BORGNAKKE • SONNTAG

Fundamentals of Thermodynamics

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Fundamental Physical Constants

Avogadro	$N_0 = 6.022\,1415 \times 10^{23}$ mol^{-1}
Boltzmann	$k = 1.380\,6505 \times 10^{-23}$ J K^{-1}
Planck	$h = 6.626\,0693 \times 10^{-34}$ Js
Gas Constant	$\overline{R} = N_0\,k = 8.314\,472$ J mol^{-1} K^{-1}
Atomic Mass Unit	$m_0 = 1.660\,538\,86 \times 10^{-27}$ kg
Velocity of light	$c = 2.997\,924\,58 \times 10^{8}$ ms^{-1}
Electron Charge	$e = 1.602\,176\,53 \times 10^{-19}$ C
Electron Mass	$m_e = 9.109\,3826 \times 10^{-31}$ kg
Proton Mass	$m_p = 1.672\,621\,71 \times 10^{-27}$ kg
Gravitation (Std.)	$g = 9.806\,65$ ms^{-2}
Stefan Boltzmann	$\sigma = 5.670\,400 \times 10^{-8}$ W m^{-2} K^{-4}

Mol here is gram mol.

Prefixes

10^{-1}	deci	d
10^{-2}	centi	c
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n
10^{-12}	pico	p
10^{-15}	femto	f
10^{1}	deka	da
10^{2}	hecto	h
10^{3}	kilo	k
10^{6}	mega	M
10^{9}	giga	G
10^{12}	tera	T
10^{15}	peta	P

Concentration

10^{-6}	parts per million ppm

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Fundamentals of Thermodynamics

8/e

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WILEY

Preface

In this eighth edition the basic objective of the earlier editions have been retained:

- to present a comprehensive and rigorous treatment of classical thermodynamics while retaining an engineering perspective, and in doing so
- to lay the groundwork for subsequent studies in such fields as fluid mechanics, heat transfer, and statistical thermodynamics, and also
- to prepare the student to effectively use thermodynamics in the practice of engineering.

The presentation is deliberately directed to students. New concepts and definitions are presented in the context where they are first relevant in a natural progression. The introduction has been reorganized with a very short introduction followed by the first thermodynamic properties to be defined (Chapter 1), which are those that can be readily measured: pressure, specific volume, and temperature. In Chapter 2, tables of thermodynamic properties are introduced, but only in regard to these measurable properties. Internal energy and enthalpy are introduced in connection with the energy equation and the first law, entropy with the second law, and the Helmholtz and Gibbs functions in the chapter on thermodynamic relations. Many real-world realistic examples have been included in the book to assist the student in gaining an understanding of thermodynamics, and the problems at the end of each chapter have been carefully sequenced to correlate with the subject matter, and are grouped and identified as such. The early chapters in particular contain a large number of examples, illustrations, and problems, and throughout the book, chapter-end summaries are included, followed by a set of concept/study problems that should be of benefit to the students.

This is the first edition I have prepared without the thoughtful comments from my colleague and coauthor, the late Professor Richard E. Sonntag, who substantially contributed to earlier versions of this textbook. I am grateful for the collaboration and fruitful discussions with my friend and trusted colleague, whom I have enjoyed the privilege of working with over the last three decades. Professor Sonntag consistently shared generously his vast knowledge and experience in conjunction with our mutual work on previous editions of this book and on various research projects, advising PhD students and performing general professional tasks at our department. In honor of my colleague's many contributions, Professor Sonntag still appears as a coauthor of this edition.

NEW FEATURES IN THIS EDITION

Chapter Reorganization and Revisions

The introduction and the first five chapters in the seventh edition have been completely reorganized. A much shorter introduction leads into the description of some background material from physics, thermodynamic properties, and units all of which is in the new Chapter 1. To have the tools for the analysis, the order of the presentation has been kept

from the previous editions, so the behavior of pure substances is presented in Chapter 2, with a slight expansion and separation of the different domains for solid, liquid, and gas phase behavior. Some new figures and explanations have been added to show the ideal gas region as a limit behavior for a vapor at low density.

Discussion about work and heat is now included in Chapter 3 with the energy equation to emphasize that they are transfer terms of energy explaining how energy for mass at one location can change because of energy exchange with a mass at another location. The energy equation is presented first for a control mass as a basic principle accounting for energy in a control volume as

$$\text{Change of storage} = \text{transfer in} - \text{transfer out}$$

The chapter then discusses the form of energy storage as various internal energies associated with the mass and its structure to better understand how the energy is actually stored. This also helps in understanding why internal energy and enthalpy can vary nonlinearly with temperature, leading to nonconstant specific heats. Macroscopic potential and kinetic energy then naturally add to the internal energy for the total energy. The first law of thermodynamics, which often is taken as synonymous with the energy equation, is shown as a natural consequence of the energy equation applied to a cyclic process. In this respect, the current presentation follows modern physics rather than the historical development presented in the previous editions.

After discussion about the storage of energy, the left-hand side of the energy equation, the transfer terms as work and heat transfer are discussed, so the whole presentation is shorter than that in the previous editions. This allows less time to be spent on the material used for preparation before the energy equation is applied to real systems.

