and is much like keeping track of your account in a checkbook.5

This same general accounting applies to an instant where time rates replace actual quantities (Fig. 1.17 bottom). Continuing with our example of mass,  $\dot{X}_{in}$  represents the mass flow rate<sup>6</sup> into the control volume and has units of kilograms per second. The storage term,  $\dot{X}_{stored}$ , now represents the time rate of change of mass within the control volume rather than the difference in mass over a finite time interval. Again, the ideas expressed in Eq. 1.2 are intuitively appealing and easy to grasp.

The challenge in the application of Eqs. 1.1 and 1.2 lies in the correct identification of all of the terms, making sure that every important term is included in an analysis and that no term is doubly counted. For example, in our study of energy conservation (Chapter 5), the *in* and *out* terms represent energy transfers as work and heat, as well as energy carried with the flow into and out of the control volume. Regardless of the complexity of the mathematical statement of any conservation principle, Eqs. 1.1 and 1.2 are at its heart; that is, *in* minus *out* plus *generated* equals *stored*.

<sup>&</sup>lt;sup>5</sup> In our consideration of both mass and energy conservation,  $X_{\text{generated}}$  will always be zero.

<sup>&</sup>lt;sup>6</sup> Flow rates are discussed at length in Chapter 3.

#### 1.4b Motivation to Study Properties

To apply these basic conservation principles to engineering problems requires a good understanding of thermodynamic properties, their interrelationships, and how they relate to various processes. Although mass conservation may require only a few thermodynamic properties—usually, the mass density  $\rho$  and its relationship to pressure *P* and temperature *T* suffice successful application of the energy conservation principle relies heavily on thermodynamic properties. To illustrate this, we preview Chapter 5 by applying the generic conservation principle (Eq. 1.1) to a particular conservation of energy statement as follows:

$$Q_{\text{net, in}} - W_{\text{net, out}} = U_2 - U_1.$$
 (1.3)

Here,  $Q_{\text{net, in}}$  is the energy that entered the system as a result of a heat-transfer process,  $W_{\text{net, out}}$  is the energy that left the system as a result of work being performed, and  $U_1$  and  $U_2$  are the internal energies of the system at the initial state 1 and at the final state 2, respectively.

This first-law statement (Eq. 1.3) immediately presents us with an important thermodynamic property, the internal energy U. Although you likely encountered this property in a study of physics, a much deeper understanding is required in our study of engineering thermodynamics. Defining internal energy and relating it to other, more common, system properties, such as temperature T and pressure P, are important topics considered in Chapter 2. We also need to know how to deal with this property when dealing with two-phase mixtures such as water and steam.

To further illustrate the importance of Chapter 2, we note that the work term in our conservation of energy statement (Eq. 1.3) also relates to system thermodynamic properties. For the special case of a reversible expansion, the work can be related to the system pressure P and volume V, both thermodynamic properties. Specifically, to obtain the work requires the evaluation of the integral of PdV from state 1 to state 2. To perform this integration, we need to know how P and V relate for the particular process that takes the system from state 1 to state 2. Much of Chapter 2 deals with, first, defining the relationships among various thermodynamic properties and, second, showing how properties relate during various specific processes. For example, the ideal-gas law,  $PV = NR_{u}T$  (where N is the number of moles contained in the system and  $R_{\rm u}$  is the universal gas constant), expresses a familiar relationship among the thermodynamic properties P,  $\vec{V}$ , and T. From this relationship among properties, we see that the product of the system pressure and volume is constant for a constanttemperature process. In addition to exploring the ideal-gas equation of state, Chapter 2 shows how to deal with the many substances that do not behave as ideal gases. Common examples here include water, water vapor, and various refrigerants.

#### **1.5 KEY CONCEPTS AND DEFINITIONS**

In addition to systems, control volumes, and surroundings, several other basic concepts permeate our study of thermodynamics and are listed in Table 1.2. We introduce these concepts in this section, recognizing that they will be revisited again, perhaps several times, in later chapters.

#### Table 1.2 Some Fundamental Thermodynamic Concepts

System (or closed system) Control volume (or open system) Surroundings Property State Process Flow process Cycle Equilibrium Quasi-equilibrium





#### **1.5a Properties**

Before we can begin a study of thermodynamic properties understood in their most restricted sense, we define what is meant by a **property** in general:

### A *property* is a quantifiable macroscopic characteristic of a system.

Examples of system properties include mass, volume, density, pressure, temperature, height, width, and color, among others. Not all system properties, however, are thermodynamic properties. Thermodynamic properties all relate in some way to the energy of a system. In our list here, height, width, and color, for example, do not qualify as thermodynamic properties, although the others do. A precise definition of thermodynamic properties often depends on restricting the system to which they apply in subtle ways. Chapter 2 is devoted to thermodynamic properties and their interrelationships.

Properties are frequently combined to create new ones. For example, a spinning baseball in flight not only has the properties of mass and velocity but also kinetic energy and angular momentum. Thus, any system may possess numerous properties.

#### 1.5b States

Another fundamental concept in thermodynamics is that of a state:

### A thermodynamic *state* of a system is defined by the values of all of the system thermodynamic properties.



When the value of any one of a system's properties changes, the system undergoes a change in state. For example, hot coffee in a thermos bottle undergoes a continual change of state as it slowly cools. Not all thermodynamic properties necessarily change when the state of a system changes; the mass of the coffee in a sealed thermos remains constant while the temperature falls. An important skill in solving problems in thermodynamics is to identify which properties remain fixed and which properties change during a change in state.





#### **1.5c Processes**

One goal of studying thermal-fluid sciences is to develop an understanding of how various devices convert one form of energy to another. For example, how does the burning coal in a power plant result in the electricity supplied to your home? In analyzing such energy transformations, we formally introduce the idea of a thermodynamic **process**:

### A *process* occurs whenever a system changes from one state to another state.

Figure 1.18a illustrates a process in which the gas contained in a cylinder– piston arrangement at state 1 is compressed to state 2. As is obvious from the sketch, one property, the volume, changes in going from state 1 to state 2. Without knowing more details of the process, we cannot know what other properties may have changed as well. In many thermodynamic analyses, a single property—for example, temperature, pressure, or entropy<sup>7</sup>—is held constant during the process. In these particular cases, we refer to the processes as a constant-temperature (isothermal) process, constant-pressure (isobaric) process, or a constant-entropy (isentropic) process, respectively.

Although formal definitions of process refer to systems, the term is also applied to control volumes, in particular, steady flows in which no properties change with time. We thus define a **flow process** as follows:

#### A *flow process* occurs whenever the state of the fluid entering a control volume is different from the state of the fluid exiting the control volume.



### <sup>7</sup> Entropy is an important thermodynamic property and is discussed in detail in Chapters 2 and 6. We only introduce it here as an example of a property.

#### FIGURE 1.18

(a) A system undergoes a process that results in a change of the system state from state 1 to state 2. (b) In a steady-flow process, fluid enters the control volume at state 1 and exits the control volume at state 2.



This jet engine test exemplifies a steady-flow process. Photograph courtesy of U.S. Air Force.

Figure 1.18b schematically illustrates a flow process. An example of a steadyflow process is constant-pressure combustion. In this process, a cold fuel–air mixture (state 1) enters the control volume (combustor) and exits as hot products of combustion (state 2). Various flow processes underlie the operation of myriad practical devices, many of which we will study in subsequent chapters.

#### 1.5d Cycles

In many energy-conversion devices, the **working fluid** undergoes a thermodynamic **cycle**. Since the word *cycle* is used in many ways, we need a precise definition for our study of thermodynamics. Our definition is the following:

#### A thermodynamic *cycle* consists of a sequence of processes in which the working fluid returns to its original thermodynamic state.



An example of a cycle applied to a fixed-mass system is presented in Fig. 1.19. Here a gas trapped in a piston–cylinder assembly undergoes four processes. A cycle can be repeated any number of times following the same sequence of processes. Although it is tempting to consider reciprocating internal combustion engines as operating in a cycle, the products of combustion never undergo a transformation back to fuel and air, as would be required for our definition of a cycle. There exist, however, types of reciprocating engines that do operate on thermodynamic cycles. A prime example of this is the Stirling engine [16]. The working fluid in Stirling engines typically is hydrogen or helium. All combustion takes place outside of the cylinder. Figure 1.20 shows a modern Stirling engine.