All the balance equations for mass, momentum, energy, and entropy follow the same format to show the uniformity in the basic principles and make the concept something to be understood and not merely memorized. This is also the reason to use the names *energy equation* and *entropy equation* for the first and second laws of thermodynamics to stress that they are universally valid, not just used in the field of thermodynamics but apply to all situations and fields of study with no exceptions. Clearly, special cases require extensions not covered in this text, like effects of surface tension in drops or for liquid in small pores, relativity, and nuclear processes, to mention a few.

The energy equation applied to a general control volume is retained from the previous edition with the addition of a section on multiflow devices. Again, this is done to reinforce to students that the analysis is done by applying the basic principles to systems under investigation. This means that the actual mathematical form of the general laws follows the sketches and figures of the system, and the analysis is not a question about finding a suitable formula in the text.

To show the generality of the entropy equation, a small example is presented applying the energy and entropy equations to heat engines and heat pumps shown in Chapter 6. This demonstrates that the historical presentation of the second law in Chapter 5 can be completely substituted by the postulation of the entropy equation and the existence of the absolute temperature scale. Carnot cycle efficiencies and the fact that real devices have lower efficiency follow from the basic general laws. Also, the direction of heat transfer from a higher temperature domain toward a lower temperature domain is predicted by the entropy equation due to the requirement of a positive entropy generation. These are examples that show the application of the general laws for specific cases and improve the student's understanding of the material.

The rest of the chapters have been updated to improve the student's understanding of the material. The word *availability* has been substituted by *exergy* as a general concept, though it is not strictly in accordance with the original definition. The chapters concerning cycles have been expanded, with a few details for specific cycles and some extensions shown to tie the theory to industrial applications with real systems. The same is done for Chapter 13 with combustion to emphasize an understanding of the basic physics of what happens, which may not be evident in the more abstract definition of terms like *enthalpy of combustion.*

Web-Based Material

Several new documents will be available from Wiley's website for the book. The following material will be accessible for students, with additional material reserved for instructors of the course.

Notes for classical thermodynamics.   A very short set of notes covers the basic thermodynamic analysis with the general laws (continuity, energy, and entropy equations) and some of the specific laws like device equations, process equations, and so on. This is useful for students doing review of the course or for exam preparation, as it gives a comprehensive presentation in a condensed form.

Extended set of study examples.   This document includes a collection of additional examples for students to study. These examples have slightly longer and more detailed solutions than the examples printed in the book and thus are excellent for self-study. There are about 8 SI unit problems with 3–4 English unit problems for each chapter covering most of the material in the chapters.

How-to notes.   Frequently asked questions are listed for each of the set of subject areas in the book with detailed answers. These are questions that are difficult to accommodate in the book. Examples:

> How do I find a certain state for R-410a in the B-section tables?
> How do I make a linear interpolation?
> Should I use internal energy (u) or enthalpy (h) in the energy equation?
> When can I use the ideal gas law?

Instructor material.   The material for instructors covers typical syllabus and homework assignments for a first and a second course in thermodynamics. Additionally, examples of two standard 1-hour midterm exams and a 2-hour final exam are given for typical Thermodynamics I and Thermodynamics II classes.

FEATURES CONTINUED FROM THE SEVENTH EDITION

In-Text-Concept Questions

The in-text concept questions appear in the text after major sections of material to allow student to reflect on the material just presented. These questions are intended to be quick self-tests for students or used by teachers as wrap-up checks for each of the subjects covered, and most of them emphasize the understanding of the material without being memory facts.

End-of-Chapter Engineering Applications

The last section in each chapter, called "Engineering Applications," has been revised with updated illustrations and a few more examples. These sections are intended to be motivating material, consisting mostly of informative examples of how this particular chapter material is being used in actual engineering. The vast majority of these sections do not have any material with equations or developments of theory, but they do contain figures and explanations of a few real physical systems where the chapter material is relevant for the engineering analysis and design. These sections are deliberately kept short and not all the details in the devices shown are explained, but the reader can get an idea about the applications relatively quickly.

End-of-Chapter Summaries with Main Concepts and Formulas

The end-of-chapter summaries provide a review of the main concepts covered in the chapter, with highlighted key words. To further enhance the summary, a list of skills that the student should have mastered after studying the chapter is presented. These skills are among the outcomes that can be tested with the accompanying set of study-guide problems in addition to the main set of homework problems. Main concepts and formulas are included after the summary for reference, and a collection of these will be available on Wiley's website.

Concept-Study Guide Problems

Additional concept questions are placed as problems in the first section of the end-of-chapter homework problems. These problems are similar to the in-text concept questions and serve as study guide problems for each chapter. They are a little like homework problems with numbers to provide a quick check of the chapter material. These questions are short and directed toward very specific concepts. Students can answer all of these questions to assess their level of understanding and determine if any of the subjects need to be studied further. These problems are also suitable for use with the rest of the homework problems in assignments and are included in the solution manual.

Homework Problems

The number of homework problems now exceeds 2800, with more than 700 new and modified problems. A large number of introductory problems cover all aspects of the chapter material and are listed according to the subject sections for easy selection according to the particular coverage given. They are generally ordered to be progressively more complex and involved. The later problems in many sections are related to real industrial processes and devices, and the more comprehensive problems are retained and grouped at the end as **review problems**.