#### FIGURE 1.19

A system undergoes a cycle when a series of processes returns the system to its original state. In this sketch, the cycle consists of the repetition of the state sequence 1-2-3-4-1.

FIGURE 1.20 A Stirling engine provides the motive power to an electrical generator set. Photograph courtesy of Stirling Technology Company.





FIGURE 1.21 A cycle can also consist of a sequence of flow processes in which the flowing fluid is returned to its original state: 1–2–3–4–1.



#### FIGURE 1.22

The flow of energy from a region of higher temperature to a region of lower temperature drives a system toward thermal equilibrium. The temperature is uniform in a system at equilibrium. Thermodynamic cycles are most frequently executed by a series of flow processes, as illustrated in Fig. 1.21. As the working fluid flows through the loop, it experiences many changes in state as it passes through various devices such as pumps, boilers, and heat exchangers, but ultimately it returns to its initial state, arbitrarily chosen here to be state 1. As we have already seen, the heart of a fossil-fueled steam power plant operates on a thermodynamic cycle of the type illustrated in Fig. 1.21 (cf. Fig. 1.1). Refrigerators and air conditioners are everyday examples of devices operating on thermodynamic cycles. In Chapter 8, we analyze various cycles for power production, propulsion, and heating and cooling.

The thermodynamic cycle is central to many statements of the second law of thermodynamics and concepts of thermal efficiency (Chapter 6).

#### **1.5e Equilibrium and the Quasi-Equilibrium Process**

The science of thermodynamics builds upon the concept of equilibrium states. For example, the common thermodynamic property temperature has meaning only for a system in equilibrium. In a thermodynamic sense, then, what do we mean when we say that a system is in equilibrium? In general, there must be no unbalanced potentials or drivers that promote a change of state. The state of a system in equilibrium remains unchanged for all time. For a system to be in equilibrium, we require that the system be simultaneously in thermal equilibrium, mechanical equilibrium, phase equilibrium, and chemical equilibrium. Other considerations may exist, but they are beyond our scope. We now consider each of these components of thermodynamic equilibrium.

**Thermal equilibrium** is achieved when a system both has a uniform temperature and is at the same temperature as its surroundings. If, for example, the surroundings are hotter than the system under consideration, energy flows across the system boundary from the surroundings to the system. This exchange results in an increase in the temperature of the system. Equilibrium thus does not prevail. Similarly, if temperature gradients exist within the system, the initially hotter regions become cooler, and the initially cooler regions become hotter, as time passes (Fig. 1.22 top). Given sufficient time the temperature of the system is identical to that of the surroundings (Fig. 1.22 bottom). Prior to achieving the final uniform temperature, the system is not in thermal equilibrium.

**Mechanical equilibrium** is achieved when the pressure throughout the system is uniform and there are no unbalanced forces at the system boundaries. An exception to the condition of uniform pressure exists when a system is under the influence of a gravitational field. For example, pressure





In the quasi-equilibrium compression of a gas, the pressure is essentially uniform throughout the gas system, that is,  $P_{\rm B} \approx P_{\rm T}$ . increases with depth in a fluid such that pressure forces balance the weight of the fluid above. In many systems, however, the assumption of uniform pressure is reasonable.

**Phase equilibrium** relates to conditions in which a substance can exist in more than one physical state; that is, any combination of vapor, liquid, and solid. For example, you are quite familiar with the three states of  $H_2O$ : water vapor (steam), liquid water, and ice. Phase equilibrium requires that the amount of a substance in any one phase not change with time; for example, liquid–vapor phase equilibrium implies that the rate at which molecules escape the liquid phase to enter the gas phase is exactly balanced by the rate at which molecules from the gas phase enter the liquid phase. We will discuss these ideas further in Chapters 2 and 6.

Our final condition for thermodynamic equilibrium requires the system to be in **chemical equilibrium**. For systems incapable of chemical reaction, this condition is trivial; however, for reacting systems this constraint is quite important. A significant portion of Chapter 6 is devoted to this topic.

From the foregoing discussion, we see that an equilibrium state is a pretty boring proposition. Nothing happens. The system just sits there. Nevertheless, considering a system to be in an equilibrium state at the beginning of a process and at the end of the process is indeed useful. In fact, it is this idea that motivates our discussion. Our development of the conservation of energy principle relies on the idea that equilibrium states exist at the beginning and end of a process, even though during the process the system may be far from equilibrium.

This discussion suggests that it is not possible to describe the details of a process because of departures from equilibrium. In some sense, this is indeed true. The often-invoked assumption of a quasi-static or quasi-equilibrium process, however, does permit an idealized description of a process as it occurs. We define a quasi-static or quasi-equilibrium process to be a process that happens sufficiently slowly such that departures from thermodynamic equilibrium are always so small that they can be neglected. For example, the compression of a gas in a perfectly insulated piston-cylinder system (Fig. 1.23) results in the simultaneous increase in temperature and pressure of the gas. If the compression is performed slowly, the pressure and temperature at each instant will be uniform throughout the gas system for all intents and purposes [i.e.,  $P_{\rm B}(t) = P_{\rm T}(t)$ ], and the system can be considered to be in an equilibrium state.<sup>8</sup> In contrast, if the piston moves rapidly, the pressure in the gas at the piston face  $(P_{\rm B})$  would be greater than at the far end of the cylinder  $(P_{T})$  and equilibrium would not be achieved. The formal requirement for a quasi-equilibrium process is that the time for a system to reach equilibrium after some change is small compared to the time scale of the process. For our example of the gas compressed by the piston, the time for the pressure to equilibrate is determined by the speed of sound, that is, the propagation speed of a pressure disturbance. For room-temperature air, the sound speed is approximately 340 m/s. If we assume that at a particular instant the piston is 100 mm (= L) from the closed end of the cylinder, the change in the pressure due to the piston motion will be communicated to the closed end in a time equal to  $2.9 \times 10^{-4}$  s [= (0.100 m)/(340 m/s)] or 0.29 ms. If during 0.29 ms the piston moves very little ( $\Delta x$ ), the pressure can be assumed to be uniform throughout the system for all practical purposes, and the compression can be considered a quasi-equilibrium process. Alternatively, we can say that the speed of the pressure waves that communicate changes in pressure is much faster than the speed of the piston that creates the increasing pressure.<sup>9</sup> Similar arguments involving time scales can be used to ascertain whether or not thermal and chemical equilibrium are approximated for any real processes. Our purposes here, however, are not to define the exact conditions for which a quasi-equilibrium process might be assumed, but rather to acquaint the reader with this commonly invoked assumption. Later in the book we use the quasi-equilibrium process as a standard to which real processes are compared.

#### **1.6 DIMENSIONS AND UNITS**

The primary dimensions used in this book are *mass*, *length*, *time*, *temperature*, *electric current*, and *amount of substance*. All other dimensions, such as force, energy, and power, are derived from these primary dimensions. Furthermore, we employ almost exclusively the International System of Units, or le Système International (SI) d'Unités. The primary dimensions thus have the following associated units:<sup>10</sup>

Mass [=] kilogram (kg),

Length [=] meter (m),

Time [=] second (s),

Temperature [=] kelvin (K),

Electric Current [=] ampere (A), and

Amount of Substance [=] mole (mol).

The derived dimensions most frequently used in this book are defined as follows:

Force 
$$\equiv 1 \text{ kg} \cdot \text{m/s}^2 = 1 \text{ newton (N)},$$
 (1.4)

Energy 
$$\equiv 1 (\text{kg} \cdot \text{m/s}^2) \cdot \text{m} = 1 \text{ N} \cdot \text{m} \text{ or } 1 \text{ joule (J), and}$$
 (1.5)

Power = 
$$1 \frac{(\text{kg} \cdot \text{m/s}^2) \cdot \text{m}}{\text{s}} = 1 \text{ J/s or } 1 \text{ watt (W)}.$$
 (1.6)

Unfortunately, a wide variety of non-SI units are used customarily in the United States, many of which are industry-specific. Conversion factors from SI units to the most common non-SI units are presented on the inside covers of this book. We refer to certain non-SI units in several examples to provide some familiarity with these important non-SI units. To have a single location for their definition, the customary units most important to our study of thermodynamics are presented here. In terms of the four primary dimensions, mass ([=] pound-mass or  $lb_m$ ), length ([=] foot), time ([=] second), and temperature ([=] degree Rankine or R), common derived dimensions and units are as follows:

Force 
$$\equiv 32.174 \frac{lb_m \cdot ft}{s^2} = 1$$
 pound-force or  $lb_f$ , (1.7)







<sup>&</sup>lt;sup>9</sup> Pressure waves travel at the speed of sound.