Tables

The tables of the substances have been carried over from the seventh edition with **alternative refrigerant R-410a**, which is the replacement for R-22, and **carbon dioxide**, which is a natural refrigerant. Several more substances have been included in the software. The ideal gas tables have been printed on a mass basis as well as a mole basis, to reflect their use on a mass basis early in the text and a mole basis for the combustion and chemical equilibrium chapters.

Software Included

The software **CATT3** includes a number of additional substances besides those included in the printed tables in Appendix B. The current set of substances for which the software can provide the complete tables are:

Water Refrigerants:	R-11, 12, 13, 14, 21, 22, 23, 113, 114, 123, 134a, 152a, 404a, 407c, 410a, 500, 502, 507a, and C318
Cryogenics:	Ammonia, argon, ethane, ethylene, isobutane, methane, neon, nitrogen, oxygen, and propane
Ideal Gases:	air, CO_2, CO, N, N_2, NO, NO_2, H, H_2, H_2O, O, O_2, and OH

Some of these are printed in the booklet *Thermodynamic and Transport Properties*, by Claus Borgnakke and Richard E. Sonntag, John Wiley and Sons, 1997. Besides the properties of the substances just mentioned, the software can provide the psychrometric chart and the compressibility and generalized charts using the Lee-Keslers equation-of-state, including an extension for increased accuracy with the acentric factor. The software can also plot a limited number of processes in the *T–s* and log *P*–log *v* diagrams, giving the real process curves instead of the sketches presented in the text material.

FLEXIBILITY IN COVERAGE AND SCOPE

The book attempts to cover fairly comprehensively the basic subject matter of classical thermodynamics, and I believe that it provides adequate preparation for study of the application of thermodynamics to the various professional fields as well as for study of more advanced topics in thermodynamics, such as those related to materials, surface phenomena, plasmas, and cryogenics. I also recognize that a number of colleges offer a single introductory course in thermodynamics for all departments, and I have tried to cover those topics that the various departments might wish to have included in such a course. However, since specific courses vary considerably in prerequisites, specific objectives, duration, and background of the students, the material is arranged in sections, particularly in the later chapters, so considerable flexibility exist in the amount of material that may be covered.

The book covers more material than required for a two-semester course sequence, which provides flexibility for specific choices of topic coverage. Instructors may want to visit the publisher's website at www.wiley.com/college/borgnakke for information and suggestions on possible course structure and schedules, and the additional material mentioned as Web material that will be updated to include current errata for the book.

ACKNOWLEDGMENTS

I acknowledge with appreciation the suggestions, counsel, and encouragement of many colleagues, both at the University of Michigan and elsewhere. This assistance has been very helpful to me during the writing of this edition, as it was with the earlier editions of the book. Both undergraduate and graduate students have been of particular assistance, for their perceptive questions have often caused me to rewrite or rethink a given portion of the text, or to try to develop a better way of presenting the material in order to anticipate such

questions or difficulties. Finally, the encouragement and patience of my wife and family have been indispensable, and have made this time of writing pleasant and enjoyable, in spite of the pressures of the project. A special thanks to a number of colleagues at other institutions who have reviewed the earlier editions of the book and provided input to the revisions. Some of the reviewers are

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Etim U. Ubong, *Kettering University*
Yanhua Wu, *Wright State University*
Walter Yuen, *University of California at Santa Barbara*

I also wish to welcome the new editor, Linda Ratts, and thank her for encouragement and help during the production of this edition.

I hope that this book will contribute to the effective teaching of thermodynamics to students who face very significant challenges and opportunities during their professional careers. Your comments, criticism, and suggestions will also be appreciated, and you may communicate those to me at claus@umich.edu.

CLAUS BORGNAKKE
Ann Arbor, Michigan
July 2012

Contents

10 Power and Refrigeration Systems—Gaseous Working Fluids   462

11 Gas Mixtures   513

Contents of Appendix 753

Answers to Selected Problems 878

Index 889

Symbols

a	acceleration
A	area
a, A	specific Helmholtz function and total Helmholtz function
AF	air-fuel ratio
B_S	adiabatic bulk modulus
B_T	isothermal bulk modulus
c	velocity of sound
c	mass fraction
C_D	coefficient of discharge
C_p	constant-pressure specific heat
C_v	constant-volume specific heat
C_{po}	zero-pressure constant-pressure specific heat
C_{vo}	zero-pressure constant-volume specific heat
COP	coefficient of performance
CR	compression ratio
e, E	specific energy and total energy
EMF	electromotive force
F	force
FA	fuel-air ratio
g	acceleration due to gravity
g, G	specific Gibbs function and total Gibbs function
h, H	specific enthalpy and total enthalpy
HV	heating value
i	electrical current
I	irreversibility
J	proportionality factor to relate units of work to units of heat
k	specific heat ratio: C_p/C_v
K	equilibrium constant
KE	kinetic energy
L	length
m	mass
$\dot{m}$	mass flow rate
M	molecular mass
M	Mach number
n	number of moles
n	polytropic exponent
P	pressure
P_i	partial pressure of component i in a mixture
PE	potential energy

P_r	reduced pressure P/P_c
P_r	relative pressure as used in gas tables
q, Q	heat transfer per unit mass and total heat transfer
$\dot{Q}$	rate of heat transfer
Q_H, Q_L	heat transfer with high-temperature body and heat transfer with low-temperature body; sign determined from context
R	gas constant
$\overline{R}$	universal gas constant
s, S	specific entropy and total entropy
S_{gen}	entropy generation
$\dot{S}_{\text{gen}}$	rate of entropy generation
t	time
T	temperature
T_r	reduced temperature T/T_c
u, U	specific internal energy and total internal energy
v, V	specific volume and total volume
v_r	relative specific volume as used in gas tables
$\mathbf{V}$	velocity
w, W	work per unit mass and total work
$\dot{W}$	rate of work, or power
w^{rev}	reversible work between two states
x	quality
y	gas-phase mole fraction
y	extraction fraction
Z	elevation
Z	compressibility factor
Z	electrical charge

Script Letters

$\mathscr{E}$	electrical potential
$\mathscr{S}$	surface tension
$\mathscr{T}$	tension

Greek Letters

α	residual volume
α	dimensionless Helmholtz function a/RT
α_p	volume expansivity
β	coefficient of performance for a refrigerator
β'	coefficient of performance for a heat pump
β_S	adiabatic compressibility
β_T	isothermal compressibility
δ	dimensionless density ρ/ρ_c
η	efficiency
μ	chemical potential
ν	stoichiometric coefficient
ρ	density
τ	dimensionless temperature variable T_c/T
τ_0	dimensionless temperature variable $1 - T_r$
Φ	equivalence ratio
ϕ	relative humidity

ϕ, Φ	exergy or availability for a control mass
ψ	exergy, flow availability
ω	humidity ratio or specific humidity
ω	acentric factor

Subscripts

c	property at the critical point
c.v.	control volume
e	state of a substance leaving a control volume
f	formation
f	property of saturated liquid
fg	difference in property for saturated vapor and saturated liquid
g	property of saturated vapor
i	state of a substance entering a control volume
i	property of saturated solid
if	difference in property for saturated liquid and saturated solid
ig	difference in property for saturated vapor and saturated solid
r	reduced property
s	isentropic process
0	property of the surroundings
0	stagnation property

Superscripts

$\overline{}$	bar over symbol denotes property on a molal basis (over V, H, S, U, A, G, the bar denotes partial molal property)
$\circ$	property at standard-state condition
$*$	ideal gas
$*$	property at the throat of a nozzle
irr	irreversible
r	real gas part
rev	reversible

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Introduction and Preliminaries

The field of thermodynamics is concerned with the science of energy focusing on energy storage and energy conversion processes. We will study the effects on different substances, as we may expose a mass to heating/cooling or to volumetric compression/expansion. During such processes we are transferring energy into or out of the mass, so it changes its conditions expressed by properties like temperature, pressure, and volume. We use several processes similar to this in our daily lives; we heat water to make coffee or tea or cool it in a refrigerator to make cold water or ice cubes in a freezer. In nature, water evaporates from oceans and lakes and mixes with air where the wind can transport it, and later the water may drop out of the air as either rain (liquid water) or snow (solid water). As we study these processes in detail, we will focus on situations that are physically simple and yet typical of real-life situations in industry or nature.

By a combination of processes, we are able to illustrate more complex devices or complete systems—for instance, a simple steam power plant that is the basic system that generates the majority of our electric power. A power plant that produces electric power and hot water for district heating burns coal, as shown in Fig. 1.1. The coal is supplied by ship, and the district heating pipes are located in underground tunnels and thus are not visible. A more technical description and a better understanding are obtained from the simple schematic of the power plant, as shown in Fig. 1.2. This includes various outputs from the plant as electric power to the net, warm water for district heating, slag from burning coal, and other materials like ash and gypsum; the last output is a flow of exhaust gases out of the chimney.

Another set of processes forms a good description of a refrigerator that we use to cool food or apply it at very low temperatures to produce a flow of cold fluid for cryogenic surgery by freezing tissue for minimal bleeding. A simple schematic for such a system is shown in Fig. 1.3. The same system can also function as an air conditioner with the dual purpose of cooling a building in summer and heating it in winter; in this last mode of use, it is also called a *heat pump*. For mobile applications, we can make simple models for gasoline and diesel engines typically used for ground transportation and gas turbines in jet engines used in aircraft, where low weight and volume are of prime concern. These are just a few examples of familiar systems that the theory of thermodynamics allows us to analyze. Once we learn and understand the theory, we will be able to extend the analysis to other cases we may not be familiar with.

Beyond the description of basic processes and systems, thermodynamics is extended to cover special situations like moist atmospheric air, which is a mixture of gases, and the combustion of fuels for use in the burning of coal, oil, or natural gas, which is a chemical and energy conversion process used in nearly all power-generating devices. Many other extensions are known; these can be studied in specialty texts. Since all the processes

FIGURE 1.1 A power station in Esbjerg, Denmark.