<sup>&</sup>lt;sup>10</sup> The symbol [=] is used to express "*has units of*" and is used throughout this book.

Energy 
$$\equiv 1 \text{ ft} \cdot \text{lb}_{\text{f}} = \frac{1}{778.17}$$
 British thermal unit or Btu, and (1.8)

Power 
$$\equiv 1 \frac{\text{ft} \cdot \text{lb}_{\text{f}}}{\text{s}} = \frac{1}{550}$$
 horsepower or hp. (1.9)

In some applications, the unit associated with mass is the slug. Using this unit to define force yields

Force 
$$\equiv 1 \frac{\text{slug} \cdot \text{ft}}{\text{s}^2} = 1$$
 pound-force or lb<sub>f</sub>. (1.10)

Further elaboration of units is found in the discussion of thermodynamic properties in Chapter 2.

The use of the units pound-force  $(lb_f)$  and pound-mass  $(lb_m)$  can cause some confusion to the casual user.<sup>11</sup> The following example clarifies their usage.

<sup>11</sup> A safe rule of thumb to avoid any confusion with units is to convert all given quantities in a problem to SI units, solve the problem using SI units, and then convert the final answer to any desired customary units.

A mass of 1 lb<sub>m</sub> is placed on a spring scale calibrated to read in poundsforce. Assuming an earth-standard gravitational acceleration of 32.174 ft/s<sup>2</sup>, what is the scale reading? What is the equivalent reading in newtons? How do these results change if the measurement is conducted on the surface of the moon where the gravitational acceleration is 5.32 ft/s<sup>2</sup>?

#### Solution

*Known*  $M = 1 \text{ lb}_m$ ,  $g_{\text{earth}} = 32.174 \text{ ft/s}^2$ *Find* Force exerted on scale

Analysis The force exerted on the scale is the weight, F = W, which equals the product of the mass and the gravitational acceleration, that is,

Thus,

$$F = (1 \text{ lb}_{\text{m}}) (32.174 \text{ ft/s}^2)$$

 $F = Mg_{\text{earth}}$ 

Using the definition of pounds-force (Eq. 1.7), we generate the identity

$$1 \equiv \left[\frac{1\frac{\mathrm{lb}_{\mathrm{f}}}{\mathrm{ft/s}^2}}{32.174\,\mathrm{lb}_{\mathrm{m}}}\right].$$

Using this identity in the previous expression for the force yields

$$F = 1 \text{ lb}_{\text{m}} \left[ \frac{1 \frac{\text{lb}_{\text{f}}}{\text{ft/s}^2}}{32.174 \text{ lb}_{\text{m}}} \right] 32.174 \text{ ft/s}^2,$$



or

$$F = 1 \, \mathrm{lb}_{\mathrm{f}}$$

To convert this result to SI units, we use the conversion factor found at the front of the book:

$$F = 1 \, \text{lb}_{\text{f}} \left[ \frac{1 \, \text{N}}{0.224809 \, \text{lb}_{\text{f}}} \right] = 4.45 \, \text{N}.$$

On the moon, the force is

$$F = Mg_{moon}$$
  
= (1 lb<sub>m</sub>) (5.32 ft/s<sup>2</sup>)  
= 1 lb<sub>m</sub>  $\left[ \frac{1 \frac{lb_f}{ft/s^2}}{32.174 lb_m} \right] 5.32 ft/s^2$   
$$F = 0.165 lb_c$$

or

F = 0.736 N.

*Comments* From this example, we see that the definition of the U.S. customary unit for force was chosen so that a one-pound mass produces a force of exactly one pound-force under conditions of standard earth gravity. In the SI system, numerical values for mass and force are *not* identical for conditions of standard gravity. For example, consider the weight associated with a 1-kg mass:

$$F = Mg$$
  
= (1 kg)(9.807 m/s<sup>2</sup>)  
= 1 kg  $\left(\frac{1 N}{kg \cdot m/s^2}\right)$ (9.807 m/s<sup>2</sup>)  
= 9.807 N.

Regardless of the system of units, care must be exercised in any unit conversions. Checking to see that the units associated with any calculated result are correct should be part of every problem solution. Such practice also helps you to spot gross errors and can save time.



Repeat Example 1.1 for a given mass of 1 slug.

(Answer: 32.174 lb<sub>f</sub>, 143.12 N, 5.32 lb<sub>f</sub>, 23.66 N)

#### **1.7 PROBLEM-SOLVING METHOD**

For you to consistently solve engineering problems successfully (both textbook and real problems) depends on your developing a procedure that aids thought processes, facilitates identification of errors along the way, allows others to easily check your work, and provides a reality check at

completion. The following general procedure has these attributes and is recommended for your consideration for most problems. Nearly all of the examples throughout the text will follow this procedure.

- 1. State what is known in a simple manner without rewriting the problem statement.
- 2. Indicate what quantities you want to find.
- 3. Draw and label useful sketches whenever possible. (What is useful generally depends on the context of the problem. Suggestions are provided at appropriate locations in the text.)
- 4. List your initial assumptions and add others to the list as you proceed with your solution.
- 5. Analyze the problem and identify the important definitions and principles that apply to your solution.
- 6. Develop a symbolic or algebraic solution to your problem, delaying substitution of numerical values as late as possible in the process.
- 7. Substitute numerical values as appropriate and indicate the source of all physical data as you proceed. (The appendices of this book contain much useful data.)
- 8. Check the units associated with each calculation. The factor-label method is an efficient way to do this.
- 9. Examine your answer critically. Does it appear to be reasonable and consistent with your expectations and/or experience?
- 10. Write out one or more comments using step 9 as your guide. What did you learn as a result of solving the problem? Are your assumptions justified?

#### **1.8 HOW TO USE THIS BOOK**



You may find the organization of this textbook different from others used previously in your study of mathematics, the fundamental sciences, and engineering. To a large degree, the organization here is hierarchical; that is, all related topics are grouped within a single chapter, with the most elementary topics appearing first and additional levels of complexity added as the chapter progresses. The purpose of this particular organization is to show in as strong a fashion as possible that various topics are actually related and not disjoint concepts [17]. Therefore, in the actual use of the book, you will not necessarily proceed linearly, going from the beginning to the end of each chapter, chapter by chapter. In particular, the following chapter dealing with thermodynamic properties provides much more information than you will need initially. You should be prepared to continually revisit Chapter 2 as you need particular information on properties. For example, a study of entropy and related properties should be concurrent with your study of the second law of thermodynamics in Chapter 6. Another example of nonlinear organization is the placement of numerous practical applications in the final chapters. This arrangement does not mean that these applications should be dealt with last; rather, they are separated to provide flexibility in coverage. Do not be surprised to have simultaneous assignments from Chapters 5 and 7, for example. It is the author's hope that this structure will make your learning thermodynamics both more efficient and more interesting than more traditional presentations.

#### SUMMARY

In this chapter, we introduced the subject of thermodynamics, a foundational topic within the thermal-fluid sciences. We also presented the following three practical applications of thermodynamics: fossil-fuel steam power plants, spark-ignition engines, and jet engines. From these discussions, you should have a reasonably clear idea of what this book is about. Also presented in this chapter are many concepts and definitions upon which we will build in subsequent chapters. To make later study easier, you should have a firm understanding of these concepts and definitions. A review of the learning objectives presented at the start of this chapter may be helpful in that regard. Finally, it is the author's hope that your interest has been piqued in the subject matter of this book.