(Courtesy of Dong Energy A/S, Denmark.)

engineers deal with have an impact on the environment, we must be acutely aware of the ways in which we can optimize the use of our natural resources and produce the minimal amount of negative consequences for our environment. For this reason, the treatment of efficiencies for processes and devices is important in a modern analysis and is required knowledge for a complete engineering consideration of system performance and operation.

Before considering the application of the theory, we will cover a few basic concepts and definitions for our analysis and review some material from physics and chemistry that we will need.

1.1 A THERMODYNAMIC SYSTEM AND THE CONTROL VOLUME

A thermodynamic system is a device or combination of devices containing a quantity of matter that is being studied. To define this more precisely, a control volume is chosen so that it contains the matter and devices inside a control surface. Everything external to the
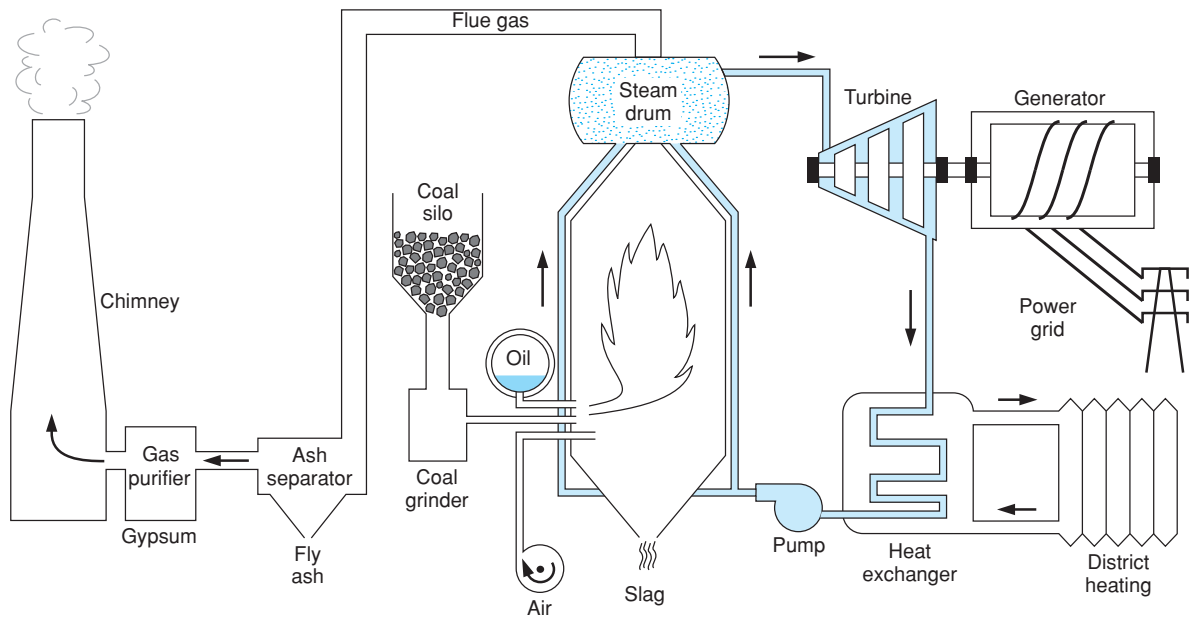
FIGURE 1.2   Schematic diagram of a steam power plant.

control volume is the surroundings, with the separation provided by the control surface. The surface may be open or closed to mass flows, and it may have flows of energy in terms of heat transfer and work across it. The boundaries may be movable or stationary. In the case of a control surface that is closed to mass flow, so that no mass can escape or enter
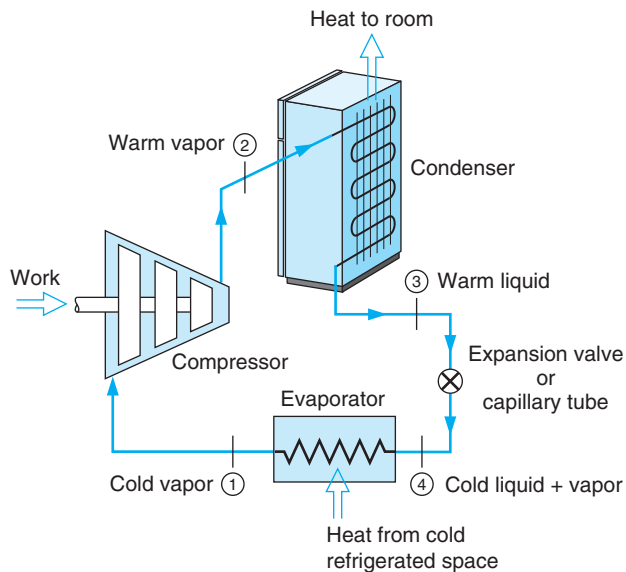
FIGURE 1.3
Schematic diagram
of a refrigerator.
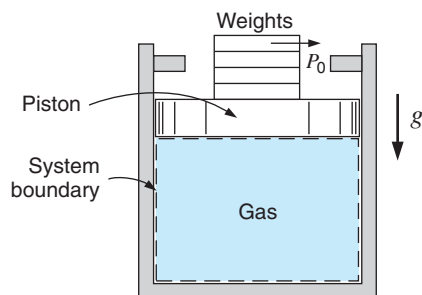
FIGURE 1.4 Example of a control mass.

the control volume, it is called a control mass containing the same amount of matter at all times.

Selecting the gas in the cylinder of Fig. 1.4 as a control volume by placing a control surface around it, we recognize this as a control mass. If a Bunsen burner is placed under the cylinder, the temperature of the gas will increase and the piston will move out. As the piston moves, the boundary of the control mass also changes. As we will see later, heat and work cross the boundary of the control mass during this process, but the matter that composes the control mass can always be identified and remains the same.

An isolated system is one that is not influenced in any way by the surroundings so that no mass, heat, or work is transferred across the boundary of the system. In a more typical case, a thermodynamic analysis must be made of a device like an air compressor which has a flow of mass into and out of it, as shown schematically in Fig. 1.5. The real system includes possibly a storage tank, as shown later in Fig. 1.20. In such an analysis, we specify a control volume that surrounds the compressor with a surface that is called the control surface, across which there may be a transfer of mass, and momentum, as well as heat and work.

Thus, the more general control surface defines a control volume, where mass may flow in or out, with a control mass as the special case of no mass flow in or out. Hence, the control mass contains a fixed mass at all times, which explains its name. The general formulation of the analysis is considered in detail in Chapter 4. The terms closed system (fixed mass) and open system (involving a flow of mass) are sometimes used to make this distinction. Here, we use the term system as a more general and loose description for a mass, device, or combination of devices that then is more precisely defined when a control volume is selected. The procedure that will be followed in presenting the first and second
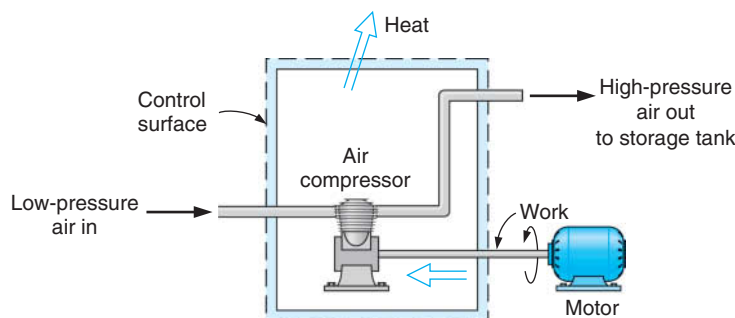
FIGURE 1.5 Example of a control volume.

laws of thermodynamics is first to present these laws for a control mass and then to extend the analysis to the more general control volume.

1.2   MACROSCOPIC VERSUS MICROSCOPIC POINTS OF VIEW

The behavior of a system may be investigated from either a microscopic or macroscopic point of view. Let us briefly describe a system from a microscopic point of view. Consider a system consisting of a cube 25 mm on a side and containing a monatomic gas at atmospheric pressure and temperature. This volume contains approximately 10^{20} atoms. To describe the position of each atom, we need to specify three coordinates; to describe the velocity of each atom, we specify three velocity components.

Thus, to describe completely the behavior of this system from a microscopic point of view, we must deal with at least 6×10^{20} equations. Even with a modern computer, this is a hopeless computational task. However, there are two approaches to this problem that reduce the number of equations and variables to a few that can be computed relatively easily. One is the statistical approach, in which, on the basis of statistical considerations and probability theory, we deal with average values for all particles under consideration. This is usually done in connection with a model of the atom under consideration. This is the approach used in the disciplines of kinetic theory and statistical mechanics.

The other approach to reducing the number of variables to a few that can be handled relatively easily involves the macroscopic point of view of classical thermodynamics. As the word *macroscopic* implies, we are concerned with the gross or average effects of many molecules. These effects can be perceived by our senses and measured by instruments. However, what we really perceive and measure is the time-averaged influence of many molecules. For example, consider the pressure a gas exerts on the walls of its container. This pressure results from the change in momentum of the molecules as they collide with the wall. From a macroscopic point of view, however, we are concerned not with the action of the individual molecules but with the time-averaged force on a given area, which can be measured by a pressure gauge. In fact, these macroscopic observations are completely independent of our assumptions regarding the nature of matter.

Although the theory and development in this book are presented from a macroscopic point of view, a few supplementary remarks regarding the significance of the microscopic perspective are included as an aid to understanding the physical processes involved. Another book in this series, *Introduction to Thermodynamics: Classical and Statistical*, by R. E. Sonntag and G. J. Van Wylen, includes thermodynamics from the microscopic and statistical point of view.

A few remarks should be made regarding the continuum approach. We are normally concerned with volumes that are very large compared to molecular dimensions and with time scales that are very large compared to intermolecular collision frequencies. For this reason, we deal with very large numbers of molecules that interact extremely often during our observation period, so we sense the system as a simple uniformly distributed mass in the volume called a continuum. This concept, of course, is only a convenient assumption that loses validity when the mean free path of the molecules approaches the order of magnitude of the dimensions of the vessel, as, for example, in high-vacuum technology. In much engineering work the assumption of a continuum is valid and convenient, consistent with the macroscopic point of view.