### Chapter 1 Key Concepts & Definitions Checklist<sup>12</sup>

- 1.1 What is thermodynamics?
- □ Definition > 1.1
- Applications > 1.2
- 1.2 Some applications > 1.3-1.5
- Basic Rankine cycle
- Rankine cycle components
- □ Spark-ignition engines
- □ Four-stroke cycle
- **U** Turbojet and turbofan engines

#### **1.3 Physical frameworks for analysis**

- Thermodynamic (or closed) system > 1.6
- □ Control volume (or open system) > 1.10
- **D** Boundaries > 1.8
- □ Surroundings > 1.11

#### 1.4 Preview of conservation principles

- General conservation law for time interval (Eq. 1.1) ► 1.13, 1.17
- General conservation law at an instant (Eq. 1.2) > 1.14, 1.19
- The need for thermodynamic properties

#### 1.5 Key concepts and definitions

- $\Box \quad \text{Property} > 1.22$
- □ State > 1.22
- $\Box \quad \text{Process} > 1.22$
- Flow process > 1.24
- $\Box \quad Cycle > 1.23$
- **Equilibrium** > 1.25
- **Q**uasi-equilibrium > 1.26

#### 1.6 Dimensions and units > 1.35, 1.40, 1.47

- The difference between dimensions and units
- Primary SI dimensions
- Derived dimensions
- U.S. customary units
- Pounds-force and pounds-mass

#### 1.7 Problem-solving method

□ Key steps in solving thermal-fluid problems

<sup>&</sup>lt;sup>12</sup> Numbers following arrows below refer to Questions and Problems at the end of the chapter.

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Some end-of-chapter problems were adapted with permission from the following:

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Chapter	Question una Froblem Subjett / neus
1.1-1.6	Applications of thermodynamics
1.7-1.12	Thermodynamic systems and control volumes
1.13-1.21	Generalized conservation principles
1.22-1.28	Key concepts and definitions
1.29-1.47	Dimensions and units
1.48	Miscellaneous

Chapter 1 Question and Problem Subject Areas

#### **QUESTIONS AND PROBLEMS**

\*Indicates computer required for solution.

- 1.1 Discuss the principal subjects of thermodynamics.
- 1.2 Make a list of practical devices for which the design was made possible by the application of thermodynamics.
- 1.3 Draw a schematic diagram of a simple steam power plant. Discuss the processes associated with each major piece of equipment.
- 1.4 Sketch and discuss the four strokes associated with the four-stroke cycle spark-ignition engine.
- 1.5 Distinguish between a turbojet engine and a turbofan engine. Which type is most commonly used for commercial airline service?
- 1.6 Create a list of the factors that differentiate a thermodynamic system from a control volume.
- 1.7 Discuss how the concepts of thermodynamics and control volumes apply to a spark-ignition engine.
- 1.8 Consider a conventional toaster—the kind used to toast bread. Sketch two different boundaries associated with an operating toaster: one in which a thermodynamic system is defined, and a second one in which a control volume is defined. Be sophisticated in your analyses. Discuss.



1.9 Discuss what would have to be done to transform the control volume shown in Fig. 1.14 to a thermodynamic system. Ignore the boundary shown in Fig. 1.14. What thermodynamic systems can be defined for the situation illustrated?

1.10 Consider a conventional house in the northeastern part of the United States. Isolate the house from the surroundings by drawing a control volume. Identify all of the locations where mass enters or exits your control volume.



1.11 Consider an automobile, containing a driver and several passengers, traveling along a country road. Isolate the automobile and its contents from the surroundings by drawing an appropriate boundary. Does your boundary enclose a thermodynamic system or a control volume? How would you have to modify your boundary to convert from one to the other? What assumptions, if any, do you have to make to perform this conversion?



- 1.12 Consider a thermodynamic analysis of the human body. Would you choose a thermodynamic system or a control volume for your analysis. Discuss.
- 1.13 Write out in words a general expression of the conservation of energy principle applied to a finite time interval. (See Eq. 1.1.)

- 1.14 Write out in words a general expression of the conservation of energy principle applied to an instant, that is, an infinitesimal time interval. (See Eq. 1.2.)
- 1.15 Repeat Questions 1.13 and 1.14, but for conservation of mass.
- 1.16 On Wednesday morning a truck delivers a load of 100 perfect ceramic flowerpots to a store. Each of these perfect flowerpots is valued at \$3 and has a mass of 2



 $lb_m$ . Half of the flowerpots are immediately put in the storeroom, while the other half are sent to the garden department to be sold. Wednesday afternoon, five customers enter the store, buy 1 flowerpot apiece, and leave the store. Another customer enters, buys 3 flowerpots, and leaves the store. Wednesday evening, three particularly clumsy customers knock 14 flowerpots on the floor and damage them. Their damaged value is \$1 each. For the entire store as the system, fill in the following table:

1.17 One shop of a roller-bearing plant produces 50-g roller bearings at the rate of 10,000 per day from steel that enters the plant during the day. Of this total production, 3,000 are judged "precision" (value = \$5 each), 5,000 are judged "standard" (value = \$3 each), and the remainder are judged to be "substandard" (value = 0). The shop sells 1,500 precision bearings per day and 2,000 standard bearings per day to another company. The remaining precision and standard bearings are stored within the shop. The substandard bearings are removed from the shop as waste along with the 20 kg/day of steel that is ground off during the production of the bearings. For the shop as the system, fill the following table for a one-day time increment:

Quantity (Units)	Mass (kg)	Precision (#)	Standard (#)	Substandard (#)	Value (k\$)
Inflow					
Produced					
Outflow					
Stored					
Destroyed					

- 1.18 A chemical plant produces the chemical furfural (FFL). The raw materials are primarily corncobs and oat hulls. One pound of corncobs will make 0.5 lb<sub>m</sub> of FFL and 0.5 lb<sub>m</sub> of residue. One pound of oat hulls will make 0.75 lb<sub>m</sub> of FFL and 0.25 lb<sub>m</sub> of residue. Corncobs are delivered to the plant at a rate of 1,000 lb<sub>m</sub>/hr and a cost of 10 cents/ lb<sub>m</sub>. Oat hulls are delivered to the plant at a rate of 200 lb<sub>m</sub>/hr at a cost of 20 cents/lb<sub>m</sub>. FFL is sold at a rate of 350 lb<sub>m</sub>/hr for a price of 50 cents/lb<sub>m</sub>. FFL is stored within the plant at a rate of 100 lb<sub>m</sub>/hr. All residue produced is sold for 25 cents/lb<sub>m</sub>. At the beginning of the 8:00 A.M. shift, there are 350 lb<sub>m</sub> of oat hulls in the plant is down to 250 lb<sub>m</sub>.
  - A. For the chemical plant as the system, complete the following table:

Quantity (Units)	Corncobs (lb <sub>m</sub> /hr)	Oat hulls (lb <sub>m</sub> /hr)	FFL (lb <sub>m</sub> /hr)	Value (\$/hr)	Money (\$/hr)
Inflow					
Produced					
Outflow					
Stored					
Destroyed					

- B. Using a closed system and balance principles, determine the change in value associated with making 1  $lb_m$  of corncobs into FFL. Show and label your system clearly.
- 1.19 The Foster-Davis Juice Company steadily takes in 1,000 oranges per hour and ships out 150 cans of juice per hour. The average orange has a mass of 0.5 lb<sub>m</sub>, costs 25 cents, and is processed into 0.4 lb<sub>m</sub> of juice and 0.1 lb<sub>m</sub> of peels and pulp (P&P). Each can of juice contains 2 lb<sub>m</sub> of juice and sells for 1 dollar. The mass of the can itself may be neglected. The P&P are sold to University Food Service for 20 cents/lb<sub>m</sub> at the rate of 50 lb<sub>m</sub>/hr. Oranges are put into cold storage in the plant at a rate of 300 oranges per hour. The remaining oranges are processed into juice and P&P. The Foster-Davis Juice Company has a "pay as you go" policy. Initially there are stockpiles of oranges, cans of juice, P&P, and money within the plant.
  - A. Considering the Foster-Davis plant as a control volume (open system), complete the following table:

Mass (lb <sub>m</sub> /hr)	Oranges (#/hr)	Juice (cans/hr)	P&P (lb <sub>m</sub> /hr)	Money (\$/hr)
	Mass (lb <sub>m</sub> /hr)	Mass Oranges (lb <sub>m</sub> /hr) (#/hr)	Mass Oranges Juice (lb <sub>m</sub> /hr) (#/hr) (cans/hr)	Mass Oranges Juice P&P (lb <sub>m</sub> /hr) (#/hr) (cans/hr) (lb <sub>m</sub> /hr)

- B. Can the plant go on operating in this way forever? Explain.
- C. Can the process within the plant be reversed? Explain.
- 1.20 Consider a machine shop that stamps washers out of metal disks as a control volume (open system). Disks enter the shop at the rate of 1000 disks per second and each disk has a mass of 2 g. The stamping machine punches out the center of each disk to make a 1.5-g washer and a 0.5-g center. The stamping machine makes washers at the rate of 800 washers per second. A conveyor belt transports 1000 washers per second from the shop. Initially there are 3000 disks and 5000 washers stockpiled in the shop but no centers. The shop then runs for a 1-s time increment.
  - A. Sketch the machine shop. Be sure to include the control-volume boundaries in your sketch.
  - B. Fill in the following table for the 1-s increment:

Quantity (Units)	Disks (#)	Washers (#)	Centers (#)	Mass (g)
Inflow				
Produced				
Outflow				
Stored				
Destroyed				

Now consider a closed system containing a single disk about to enter the shop. For this system, consider the time increment required for the system to go from the shop entrance to the exit of the stamping machine.

- C. Show this system on the machine-shop sketch at the start of the time increment.
- D. Show this system on the machine-shop sketch at the *end* of the time increment.
- E. For this new system, fill in the table given in Part B.
- 1.21 A cook (200  $lb_m$ ) brings 100 apples (0.5  $lb_m$  each) into the kitchen, stores 36 of the apples in the refrigerator, and puts the rest on the table to make applesauce. While the cook is mashing the apples into sauce, three young friends (70  $lb_m$  each) enter the kitchen. The cook gives them 6 apples each from the table, and they take them outdoors. After finishing the sauce, the cook leaves the kitchen. Considering the kitchen as a control volume (open system), complete the following table:

Quantity (Units)	Mass (lb <sub>m</sub> )	Apples (#)	Sauce (lb <sub>m</sub> )
Inflow			
Produced			
Outflow			
Stored			
Destroyed			

- 1.22 Write out the formal definitions of the following terms: property, state, and process. Discuss the interrelationships of these three terms.
- 1.23 Can you identify any devices that operate in a thermodynamic cycle? If so, list them. Also identify the working fluids, if known.
- 1.24 Distinguish between a system process and a flow process.

- 1.25 List the conditions that must be established for thermodynamic equilibrium to prevail (i.e., list the subtypes of equilibrium).
- 1.26 Define a quasi-static or quasi-equilibrium process and give an example of such a process. Also give an example of a non–quasi-equilibrium process.
- 1.27 What is the key property associated with thermal equilibrium? With mechanical equilibrium?
- 1.28 At what speed are changes in pressure communicated throughout a thermodynamic system.
- 1.29 What is your approximate weight in pounds-force? In newtons? What is your mass in pounds-mass? In kilograms? In slugs?
- 1.30 Repeat Problem 1.29 assuming you are now on the surface of Mars where the gravitational acceleration is  $3.71 \text{ m/s}^2$ .
- 1.31 A residential natural gas-fired furnace has an output of 86,000 Btu/hr. What is the output in kilowatts? How many 100-W incandescent light bulbs would be required to provide the same output as the furnace?



1.32 The 1964 Pontiac GTO was one of the first so-called muscle cars produced in the United States in the 1960s and 1970s. The 389-in<sup>3</sup> displacement V-8



engine in the GTO delivered a maximum power of 348 hp and a maximum torque of 428 lb<sub>f</sub>  $\cdot$  ft. From a standing start, the GTO traveled 1/4 mile in 14.8 s, accelerating to 95 mph. Convert all of the U.S. customary units in these specifications to SI units.

1.33 Coal-burning power plants convert the sulfur in the coal to sulfur dioxide  $(SO_2)$ , a regulated air pollutant. The maximum allowable  $SO_2$  emission for new power plants (i.e., the maximum allowed ratio of the mass of  $SO_2$  emitted per input of fuel energy) is 0.80 lb<sub>m</sub>/(million Btu). Convert this emission factor to units of grams per joule.



- 1.34 The National Ambient Air Quality Standard (NAAQS) for lead (Pb) in the air is  $1.5 \ \mu g/m^3$ . Convert this standard to U.S. customary units of  $lb_m/ft^3$ .
- 1.35 The astronauts of *Apollo 17*, the final U.S. manned mission to the moon, collected 741 lunar rock and soil samples having a total mass of 111 kg. Determine the weight of samples in SI and U.S. customary units (a) on the lunar surface  $(g_{moon} = 1.62 \text{ m/s}^2)$  and (b) on the earth  $(g_{earth} = 9.807 \text{ m/s}^2)$ .



Also determine (c) the mass of the samples in U.S. customary units.

\*1.36 The gravitational acceleration on the earth varies with latitude and altitude as follows [18]:

 $g (m/s^2) = 9.780356 [1 + 0.0052885 \sin^2 \theta$  $- 0.0000059 \sin^2 (2\theta)] - 0.003086 z,$ 

where  $\theta$  is the latitude and z is the altitude in kilometers. Use this information to determine the weight (in newtons and pounds-force) of a 54-kg mountain climber at the following locations:

- A. Summit of Kilimanjaro in Tanzania (3.07° S and 5895 m)
- B. Summit of Cerro Aconcagua in Argentina (32° S and 6962 m)
- C. Summit of Denali in Alaska (63° N and 6,194 m)



How do these values compare with the mountain climber's weight at 45° N latitude at sea level? Use spreadsheet software to perform all calculations.

- 1.37 The gravitational acceleration at the surfaces of Jupiter, Pluto, and the sun are 23.12 m/s<sup>2</sup>, 0.72 m/s<sup>2</sup>, and 273.98 m/s<sup>2</sup>, respectively. Determine your weight at each of these locations in both SI and U.S. customary units. Assume no loss of mass results from the extreme conditions.
- 1.38 A coal-burning power plant consumes fuel energy at a rate of 4845 million Btu/hr and produces 500 MW



of net electrical power. Determine the overall efficiency of the power plant (i.e., the dimensionless ratio of the net output and input energy rates).

- 1.39 Derive a conversion factor relating pressures in pascals  $(N/m^2)$  and psi  $(lb_f/in^2)$ . Compare your result with the conversion factor provided inside the front cover of this book.
- 1.40 The Space Shuttle main engine had the following specifications ca. 1987. Convert these values to SI units.



Maximum Thrust	
At sea level	408,750 lb <sub>f</sub>
In vacuum	512,300 lb <sub>f</sub>
Pressures	
Hydrogen pump discharge	6872 psi
Oxygen pump discharge	7936 psi
Combustion chamber	3277 psi
Flow Rates	
Hydrogen	160 lb <sub>m</sub> /s
Oxygen	970 lb <sub>m</sub> /s
Power	
High-pressure H <sub>2</sub> turbopump	74,928 hp
High-pressure O <sub>2</sub> turbopump	28,229 hp
Weight	$7000 \ lb_{\rm f}$
Length	14 ft
Diameter	7.5 ft

- 1.41 Determine the acceleration of gravity for which the weight of an object will be numerically equal to its mass in the SI unit system.
- 1.42 Determine the mass in  $lb_m$  of an object that weighs 200  $lb_f$  on a planet where g = 50 ft/s<sup>2</sup>.
- 1.43 Determine the mass in kg of an object that weighs 1000 N on a planet where  $g = 15 \text{ m/s}^2$ .
- 1.44 You are given the job of setting up an experiment station on another planet. While on the surface of this planet, you notice that an object with a known mass of 50 kg has a weight (when measured on a spring scale calibrated in  $lb_f$  on earth at standard gravity) of 50  $lb_f$ . Determine the local acceleration of gravity in m/s<sup>2</sup> on the planet.



- 1.45 In an environmental test chamber, an artificial gravity of 1.676 m/s<sup>2</sup> is produced. How much would a 92.99-kg man weigh inside the chamber?
- 1.46 Compare the acceleration of a 5-lb<sub>m</sub> stone acted on by 20 lb<sub>f</sub> vertically upward and vertically downward at a place where g = 30 ft/s<sup>2</sup>. Ignore any frictional effects.