1.3 PROPERTIES AND STATE OF A SUBSTANCE

If we consider a given mass of water, we recognize that this water can exist in various forms. If it is a liquid initially, it may become a vapor when it is heated or a solid when it is cooled. Thus, we speak of the different phases of a substance. A phase is defined as a quantity of matter that is homogeneous throughout. When more than one phase is present, the phases are separated from each other by the phase boundaries. In each phase the substance may exist at various pressures and temperatures or, to use the thermodynamic term, in various states. The state may be identified or described by certain observable, macroscopic properties; some familiar ones are temperature, pressure, and density. In later chapters, other properties will be introduced. Each of the properties of a substance in a given state has only one definite value, and these properties always have the same value for a given state, regardless of how the substance arrived at the state. In fact, a property can be defined as any quantity that depends on the state of the system and is independent of the path (that is, the prior history) by which the system arrived at the given state. Conversely, the state is specified or described by the properties. Later we will consider the number of independent properties a substance can have, that is, the minimum number of properties that must be specified to fix the state of the substance.

Thermodynamic properties can be divided into two general classes: intensive and extensive. An intensive property is independent of the mass; the value of an extensive property varies directly with the mass. Thus, if a quantity of matter in a given state is divided into two equal parts, each part will have the same value of intensive properties as the original and half the value of the extensive properties. Pressure, temperature, and density are examples of intensive properties. Mass and total volume are examples of extensive properties. Extensive properties per unit mass, such as specific volume, are intensive properties.

Frequently we will refer not only to the properties of a substance but also to the properties of a system. When we do so, we necessarily imply that the value of the property has significance for the entire system, and this implies equilibrium. For example, if the gas that composes the system (control mass) in Fig. 1.4 is in thermal equilibrium, the temperature will be the same throughout the entire system, and we may speak of the temperature as a property of the system. We may also consider mechanical equilibrium, which is related to pressure. If a system is in mechanical equilibrium, there is no tendency for the pressure at any point to change with time as long as the system is isolated from the surroundings. There will be variation in pressure with elevation because of the influence of gravitational forces, although under equilibrium conditions there will be no tendency for the pressure at any location to change. However, in many thermodynamic problems, this variation in pressure with elevation is so small that it can be neglected. Chemical equilibrium is also important and will be considered in Chapter 14. When a system is in equilibrium regarding all possible changes of state, we say that the system is in thermodynamic equilibrium.

1.4 PROCESSES AND CYCLES

Whenever one or more of the properties of a system change, we say that a change in state has occurred. For example, when one of the weights on the piston in Fig. 1.6 is removed, the piston rises and a change in state occurs, for the pressure decreases and the specific
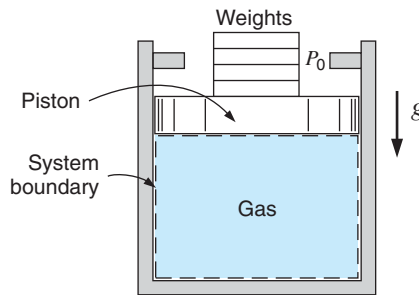
FIGURE 1.6 Example of a system that may undergo a quasi-equilibrium process.

volume increases. The path of the succession of states through which the system passes is called the process.

Let us consider the equilibrium of a system as it undergoes a change in state. The moment the weight is removed from the piston in Fig. 1.6, mechanical equilibrium does not exist; as a result, the piston is moved upward until mechanical equilibrium is restored. The question is this: Since the properties describe the state of a system only when it is in equilibrium, how can we describe the states of a system during a process if the actual process occurs only when equilibrium does not exist? One step in finding the answer to this question concerns the definition of an ideal process, which we call a *quasi-equilibrium* process. A quasi-equilibrium process is one in which the deviation from thermodynamic equilibrium is infinitesimal, and all the states the system passes through during a quasi-equilibrium process may be considered equilibrium states. Many actual processes closely approach a quasi-equilibrium process and may be so treated with essentially no error. If the weights on the piston in Fig. 1.6 are small and are taken off one by one, the process could be considered quasi-equilibrium. However, if all the weights are removed at once, the piston will rise rapidly until it hits the stops. This would be a nonequilibrium process, and the system would not be in equilibrium at any time during this change of state.

For nonequilibrium processes, we are limited to a description of the system before the process occurs and after the process is completed and equilibrium is restored. We are unable to specify each state through which the system passes or the rate at which the process occurs. However, as we will see later, we are able to describe certain overall effects that occur during the process.

Several processes are described by the fact that one property remains constant. The prefix *iso-* is used to describe such a process. An isothermal process is a constant-temperature process, an isobaric process is a constant-pressure process, and an isochoric process is a constant-volume process.

When a system in a given initial state goes through a number of different changes of state or processes and finally returns to its initial state, the system has undergone a cycle. Therefore, at the conclusion of a cycle, all the properties have the same value they had at the beginning. Steam (water) that circulates through a steam power plant undergoes a cycle.

A distinction should be made between a thermodynamic cycle, which has just been described, and a mechanical cycle. A four-stroke-cycle internal-combustion engine goes through a mechanical cycle once every two revolutions. However, the working fluid does not go through a thermodynamic cycle in the engine, since air and fuel are burned and changed to products of combustion that are exhausted to the atmosphere. In this book, the term *cycle* will refer to a thermodynamic cycle unless otherwise designated.