1.47 Use the conversion factors found on the inside covers of the book to convert the flowing quantities to SI units:

Density,  $\rho = 120 \text{ lb}_{\text{m}}/\text{ft}^3$ 

Thermal conductivity,  $k = 170 \text{ Btu/(hr \cdot ft \cdot F)}$ 

Convective heat-transfer coefficient,  $h_{conv} = 211$ Btu/(hr · ft<sup>2</sup> · F)

Specific heat,  $c_p = 175 \text{ Btu}/(\text{lb}_m \cdot \text{F})$ 

Viscosity,  $\mu = 20$  centipoise

Viscosity,  $\mu = 77 \text{ lb}_{\text{f}} \cdot \text{s/ft}^2$ 

Kinematic viscosity,  $\nu = 3.0 \text{ ft}^2/\text{s}$ 

Stefan–Boltzmann constant,  $\sigma = 0.1713 \times 10^{-8}$ Btu/(ft<sup>2</sup> · hr · R<sup>4</sup>)

Acceleration, a = 12.0 ft/s<sup>2</sup>

\*1.48 Given the following geometric parameters for a spark-ignition engine, plot the instantaneous combustion chamber volume and its time rate of change for a complete cycle (see Appendix 1A):

Bore, 80 mm

Stroke, 70 mm

Connecting-rod length to crank radius ratio, 3.4

Compression ratio, 7.5

Engine speed, 2000 rpm

Since we will be revisiting the SI engine, it is useful to define a few enginerelated geometrical terms at this point, rather than repeating them in a variety of locations. These are:

- *B*: The **bore** is the diameter of the cylinder.
- *S*: The **stroke** is the distance traveled by the piston in moving from top center to bottom center, or vice versa.
- $V_c$  (or  $V_{TC}$ ): The **clearance volume** is the combustion chamber volume when the piston is at top center.

 $V_d$  (or  $V_{disp}$ ): The **displacement** is the difference in the volume at bottom center and at top center, that is,

$$\mathcal{V}_{disp} = \mathcal{V}_{BC} - \mathcal{V}_{TC}$$
 (1A.1)

The displacement is also equal to the product of the stroke and the cross-sectional area of the cylinder:

$$\mathcal{P}_{\rm disp} = S \ \pi B^2 / 4.$$
 (1A.2)

CR:

The **compression ratio** is the ratio of the volume at bottom center to the volume at top center, that is,

$$CR = \frac{\mathcal{V}_{BC}}{\mathcal{V}_{TC}} = \frac{\mathcal{V}_{disp}}{\mathcal{V}_{TC}} + 1.$$
(1A.3)

The following geometrical parameters associated with a reciprocating engine are illustrated in Fig. 1A.1:

ľ

 $B \equiv \text{bore}$ 

 $S \equiv \text{stroke}$ 

 $\ell \equiv \text{connecting-rod length}$ 

 $a \equiv \operatorname{crank} \operatorname{radius}$ 

 $\theta \equiv \text{crank angle}$ 

 $V_{\rm TC} \equiv$  volume at top center

 $V_{\rm BC} \equiv$  volume at bottom center

 $CR \equiv \text{compression ratio} (= \mathcal{V}_{\text{BC}} / \mathcal{V}_{\text{TC}})$ 



Definition of geometrical parameters

for reciprocating engines. After

FIGURE 1A.1

Ref. [9].

From geometric and kinematic analyses [9], the instantaneous volume,  $\hat{V}(\theta)$ , and its time derivative,  $d\hat{V}(\theta)/dt$ , are given by

$$\mathcal{V}(\theta) = \mathcal{V}_{\rm TC} \left\{ 1 + \frac{1}{2} (CR - 1) \left[ \frac{\ell}{a} + 1 - \cos \theta - \left( \frac{\ell^2}{a^2} - \sin^2 \theta \right)^{1/2} \right] \right\}$$
(1A.4)

and

$$\frac{d\hat{\mathbf{V}}(\theta)}{dt} = SN\left(\frac{\pi B^2}{4}\right)\pi\sin\theta \left[1 + \frac{\cos\theta}{\left(\frac{\ell^2}{a^2} - \sin^2\theta\right)^{1/2}}\right],$$
(1A.5)

where N is the crank rotational speed in rev/s.

# THERMODYNAMIC PROPERTIES, PROPERTY RELATIONSHIPS, AND PROCESSES



### After studying Chapter 2, you should:

- Be able to explain the meaning of the continuum limit and its importance to thermodynamics.
- Be familiar with the following basic thermodynamic properties: pressure, temperature, specific volume and density, specific internal energy and enthalpy, constant-pressure and constant-volume specific heats, entropy, and Gibbs free energy.
- Understand the relationships among absolute, gage, and vacuum pressures.
- Know the four common temperature scales and be proficient at conversions among all four.
- Know how many independent intensive properties are required to determine the thermodynamic state of a simple compressible substance.
- Be able to indicate what properties are involved in the following state relationships: equation of state, calorific equation of state, and the Gibbs (or T–ds) relationships.
- Explain the fundamental assumptions used to describe the molecular behavior of an ideal gas and under what conditions these assumptions break down.

- Be able to write one or more forms of the ideal gas equation of state and from this derive all other (mass, molar, mass-specific, and molarspecific) forms.
- Be proficient at obtaining thermodynamic properties for liquids and gases from NIST software or online databases and from printed tables.
- Be able to explain in words and write out mathematically the meaning of the thermodynamic property quality.
- Be able to draw and identify the following on T-v, P-v, and T-s diagrams: saturated liquid line, saturated vapor line, critical point, compressed liquid region, liquid-vapor region, and the superheated vapor region.
- Be able to draw an isobar on a T-v diagram, an isotherm on a P-v diagram, and both isobars and isotherms on a T-s diagram.
- Be proficient at plotting simple isobaric, isochoric, isothermal, and isentropic thermodynamic processes on T-v, P-v, and T-s coordinates.
- Be able to explain the approximations used to

estimate properties for liquids and solids.

- Be able to derive all of the isentropic process relationships for an ideal gas given that Pvγ = constant.
- Be able to explain the meaning of a polytropic process and write the general state relationship expressing a polytropic process.
- Be able to explain the principle of corresponding states and the use of generalized compressibility charts.
- Be able to express the composition of a gas mixture using both mole and mass fractions.
- Be able to calculate the thermodynamic properties of an ideal-gas mixture knowing the mixture composition and the properties of the constituent gases.
- Understand the concept of standardized properties, in particular, standardized enthalpies, and their application to ideal-gas systems involving chemical reaction.
- Be able to apply the concepts and skills developed in this chapter throughout this book.

# Chapter 2 Overview

THIS IS ONE OF THE LONGER chapters in this book and should be revisited many times at various levels. To cover in detail the subject of the properties of gases and liquids would take an entire book. Reference [1] is a classic example of such a book. We begin our study of properties by defining a few basic terms and concepts. This is followed by a treatment of ideal-gas properties that originate from the equation of state, calorific equations of state, and the second law of thermodynamics. Various approaches for obtaining properties of nonideal gases, liquids, and solids follow. The properties of substances that have coexisting liquid and vapor phases are emphasized. The concept of illustrating processes graphically using thermodynamic property coordinates (i.e., T-v, P-v, and T-s coordinates) is developed. In addition to dealing with pure substances, we treat the thermodynamic properties of nonreacting and reacting ideal-gas mixtures.

#### 2.1 KEY DEFINITIONS

To start our study of thermodynamic properties, you should review the definitions of **properties**, **states**, and **processes** presented in Chapter 1, as these concepts are at the heart of the present chapter.

The focus of this chapter is not on the properties of the generic system discussed in Chapter 1—a system that may consist of many clearly identifiable subsystems—but rather on the properties of a pure substance and mixtures of pure substances. We formally define a **pure substance** as follows:



### A *pure substance* is a substance that has a homogeneous and unchanging chemical composition.

Each element of the periodic table is a pure substance. Compounds, such as  $CO_2$  and  $H_2O$ , are also pure substances. Note that pure substances may exist in various physical phases: **vapor**, **liquid**, and **solid**. You are well acquainted with these phases of  $H_2O$  (i.e., steam, water, and ice). Carbon dioxide also readily exhibits all three phases. In a compressed gas cylinder at room temperature, liquid  $CO_2$  is present with a vapor phase above it at a pressure of 56.5 atmospheres. Solid  $CO_2$  or "dry ice" exists at temperatures below  $-78.5^{\circ}C$  at a pressure of 1 atmosphere.

In most of our discussions of properties, we further restrict our attention to those pure substances that may be classified as **simple compressible substances**.



The high pressure beneath the blade of an ice skate results in a thin layer of liquid between the blade and the solid ice (top). Surface tension complicates specifying the thermodynamic state of very small droplets (bottom).

# A *simple compressible substance* is one in which the effects of the following are negligible: motion, fluid shear, surface tension, gravity, and magnetic and electrical fields.<sup>1</sup>

The adjectives *simple* and *compressible* greatly simplify the description of the state of a substance. Many systems of interest to engineering closely approximate simple compressible substances. Although motion, fluid shear, and gravity are present in many engineering systems, their effects on local thermodynamic properties are quite small; thus, fluid properties are very well approximated as those of a simple compressible substance. Free surface, magnetic, and electrical effects are not considered in this book.

We conclude this section by distinguishing between **extensive properties** and **intensive properties**:

### An *extensive property* depends on how much of the substance is present or the "extent" of the system under consideration.

Examples of extensive properties are volume  $\forall$  and energy *E*. Clearly, numerical values for  $\forall$  and *E* depend on the size, or mass, of the system. In contrast, intensive properties do not depend on the extent of the system:

### An *intensive property* is independent of the mass of the substance or system under consideration.

Two familiar thermodynamic properties, temperature T and pressure P, are intensive properties. Numerical values for T and P are independent of the mass or the amount of substance in the system.

Intensive properties are generally designated using lowercase symbols, although both temperature and pressure violate the rule in this text. Any extensive property can be converted to an intensive one simply by dividing by the mass M. For example, the **specific volume** v and the **specific energy** e can be defined, respectively, by

$$v \equiv V/M \quad [=] \text{ m}^3/\text{kg} \tag{2.1a}$$

and

$$e \equiv E/M \quad [=] \text{ J/kg.} \tag{2.1b}$$

Intensive properties can also be based on the number of moles present rather than the mass. Thus, the properties defined in Eqs. 2.1 would be more accurately designated as **mass-specific** properties, whereas the corresponding **molar-specific** properties would be defined by

$$\overline{v} \equiv \sqrt[n]{N} \quad [=] \text{ m}^3/\text{kmol} \tag{2.2a}$$

and

$$\bar{e} \equiv E/N \quad [=] \text{ J/kmol}, \tag{2.2b}$$

<sup>1</sup> A more rigorous definition of a simple compressible substance is that, in a system comprising such a substance, the only reversible work mode is that associated with compression or expansion, work, that is, P-dV work. To appreciate this definition, however, requires an understanding of what is meant by *reversible* and by P-dV work. These concepts are developed at length in Chapters 4 and 6. where N is the number of moles under consideration. Molar-specific properties are designated using lowercase symbols with an overbar, as shown in Eqs. 2.2. Conversions between mass-specific properties and molar-specific properties are accomplished using the following simple relationships:

$$\overline{z} = z\mathcal{M} \tag{2.3}$$

and

$$= \bar{z}/\mathcal{M} \tag{2.4}$$

where z (or  $\overline{z}$ ) is any intensive property and  $\mathcal{M}([=] \text{ kg/kmol})$  is the molecular weight of the substance (see also Eq. 2.6).

Z

#### 2.2 FREQUENTLY USED THERMODYNAMIC PROPERTIES

One of the principal objectives of this chapter is to see how various thermodynamic properties relate to one another, expressed 1. by an **equation of state**, 2. by a **calorific equation of state**, and 3. by **temperature–entropy, or Gibbs, relationships**. Before we do that, however, we list in Table 2.1 the most common properties so that you might have an overview of the scope of our study. You may be familiar with many of these properties, although others will be new and may seem strange. As we proceed in our study, this strangeness should disappear as you work with these new properties. We begin with a discussion of three extensive properties: mass, number of moles, and volume.

#### 2.2a Properties Related to the Equation of State

#### Mass

As one of our fundamental dimensions (see Chapter 1), **mass**, like time, cannot be defined in terms of other dimensions. Much of our intuition of what mass is follows from its role in Newton's second law of motion

$$F = Ma. \tag{2.5}$$

In this relationship, the force F required to produce a certain acceleration a of a particular body is proportional to its mass M. The SI mass standard is a platinum–iridium cylinder, defined to be one kilogram, which is kept at the International Bureau of Weights and Measures near Paris.

#### Number of Moles

In some applications, such as reacting systems, the number of moles N comprising the system is more useful than the mass. The **mole** is formally defined as the amount of substance in a system that contains as many elementary entities as there are in exactly 0.012 kg of carbon 12 (<sup>12</sup>C). The elementary entities may be atoms, molecules, ions, electrons, etc. The abbreviation for the SI unit for a mole is *mol*, and *kmol* refers to 10<sup>3</sup> *mol*.

The number of moles in a system is related to the system mass through the **atomic** or **molecular weight**<sup>2</sup>  $\mathcal{M}$ ; that is,

$$M = N\mathcal{M},\tag{2.6}$$

<sup>&</sup>lt;sup>2</sup> Strictly, the atomic weight is not a weight at all but is the relative atomic mass.

	Symbolic D	esignation	Units		Relation to	
Property	Extensive	Intensive*	Extensive	Intensive*	Other Properties	Classification
Mass	М	_	kg	_	_	Fundamental property appearing in equation of state
Number of moles	Ν		kmol		_	Fundamental property appearing in equation of state
Volume and specific volume	V	V	m <sup>3</sup>	m³/kg	_	Fundamental property appearing in equation of state
Pressure		Р		Pa or N/m <sup>2</sup>	_	Fundamental property appearing in equation of state
Temperature		Т		Κ	_	Fundamental property appearing in equation of state
Density	—	ρ	—	kg/m <sup>3</sup>	—	Fundamental property appearing in equation of state
Internal energy	U	и	J	J/kg	_	Based on first law and calculated from calorific equation of state
Enthalpy	Н	h	J	J/kg	$U + P \forall$	Based on first law and calculated from calorific equation of state
Constant-volume specific heat	—	C <sub>v</sub>	—	J/kg·K	$(\partial u/\partial T)_v$	Appears in calorific equation of state
Constant-pressure specific heat	—	C <sub>p</sub>	—	J/kg·K	$(\partial h/\partial T)_p$	Appears in calorific equation of state
Specific-heat ratio		$\gamma$	—	Dimensionless	$c_p/c_v$	—
Entropy	S	S	J/K	J/kg·K	_	Based on second law of thermodynamics
Gibbs free energy (or Gibbs function)	G	g	J	J/kg	H-TS	Based on second law of thermodynamics
Helmholtz free energy (or Helmholtz function)	A	а	J	J/kg	U - TS	Based on second law of thermodynamics

#### Table 2.1 Common Thermodynamic Properties of Single-Phase Pure Substances

\* Molar intensive properties are obtained by substituting the number of moles, N, for the mass and changing the units accordingly. For example,  $s \equiv S/M$  [=] J/kg·K becomes  $\bar{s} \equiv S/N$  [=] J/kmol·K.
where  $\mathcal{M}$  has units of g/mol or kg/kmol. Thus, the atomic weight of carbon 12 is exactly 12. The **Avogadro constant**  $\mathcal{H}_{AV}$  is used to express the number of particles (atoms, molecules, etc.) in a mole:

$$\mathcal{N}_{AV} = \begin{cases} 6.02214199 \times 10^{23} \text{ particles/mol} \\ 6.02214199 \times 10^{26} \text{ particles/kmol.} \end{cases}$$
(2.7)

For example, we can use the Avogadro constant to determine the mass of a single <sup>12</sup>C atom:

$$M_{^{12}C} = \frac{M(1 \text{ mol } ^{12}C)}{\mathcal{M}_{AV}N_{^{12}C}}$$
  
=  $\frac{0.012}{6.02214199 \times 10^{23}(1)} = 1.9926465 \times 10^{-26}$   
[=] $\frac{\text{kg}}{(\text{atom/mol})\text{mol}} = \frac{\text{kg}}{\text{atom}}.$ 

Although not an SI unit, one-twelfth of the mass of a single <sup>12</sup>C atom is sometimes used as a mass standard and is referred to as the **unified atomic mass unit**, defined as

$$1 m_{\rm u} \equiv (1/12) M_{12_{\rm c}} = 1.66053873 \times 10^{-27} \,\rm kg.$$

## Volume

The familiar property, **volume**, is formally defined as the amount of space occupied in three-dimensional space. The SI unit of volume is cubic meters (m<sup>3</sup>).