1.5 UNITS FOR MASS, LENGTH, TIME, AND FORCE

Since we are considering thermodynamic properties from a macroscopic perspective, we are dealing with quantities that can, either directly or indirectly, be measured and counted. Therefore, the matter of units becomes an important consideration. In the remaining sections of this chapter we will define certain thermodynamic properties and the basic units. Because the relation between force and mass is often difficult for students to understand, it is considered in this section in some detail.

Force, mass, length, and time are related by Newton's second law of motion, which states that the force acting on a body is proportional to the product of the mass and the acceleration in the direction of the force:

$$F \propto ma$$

The concept of time is well established. The basic unit of time is the second (s), which in the past was defined in terms of the solar day, the time interval for one complete revolution of the earth relative to the sun. Since this period varies with the season of the year, an average value over a 1-year period is called the *mean solar day*, and the mean solar second is 1/86 400 of the mean solar day. In 1967, the General Conference of Weights and Measures (CGPM) adopted a definition of the second as the time required for a beam of cesium-133 atoms to resonate 9 192 631 770 cycles in a cesium resonator.

For periods of time less than 1 s, the prefixes *milli*, *micro*, *nano*, *pico*, or *femto*, as listed in Table 1.1, are commonly used. For longer periods of time, the units minute (min), hour (h), or day (day) are frequently used. It should be pointed out that the prefixes in Table 1.1 are used with many other units as well.

The concept of length is also well established. The basic unit of length is the meter (m), which used to be marked on a platinum–iridium bar. Currently, the CGPM has adopted a more precise definition of the meter in terms of the speed of light (which is now a fixed constant): The meter is the length of the path traveled by light in a vacuum during a time interval of 1/299 792 458 of a second.

The fundamental unit of mass is the kilogram (kg). As adopted by the first CGPM in 1889 and restated in 1901, it is the mass of a certain platinum–iridium cylinder maintained under prescribed conditions at the International Bureau of Weights and Measures. A related unit that is used frequently in thermodynamics is the mole (mol), defined as an amount of substance containing as many elementary entities as there are atoms in 0.012 kg of carbon-12. These elementary entities must be specified; they may be atoms, molecules, electrons, ions, or other particles or specific groups. For example, 1 mol of diatomic oxygen, having a

TABLE 1.1
Unit Prefixes

Factor	Prefix	Symbol	Factor	Prefix	Symbol
10^{15}	peta	P	10^{-3}	milli	m
10^{12}	tera	T	10^{-6}	micro	μ
10^{9}	giga	G	10^{-9}	nano	n
10^{6}	mega	M	10^{-12}	pico	p
10^{3}	kilo	k	10^{-15}	femto	f

molecular mass of 32 (compared to 12 for carbon), has a mass of 0.032 kg. The mole is often termed a *gram mole*, since it is an amount of substance in grams numerically equal to the molecular mass. In this book, when using the metric SI system, we will find it preferable to use the kilomole (kmol), the amount of substance in kilograms numerically equal to the molecular mass, rather than the mole.

The system of units in use presently throughout most of the world is the metric International System, commonly referred to as *SI units* (from Le Système International d'Unités). In this system, the second, meter, and kilogram are the basic units for time, length, and mass, respectively, as just defined, and the unit of force is defined directly from Newton's second law.

Therefore, a proportionality constant is unnecessary, and we may write that law as an equality:

$$F = ma \tag{1.1}$$

The unit of force is the newton (N), which by definition is the force required to accelerate a mass of 1 kg at the rate of 1 m/s^2:

$$1 \text{ N} = 1 \text{ kg m/s}^2$$

It is worth noting that SI units derived from proper nouns use capital letters for symbols; others use lowercase letters. The liter, with the symbol L, is an exception.

The traditional system of units used in the United States is the English Engineering System. In this system the unit of time is the second, which was discussed earlier. The basic unit of length is the foot (ft), which at present is defined in terms of the meter as

$$1 \text{ ft} = 0.3048 \text{ m}$$

The inch (in.) is defined in terms of the foot:

$$12 \text{ in.} = 1 \text{ ft}$$

The unit of mass in this system is the pound mass (lbm). It was originally defined as the mass of a certain platinum cylinder kept in the Tower of London, but now it is defined in terms of the kilogram as

$$1 \text{ lbm} = 0.453\,592\,37 \text{ kg}$$

A related unit is the pound mole (lb mol), which is an amount of substance in pounds mass numerically equal to the molecular mass of that substance. It is important to distinguish between a pound mole and a mole (gram mole).

In the English Engineering System of Units, the unit of force is the pound force (lbf), defined as the force with which the standard pound mass is attracted to the earth under conditions of standard acceleration of gravity, which is that at 45° latitude and sea level elevation, 9.806 65 m/s^2 or 32.1740 ft/s^2. Thus, it follows from Newton's second law that

$$1 \text{ lbf} = 32.174 \text{ lbm ft/s}^2$$

which is a necessary factor for the purpose of units conversion and consistency. Note that we must be careful to distinguish between an lbm and an lbf, and we do not use the term *pound* alone.

The term *weight* is often used with respect to a body and is sometimes confused with mass. Weight is really correctly used only as a force. When we say that a body weighs so