### Density

Consider the small volume  $\Delta \hat{V} (= \Delta x \Delta y \Delta z)$  as shown in Fig. 2.1. We formally define the density to be the ratio of the mass of this element to the volume of the element, under the condition that the size of the element shrinks to the continuum limit, that is,

$$\rho \equiv \lim_{\Delta \mathcal{V} \to \mathcal{V}_{\text{continuum}}} \frac{\Delta M}{\Delta \mathcal{V}} \quad [=] \text{ kg/m}^3.$$
(2.8)

What is meant by the **continuum limit** is that the volume is very small, but yet sufficiently large so that the number of molecules within the volume is essentially constant and unaffected by any statistical fluctuations. For a volume smaller than the continuum limit, the number of molecules within the



A finite volume element shrinks to the continuum limit to define macroscopic properties. Volumes smaller than the continuum limit experience statistical fluctuations in properties as molecules enter and exit the volume.





Table 2.2 Si	ize of Gas	Volume	Containing n	Molecules	at 25°C and	1 atm
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Number of	Volume	Size of Equivalent
Molecules ( <i>n</i> )	(mm <sup>3</sup> )	Cube (mm)
10 <sup>5</sup> 10 <sup>6</sup> 10 <sup>10</sup> 10 <sup>12</sup>	$\begin{array}{l} 4.06 \times 10^{-12} \\ 4.06 \times 10^{-11} \\ 4.06 \times 10^{-7} \\ 4.06 \times 10^{-5} \end{array}$	0.00016 0.0003 0.0074 0.0344

volume fluctuates with time as molecules randomly enter and exit the volume. As an example, consider a volume such that, on average, only two molecules are present. Because the volume is so small, the number of molecules within may fluctuate wildly, with three or more molecules present at some times, and one or none at other times. In this situation, the volume is below the continuum limit. In most practical systems, however, the continuum limit is quite small, and the density, and other thermodynamic properties, can be considered to be smooth functions in space and time. Table 2.2 provides a quantitative basis for this statement.

## Specific Volume

The specific volume is the inverse of the density, that is,

$$v \equiv \frac{1}{\rho} \quad [=] \text{ m}^3/\text{kg.} \tag{2.9}$$

Physically it is interpreted as the amount of volume per unit mass associated with a volume at the continuum limit. The specific volume is most frequently used in thermodynamic applications, whereas the density is more commonly used in fluid mechanics and heat transfer. You should be comfortable with both properties and immediately recognize their inverse relationship.

#### Pressure

For a fluid (liquid or gaseous) system, the pressure is defined as the normal force exerted by the fluid on a solid surface or a neighboring fluid element, per unit area, as the area shrinks to the continuum limit, that is,

$$P \equiv \lim_{\Delta A \to A_{\text{continuum}}} \frac{F_{\text{normal}}}{\Delta A}.$$
 (2.10)

This definition assumes that the fluid is in a state of equilibrium at rest. It is important to note that the pressure is a scalar quantity, having no direction associated with it. Figure 2.2 illustrates this concept showing that the pressure at a point<sup>3</sup> is independent of orientation. That the pressure force is always directed normal to a surface (real or imaginary) is a consequence of a fluid being unable to sustain any tangential force without movement. If a tangential force is present, the fluid layers simply slip over one another.

<sup>&</sup>lt;sup>3</sup> Throughout this book, the idea of a *point* is interpreted in light of the continuum limit, that is, a point is of some small dimension rather than of zero dimension required by the mathematical definition of a point.

#### FIGURE 2.2

Pressure at a point is a scalar quantity independent of orientation. Regardless of the orientation of  $\Delta A$ , application of the defining relationship (Eq. 2.10) results in the same value of the pressure.



From a microscopic (molecular) point of view, the pressure exerted by a gas on the walls of its container is a measure of the rate at which the momentum of the molecules colliding with the wall is changed.

The SI unit for pressure is a *pascal*, defined by

$$P [=] Pa \equiv 1 \text{ N/m}^2.$$
 (2.11a)

Since one pascal is typically a small number in engineering applications, multiples of  $10^3$  and  $10^6$  are employed that result in the usage of kilopascal, kPa ( $10^3$  Pa), and megapascal, MPa ( $10^6$  Pa). Also commonly used is the **bar**, which is defined as

$$1 \text{ bar} \equiv 10^5 \text{ Pa.}$$
 (2.11b)

Pressure is also frequently expressed in terms of a standard atmosphere:

1 standard atmosphere (atm) 
$$\equiv$$
 101,325 Pa. (2.11c)

As a result of some practical devices measuring pressures relative to the local atmospheric pressure, we distinguish between **gage pressure** and **absolute pressure**. Gage pressure is defined as

$$P_{\text{gage}} \equiv P_{\text{abs}} - P_{\text{atm, abs}}, \qquad (2.12)$$

where the absolute pressure  $P_{abs}$  is that as defined in Eq. 2.10. In a perfectly evacuated space, the absolute pressure is zero. Figure 2.3 graphically illustrates the relationship between gage and absolute pressures. The term *vacuum* or *vacuum pressure* is also employed in engineering applications (and leads to confusion if one is not careful) and is defined as

$$P_{\text{vacuum}} = P_{\text{atm, abs}} - P_{\text{abs.}}$$
(2.13)

This relationship is also illustrated in Fig. 2.3.

In addition to SI units, many other units for pressure are commonly employed. Most of these units originate from the application of a particular measurement method. For example, the use of manometers results in pressures expressed in inches of water or millimeters of mercury. American (or British) customary units (pounds-force per square inch or *psi*) are frequently appended with a "g" or an "a" to indicate gage or absolute pressures, respectively (i.e., *psig* and *psia*). Conversion factors for common pressure units are provided at the front of this book.





Example 2.1



A pressure gage is used to measure the inflation pressure of a tire. The gage reads 35 psig in State College, PA, when the barometric pressure is 28.5 in of mercury. What is the absolute pressure in the tire in kPa and psia?

### Solution



Sketch



Analysis From the sketch and from Eq. 2.12, we know that

$$P_{\text{tire, abs}} = P_{\text{tire, g}} + P_{\text{atm, abs}}.$$

We need only to deal with the mixed units given to apply this relationship. Applying the conversion factor from the front of this book to express the atmospheric pressure in units of psia yields

$$P_{\text{atm, abs}} = (28.5 \text{ in Hg}) \left[ \frac{14.70 \text{ psia}}{29.92 \text{ in Hg}} \right] = 14.0 \text{ psia.}$$

Thus,

$$P_{\text{tire, abs}} = 35 + 14.0 = 49 \text{ psia.}$$



Converting this result to units of kPa yields

$$P_{\text{tire, abs}} = 49 \text{ lb}_{\text{f}}/\text{in}^2 \left[ \frac{1 \text{ Pa}}{1.4504 \times 10^{-4} \text{ lb}_{\text{f}}/\text{in}^2} \right] \left[ \frac{1 \text{ kPa}}{1000 \text{ Pa}} \right] = 337.8 \text{ kPa}.$$

*Comments* Note the use of three different units to express pressure: Pa (or kPa), psi (or  $lb_f/in^2$ ), and in Hg. Other commonly used units are mm Hg and in H<sub>2</sub>O. You should be comfortable working with any of these. Note also the usage *psia* and *psig* to denote *absolute* and *gage* pressures, respectively, when working with  $lb_f/in^2$  units.



A car tire suddenly goes flat and a pressure gage indicates zero psig. Is the absolute pressure in the tire also zero psia?

(Answer: No. A zero gage reading indicates the absolute pressure in the tire is the atmospheric pressure.)

# Example 2.2 SI Engine Application



A vintage automobile has an intake manifold vacuum gage in the dashboard instrument cluster. Cruising at 20.1 m/s (45 mph), the gage reads 14 in Hg vacuum. If the local atmospheric pressure is 99.5 kPa, what is the absolute intake manifold pressure in kPa?

## Solution





### Sketch



*Analysis* From the sketch and a rearrangement of Eq. 2.13, we find the intake manifold absolute pressure to be

$$P_{\text{man, abs}} = P_{\text{atm, abs}} - P_{\text{man, vac}}$$

Substituting numerical values and converting units yields

$$P_{\text{man, abs}} = 99.5 \text{ kPa} - (14 \text{ in Hg}) \left[ \frac{1 \text{ atm}}{29.92 \text{ in Hg}} \right] \left[ \frac{101.325 \text{ kPa}}{\text{ atm}} \right]$$
$$= 99.5 \text{ kPa} - 47.4 \text{ kPa} = 52.1 \text{ kPa}$$

